

Kinetics and Scale-up of Electrochemical Reduction of Aqueous CO₂ at Sn Cathodes

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DECLARATION

I confirm that this thesis is my own work and all references made to other researches are referenced in the text.

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Abstract

Electrochemical reduction of CO₂ in aqueous buffer solutions of different pHs at tin electrodes was studied. The partial current densities exhibited the expected two Tafel regions; with increasingly negative electrode potential, the first to be encountered depended on pH strongly, while the second showed only weak dependence. Formate and CO were observed as the main products. In the range of potentials studied, the highest charge yield of 0.67 was achieved at -1.55 V (AgCl|Ag) in 0.5 M NaOH saturated with 1 atm CO₂ with a total current density of 36.2 A m⁻². pH was also found to affect the formation ratios of CO to formate, the value of which ranged from 1 to 0.15 as pH was increased from 2.9 to 7.8. However, pH was not an ideal variable to adjust the product distributions because lower pH led to a lower charge yield of CO₂ reduction due to increasingly competing hydrogen evolution.

Two mathematical kinetic models based on slightly different concepts were developed to quantify the dependence of the formation ratios on pH and to predict partial current densities of CO₂ reduction at different pHs and electrode potentials. The first model assumed that there could be multiple reactions having different stoichiometric coefficients of proton consumption occurring simultaneously; the greater the coefficient, the stronger was the preference for CO production from the reaction. The other concept was that there were multiple protonation states of the intermediate in CO₂ reduction; the higher the protonation state, the higher was the tendency to form CO from the intermediate. Both concepts allowed variations of the product ratios as a function of pH, but the latter model was preferred because more accurate predictions of the partial current densities were achieved and a generalised reaction mechanism could be derived.

Electrochemical reduction of CO₂ in 0.5 M NaOH saturated with 1 atm CO₂ at tin-coated graphite felt electrodes was also studied. Tin was deposited on graphite felt from aqueous solutions of 0.3 M K₂[Sn(OH)₆], 0.4 M KOH and 0.5 M K₃PO₄. The effects of electrode potential and electrolyte flow rates on the performances of CO₂ reduction at 3D electrodes were explored. The best performance was achieved at -1.62 V (AgCl|Ag) and 99 ml min⁻¹ electrolyte flow rate; the total current density and

the charge yield of formate were 971 A m^{-2} and 0.58, respectively. Accumulation of gas bubbles composed of H_2 and CO was found to have detrimental effects on superficial electrolyte conductivities and mass transport of CO_2 , but can be partially alleviated by increasing the electrolyte flow rate.

Two mathematical models were developed to include the effect of flow rates into account in predicting total current densities and formate charge yields from 3D electrodes. The first model assumed that the gas bubbles inside porous electrodes travelled at the same velocities as the electrolyte solutions; this led to highly under-predicted potential drops across the electrode thickness and over-predicted total current densities. On the other hand, the second model allowed slip between bubble flows and electrolyte flows, resulting in more accurate predictions. Bubbles were found to travel 0.0016 times slower than electrolyte flow velocities.

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Nomenclature

A	area
a	specific surface area of felt electrode
a_i	activity of species i
$a^\ddagger$	activity of activated complex
C_D	drag coefficient
c_i	concentration of species i
$c_{i,0}$	standard concentration of species i
D_i	diffusion coefficient of species i
d	diameter
E	electrode potential
E_0	standard electrode potential
E_e	equilibrium electrode potential
F	Faraday constant
f	relative velocity factor
G_i	Gibbs free energy of species i
h	Planck constant
j_0	exchange current density
j_i	current density for formation or consumption of species i
j_L	limiting current density
j_s	superficial current density
K	equilibrium constant
k	rate coefficient

k_B	Boltzmann constant
N_i	molar flux
n_i	mole of species i
P	pressure
R	gas constant
r	rate of reaction
Re	Reynolds number
T	absolute temperature
V	volume
z_i	valency of species i
α	transfer coefficient
δ	thickness of diffusion layer
ε	volume fraction
ε_b	bubble fraction based on felt void
ε_f	void fraction of felt
Φ	efficiency
ϕ	electrical potential
Γ	concentration of surface sites
γ_i	activity coefficient of species i in solution
η	overpotential
κ	conductivity
κ_s	superficial conductivity
μ_i	electrochemical potential of species i
$\mu_{i,0}$	standard electrochemical potential of species i

ν_i	stoichiometric coefficient of species i
θ_i	surface coverage of species i
ρ_i	density of phase i
v	flow velocity
v_i	interstitial flow velocity
v_s	superficial flow velocity
ξ	extent of reaction

1 Introduction

1.1 Background

The energy crisis, rising oil and gas prices in particular, have led to propagated exploitation of renewable energy sources. Highly accessible sources, i.e. the sun and the wind, enable localised energy production, which in theory reduces delivery costs, though technological advancements are still required for efficient implementation. Good management of mismatches between demands and supplies of energy is also crucial to successful applications because the availability of a number of renewable energy sources is periodic. For example, solar energy is available only during daytimes but humans are generally active at slightly delayed phases; excess energy during daytimes should be stored for night-time consumption. This is possible only if a technology for energy storage is in place.

The current widely-adopted means of energy storage is conversion to electrical potential energy in batteries. Though the systems are efficient, typical energy carriers are heavy metals that present hazards to the environment and hence cannot be easily mitigated. More environmentally friendly but less successful options include water electrolysis and electrochemical reduction of CO₂. Both technologies employ heavy metals only as catalysts and produce relatively biologically safe products; while the reduction product from water electrolysis is limited to only hydrogen, those from CO₂ reduction include formic acid, carbon monoxide, methanol, ethanol, methane and ethylene. Some of these fuels can be readily converted into electricity in dedicated fuel cells at room temperatures and atmospheric pressure.

While water electrolysis is generally recognised as producing hydrogen as a clean fuel, electrochemical reduction of CO₂ has potential for productive CO₂ sequestration. However, even state-of-the-art processes are still efficient only in reduction of concentrated CO₂. Its current application may be limited to only conversion of flue gases and not atmospheric CO₂, which comprises less than 1% of the atmosphere. Ideally, a closed system of energy storage and energy production could be devised as in Figure 1-1. A fuel cell is preferred to a combustion engine for energy production because a fuel and oxygen react in different compartments of a

fuel cell and therefore a clean CO_2 stream can be obtained without contamination by unreacted oxygen.

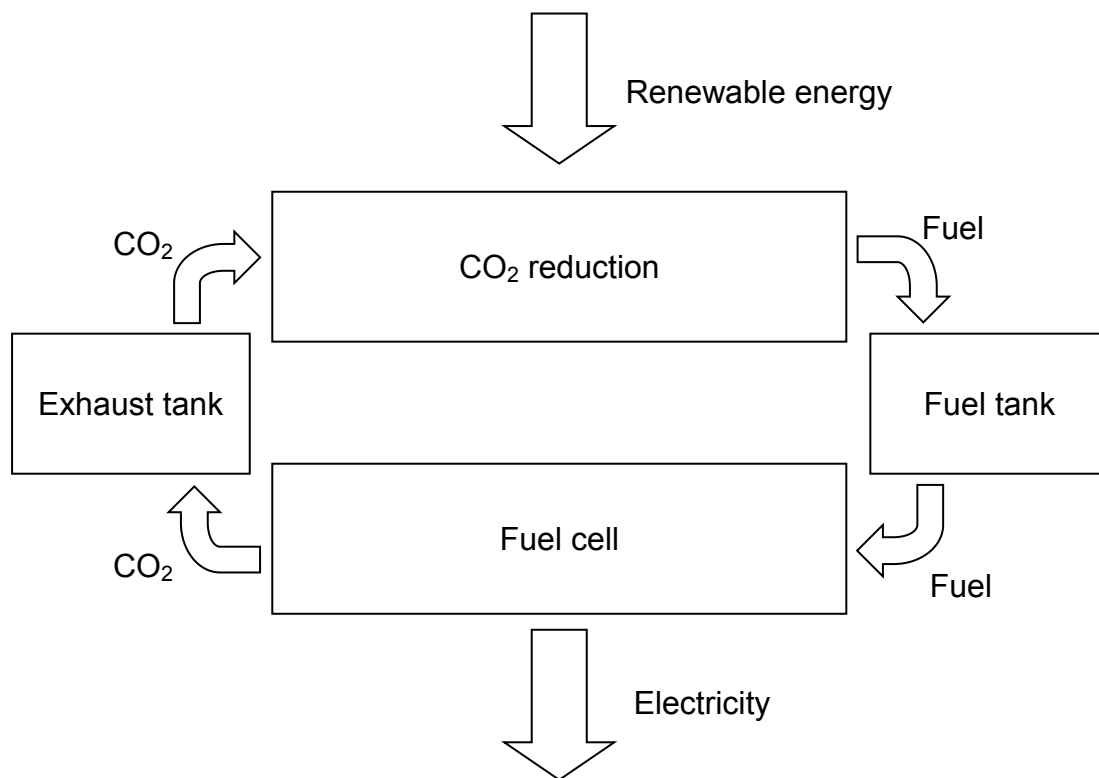


Figure 1-1: Schematic diagram of ideal cycle for storing and releasing energy

It may also be useful to consider thermochemical conversion of CO_2 for comparison. The industrial process for the production of methanol is a good example because it takes CO_2 , CO and H_2 as the feedstocks. The reactor usually operates at 200-400 °C and 5 MPa (English et al., 2004) and therefore significant energy loss could be expected. Furthermore, syngas must be obtained separately as a source of CO and H_2 . On these grounds, electrochemical reduction of CO_2 , which can perform at room temperatures and atmospheric pressure and require only water as a source of hydrogen, may be more economical.

1.2 Background theory of electrochemistry

1.2.1 Electrochemical thermodynamics

Electrochemical changes involve at least a charged species – electrons. Therefore, thermodynamic equations for such processes must include the effect of electrical potential on charged species. The chemical potential is replaced by the electrochemical potential defined as:

$$\mu_i = \mu_{i,0} + RT \ln a_i + z_i F \phi_i \quad \text{E1-1.}$$

An equation for thermodynamic equilibrium at an electrode immersed in an electrolyte containing reactants and products can be derived by considering the Gibbs energy of involved species including electrons near the electrode;

$$nG = \sum n_i \mu_i \quad \text{E1-2.}$$

As the reaction occurs, the numbers of moles change accordingly:

$$(n + \xi \sum \nu_i)G = \sum (n_i + \nu_i \xi) \mu_i \quad \text{E1-3.}$$

Differentiating the equation with respect to the reaction coordinate, ξ , and setting it to zero to find the lowest point yield:

$$\frac{\partial (n + \xi \sum \nu_i)G}{\partial \xi} = 0 = \sum (n_i + \nu_i \xi) \frac{\partial \mu_i}{\partial \xi} + \sum \nu_i \mu_i \quad \text{E1-4.}$$

Applying Gibbs-Duhem equation at a constant temperature and pressure gives:

$$\begin{aligned} 0 &= \sum \nu_i \mu_i \\ &= \Delta \mu_0 + RT \ln \prod a_i^{\nu_i} + F \sum \nu_i z_i \phi_i + \nu_e \mu_{e,0} + \nu_e z_e F \phi_e \end{aligned} \quad \text{E1-5.}$$

The potentials of the species in the electrolyte are in the same phase and therefore equal to the potential of the electrolyte:

$$\begin{aligned} 0 &= \Delta \mu_0 + RT \ln \prod a_i^{\nu_i} + F \phi_{electrolyte} \sum \nu_i z_i + \nu_e \mu_{e,0} + \nu_e z_e F \phi_e \\ &= \Delta \mu_0 + RT \ln \prod a_i^{\nu_i} - \nu_e z_e F \phi_{electrolyte} + \nu_e \mu_{e,0} + \nu_e z_e F \phi_e \\ &= \frac{\Delta \mu}{\nu_e} + \mu_e \end{aligned} \quad \text{E1-6.}$$

The potentials of the electrolyte and the electrons are not readily accessible and therefore practically measured against the equilibrium potential of another reference electrochemical reaction:

$$\begin{aligned} \mu_e - \mu_{e,ref} &= - \left(\frac{\Delta \mu}{\nu_e} - \frac{\Delta \mu_{ref}}{\nu_{e,ref}} \right) \\ \mu_{e,0} - \mu_{e,ref,0} + z_e F (\phi_e - \phi_{e,ref}) &= - \left(\frac{\Delta \mu_0 + RT \ln \prod a_i^{\nu_i}}{\nu_e} - \frac{\Delta \mu_{ref,0} + RT \ln \prod a_{i,ref}^{\nu_{i,ref}}}{\nu_{e,ref}} \right) \end{aligned} \quad \text{E1-7.}$$

If the electrical leads at which measurement is made are made of the same material, they share the same chemical part of the electrochemical potentials of electrons:

$$z_e F (\phi_e - \phi_{e,ref}) = - \left(\frac{\Delta\mu_0 + RT \ln \prod a_i^{\nu_i}}{\nu_e} - \frac{\Delta\mu_{ref,0} + RT \ln \prod a_{i,ref}^{\nu_{i,ref}}}{\nu_{e,ref}} \right)$$

$$\phi_e - \phi_{e,ref} = \left(- \frac{\Delta\mu_0}{\nu_e z_e F} - \frac{RT}{\nu_e z_e F} \ln \prod a_i^{\nu_i} \right) - \left(- \frac{\Delta\mu_{0,ref}}{\nu_{e,ref} z_e F} - \frac{RT}{\nu_{e,ref} z_e F} \ln \prod a_{i,ref}^{\nu_{i,ref}} \right) \quad \text{E1-8.}$$

$$E_e = E_0 - \frac{RT}{\nu_e z_e F} \ln \prod a_i^{\nu_i}$$

An equilibrium potential measured against a reference equilibrium potential is called the equilibrium electrode potential. Its value also depends on the reference electrochemical reaction employed to produce the reference potential. Hydrogen evolution from an aqueous solution containing protons of 1 M activity at 1 atm H₂ is historically set as a reference electrochemical reaction and called a standard hydrogen electrode (SHE); hence, the standard electrochemical potential of proton is set arbitrarily to zero J mol⁻¹, on which standard electrochemical potentials of other ions are based.

In many instances, hydrogen evolution is impractical and a simpler reference electrode is needed. The value of an equilibrium electrode potential measured against another reference electrode can be obtained by subtracting the equilibrium electrode potential of the reference electrode measured against an SHE from that of the electrode in question also measured against an SHE.

1.2.2 Electrochemical kinetics

The kinetics of electrochemical reactions in this project were assumed to follow the transition state theory. The forward and reverse rates of an electrochemical reaction,



can be determined through the activities of its activated complexes with a unity transmission coefficient:

$$r_f = \frac{k_B T}{h} a_f^\ddagger \quad \text{E1-9}$$

and

$$r_r = \frac{k_B T}{h} a_r^\ddagger \quad \text{E1-10,}$$

respectively. The activated complex is assumed to be in equilibrium with the reactant for the forward reaction and the product for the reverse reaction. In order to determine the activities of the activated complexes, equations for their electrochemical potentials must be derived.

The electrochemical potential of the activated complexes consists of a chemical and an electronic part. The dependence of the latter on electrode potential requires a specific approach. A 4-step process for transfer of electrons at the electrode has been suggested as a basis for this consideration (Delahay & Tobias, 1965):

- I. The reactant, R, is in the bulk of the electrolyte, where the potential in the solution is ϕ_{ref} .
- II. The reactant moves to the outer Helmholtz plane, where the potential in the solution is ϕ_2 .
- III. The product, P, forms at the outer Helmholtz plane.
- IV. The product moves away from the Helmholtz plane to the bulk of the electrolyte.

The transfer of electrons occurs between step II and III. The activated complexes are also loosely implied during the transition between the two steps. The Gibbs free energy of the reactant and the product undergoing the reaction in each step can be written as:

$$I. \quad G_I = \mu_{R,0} + RT \ln a_R + z_R F \phi_{ref} + |v_e| (\mu_{e,0} - F \phi_m)$$

$$II. \quad G_{II} = \mu_{R,0} + RT \ln a_R + z_R F \phi_2 + |v_e| (\mu_{e,0} - F \phi_m)$$

$$III. \quad G_{III} = \mu_{P,0} + RT \ln a_P + (z_R - |v_e|) F \phi_2$$

$$IV. \quad G_{IV} = \mu_{P,0} + RT \ln a_P + (z_R - |v_e|) F \phi_{ref}$$

The activation energy for the forward reaction is

$$G^\ddagger - G_I = \Delta G_f^\ddagger \quad E1-11$$

$$\text{and for the reverse reaction is} \quad G^\ddagger - G_{IV} = \Delta G_r^\ddagger \quad E1-12.$$

Each also consists of a chemical and an electronic part. A change in the latter between step II and the transition state is assumed to be a fraction of a change in the electronic part of the Gibbs free energy between step II and III. Therefore, the activation energy for the forward reaction is:

$$\begin{aligned}
\Delta G_f^\ddagger &= [\Delta G_f^\ddagger]_c + [\Delta G_f^\ddagger]_e \\
&= [\Delta G_f^\ddagger]_c + \alpha([G_{III}]_e - [G_{II}]_e) + ([G_{II}]_e - [G_I]_e) \\
&= [G^\ddagger]_c - (\mu_{R,0} + RT \ln a_R + |v_e| \mu_{e,0}) + \alpha |v_e| F(\phi_m - \phi_2) + z_R F(\phi_2 - \phi_{ref}) \quad \text{E1-13} \\
&= \Delta \mu_f^\ddagger + RT \ln \frac{a_f^\ddagger}{a_R} + \alpha |v_e| F \phi_m + (z_R - \alpha |v_e|) F \phi_2 - z_R F \phi_{ref} \\
&= \Delta \mu_f^\ddagger + RT \ln \frac{a_f^\ddagger}{a_R} + \alpha |v_e| FE + (z_R - \alpha |v_e|) F(\phi_2 - \phi_{ref})
\end{aligned}$$

and, similarly, for the reverse reaction is:

$$\begin{aligned}
\Delta G_r^\ddagger &= [\Delta G_r^\ddagger]_c + [\Delta G_r^\ddagger]_e \\
&= [\Delta G_r^\ddagger]_c + (1 - \alpha)([G_{II}]_e - [G_{III}]_e) + ([G_{III}]_e - [G_{IV}]_e) \\
&= [G^\ddagger]_c - (\mu_{P,0} + RT \ln a_P) + (1 - \alpha) |v_e| F(\phi_2 - \phi_m) + (z_R - |v_e|) F(\phi_2 - \phi_{ref}) \quad \text{E1-14.} \\
&= \Delta \mu_r^\ddagger + RT \ln \frac{a_r^\ddagger}{a_P} - (1 - \alpha) |v_e| FE + (z_R - \alpha |v_e|) F(\phi_2 - \phi_{ref})
\end{aligned}$$

The activities of the activated complex at equilibrium can be derived promptly. That of the forward reaction is:

$$a_f^\ddagger = a_R \exp\left(-\frac{\Delta \mu_f^\ddagger}{RT}\right) \exp\left(-\frac{\alpha |v_e| FE}{RT}\right) \exp\left(\frac{\{\alpha |v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-15}$$

and that of the reverse reaction is:

$$a_r^\ddagger = a_P \exp\left(-\frac{\Delta \mu_r^\ddagger}{RT}\right) \exp\left(\frac{\{1 - \alpha\} |v_e| FE}{RT}\right) \exp\left(\frac{\{\alpha |v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-16.}$$

Substitution of the activities in equation E1-9 and E1-10 with equation E1-15 and E1-16, respectively, gives:

$$\begin{aligned}
r_f &= \frac{k_B T}{h} a_R \exp\left(-\frac{\Delta \mu_f^\ddagger}{RT}\right) \exp\left(-\frac{\alpha |v_e| FE}{RT}\right) \exp\left(\frac{\{\alpha |v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right) \\
&= k_f a_R \exp\left(-\frac{\alpha |v_e| FE}{RT}\right) \exp\left(\frac{\{\alpha |v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-17}
\end{aligned}$$

and

$$\begin{aligned}
r_r &= \frac{k_B T}{h} a_P \exp\left(-\frac{\Delta \mu_r^\ddagger}{RT}\right) \exp\left(\frac{\{1 - \alpha\} |v_e| FE}{RT}\right) \exp\left(\frac{\{\alpha |v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right) \\
&= k_r a_P \exp\left(\frac{\{1 - \alpha\} |v_e| FE}{RT}\right) \exp\left(\frac{\{\alpha |v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-18.}
\end{aligned}$$

These kinetic expressions for reduction and oxidation are already in usable forms. The net rate can be obtained by subtracting the reverse rate from the forward rate but, in many cases, either the forward or the reverse rate is sufficient to describe experimental results due to exponential dependence of electrochemical reaction rates on electrode potential. However, further modifications can be done to include the equilibrium electrode potential of the reaction. At equilibrium, the forward and the reverse rate are equal:

$$\begin{aligned}
 r_f &= r_r \\
 \frac{k_f a_R}{k_r a_P} &= \exp\left(\frac{|v_e| F E_e}{RT}\right) \\
 E_e &= -\frac{RT}{|v_e| F} \ln \frac{k_r}{k_f} - \frac{RT}{|v_e| F} \ln \frac{a_P}{a_R}
 \end{aligned} \tag{E1-19}$$

Comparing this equation with equation E1-8 yields:

$$\begin{aligned}
 E_0 &= -\frac{RT}{|v_e| F} \ln \frac{k_r}{k_f} \\
 &= -\frac{RT}{|v_e| F} \ln \frac{\exp\left(-\frac{\Delta\mu_r^\ddagger}{RT}\right)}{\exp\left(-\frac{\Delta\mu_f^\ddagger}{RT}\right)} \\
 &= -\frac{\Delta\mu_0}{|v_e| F}
 \end{aligned} \tag{E1-20}$$

Therefore,

$$E_e = -\frac{\Delta\mu_0}{|v_e| F} - \frac{RT}{|v_e| F} \ln \frac{a_P}{a_R} \tag{E1-21}$$

Multiplying and dividing equation E1-17 by $\exp\left(\frac{-\alpha|v_e| F E_e}{RT}\right)$ gives

$$\begin{aligned}
 r_f &= \frac{k_B T}{h} a_R^{1-\alpha} a_P^\alpha \exp\left(\frac{\{\alpha-1\}\Delta\mu_f^\ddagger - \alpha\Delta\mu_r^\ddagger}{RT}\right) \exp\left(-\frac{\alpha|v_e| F \eta}{RT}\right) \\
 &\times \exp\left(\frac{\{\alpha|v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right)
 \end{aligned} \tag{E1-22}$$

Similarly, multiplying and dividing equation E1-18 by $\exp\left(\frac{\{1-\alpha\}|v_e|FE_e}{RT}\right)$ gives

$$r_r = \frac{k_B T}{h} a_R^{1-\alpha} a_P^\alpha \exp\left(\frac{\{\alpha-1\}\Delta\mu_f^\ddagger - \alpha\Delta\mu_r^\ddagger}{RT}\right) \exp\left(\frac{\{1-\alpha\}|v_e|F\eta}{RT}\right) \times \exp\left(\frac{\{\alpha|v_e| - z_R\}F\{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-23.}$$

The net reaction rate can be obtained by adding the negative reduction rate to the positive oxidation rate:

$$r = r_0 \left[\exp\left(\frac{\{1-\alpha\}|v_e|F\eta}{RT}\right) - \exp\left(\frac{-\alpha|v_e|F\eta}{RT}\right) \right] \quad \text{E1-24,}$$

where $r_0 = \frac{k_B T}{h} a_R^{1-\alpha} a_P^\alpha \exp\left(\frac{\{\alpha-1\}\Delta\mu_f^\ddagger - \alpha\Delta\mu_r^\ddagger}{RT}\right) \exp\left(\frac{\{\alpha|v_e| - z_R\}F\{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-25.}$

Practically, rates of electrochemical reactions are expressed in $\text{mol m}^{-2} \text{s}^{-1}$; this can be achieved by multiplying both sides of equation E1-24 by the standard concentration of activated complexes, $c_0^\ddagger$, in mol m^{-2} . The new rate expression with equation E1-25 rearranged to employ concentrations instead of activities is:

$$r' = r'_0 \left[\exp\left(\frac{\{1-\alpha\}|v_e|F\eta}{RT}\right) - \exp\left(\frac{-\alpha|v_e|F\eta}{RT}\right) \right] \quad \text{E1-26,}$$

$$r'_0 = \left(\frac{k_B T}{h} \frac{c_0^\ddagger}{c_{R,0}^{1-\alpha} c_{P,0}^\alpha} \right) \gamma_R^{1-\alpha} c_R^{1-\alpha} \gamma_P^\alpha c_P^\alpha \exp\left(\frac{\{\alpha-1\}\Delta\mu_f^\ddagger - \alpha\Delta\mu_r^\ddagger}{RT}\right) \times \exp\left(\frac{\{\alpha|v_e| - z_R\}F\{\phi_2 - \phi_{ref}\}}{RT}\right) \quad \text{E1-27.}$$

$$= k \gamma_R^{1-\alpha} c_R^{1-\alpha} \gamma_P^\alpha c_P^\alpha \exp\left(\frac{\{\alpha-1\}\Delta\mu_f^\ddagger - \alpha\Delta\mu_r^\ddagger}{RT}\right) \exp\left(\frac{\{\alpha|v_e| - z_R\}F\{\phi_2 - \phi_{ref}\}}{RT}\right)$$

Hence, the net current density is:

$$j = j_0 \left[\exp\left(\frac{\{1-\alpha\}|v_e|F\eta}{RT}\right) - \exp\left(\frac{-\alpha|v_e|F\eta}{RT}\right) \right] \quad \text{E1-28,}$$

$$j_0 = |v_e| F k \gamma_R^{1-\alpha} c_R^{1-\alpha} \gamma_P^\alpha c_P^\alpha \exp\left(\frac{\{\alpha-1\} \Delta\mu_f^\ddagger - \alpha \Delta\mu_r^\ddagger}{RT}\right) \times \exp\left(\frac{\{\alpha|v_e| - z_R\} F \{\phi_2 - \phi_{ref}\}}{RT}\right)$$

where

E1-29.

It can be seen that rates of electrochemical reactions depend on not only electrode potential but also the potential at the outer Helmholtz plane, which is mostly affected by the composition of the electrolyte. In aqueous solutions, the valencies, the radii and the concentrations of ions play important roles in determining the structure of the electrical double layer. Electrolytes of high concentrations are recommended to maximise gradients of the potential within the electrical double layer, minimising the dependence of the potential at the outer Helmholtz plane on electrode potential. Only under this circumstance should this dependence be discarded. Kinetic equations for electrochemical reactions with more than one reactant can also be derived similarly.

2 Literature survey

2.1 Reaction mechanisms of electrochemical reduction of CO₂

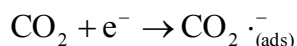
A number of products can be produced via electrochemical reduction of CO₂. The main factor determining their distribution is cathode materials, each of which has a particular set of possible products in aqueous electrolytes and, mostly, a different one in non-aqueous electrolytes. The distributions of the products in a set can be fine-tuned by adjusting parameters such as electrolyte composition and overpotential.

Most works on electrochemical reduction of CO₂ were conducted in aqueous electrolytes. Some cathode materials and their respective product distributions expressed in Faradaic efficiencies are presented in Table 1. Hori et al. (1994) categorised these electrodes into four groups according to their main products: hydrocarbons, carbon monoxide, formate, and hydrogen.

Table 1: Some cathode materials and their respective product distributions from electrochemical reduction of CO₂ in 0.5 M KHCO₃ saturated with 1 atm CO₂ (Hori et al., 1994a)

Electrode	Potential (V) vs. <i>nhe</i>	Current density (mA cm ⁻²)	Faradaic efficiency/%							Total
			CH ₄	C ₂ H ₄	EtOH	PrOH	CO	HCOO ⁻	H ₂	
Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5*
Au	-1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	-1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	-1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	-1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	-1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4†
Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	-1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

The formation mechanisms of products from CO₂ reduction are not yet firmly established and still being investigated. However, a widely accepted part of mechanisms is the formation of CO₂⁻ as the first step in CO₂ reduction:



R2-1

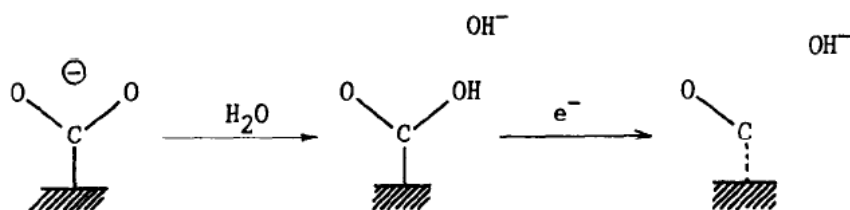
with an estimated standard equilibrium potential of -1.90 V (SHE) (Benson et al., 2009). This radical then undergoes different reaction pathways to form various products. The subsequent reduction of $\text{CO}_2^{\cdot-}$ in aqueous solutions mainly results in either formate or CO. While the former is widely recognised as a dead end, the latter can be further reduced to hydrocarbons including various alcohols notably at copper electrodes.

Hori et al. (1994) proposed generalised reaction mechanisms for CO_2 reduction at metal electrodes, which are summarised in Figure 2-1. Their proposed mechanisms were based on the combinations of adsorption characteristics of $\text{CO}_2^{\cdot-}$ at different cathode materials, i.e. adsorbed or not adsorbed, and the nature of electrolytes, i.e. aqueous or non-aqueous. Thus, there are four possible combinations:

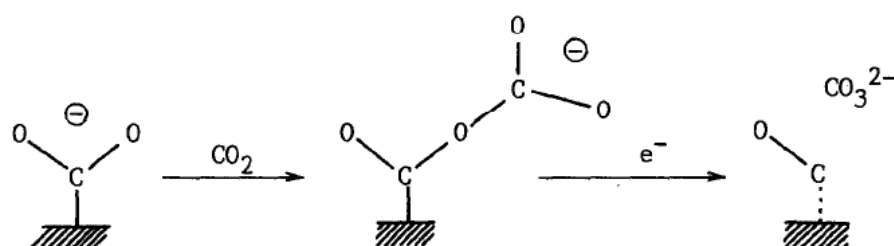
- **$\text{CO}_2^{\cdot-}$ is adsorbed at the cathode and the electrolyte is aqueous.**
Adsorbed $\text{CO}_2^{\cdot-}$ is attacked by water and reduced to adsorbed CO.
- **$\text{CO}_2^{\cdot-}$ is adsorbed at the cathode and the electrolyte is non-aqueous.**
Adsorbed $\text{CO}_2^{\cdot-}$ is attacked by CO_2 instead of water. Following further reduction, CO forms and CO_3^{2-} is released.
- **$\text{CO}_2^{\cdot-}$ is not adsorbed at the cathode and the electrolyte is aqueous.**
 $\text{CO}_2^{\cdot-}$ is released into the electrolyte and attacked by water. Subsequent reduction results in formate formation.
- **$\text{CO}_2^{\cdot-}$ is not adsorbed at the cathode and the electrolyte is non-aqueous.**
Either $\text{CO}_2^{\cdot-}$ is attacked by CO_2 and reduced to oxalate or $\text{CO}_2^{\cdot-}$ reacts with another $\text{CO}_2^{\cdot-}$ to form oxalate.

(1) $\text{CO}_2^{\bullet-}$ adsorbed on metal electrode

Aqueous media (Au, Ag, Cu, Zn)

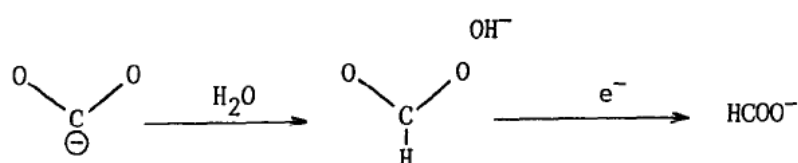


Nonaqueous media (Au, Ag, Cu, Zn, Cd, Sn, In)



(2) $\text{CO}_2^{\bullet-}$ not adsorbed on metal electrode

Aqueous media (Cd, Sn, In, Pb, Tl, Hg)



Nonaqueous media (Pb, Tl, Hg)

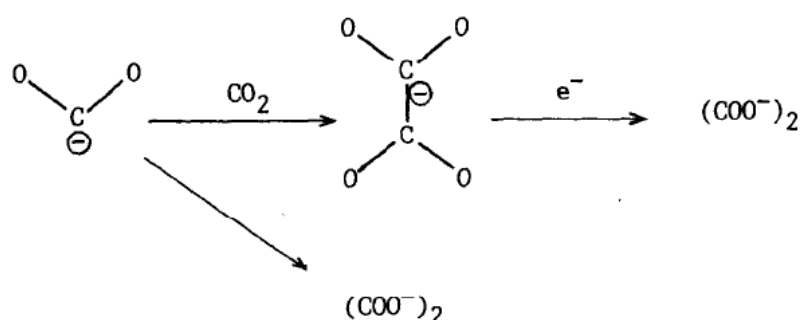


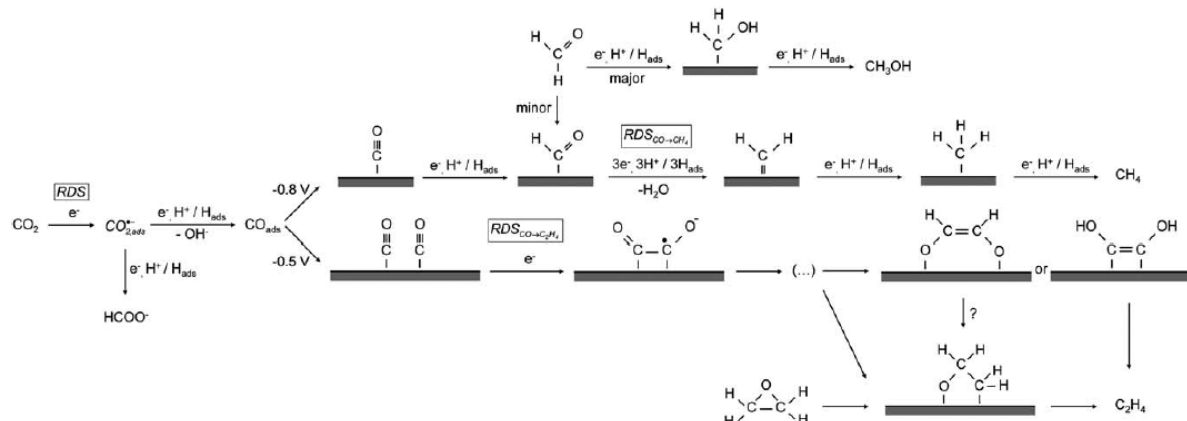
Figure 2-1: Generalised mechanisms of formation of formate, CO and oxalate, proposed by Hori et al. (1994)

2.1.1 Carbon monoxide and hydrocarbons

Although carbon monoxide and formate are observed as products at many cathode materials, hydrocarbons including alcohols are produced with significant current efficiencies at only a few and notably copper. Hori et al. (1987, 1989) studied CO_2

$$\begin{array}{c}
 \text{CO}_2 \xrightarrow{e^-} \text{CO}_2^- (\text{ads}) \xrightarrow{e^-} \text{CO} (\text{ads}) \begin{cases} \xrightarrow{\text{H}_2^+, e^-} \text{CHOH} (\text{ads}) \xrightarrow{\text{H}_2^+, e^-} \text{CH}_2 (\text{ads}) \\ \xrightarrow{\quad \quad \quad} \text{C} (\text{ads}) + \text{O} (\text{ads}) \xrightarrow{2\text{H}_2^+, 2e^-} \text{CH}_2 (\text{ads}) \end{cases} \\
 \\
 \text{CH}_2 (\text{ads}) \begin{cases} \xrightarrow{\text{H}_2^+, e^-} \text{CH}_4 \\ \xrightarrow{\quad \quad \quad} \text{C}_2\text{H}_4 \\ \xrightarrow{\text{CO}} \text{CH}_2=\text{C}=\text{O} (\text{ads}) \end{cases} \\
 \text{CH}_2=\text{C}=\text{O} (\text{ads}) \begin{cases} \xrightarrow{\text{H}_2^+, e^-} \text{CH}_2=\overset{\text{OH}}{\text{CH}} (\text{ads}) \xrightarrow{\text{H}_2^+, e^-} \text{CH}_3-\text{CH}_2\text{OH} \\ \xrightarrow{\text{H}_2^+, e^-} \text{CH}_3-\text{CH} (\text{ads}) \xrightarrow{\text{CO}, 2\text{H}_2^+, 2e^-} \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH} \end{cases}
 \end{array}$$

Minor modifications to the pathways shown in Figure 2-2 are still ongoing. Schouten et al. (2011) conducted experiments with Online Electrochemical Mass Spectrometry (OLEMS) and believed that CHO, rather than COH, is parts of the intermediates in hydrocarbon formation. Their proposed reaction pathways are shown in Figure 2-3.

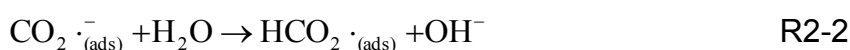


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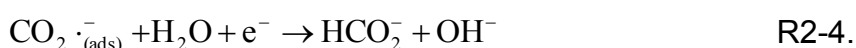
Furthermore, Schouten et al. (2012) found that ethylene may form from two different pathways at different crystal surfaces.

2.1.2 Formate

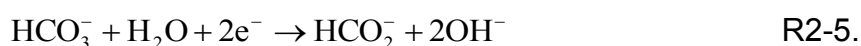
Formate is produced as a main product with current efficiencies reaching 100% at various cathode materials (Table 1). Its formation mechanism is perhaps the simplest amongst those of possible products from CO₂ reduction. Paik, Andersen and Eyring (1969) proposed:



The difference between this mechanism and that in Figure 2-1 is that CO₂^{·-} is adsorbed in this mechanism. This scheme is probably the most widely accepted, though other similar variants exist. For example, Vassiliev et al. (1985) believed that the first electron was transferred to an adsorbed CO₂ molecule rather than solvated one on the basis that electrode materials strongly affect both Tafel regions and they also combine the hydration reaction and the second electron transfer:



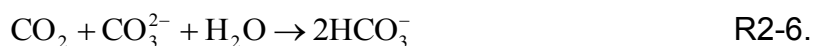
There is also another school believing that, in addition to CO₂, HCO₃⁻ is also reduced to formate. Innocent et al. (2009), for example, suggested:



However, Hori and Suzuki (1983)'s quantitative analyses showed earlier that, if bicarbonate were electrochemically active, current densities higher than those observed at pH between 8 and 9 would be obtained because bicarbonate concentrations are higher than that of CO₂ by an order of magnitude.

Li and Oloman (2006) studied electrochemical reduction of CO₂ to formate in various aqueous solutions containing inorganic salts: NaCl, KCl, Na₂CO₃, K₂CO₃ and KHCO₃. They found that current efficiencies of formate were high in KHCO₃.

solutions, but severely reduced in the presence of CO_3^{2-} . They proposed that CO_2 was eliminated by CO_3^{2-} at the electrode via:



2.1.3 Methanol

As mentioned earlier, the production of methanol is not always observed in electrochemical reduction of CO_2 . Hori, Murata, and Takahashi (1989) did not detect methanol in the reduction of CO_2 , but did in the reduction of formaldehyde as a main product. However, they did not always observe formaldehyde as a product of CO_2 reduction. Schouten et al. (2011) also showed that methanol was a product of formaldehyde reduction, but was not detected in the reduction of CO_2 . Thereby, they concluded that formaldehyde is not a product of CO_2 reduction but formaldehyde and methanol are also included in their reaction pathways (Figure 2-3) as complements. These reports suggest that methanol should not have formed from CO_2 reduction.

Nevertheless, a recent comprehensive list of products from electrochemical reduction of CO_2 at copper produced by Kuhl et al. (2012) included methanol, though at low concentrations. Russell et al. (1977) observed methanol formation from the reduction of both formate and formaldehyde, providing a possible pathway for methanol formation from CO_2 reduction. Furthermore, a few papers reported the production of methanol from CO_2 reduction at some metal cathodes not listed in Table 1 such as molybdenum (Summers et al., 1986) and rubidium (Frese & Leach, 1985).

Reducing CO_2 electrochemically to methanol is generally achieved at low current densities. The work by Summers et al. (1986) featured a current density of 0.12 mA cm^{-2} with 84% current efficiency, while the production of hydrocarbons and formate can be observed at current densities larger than 1 mA cm^{-2} (Table 1). Kobayashi and Takahashi (2004) reported the formation of methanol at a cathode made of mixed oxides of Cu, Zn and Al, the combination of which was actually a catalyst for industrial thermochemical production of methanol, at slightly larger current densities and with current efficiencies reaching 97%. Schizodimou and Kyriacou (2012) reduced CO_2 at cathodes made of a Cu-Sn-Pb alloy and observed methanol formation at 0.2 mA cm^{-2} with a current efficiency of 34%. Chang et al. (2009) reported methanol formation at Cu_2O -catalysed carbon cloth at a higher current

density of 4.5 mA cm^{-2} at -1.7 V (SCE) . However, the higher value might have been attributed to the high surface area of carbon cloth.

Methanol forms as a product with current efficiencies up to 30% when CO_2 was reduced electrochemically at palladium in the presence of pyridine, according to Seshadri et al. (1994). Schemes of electron shuttled by the chemical to CO_2 and intermediates were proposed in a study by Barton Cole et al. (2010). In both papers, electrolyses were carried out at small overpotentials to avoid hydrogen evolution and ensure high current efficiencies of CO_2 reduction to methanol. Consequently, the current densities were low and in the order of $10 \text{ } \mu\text{A cm}^{-2}$, which was lower than those reported in other works. Neither the current efficiencies nor the partial current densities of methanol formation at larger overpotentials were reported.

Perhaps, to date, the only reliable paper showing the formation rates of methanol at large overpotentials was that by Kuhl et al. (2012). This rare data showed that the formation rate of methanol was not an exponential function of electrode potential. The partial current densities were close to $1\text{-}20 \text{ } \mu\text{A cm}^{-2}$ at all electrode potentials in the study. The authors also pointed out that the trend is inconclusive because of low methanol concentrations achieved. This report was important because it showed that the formation of methanol was probably limited by a non-electrochemical process.

It is worth mentioning that Cu-Zn-Al mixed oxides and Cu_2O catalyst are based on the same copper catalyst. Both should be reduced to copper at the potentials applied during electrochemical reduction of CO_2 . The presence of zinc oxide in Cu-Zn-Al mixed oxides is reportedly to reduce light products, while aluminium oxide serves as a support (English et al., 2004).

2.1.4 Products obtained in non-aqueous electrolytes

The low solubilities of CO_2 in water are thought to be partly responsible for the limited rates of reduction. Therefore, some research groups conducted electrochemical reduction of CO_2 in hydrocarbon solvents with higher CO_2 solubilities such as methanol and propylene carbonate. Furthermore, hydrogen evolution was less problematic in such systems. However, distorted product distributions and even additional products such as oxalate and glyoxylate should have been expected due to lower proton availability.

CO₂ reduction at Cu in methanol generally yields products similar to those obtained in aqueous electrolytes such as methane, ethylene, formic acid and carbon monoxide, although with slightly different distribution. Kaneco et al. (2002) studied effects of different Li salts added to methanol as supporting electrolytes and found that they strongly affected the product distribution. The highest current efficiency of methane was 71.8% at 27 mA cm⁻² with LiClO₄ as the supporting electrolyte. The formation of the products was described through the same mechanisms for the reduction in aqueous electrolytes. The formation of hydrogen-containing products indicated that methanol donated protons during the reduction and was also likely to be oxidised at the anode.

An aprotic solvent, i.e. propylene carbonate, yields completely distorted product distributions when used as an electrolyte in CO₂ reduction. Ito et al. (1985) studied the reduction at Pb, Sn, In and Zn electrodes in propylene carbonate and observed, apart from CO and formic acid, oxalic acid, glyoxylic acid and glycolic acid. The formation of oxalate is generally described as presented earlier in Figure 2-1. Further reduction produces glyoxylate as shown in Figure 2-4.

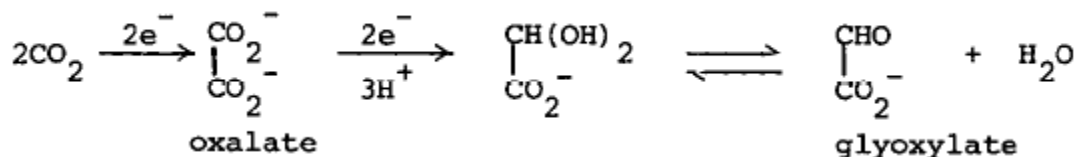


Figure 2-4: Formation mechanism of glyoxylate (Eggins et al., 1988)

CO₂ reduction in aprotic solvents is highly sensitive to water contents. Ikeda, Takagi and Ito (1987) studied CO₂ reduction at Pb and In electrodes in 0.1 M tetraethylammonium phosphate/propylene carbonate. They showed that the main products shifted completely from oxalate to formate for Pb and from CO to formate for In as water contents were increased from 0 to 4.2 per cent by weight.

Oxalate and glyoxylate can also form in aqueous solutions with the surface of the cathode emulating the low proton availability in aprotic solvents. When CO₂ was reduced electrochemically in aqueous solutions of tetraalkylammonium salts, these products were obtained (Eggins et al., 1988). The cations of tetraalkylammonium salts dehydrated the surfaces of cathodes, lowering proton availability. The formation of these species, which normally form in aprotic solvents, in aqueous solutions was then observed.

2.2 Factors affecting product distributions from CO₂ reduction at copper cathodes

Copper electrodes are known to produce various energy-rich fuels such as methane, ethylene and alcohols. However, having a single product with its selectivity reaching 100% is often highly appreciated for industrial reasons. Therefore, tailoring product distributions is also a popular topic. The studies have also revealed some aspects of the complex reaction mechanisms.

Hori et al. (1989) studied formation of hydrocarbons in CO₂-saturated aqueous solutions of KHCO₃ at various concentrations from 0.03 M to 2 M. The results are presented in Figure 2-5. With increasing concentrations, the charge yields of methane increased before starting to drop at approximately 0.4 M, while those of ethylene decreased steadily. On the other hand, those of hydrogen evolution increased exponentially across the entire range of concentrations studied. They explained these results in terms of local pH at the surfaces of Cu electrodes. OH⁻ ions produced from the reduction of CO₂ (Figure 2-1) and water were the cause for local increases in pH. However, it was mitigated by HCO₃⁻ in solutions. At low HCO₃⁻ concentrations, the kinetics of OH⁻ elimination were slow. This caused the local pHs at the cathode surface to be significantly higher than those in the bulks. The high local pHs suppressed hydrogen evolution and increased the total current efficiencies of CO₂ reduction. In contrast, the elimination of generated OH⁻ ions by HCO₃⁻ ions at higher concentrations was more effective, resulting in smaller differences in pH between the bulks and the cathode surface. Therefore, hydrogen evolution became more intense and CO₂ reduction occurred at lower efficiencies. The increases in the production of methane with increasing KHCO₃ concentrations in the low concentration range were thought to show that proton availability enhanced methane formation. The production of ethylene was believed to be inversely proportional to methane production due to the competition for the same intermediate (Figure 2-2).

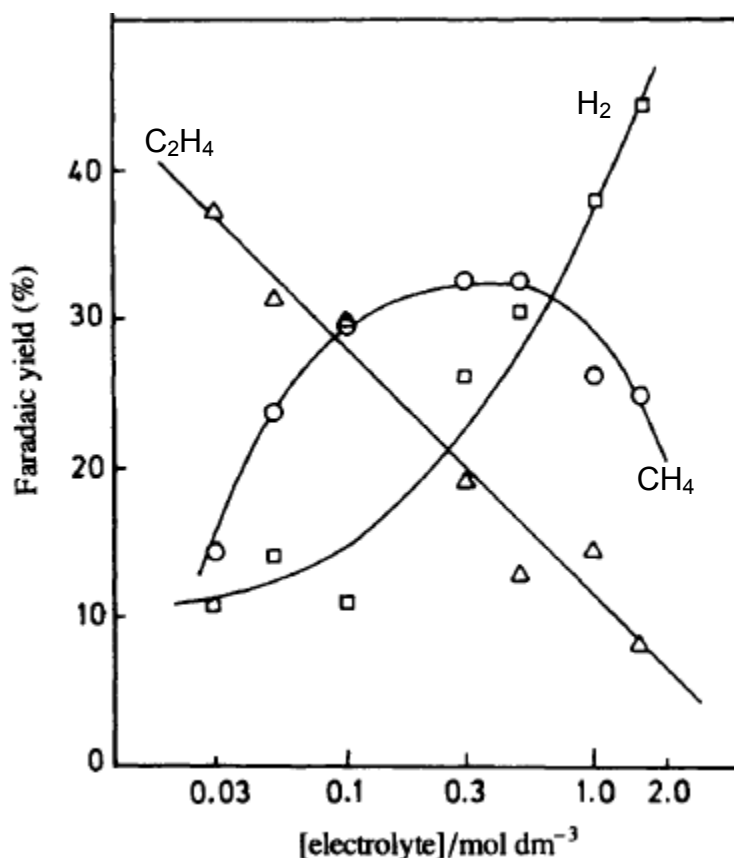


Figure 2-5: Effects KHCO_3 concentrations on faradaic yields of hydrocarbon products from electrochemical reduction of CO_2 at Cu electrodes (Hori et al., 1989)

The effect of cations on product distributions from electrochemical reduction of CO_2 at copper electrodes was studied by Kyriacou and Anagnostopoulos (1993). The catholytes in the study were aqueous solutions of LiHCO_3 , NaHCO_3 , KHCO_3 , CsHCO_3 and NH_4HCO_3 . The latter was found to severely inhibit CO_2 reduction and gave hydrogen as the main product, probably due to the acidic nature of ammonium ions. The current efficiencies of CO_2 reduction increased with the cations in this order: Li^+ , Na^+ , K^+ and Cs^+ . This effect was thought to be attributed to the hydration numbers of these cations. Smaller ions generally have larger hydration numbers, having larger total radii than larger ones. Therefore, larger cations were closer to the electrode surface, increasing the potential at the outer Helmholtz plane. According to equation E1-17, the reduction of neutral CO_2 molecules was hence faster in the presence of larger cations. The dependence of the product ratios of methane to ethylene on cation radii was also observed. Schizodimou and Kyriacou (2012) studied the effect of multivalent cations such as Ba^{2+} and La^{3+} on the current efficiencies of CO_2 reduction at electrodes made of a Cu-Sn-Pb alloy and found that the current efficiencies increased as the charges of the cations were increased. The

results were also discussed in terms of the effect of the ions on the potential at the outer Helmholtz plane.

The nature of an electrolyte also affects product distributions. The results from CO₂ reduction at copper cathodes in methanol by Kaneco et al. (2007) showed that this system tended to produce methane at current efficiencies as high as 60%, which was higher than those achieved from aqueous systems. Nevertheless, the current densities obtained from this system were very low; only 5 mA cm⁻² was obtained at -3.0 V (AgCl|Ag).

2.3 Electrode designs

Apart from the kinetic aspects of CO₂ reduction, there are also parallel developments on the engineering side. Current densities and current efficiencies can often be improved by proper design of electrodes. Increasing electrode surface areas is a widely adopted means to increase the current densities. This is often accompanied by forced flows of electrolyte solutions to enhance mass transport of CO₂, which directly affects partial current densities and current efficiencies.

2.3.1 Electrodes for aqueous systems

Packed-bed electrodes can be used instead of planar electrodes to increase active surface areas without drastic changes in the kinetics. Köleli et al. (2003) studied reduction of CO₂ at beds of Pb and Sn granules submerged in aqueous electrolytes. CO₂ gas was introduced to the cell constantly through glass frit supporting the beds. Better performances were obtained from Pb, but still inferior to that of a planar electrode in Table 1; the current densities failed to reach 5 mA cm⁻² and the highest current efficiency of 90% was achieved at a current density of only 0.8 mA cm⁻². In contrast, experiments conducted by Li and Oloman (2007) with packed beds of Sn granules with flowing electrolyte solutions and CO₂ gas showed markedly better results. Current efficiencies above 60% at superficial current densities as large as 3 kA m⁻² were reported.

Metal powders can be bonded to ionic membranes to form membrane-electrode assemblies (MEA) with larger true surface areas. Narayanan et al. (2011) fabricated Pb and In MEAs and used them as cathodes for CO₂ reduction to formate. CO₂-saturated aqueous solutions were pumped across the surface of the MEAs to enhance mass transport. At 40 mA cm⁻², the cumulative current efficiency over time

dropped rapidly from 80% to 30% within 30 minutes of the electrolysis. However, they successfully simulated the decrease in terms of slow diffusion rates of CO₂-related species within the porous structure. Dufek, Lister and Mclwain (2011) conducted similar experiments with commercially available Ag-MEAs. Separate streams of electrolytes and CO₂ gas were pumped across the electrode surface to facilitate mass transport. A current efficiency of 90% was achieved at 30 mA cm⁻². MEAs can also function with only gaseous mixtures on the cathode sides as demonstrated by Delacourt et al. (2008) in their study of the effect of different ionic membranes on the performances of MEAs. Another variant of MEAs can be produced by electroless plating of metals on ionic membranes, but this alternative method did not appear to yield better performances. MEAs of this type were fabricated with Au (Maeda et al., 1987), Cu (Cook et al., 1988, Komatsu et al., 1995) and Ag (Hori et al., 2003).

The performance of an MEA is sensitive to the type of the membrane and the electrolyte on the other side of the cathode if used. Cationic membranes often give poorer performance because protons are transported to the cathodes for intense hydrogen evolution (Delacourt et al., 2008) or, if alkaline cations are present, they migrate to the cathodes, form basic salts and then peel the cathode layers off the MEAs (Hori et al., 2003). Anionic membranes do not present these problems but CO₂ can escape through the membranes by turning into bicarbonate or carbonate and migrating away from the cathodes (Delacourt et al., 2008).

Porous layers of catalysts can be fabricated without any membrane and used as cathodes for CO₂ reduction. Mahmood, Masheder and Harty (1987) experimented on CO₂ reduction at lead-, indium- and tin-impregnated gas-diffusion electrodes (GDE). Formate was obtained as the main product and 100% current efficiencies were observed at lead GDEs at 115 mA cm⁻². Hara and Sakata (1997) conducted experiments on CO₂ reduction at GDEs made of platinum deposited on carbon-black gas-diffusion layers at higher pressures. Methane was obtained as a main hydrocarbon product from this system. At a CO₂ pressure of 20 atm, the current efficiency of methane was 39% at 500 mA cm⁻². This is contrary to the common knowledge that CO₂ in aqueous solutions is virtually not reduced at Pt cathodes; almost all of the charges passed into the cell result in hydrogen evolution. It appeared that the pressure of CO₂ also affected product distributions.

2.3.2 Electrodes for solid-oxide systems

MEAs can be constructed with solid-oxide electrolytes instead of polymeric membranes, but the requirement of high temperatures of at least 500 °C to activate conductivities poses energy concerns. Nonetheless, such temperatures also supply a large portion of energy to the activation barriers of CO₂ reduction, lowering a demand on electrical energy. Huang and Chou (2009) successfully reduced CO₂ to CO in solid-oxide cells with yttria-stabilised zirconia (YSZ) as the electrolytes and Cu-added La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} as the cathodes at temperatures higher than 800 °C. Though copper is known to produce hydrocarbons in aqueous systems, none could be expected because of the lack of proton sources in their experiments. Another similar work was also done by Bidrawn et al. (2008).

2.4 Electrode deactivation

Electrode deactivation has been occasionally reported during electrochemical reduction of CO₂. DeWulf, Jin and Bard (1989) observed formation of black graphitic carbon films on copper cathodes during CO₂ reduction and decreases in its current efficiencies over time. Kyriacou and Anagnostopoulos (1992) also observed similar decreases in the current efficiencies of CO₂ reduction at copper electrodes. Yano et al. (2002) studied electrochemical reduction of CO₂ at silver electrodes and observed rapid decreases in its current efficiencies over a period of 5 hours of electrolysis. Their analysis of the electrodes after experiments showed that graphitic carbon particles had formed on the electrode surfaces. Co-deposition of silver during CO₂ reduction was found to partially alleviate the problem. Hori et al. (2005) found that heavy-metal impurities present in reagents were deposited on electrodes during CO₂ reduction, thus also taking part in the poisoning of the electrodes, and that pre-electrolyses of solutions to remove the ions significantly improved electrode activity. Furthermore, Chiacchiarelli et al. (2012) described rapid degradation of tin electrodes during hydrogen evolution due to the deposition of alkali metal ions present in electrolytes.

2.5 Modelling works

Only a few papers report mathematical modelling of electrochemical reduction of CO₂, probably due to the complexity of the systems, which always involve hydrogen evolution in addition to CO₂ reduction if a proton source is present. Attempts to

model CO₂ reduction at copper cathodes in particular are further discouraged by the number of expected products. Despite this difficulty, Gupta, Gattrell and Macdougall (2006) developed only a mass transport model for experimental data of CO₂ reduction at copper cathodes from another research group in order to examine the relationships between local concentrations of species in solutions and kinetics of CO₂ reduction.

More works on modelling can be found for CO₂ reduction at cathode materials other than copper. Both mass transport and kinetic model were developed for the reduction of CO₂ to CO at silver and gold electrodes (Delacourt et al., 2010) and their GDEs (Delacourt & Newman, 2010). General mathematical expressions for the kinetics of CO₂ reduction at different cathode materials were proposed (Vassiliev et al., 1985). A model was also successfully developed to predict the performance of an electrochemical reactor for the reduction of CO₂ to formate at tin (Li & Oloman, 2007).

2.6 Evaluation of some products as fuels

Evaluating fuels is a subjective task due to varying criteria amongst different applications. Quantitative properties of fuels may be directly compared, but qualitative characteristics are differently appreciated depending on the nature of processes and some of them sometimes take priority over the former. The following discussions will focus on some common quantitative properties of fuels: heat of combustion, specific energy, energy density and hydrogen atom density. The values of some common products are presented in Table 2.

Table 2: Properties at 298.15 K and 1 bar (25 K and 100 bars for liquid hydrogen) of some fuels commonly produced from electrochemical reduction of CO₂¹, including those of gasoline (Eyidogan et al., 2010)

Fuel	Heat of combustion / kJ mol ⁻¹	Specific energy / MJ kg ⁻¹	Energy density / MJ L ⁻¹	Hydrogen atom density / mol _H L ⁻¹
Gaseous hydrogen	-285.8	141.8	0.01	0.08
Liquid hydrogen	-285.8	141.8	10.85	75.89
Formic acid	-254.6	5.5	6.75	53.01
Carbon monoxide	-283.0	10.1	0.01	0.00
Methanol	-725.7	22.6	17.81	98.16
Ethanol	-1367.6	29.7	23.42	102.76
Methane	-890.7	55.5	0.04	0.16
Ethylene	-1411.2	50.3	0.06	0.16
Gasoline	-4160.3	42.6	31.98	107.78

2.6.1 Characteristics of heat of combustion, specific energy, energy density and hydrogen atom density

Probably the most fundamental property of a fuel is the heat of combustion, which is directly related to the formation reaction of the fuel. Consequently, the number is generally in proportion to the number of electrons participating in the formation reaction of the fuel; -120 kJ per mole of electrons is often a good estimate. For example, a mole of formic acid requires 2 moles of electrons and hence its approximate heat of combustion is -240 kJ mol⁻¹, which is close to the actual value of -254.6 kJ mol⁻¹.

The specific energy and the energy density of a fuel are useful indices that take into consideration physical properties of the fuel. Different processes and devices have different criteria for the two properties. For example, a design of a stationary generator may specify a fuel with higher energy density to minimise its space requirement but place fewer restrictions on the fuel's weight. On the other hand, both weight and space are limited for vehicles. These indices have less obvious relationships with formation reactions of fuels, especially the energy densities, which also depend on compression. A fuel with larger heat of combustion does not necessarily have larger specific energy; the values of ethanol and methane are a good example. Nevertheless, in general, a fuel with fewer oxygen atoms tends to

¹ Raw values obtained from or calculated by an online application in NIST Chemistry WebBook: <http://webbook.nist.gov/chemistry/>

have a higher value of specific energy because an oxygen atom can be considered as a 'dead weight' that is sixteen times the weight of a hydrogen atom. Therefore, reduction that results in removal of oxygen atoms is more economical than that which results in addition of hydrogen atoms in this sense. This can be seen clearly between formic acid and carbon monoxide, which have comparable values of heat of combustion but the specific energy of CO is almost double of that of formic acid. The values of methanol and methane are another good example; both molecules have the same number of hydrogen atoms, but the absence of oxygen atom in methane results in its specific energy being more than double of methanol's, while its heat of combustion being larger in a much smaller proportion. However, complete removal of oxygen from a molecule is equivalent to termination of its polarity, resulting in weak intermolecular interactions. A fuel with exceptionally high specific energy therefore tends to be gaseous at room temperatures and atmospheric pressure unless its molecular weight is sufficiently large. The value can be increased by compression but the process consumes additional energy and the compressed gas also presents a hazard.

The hydrogen atom density of a fuel is useful if it is to be fed into a proton-exchange membrane (PEM) fuel cell. As each electron extracted from a fuel is accompanied by a proton passing through the membrane, the number of protons in the fuel is an approximate index of the fuel's energy content. In other words, hydrogen atoms in a fuel can be viewed as what actually contain energy. It is also interesting that the hydrogen atom densities of hydrocarbons are higher than that of gaseous hydrogen and the values of methanol and ethanol are even higher than that of liquid hydrogen. In addition, the energy densities seem to have a strong relationship with hydrogen atom densities. Therefore, carbon and oxygen atoms in a hydrocarbon could be considered as molecular binders that hold hydrogen atoms closer at the expense of its specific energy due to the atomic mass of carbon and oxygen atoms. Hence, CO₂ reduction is also called chemical storage of hydrogen.

2.6.2 Hydrogen versus carbon-based fuels

High concentrations of CO₂ gas are necessary for its efficient conversion due to current technological limitations. Thus, the process currently cannot be used to sequester CO₂ from the atmosphere and is limited to close systems in which CO₂ produced from oxidation of fuels are relatively pure. On these grounds, it is

questionable whether CO₂ reduction presents any advantage over water electrolysis whereby a 100% current efficiency for hydrogen evolution can be achieved relatively easily. Consideration of the fuels that the two processes can produce may reveal additional aspects for justification.

Hydrogen is almost unavoidably produced from electrochemical processes having proton sources in contact with cathodes, including electrochemical reduction of CO₂ in aqueous systems. It is an efficient fuel due to its simple oxidation kinetics, especially in PEM fuel cells, which often yield highest power densities from the fuel (Yeom et al., 2005). It is frequently marketed as a clean fuel that produces water as the only combustion product. Technically, its specific energy is probably highest amongst those of combustible fuels, but the low energy density and various storage issues including high diffusivities in many materials and incompatibility with some metals limit its successful implementations.

Carbon-based fuels have significantly lower specific energy but their generally higher energy densities and fewer restrictions on their storage are highly appreciated. The benefit in switching from gaseous hydrogen to a carbon-based fuel may be judged by the factors by which the specific energy becomes smaller and the energy density becomes larger. For example, the former and the latter factor of methane are respectively 2.6 and 4, which are comparable, whereas those of formic acid are respectively 26 and 675, which are of different orders of magnitude. It is also an observed feature that the latter factor of a liquid carbon-based product is always larger than the former by at least an order of magnitude. Therefore, liquid carbon-based fuels are more attractive than gaseous ones under this criterion. Liquefying the gases is an option but all of them in Table 2 also require cooling, which further complicates their storage facilities. Furthermore, the gaseous carbon-based products in Table 2 require elevated temperatures to activate, while the liquid fuels can be oxidised in dedicated fuel cells operated at room temperatures. Electrochemical reduction of CO₂ could be considered as superior to water electrolysis in this regard. However, the comparison described earlier does not take into account the concentrations of fuels. Both gaseous products and liquid products are always diluted by the unreacted CO₂ gas and liquid electrolyte solutions, respectively, and therefore purifications may be necessary.

2.7 Conclusions

Electrochemical reduction of CO_2 in aqueous solutions has been extensively explored. Many cathode materials and their products produced in various conditions have been identified. Formation mechanisms of many products have been proposed, though they are still debatable. Emphasis was frequently placed on Faradaic efficiencies of products from CO_2 reduction. The effects of basic parameters, such as electrolytes, types of membranes, potentials, temperatures and pressures, have been studied.

A relatively intensive investigation into the elusive production of methanol was conducted due to its high specific energy and energy density. Contradicting reports indicate unsettled arguments. However, those featuring the production of methanol consistently share low partial current densities.

Low solubilities of CO_2 in water are one of the problems of CO_2 reduction in aqueous solutions. This leads to studies of the reduction of CO_2 in hydrocarbon solvents such as methanol and propylene carbonate, which can absorb more CO_2 than water. The use of aprotic solvents results in additional products and different product distributions, which can revert to those obtained from aqueous systems with small water contamination.

Factors affecting product distributions from copper and copper-based electrodes were studied by many research groups. Local pH, affected by concentrations of buffer species and agitation, appeared to strongly influence the ratios of methane to ethylene. The radii of cations also affected product distributions from Cu cathodes. However, analyses of these results were still limited to qualitative aspects due to the complex product distributions.

Different electrode configurations were fabricated with intent to increase true surface areas of electrodes. Flowing streams of electrolyte solutions and CO_2 gas were always employed to enhance mass transport of CO_2 to these electrodes. Improvements were limited in general despite the increased complexity of the systems.

Properties in terms of heat of combustion, specific energy, energy densities and hydrogen atom densities of some common products obtained from electrochemical reduction of CO_2 were presented. The relationships between fuels and properties

were discussed. Justification for CO₂ reduction as a means to produce fuels based on the benefits of switching from hydrogen to carbon-based fuels was given.

3 Project formulation and outline

The literature survey reveals that a great deal of works have been done on copper mainly because it offers various hydrocarbon products. However, the complexity of the formation mechanisms of the products discourages modelling attempts. On the other hand, successful mathematical expressions for the current densities of CO₂ reduction at Au, Ag and Sn were proposed, though with little or no regard to possible product distributions.

Table 1 shows that most cathode materials suitable for CO₂ reduction always produce at least two carbon-containing products, notably formate and CO. The splits between the two have always been ignored, as opposed to the extensive studies of the product distributions from copper cathodes. Careful examinations may reveal the dependence of the production ratios of formate to CO on some process variables, introducing a means to shift the product preferences.

The metals that produce formate as a main product are of interest according to the comparison between gaseous and liquid fuels described in section 2.6.2. Those that do not possess extreme preferences for formate are only indium, tin and cadmium and therefore good candidates for the purpose. However, the rarity of indium and the toxicity of cadmium render them unsuitable, leaving tin as the only choice.

Local pH was shown to be a factor in determining the production ratios of methane to ethylene from the reduction of CO₂ at copper cathodes and thereby possibly influences the formate-CO splits from tin electrodes. Electrode potential also likely affects the product distributions. If they do, the relationships will be investigated. Mathematical expressions will be derived if it is possible.

The literature survey also shows that different electrode designs were invented for scale-up of electrochemical cells including MEAs, GDEs, and packed-bed electrodes, but none employed the large specific surface areas of graphite felt. It can be used as a structure on which a metal is deposited to make an electrode with a high superficial surface area. An electrode of this design should offer increased superficial current densities, while mass transport of CO₂ can be enhanced by pumping CO₂-saturated electrolyte solutions through the porous electrode.

Furthermore, the metal layer can be stripped electrochemically with little or no damage to the inert graphite fibres as a means to address the deteriorating performance frequently experienced in CO₂ reduction at many metal electrodes due to surface poisoning.

The first challenge is expected to be obtaining good coverage of tin on graphite felt, for which a suitable deposition method will be developed. During operation, the mass transport of CO₂ will also have to keep up with its increased consumption rates due to the higher surface areas of three-dimensional electrodes. Therefore, the effect of electrolyte solution flow rates on the performances of the electrodes will also be studied.

4 Electrochemical cell design

4.1 Experimental requirements

The kinetic study of CO₂ reduction at planar tin cathodes will involve multiple electrolysis batches of electrolytes of different pHs at different electrode potentials. The experimental time of each batch should be as short as possible to minimise electrode deactivation described in section 2.4, but not too short that product concentrations are too low to be detected. This leads to a requirement that the electrolyte volume must be small in relation to the electrode surface area. This criterion excludes continuous-flow experiments as they require extra volumes of electrolytes to fill a reservoir, tubes and a pump; batch experiments are preferred in this regard. The electrode area must be known and remain the same in all experiments. Products forming at the cathode must not be allowed to reach the anode lest they be oxidised. Electrolyte solutions should be circulated in some manner during electrolyses to enhance mass transport of various species in solutions. Samples of the liquid and the gas generated from the cathode from each batch will be analysed for the amounts of formate and carbon monoxide, respectively. The experiments with tinned graphite felt electrodes will in general be similar to those with planar electrodes, but the main difference will be that electrolyte solutions are required to flow directly through the porous electrodes.

4.2 Concepts

The planned experiments call for a small electrochemical cell that is chemically stable in acidic and slightly basic aqueous solutions and facilitates a short experimental time for each batch. The cell should have dedicated slots for a working electrode, a counter-electrode and a reference electrode so that the relative distances between pairs of the electrodes remain the same in every experiment and also that the cell can be assembled and disassembled in a short time. The working electrode will be masked in a way that the exposed area is known and constant. The anode and the cathode must be placed in two separate compartments partitioned by an ionic membrane to prevent the products from reaching the anode. The equipment will have a quantifiable means to enhance mass transport of various species in electrolytes. The cell must also facilitate efficient collection of samples. The reactor

design should also make provision for the experiments with tinned graphite felt electrodes so that the same cell can be used for both series of experiments, hence incorporating an inlet and an outlet for flowing electrolyte solutions.

4.3 Design

PVDF is chosen as cell material due to its chemical stability. PTFE was considered at first but eventually discarded because of its inferior robustness. Three drilled blocks of PVDF constitute the main body of the cell as shown in Figure 4-1. The left block served as the compartment for the counter-electrode, which is made of RuO₂-coated titanium mesh; the hole on the top is for an electrical lead from the counter-electrode. The middle and the right block comprise the compartment for the working electrode, which is actually a piece of tin foil and can be held between the two. An electrical lead can be connected to the foil at its extra length. The exposed surface of the tin foil can be limited by a piece of gasket placed between the working electrode and the middle block. A small magnetic stirrer can be placed inside the middle block and rotated to enhance mass transport. The top surface inside the middle block is tapered to direct gases generated at the electrode to the drilled hole at the top, which leads to a gas collector. Drilled into the side of the middle block is the port for the reference electrode, which is a small AgCl|Ag reference electrode for electrochemical quartz crystal microbalance (EQCM) cell from Metrohm. A small-diameter hole is drilled from the inside of the block where it is expected to be closest to the working electrode to connect the port to the inside of the cell, i.e. to form a Luggin probe. The reference electrode is secured to the middle block by a plug also made of PVDF. The right block serves only as a holder for the working electrode during experiments with the planar electrode but also contains an inlet for electrolytes during experiments with porous electrodes, which will be similarly placed between the middle and the right block. Flowing electrolyte solutions exit the cell through an outlet at the middle block opposite the port for the reference electrode. Concentric holes were drilled at the four corners of each block for bolts. The actual assembled cell is shown in Figure 4-2 and the plug for the reference electrode is in Figure 4-3.

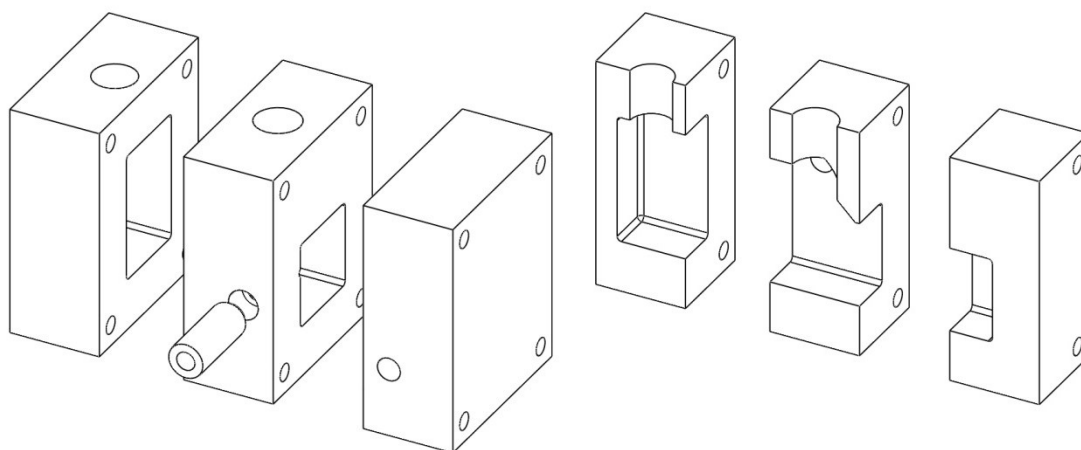


Figure 4-1: Cell designed for electrolyses of small electrolyte volumes with cross-sectional view on the right

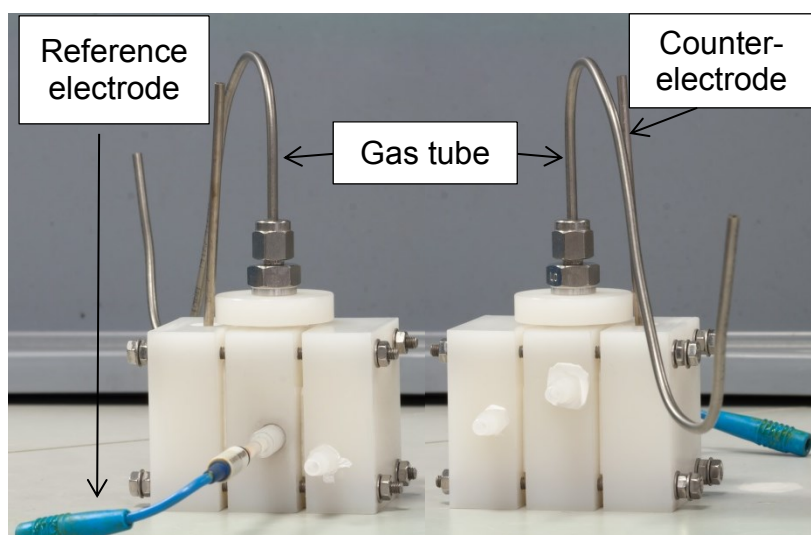


Figure 4-2: Photographs of cell; left: front, right: back



Figure 4-3: Plug for reference electrode

Combinations of ionic membranes and anolytes are believed to affect the experiments. Electrochemical reduction of CO₂ in aqueous solutions always consumes protons either directly or indirectly; the latter occurs through the direct reduction of water and leaves hydroxide ions in electrolytes. To maintain pH, the catholyte should be resupplied with protons from anolytes; this requires a cationic membrane, preferably Nafion due to its robustness. The anolyte must also be acidic without any cation, transportation of which to the other side of the membrane increases catholyte pH.

Liquid samples are analysed with an HPLC equipped with a Thermo Scientific's HyperREZ XP Organic Acids column to determine amounts of formate and other possible soluble products. Electrogenated gases are collected by water displacement in a burette with a septum. The amounts of gaseous products can be determined from their concentrations analysed by a GC equipped with a Restek's ShinCarbon ST 100/120 mesh micropacked column and the total volume of the collected gases. This is different from the conventional method by which a gaseous mixture is constantly purged from a reactor by a stream of CO₂ and formation rates of products are determined from their concentrations and the total gas flow rate. This method allows only infrequent determination of pseudo-instantaneous formation rates due to a typically long run time of a GC, whereas the method employed here yields total amounts of gaseous products produced during an experiment, being consistent with how liquid products are analysed.

4.4 Characterisation of cell mass transport

Mass transport in the cell is enhanced by rotating a 12 mm magnetic stirrer in the middle compartment. It was characterised in terms of the thicknesses of Nernst diffusion layers at different rotation speeds, which are labelled with integers instead of actual values at the motor. The thickness of a Nernst diffusion layer was derived from the limiting current density of the reduction of ferricyanide at each rotation speed through:

$$D \frac{c}{\delta} = \frac{j_L}{F} \quad \text{E4-1.}$$

The solutions of ferri/ferrocyanide for this characterisation consist of 0.03 M of each species with 0.5 M Na₂SO₄ as a supporting electrolyte. The cyclic voltammogram of

a quiescent solution is shown in Figure 4-4. The negative-going potential scan started from 0.8 V to -0.8 V, at which the scan reversed to the start potential. The voltammogram exhibited the classic shape expected from reversible redox couples.

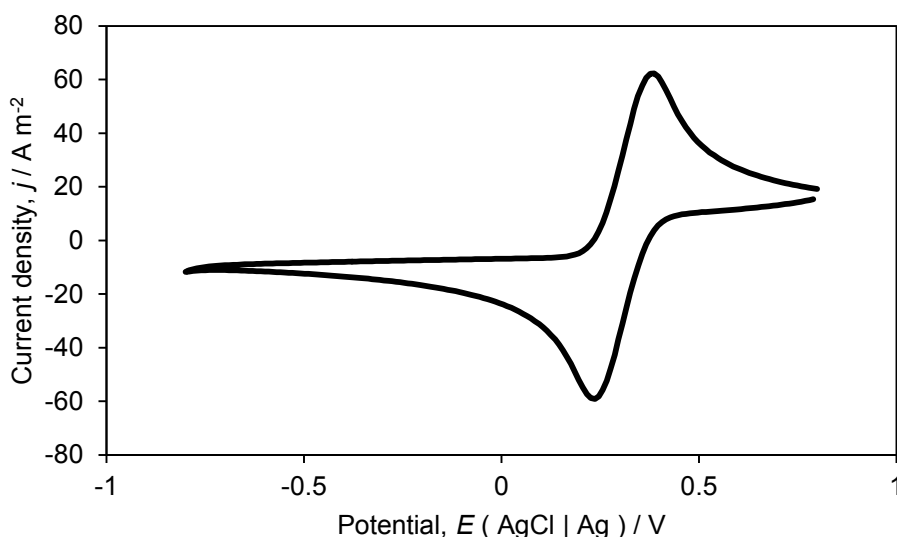


Figure 4-4: Cyclic voltammogram of Pt | quiescent aqueous solution containing 0.03 M ferricyanide, 0.03 M ferrocyanide and 0.5 M Na₂SO₄ at 50 mV s⁻¹

Cyclic voltammetry was then conducted with enhanced mass transport by rotating the magnetic stirrer at three different speeds. The results are shown in Figure 4-5. The limiting current densities of the reduction and oxidation were close because the concentrations of both species were equimolar and the diffusion coefficients are similar. The rotation speed at number three was highest before the magnetic stirrer started to move chaotically in the middle compartment. This rotation speed was therefore used in all subsequent experiments at planar electrodes. The limiting current density at this rotation speed was 58 A m⁻² as seen in Figure 4-5. The thickness of the Nernst diffusion layer calculated from E4-1 with the limiting current density and a diffusion coefficient of $7.28 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Eroğlu et al., 2011) was $3.63 \times 10^{-5} \text{ m}$.

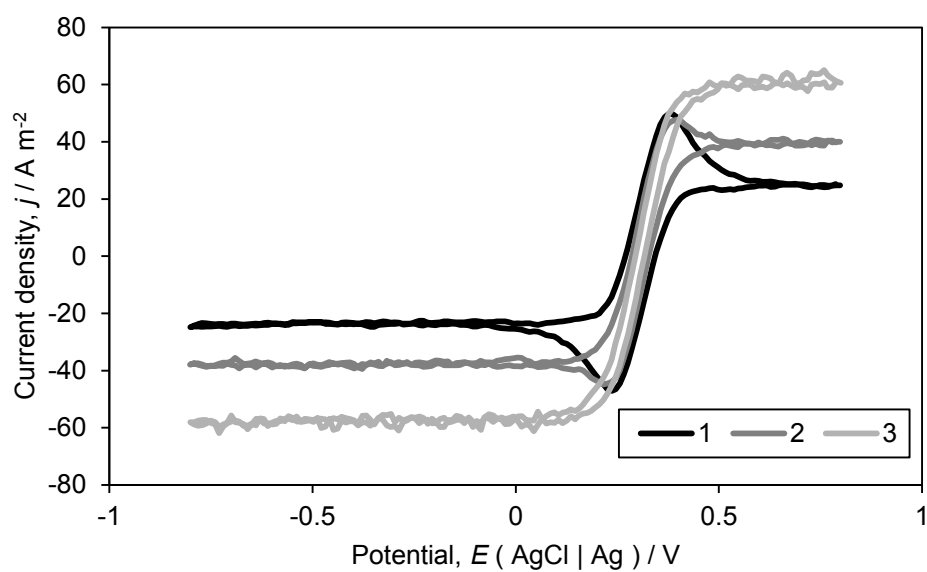


Figure 4-5: Cyclic voltammograms of Pt in aqueous solutions containing 0.03 M ferrocyanide, 0.03 M ferricyanide and 0.5 M Na_2SO_4 stirred at three different rotation speeds labelled with integers

5 Electrochemical reduction of CO₂ in aqueous solutions at planar tin electrode

The main purpose of this chapter was to determine whether formation ratios of carbon monoxide to formate can be changed and, if they can, to understand the causes. Electrode potential and pH were the two variables most likely to affect the product ratios as suggested by various reports and were the focus of this chapter. The studies were conducted by multiple batches of electrolyses of CO₂-saturated aqueous solutions of different pHs at different electrode potentials. Formate and carbon monoxide were detected as the only main products from CO₂ reduction at tin and the formation ratios of CO to formate were found to follow a systematic trend.

5.1 Experimental details

5.1.1 Electrolytes

pH was controlled by a number of aqueous buffer solutions with the concentrations of both the acids and the bases kept above 0.1 M in most cases so that local concentrations of protons at the electrode do not deviate excessively from the bulk values during electrolyses. This criterion limited the number of pHs that can be prepared to three values: 2.9, 5.9 and 7.8, obtained from 0.1 M H₃PO₄/1 M NaH₂PO₄, 1 M NaH₂PO₄/0.4 M Na₂HPO₄ and 0.5 M NaOH saturated with CO₂, respectively.

5.1.2 Sn electrode preparation

A piece of 0.5 mm thick Sn foil (Sigma Aldrich, 99.998%) was used as the working electrode. The foil was cleaned electrochemically in 70% HClO₄ at 0.5 V (SCE) for 20 seconds prior to each experiment in order to remove impurities from the electrode surface. The foil was then rinsed with high purity water and dried under a stream of nitrogen. The same Sn foil was used in every experiment.

5.1.3 Cell assembly and electrolysis

10 ml of a catholyte was sparged with CO₂ for 15 minutes, which was found to be adequate to saturate any aqueous solution studied in this project. The solution was then poured into the middle compartment of the cell, where it was further sparged

with CO₂ for 5 minutes, during which 10 ml of 10 mM H₂SO₄ was poured into the counter-electrode compartment. The sparger was removed and the gas tube was screwed to the middle compartment immediately afterwards to minimise air contamination. The end of the tube was submerged in a water bath filled with water and positioned in the water-filled burette with a septum. Electrolyses were then performed at constant potentials for 600 s.

5.1.4 Corrections of measured electrode potentials

An uncorrected electrode potential measured against a reference electrode always contains a potential drop between a Luggin probe and a working electrode. The potential drop follows Ohm's law and is therefore larger at larger current densities. The resistances of the solutions between the two points were measured with electrochemical impedance spectroscopy, estimated from the high-frequency intercepts at the real-component axis. A low current density was employed for better accuracy in each solution.

5.2 Results and discussion

Only formate and carbon monoxide were observed as CO₂ reduction products. The partial current densities of CO₂ reduction in aqueous solutions saturated with CO₂ at different pHs were calculated from the two products and are plotted against potential in Figure 5-1. The remaining partial current densities were attributed to hydrogen evolution.

Before any further analysis was performed, the local concentrations of CO₂ at the electrode were estimated to ensure that the experimental results were not limited by mass transport of CO₂. The calculation showed that the local concentration of CO₂ is 93% of the bulk concentration, 0.034 M at 1 atm CO₂ (Carroll et al., 1991), at the largest observed partial current density of CO₂ reduction, 25 A m⁻², indicating sufficient transport of CO₂.

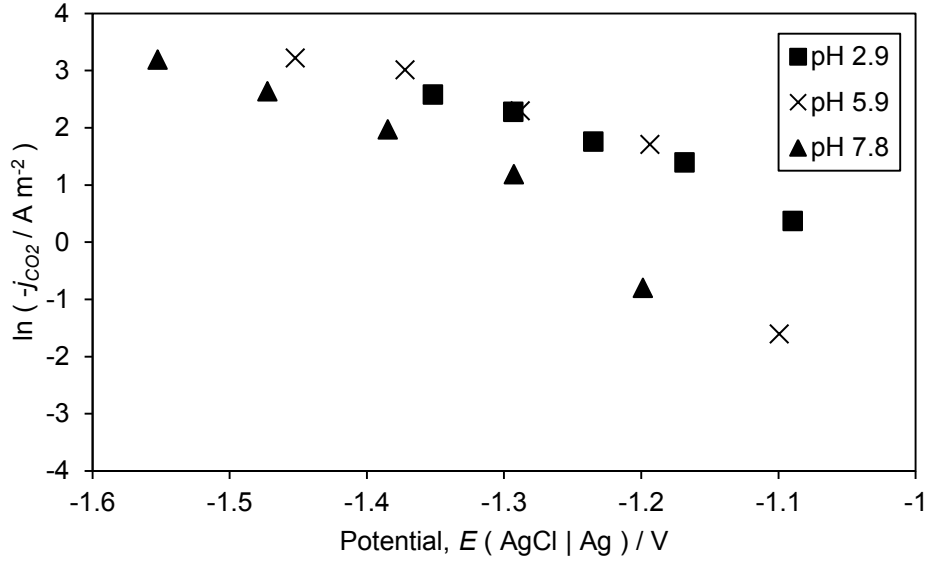
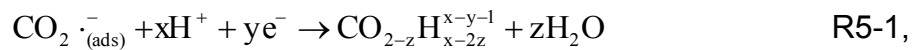


Figure 5-1: Effect of electrode potential and pH on logarithmic partial current densities of CO₂ reduction

The partial current densities of CO₂ reduction shown in Figure 5-1 appeared to be strongly dependent on solution pH, especially at high potentials, at which larger partial current densities were measured at low pH. The differences in the partial current densities observed at different pHs then diminished gradually with increasingly negative potential. Two Tafel regions were also observed, suggesting that the kinetics agreed with the generally accepted scheme of two-step electron transfer:



where x, y and z are integers. The stronger dependence of the partial current densities on pH at high potentials suggested that reaction R5-1 was limiting in this region, while reaction R2-1 was at low potentials.

The results in Figure 5-1 alone might suggest that low pH was a more favourable condition for CO₂ reduction as it offered larger partial current densities. Nevertheless, low pH also contributed even more towards the partial current densities for hydrogen evolution. This was evident from Figure 5-2 in which the total charge yields of CO₂ reduction were generally higher at higher pH. As electrode potential was decreased, the total charge yields of CO₂ reduction at pH 2.9, which were already small, decreased steadily. The values at pH 5.9 increased abruptly

between -1.1 and -1.2 V but decreased at lower potentials. The charge yields at pH 7.8 increased sharply between -1.1 and -1.2 V and, in contrast, continued to increase at lower potentials, though at a slower rate. For the range of conditions studied, the maximum charge yield of 0.67 was achieved at -1.55 V and pH 7.8.

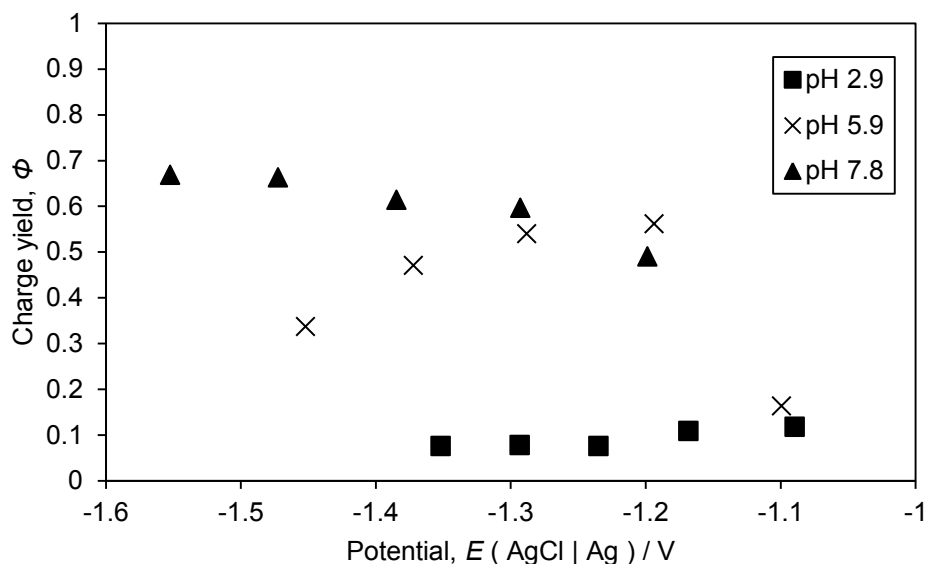


Figure 5-2: Effect of electrode potential and pH on total charge yields of CO₂ reduction

The partial current densities of CO₂ reduction in Figure 5-1 could be separated into two parts: the partial current densities for the formation of formate and carbon monoxide, which are presented in Figure 5-3 and Figure 5-4, respectively. Solution pH appeared to have a strong effect on the formation rates of both products. Decreasing pH generally increased the partial current densities for both formate and CO, but the effect was significantly stronger on the latter. The rates of the formation of CO were generally smaller than those of formate at the same potential but became comparable at pH 2.9 as pH was decreased. The partial current densities of both products exhibited two Tafel regions, but the Tafel slopes of the formation of CO at low potentials appeared to be smaller than those of formate at the same pH.

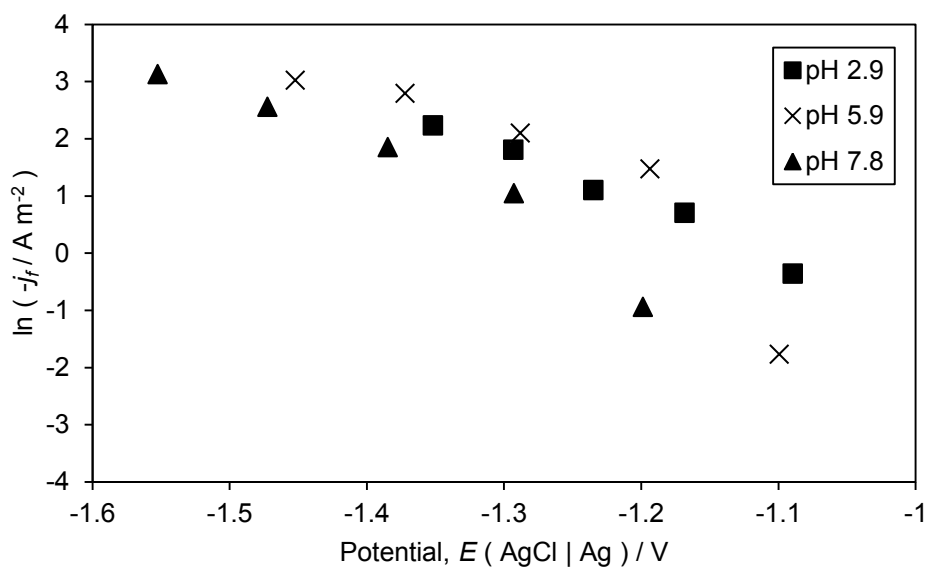


Figure 5-3: Effect of electrode potential and pH on logarithmic partial current densities of formate formation

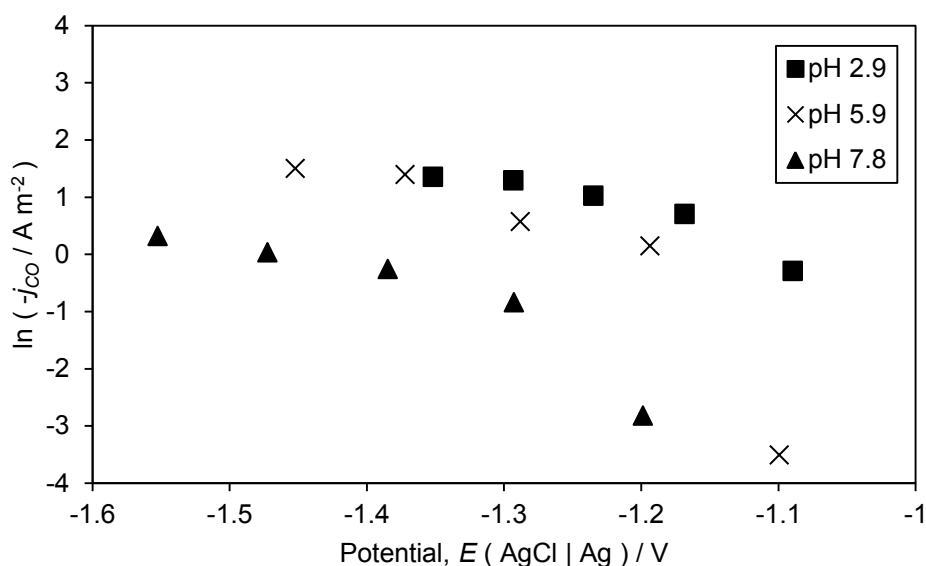


Figure 5-4: Effect of electrode potential and pH on logarithmic partial current densities of CO formation

The charge yields of formate and CO are also presented respectively in Figure 5-5 and Figure 5-6. It can be seen that they also reflected the characteristics of the partial current densities of both products. The charge yields of formate at pH 7.8 were almost identical to the corresponding total charge yields presented in Figure 5-2 due to the relatively small partial current densities of CO formation. As pH was decreased, the charge yields of formate decreased, while those of CO were

relatively unaffected; the values of both products eventually became comparable at pH 2.9.

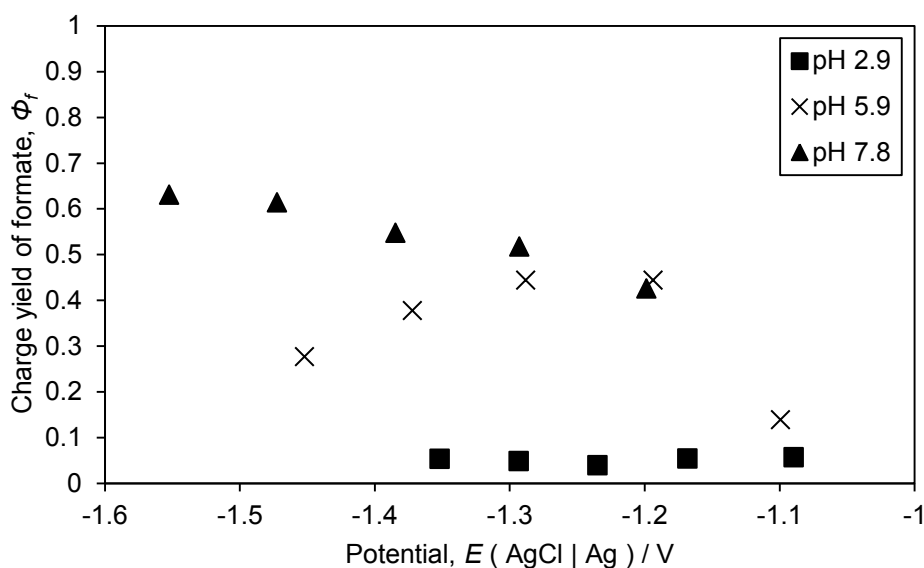


Figure 5-5: Effect of electrode potential and pH on charge yields of formate

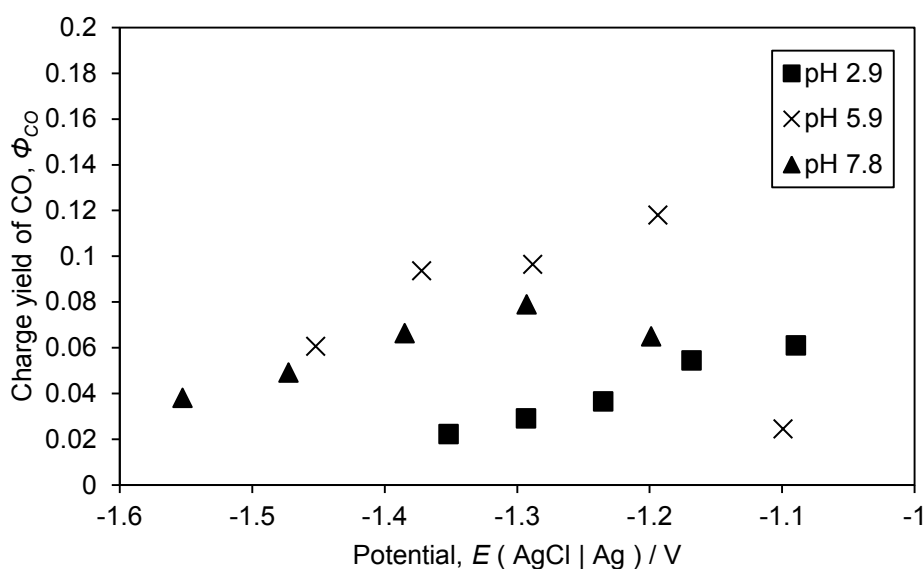


Figure 5-6: Effect of electrode potential and pH on charge yields of CO

The logarithmic formation ratios of CO to formate, as measured by the partial current densities of the products, at different pHs are plotted against potentials in Figure 5-7, which showed that the ratios remained relatively constant at less negative potentials, but became smaller at more negative potentials, with the exception that the ratios at pH 5.9 were relatively independent of electrode potential. The product ratios also seemed to depend on pH; a larger ratio was obtained at a lower pH.

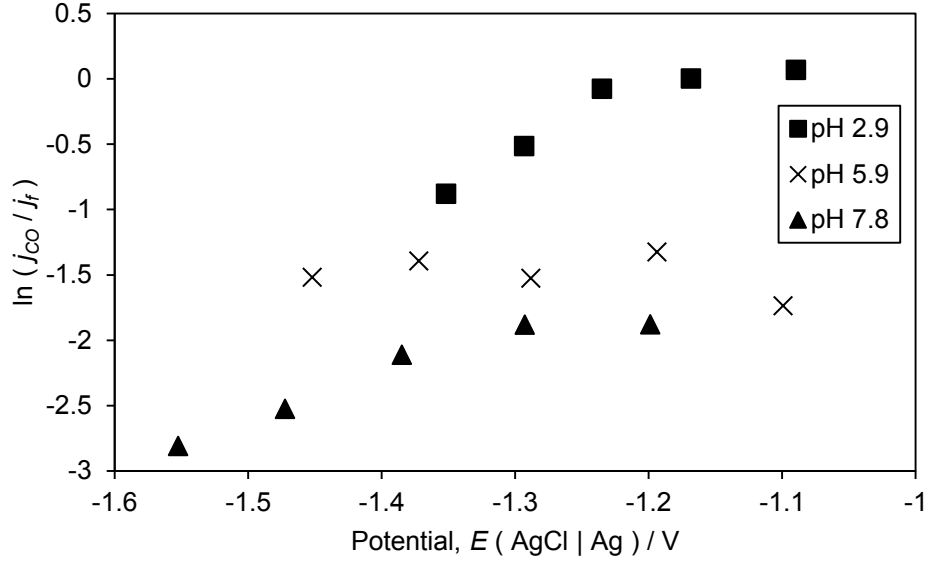
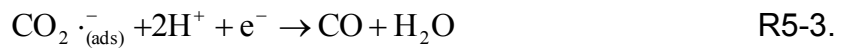


Figure 5-7: Effect of electrode potential and pH on logarithmic formation ratios of CO to formate

Investigation into the dependence of the formation ratios on pH and potential started by considering the kinetics. As the ratios increased with decreasing pH, the stoichiometric coefficient of proton consumption in CO formation was believed to be larger than that in formate formation. At this point, it was assumed that two moles of protons were required for formation of one mole of CO, but only one mole of protons was needed to form one mole of formate. Reaction R5-1 was rewritten for the formation of formate and CO:



The equation for the partial current density for formate formation based on reaction R5-2 with Langmuirian adsorption is:

$$j_f = 2Fk_f a_{\text{H}^+} \theta \exp\left(\frac{-\alpha_f FE}{RT}\right) \quad \text{E5-1}$$

and that for CO formation based on reaction R5-3 is:

$$j_{\text{CO}} = 2Fk_{\text{CO}} a_{\text{H}^+}^2 \theta \exp\left(\frac{-\alpha_{\text{CO}} FE}{RT}\right) \quad \text{E5-2.}$$

The coefficients of 2 appear only outside the exponential functions because both equations are based on only the second step of CO₂ reduction (reaction R5-1). At a

steady state, the current density from the first step (reaction R2-1) equals that from the second step; the coefficient merely adds the current density from the first step.

It then follows that the logarithmic formation ratio of CO to formate is:

$$\ln\left(\frac{j_{CO}}{j_f}\right) = \ln\left(\frac{k_{CO}}{k_f}\right) - \frac{pH}{\log e} - \frac{(\alpha_{CO} - \alpha_f)FE}{RT} \quad \text{E5-3.}$$

Equation E5-3 predicts that the logarithmic formation ratio increases with decreasing pH and is linearly dependent on electrode potential if the value of α_{CO} differs from that of α_f . Therefore, plots of the logarithmic ratio against electrode potential at different pHs were expected to have a single and common gradient. Nonetheless, different gradients were observed in the plots at all pHs in Figure 5-7. The experimental data at pH 2.9 and 7.8 even showed at least two slopes within the same series. The disagreement between the predictions of equation E5-3 and the observed experimental results necessitated an alternative explanation of the gradients.

Different slopes are predicted if the local pH in equation E5-3 deviates from the bulk value due to surface depletion of protons caused by rates of reactions exceeding mass transport rates of protons. With increasingly negative electrode potential, the cathodic partial current densities of both hydrogen evolution and CO₂ reduction increased. The local concentration of protons decreased in response to their increased consumption rate; this created a steeper proton concentration gradient, which in turn increased the proton transport rate. Equation E5-3 predicts a decrease in the formation ratio for an increase in pH and hence the apparent relationship between the ratio and electrode potential could be explained through changes in local pH.

At less negative potentials, the dependence of the logarithmic formation ratios at different pHs on electrode potential was significantly weaker. This was thought to be due to the exponential relationships between rates of electrochemical reactions and potential, which resulted in smaller consumption rates of protons at less negative potentials and hence smaller increases in local pH. Thereby, it could be assumed that the local concentrations of protons at less negative potentials were close to the values in the bulks of the solutions and that the formation ratios in these potential ranges represented the true ratios of their respective bulk pHs. Furthermore, the

slopes of the ratios against electrode potential of essentially zero in these potential regions also implied that α_{CO} probably does not differ from α_f significantly.

These concepts could also explain the largely constant ratios at pH 5.9 when the concentrations of the buffer solutions are considered: 0.1 M H_3PO_4 /1 M NaH_2PO_4 for pH 2.9, 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 for pH 5.9 and 0.5 M NaOH saturated with CO_2 for pH 7.8. The relatively high concentrations of both the weak acid and the conjugate base in the buffer solutions for pH 5.9 allowed the local pH to withstand higher consumption rates without increasing significantly. This resulted in the ratios at pH 5.9 being largely constant over the range of the potentials while the others decreased significantly.

An additional series of experiments was conducted to study the effect of proton mass transport on the product ratios. Figure 5-8 shows the results of the electrolyses of more dilute buffer solutions (0.02 M H_3PO_4 /0.2 M NaH_2PO_4) saturated with CO_2 at pH 2.9, compared with the previous results in the more concentrated buffer solutions. The product ratios from both buffer concentrations at less negative potentials were essentially the same, with slight differences probably due to small variations in the bulk pH of the two buffer solutions. The formation ratios from the dilute solutions started to decrease at a less negative potential than those of the more concentrated solutions. If the mechanism described earlier is correct, it follows that local pH is relatively poorly sustained by the dilute buffer solutions so that, at the same current density, the local pH is higher than that in the concentrated solution.

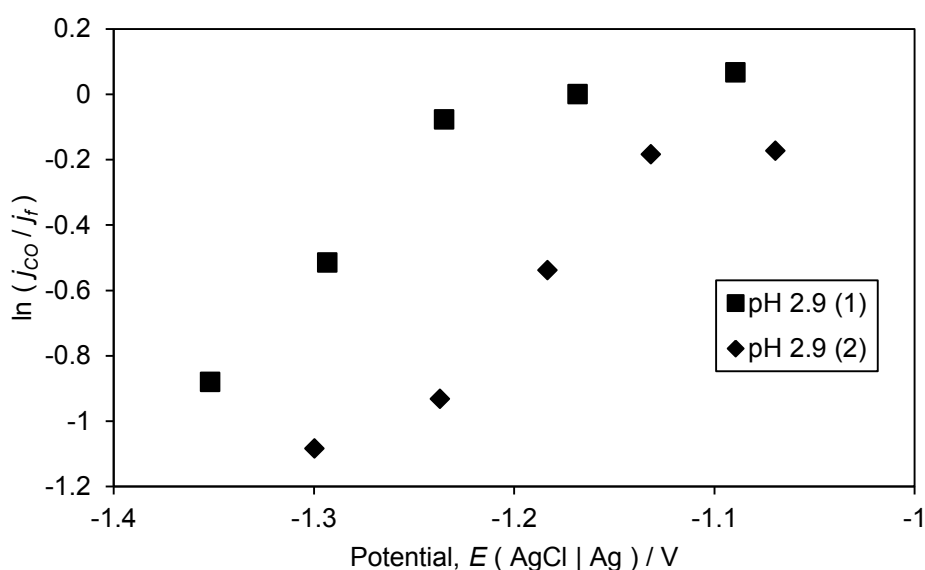


Figure 5-8: Effect of electrode potential and pH on logarithmic formation ratios of CO to formate at pH 2.9; (1) 0.1 M H_3PO_4 /1 M NaH_2PO_4 and (2) 0.02 M H_3PO_4 /0.2 M NaH_2PO_4

Figure 5-9 shows the non-linear effect of pH on the experimental values of the product ratios, though there are only three data points. As pH was increased, the logarithmic ratios decreased, but the rates of the decreases appeared to be slower at higher pH.

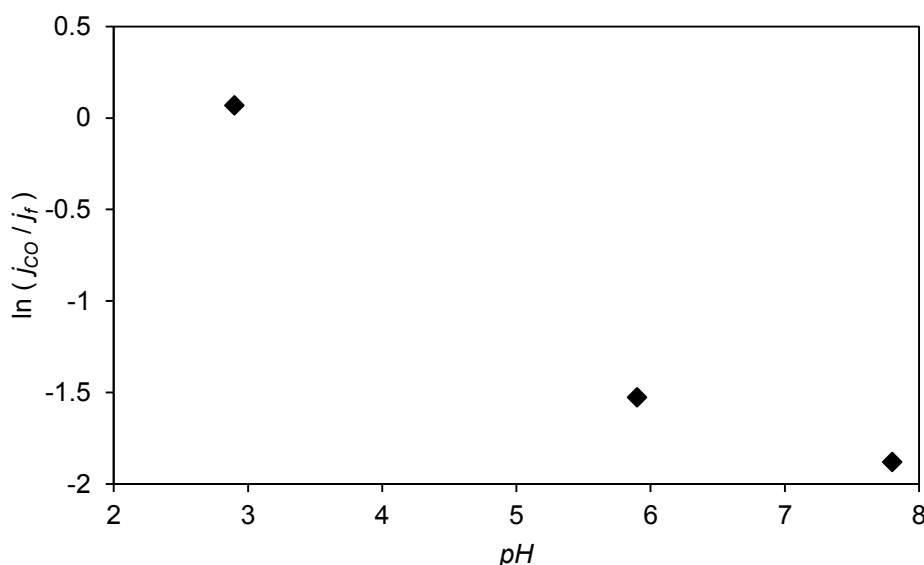


Figure 5-9: Effect of bulk pH on logarithmic formation ratios of CO to formate

Equation E5-3 allows variable slopes of the logarithmic product ratios against electrode potential through changes in local pH and therefore predicts only a single and common slope of the logarithmic true ratios against potential. The contrast between the theory and the experimental results suggested that the relationship between the product ratios and pH is actually more complex than what was described by equation E5-3. A more elaborate approach to the kinetics of CO_2 reduction at tin would be covered in a dedicated chapter. In addition, models for mass transport of various species in the electrolyte solutions would also be developed to estimate local pH in an attempt to fully describe the observed experimental results.

It is also worth pointing out that the trend in Figure 5-9 could have been clearer if there had been at least one more data point between pH 3 and 5, but this was difficult to achieve experimentally. Buffer systems that can produce pH within this range with comparable concentrations of acids and bases are often combinations of organic acids and their salts. Their presence in liquid samples could be problematic

in analysis with HPLC. Their high concentrations as buffer agents tended to produce exceedingly large peaks in chromatograms that obscured the peak of formate. This problem was encountered in a preliminary experiment with citrates as buffer agents.

5.3 Conclusions

The electrochemical reduction of CO_2 at tin in aqueous solutions of different pH was studied. The observed relationship between the partial current densities of CO_2 reduction and electrode potential suggested that the reaction followed the widely accepted mechanism of two successive electron transfers; the first step is pH-independent and limiting at low potentials, while the second depends on local pH at the electrode surface and is the rate-determining step at high potentials. Carbon monoxide and formate were the main products and the formation ratios of CO to formate measured by their respective current densities were strongly dependent on local pH; CO was favoured at low pH and formate was at high pH. An equation was developed under strict assumptions in order to explain the phenomenon, but the actual relationship between the product ratios and pH proved to be more complicated and required a more rigorous kinetic model.

6 Modelling of kinetics of electrochemical reduction of CO₂ at tin

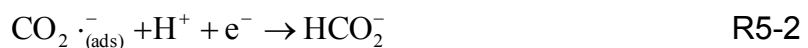
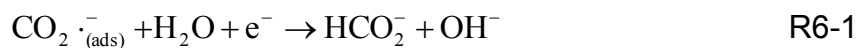
The findings in the previous chapter pointed to the lack of an accurate model for the kinetics of CO₂ reduction at tin and left the development of a more elaborate model to this chapter. The main purpose of the model was to accurately predict the product ratios and the partial current densities as a function of pH. An additional model was also required to estimate local pH in order to show that the apparent dependence of the product ratios on electrode potential was likely caused by changes in local pH.

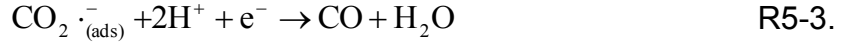
6.1 Kinetic model development

The non-linearity of the relationship between the logarithmic true product ratios and pH was the first to be considered. The plot in Figure 5-9 shares a similarity with the relationship between the current densities of hydrogen evolution and pH; the current densities of hydrogen evolution have a linear relationship with concentrations of protons at low pH but, as pH is increased, deviate from this trend gradually and eventually become independent of pH. The participation of water in the reaction scheme is the cause of this non-linearity, especially at high pH, and was probably applicable to the observed relationship between the product ratios and pH in CO₂ reduction. The formation ratios of CO to formate was assumed to be a sole function of pH, i.e. $\alpha_f = \alpha_{CO}$. Several reaction schemes based on this concept were devised but only two most successful models would be presented.

6.1.1 Scheme 1: reactions with protons in solution phase

It was hypothesised that the formation of CO and formate occurred with different stoichiometric coefficients of proton consumption and even with water instead of protons. The reaction scheme was first set as follows:





Based on Langmuirian adsorption, expressions for the partial current densities of reaction R2-1, R6-1, R6-2, R5-2 and R5-3 are respectively:

$$j_1 = -Fk_{1,0}a_{\text{CO}_2}(1-\theta)\exp\left(\frac{-\alpha_1 FE}{RT}\right) \quad \text{E6-1}$$

$$j_2 = -Fk_{2,0}\theta\exp\left(\frac{-\alpha_2 FE}{RT}\right) \quad \text{E6-2}$$

$$j_3 = -Fk_{3,0}a_{\text{H}^+}\theta\exp\left(\frac{-\alpha_2 FE}{RT}\right) \quad \text{E6-3}$$

$$j_4 = -Fk_{4,0}a_{\text{H}^+}\theta\exp\left(\frac{-\alpha_2 FE}{RT}\right) \quad \text{E6-4}$$

$$j_5 = -Fk_{5,0}a_{\text{H}^+}^2\theta\exp\left(\frac{-\alpha_2 FE}{RT}\right) \quad \text{E6-5.}$$

These expressions are shortened to:

$$j_1 = -Fk_1a_{\text{CO}_2}(1-\theta) \quad \text{E6-6}$$

$$j_2 = -Fk_2\theta \quad \text{E6-7}$$

$$j_3 = -Fk_3a_{\text{H}^+}\theta \quad \text{E6-8}$$

$$j_4 = -Fk_4a_{\text{H}^+}\theta \quad \text{E6-9}$$

$$j_5 = -Fk_5a_{\text{H}^+}^2\theta \quad \text{E6-10,}$$

where:

$$k_1 = k_{1,0}\exp\left(\frac{-\alpha_1 FE}{RT}\right) \quad \text{E6-11,}$$

$$k_i = k_{i,0}\exp\left(\frac{-\alpha_2 FE}{RT}\right) \quad \text{E6-12}$$

with $i = 2, 3, 4, \dots$ All activities are based on standard concentrations of 1 mol L⁻¹.

The logarithmic formation ratio of CO to formate can be readily derived:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{j_3 + j_5}{j_2 + j_4}\right) \\
&= \ln\left(\frac{Fk_3a_{H^+}\theta + Fk_5a_{H^+}^2\theta}{Fk_2\theta + Fk_4a_{H^+}\theta}\right) \\
&= \ln\left(\frac{[k_3/k_2]a_{H^+} + [k_5/k_2]a_{H^+}^2}{1 + [k_4/k_2]a_{H^+}}\right)
\end{aligned}
\tag{E6-13}$$

The derived logarithmic ratio can be approximated with three components. The first is the expression at high pH:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{[k_3/k_2]a_{H^+} + [k_5/k_2]a_{H^+}^2}{1 + [k_4/k_2]a_{H^+}}\right) \\
&\approx \ln\left(\frac{k_3}{k_2}\right) - \frac{pH}{\log e}
\end{aligned}
\tag{E6-14}$$

This is characterised by dominating R6-1 and R6-2, which are respectively the formation of formate with water and the formation of CO with one proton. Other reactions are strongly dependent on proton concentrations and therefore insignificant at high pH.

The second component is the expression at low pH:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{[k_3/k_2]a_{H^+} + [k_5/k_2]a_{H^+}^2}{1 + [k_4/k_2]a_{H^+}}\right) \\
&\approx \ln\left(\frac{k_5}{k_4}\right) - \frac{pH}{\log e}
\end{aligned}
\tag{E6-15}$$

R5-2 and R5-3 are prominent in this region. These are respectively the formation of formate with one proton and the formation of CO with two protons. High proton concentrations promote these reactions and make their rates significant.

The last component is the transition region between the previous two:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{[k_3/k_2]a_{H^+} + [k_5/k_2]a_{H^+}^2}{1 + [k_4/k_2]a_{H^+}}\right) \\
&\approx \ln\left(\frac{k_3}{k_4}\right)
\end{aligned}
\tag{E6-16}$$

The logarithmic ratio is expressed by R6-2 and R5-2, which are respectively the formation of CO and formate with one proton. The same stoichiometric coefficient of proton consumption of the two reactions eliminates the effect of pH on the logarithmic ratio in this region.

The logarithmic ratios calculated from equation E6-13 with an appropriate set of parameters are plotted against pH, together with the experimental values, in Figure 6-1. It can be seen that the three parameters of the equation were actually more than enough to produce a perfect fit between the experimental values and the model's predictions, but they were necessary in order to make provision for the expected decreases in the product ratios beyond pH 7.8 due to the increased local pH at low potentials. The model at this point was able to describe the logarithmic formation ratios of CO to formate satisfactorily. It would be tested whether the actual partial current densities of the formation of CO and formate can also be reproduced accurately with an appropriate set of model parameters. The next step is to derive an explicit function for the surface coverage of CO_2^- .

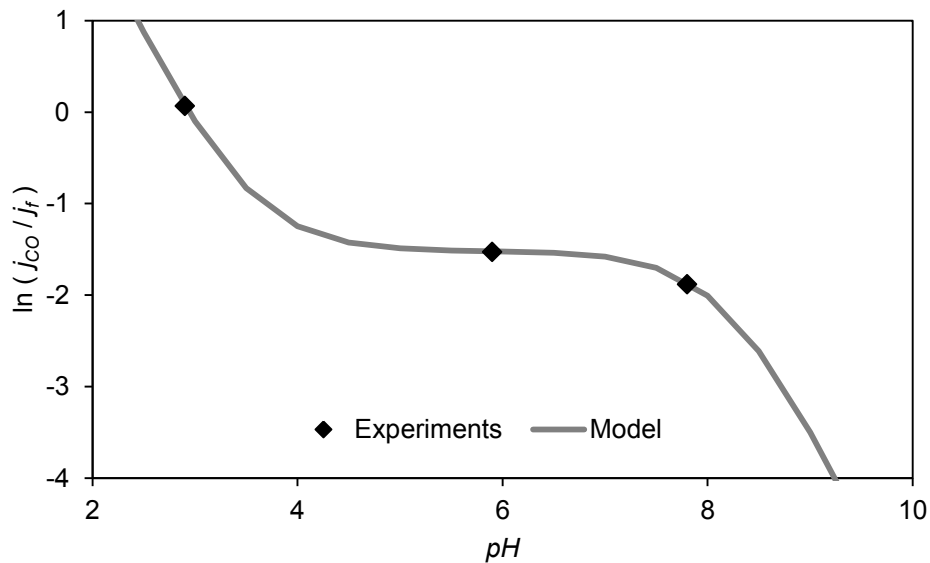


Figure 6-1: Comparison between experimental and predicted logarithmic formation ratios of CO to formate from equation E6-13 with $k_3/k_2 = 3.5 \times 10^7$, $k_5/k_2 = 1.1 \times 10^{11}$ and $k_4/k_2 = 1.6 \times 10^8$

The surface coverage at a steady state can be determined by performing a material balance of the adsorbed species. Based on the proposed reaction scheme, the adsorbed intermediate is generated only by reaction R2-1 and consumed by the others:

$$\Gamma \frac{\partial \theta}{\partial t} = \frac{-(j_1 - j_2 - j_3 - j_4 - j_5)}{F} = 0 \quad \text{E6-17.}$$

After substitution and rearranging,

$$\theta_{CO_2^-(ads)} = \frac{k_1 a_{CO_2}}{k_1 a_{CO_2} + k_2 + k_3 a_{H^+} + k_4 a_{H^+} + k_5 a_{H^+}^2} \quad \text{E6-18.}$$

Curve fitting was done with k_3/k_2 , k_5/k_2 and k_4/k_2 having the same values as those used to produce the plot in Figure 6-1. This left only k_1 , k_2 , α_1 and α_2 for adjustment. The strategy was to tune k_1 and α_1 for good agreement between the experimental values and the model predictions at low potentials, and k_2 and α_2 for that at high potentials. The predicted values of the partial current densities of formate formation, the partial current densities for CO formation, and the logarithmic formation ratios of CO to formate are shown in Figure 6-2, Figure 6-3 and Figure 6-4, respectively, together with the experimental values.

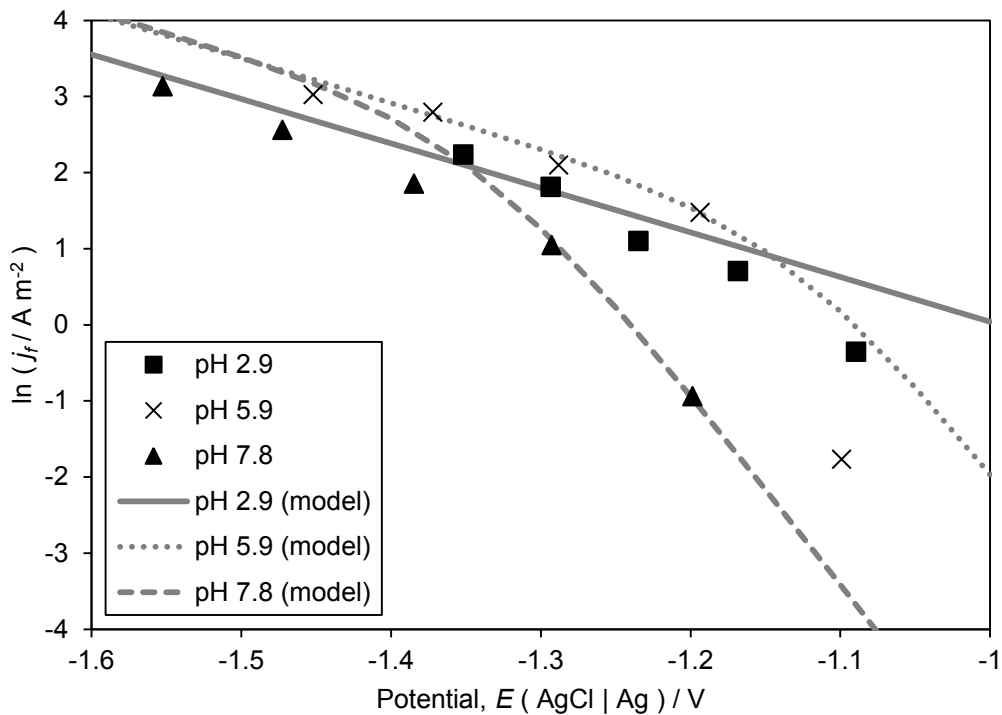


Figure 6-2: Predicted effects of electrode potential and pH on logarithmic partial current densities of formate formation with $k_{1,0} = 9.71 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_1 = 0.15$, $k_{2,0} = 4.00 \times 10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_2 = 0.65$

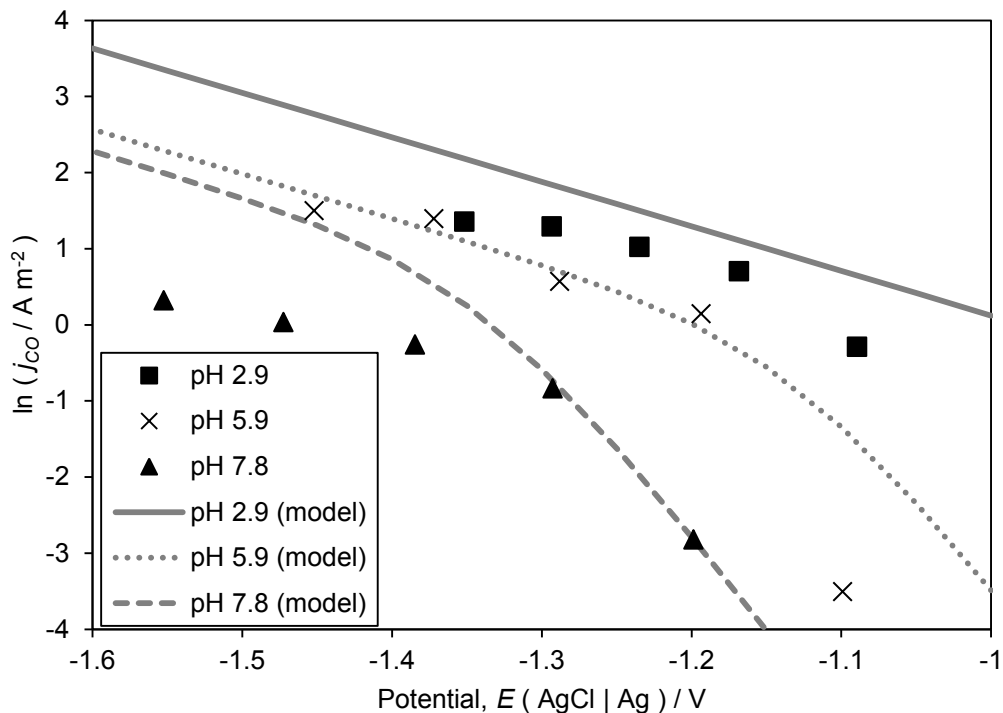


Figure 6-3: Predicted effects of electrode potential and pH on logarithmic partial current densities of CO formation with $k_{1,0} = 9.71 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_1 = 0.15$, $k_{2,0} = 4.00 \times 10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_2 = 0.65$

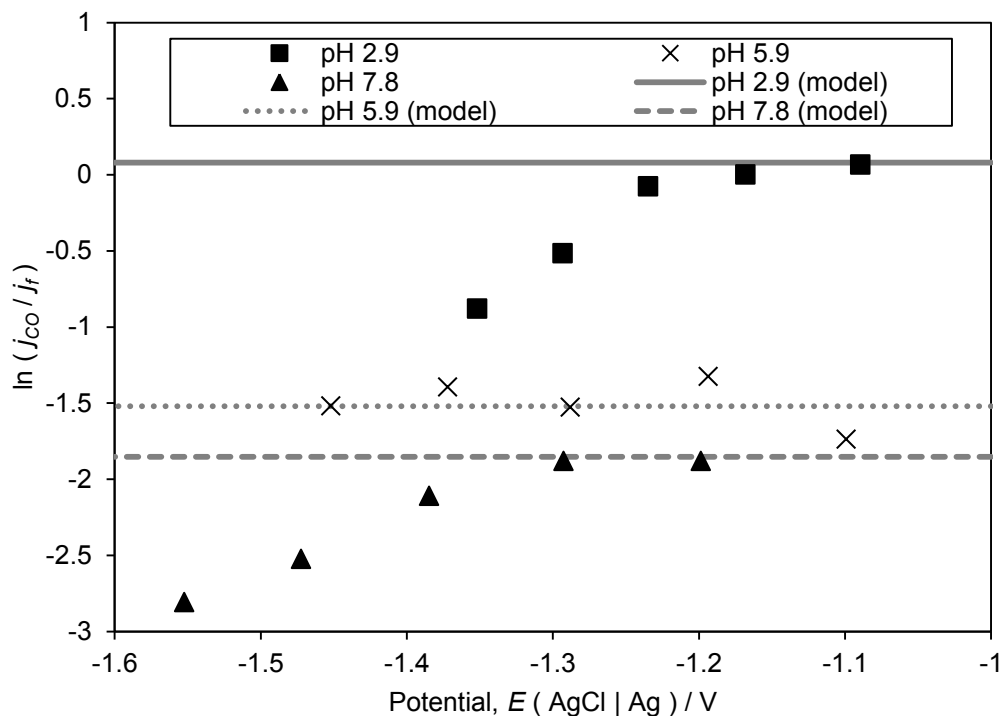


Figure 6-4: Predicted effects of electrode potential and pH on logarithmic formation ratios of CO to formate with $k_{1,0} = 9.71 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_1 = 0.15$, $k_{2,0} = 4.00 \times 10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_2 = 0.65$

It can be seen that there were general mismatches between the model and the experimental data in all three plots. Adjusting the kinetic parameters so that the model can predict accurately the partial current densities at a particular pH resulted in mismatches at other pHs. However, $k_{1,0}$ and α_1 was set so that the best fit at low potentials was obtained at pH 5.9, because it would result in good agreement in the formation of both formate and CO at this pH. This was also in agreement with the largely constant logarithmic ratio at this pH observed in Figure 6-4. Figure 6-2 shows that this approach resulted in moderately accurate predictions of the partial current densities of formate formation at pH 2.9 but significant over-predictions of those at pH 7.8. In contrast, Figure 6-3 shows over-predictions in the partial current densities of CO formation at both pHs.

On the other hand, $k_{2,0}$ and α_2 were set so that the predicted partial current densities of CO formation at high potentials matched the experimental data at pH 7.8 because this resulted in smaller mismatches at other pHs. Despite this, Figure 6-3 shows that the model still significantly over-predicted the partial current densities at both pH 2.9 and pH 5.9.

It is also worth pointing out that the partial current densities of formate formation at pH 2.9 being smaller than those at pH 5.9 at low potentials were also predicted by the model (Figure 6-2). This could be explained by first realising that, in this range of potentials, the rate-determining step was the formation of $\text{CO}_2^{\cdot-}$ (reaction R2-1), which was independent of pH. At the same potential, a shift in the ratio of the formation rates of the products resulted in a decrease in the formation rate of one and an increase in that of the other, while the sum of the partial current densities of the two products was constant. Although weak dependence of the logarithmic partial current densities of CO_2 reduction on pH at low potentials in Figure 5-1 could be observed, they were rather attributed to delayed transitions of the partial current densities between the two Tafel regions specifically at pH 7.8 due to changes in local pH. Nevertheless, this behaviour reaffirmed that the formation of formate and CO shared the same sites. Had the formation of the two products occurred at different sites, an increase in the formation rate of one product would not have led to a decrease in that of the other at the same potential.

Figure 6-4 shows that the model could predict accurately the logarithmic formation ratios of CO to formate at all three pHs at high potentials, at which the local pHs

were close to the bulk values. The disparities grew as potential was decreased because the local concentrations of protons departed from the bulk concentrations as described in Chapter 5. This was expected because the current model contained only the kinetics of the reactions without any influence of mass transport.

The calculated surface coverages of the intermediate of CO₂ reduction at different pHs are shown in Figure 6-5. The surface coverages were higher at high potentials because the rate-determining step was the second electron transfer (R5-1), which consumed the intermediate. It then decreased with increasingly negative potential as the limiting reaction was gradually shifted to the first electron transfer (R2-1), which produced the intermediate. The value at a higher pH was always higher than that at a lower pH because a higher concentration of protons resulted in a faster rate of the second electron transfer, moving the transition between the rate-determining steps towards a less negative potential.

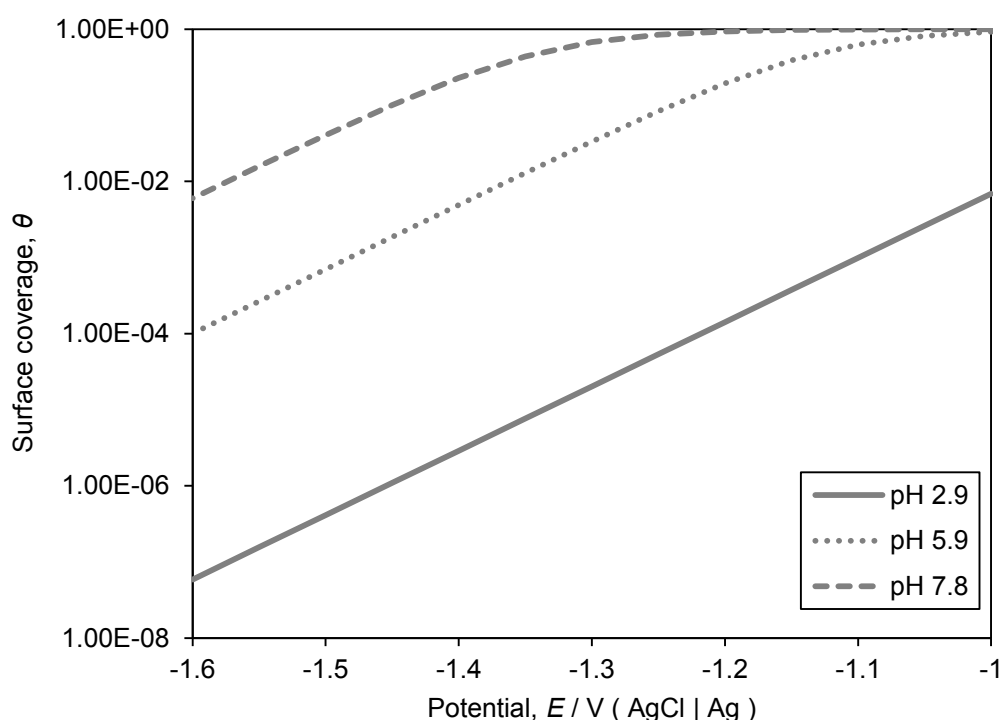


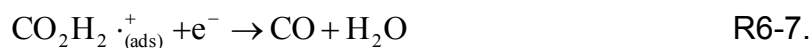
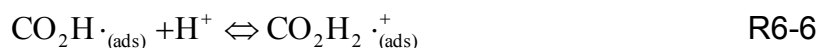
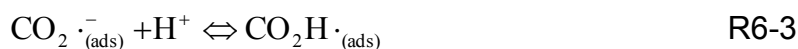
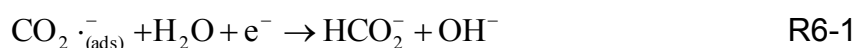
Figure 6-5: Effects of electrode potential and pH on predicted surface coverages of intermediate of CO₂ reduction

The proposed reaction scheme was shown to be able to reproduce the relationship between the true product ratios and pH successfully, but the partial current densities for product formation were mostly over-predicted, especially at high potentials. The limited success reaffirmed the concept of different stoichiometric coefficients of

proton consumption but also prompted further modifications to improve the agreement between the model predictions and the experimental results.

6.1.2 Scheme 2: protonation of $\text{CO}_2^{\cdot-}$ before electron transfer

The over-predictions of the partial current densities at high potentials suggested that the partial current densities did not depend linearly on proton concentrations as they would have had the second electron transfer occurred with protons in solutions. The over-predicted partial current densities at low pH gave an impression that the measured partial current densities were suppressed through adsorption processes whereby surface saturation of adsorbed species was induced by high concentrations of the species in solution phases. Similarly, protons were believed to participate in CO_2 reduction through adsorption. The reaction scheme was modified by breaking down each of reaction R6-2, R5-2 and R5-3 into two sub-steps of protonation and subsequent electron transfer. The modified scheme is:



It can be seen that this new scheme introduced three intermediates: $\text{CO}_2^{\cdot-}$, $\text{CO}_2\text{H}^{\cdot}$ and $\text{CO}_2\text{H}_2^{\cdot+}$. The first two have been frequently proposed in separate papers as the precursors to formate but both are included together here as parts of the same scheme. In contrast, the last intermediate, $\text{CO}_2\text{H}_2^{\cdot+}$, was never mentioned before but is needed in this scheme in order to explain the increased product ratios at low pH.

A new set of variables was introduced so that the system could be more easily described and that the mathematical equations reflect the multiple-layer adsorption. Figure 6-6 shows a schematic depiction of the new variables.

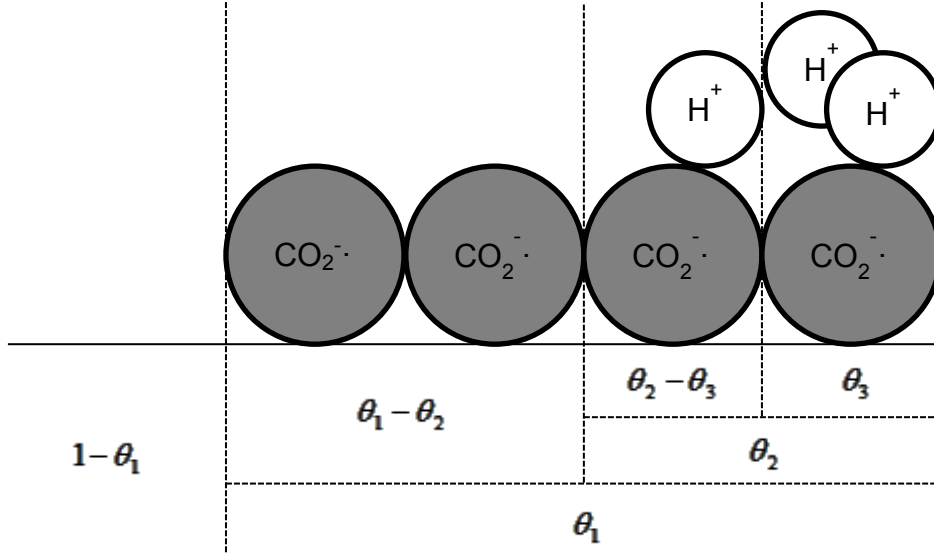


Figure 6-6: Schematic diagram of intermediate adsorption

θ_1 is defined as the fractional surface coverage of the underlying $\text{CO}_2^{\cdot-}$ and all other protonated forms. θ_2 represents the fractional surface coverage of $\text{CO}_2\text{H}^{\cdot}$ and $\text{CO}_2\text{H}_2^{\cdot+}$. Lastly, θ_3 is the fractional surface coverage of $\text{CO}_2\text{H}_2^{\cdot+}$ alone.

The protonated species can be related to proton concentrations and underlying adsorbed species through Langmuir isotherms; those of R6-3 and R6-6 are:

$$K_1 a_{\text{H}^+} = \frac{\theta_2 - \theta_3}{\theta_1 - \theta_2} \quad \text{E6-19}$$

$$K_2 a_{\text{H}^+} = \frac{\theta_3}{\theta_2 - \theta_3} \quad \text{E6-20.}$$

The equations for the rates of reaction R2-1 and R6-1 also have to be modified according to the new definitions. This together with the rate equations of reaction R6-4, R6-5 and R6-7 are respectively:

$$j_1 = -Fk_1 a_{\text{CO}_2} (1 - \theta_1) \quad \text{E6-21}$$

$$j_2 = -Fk_2 (\theta_1 - \theta_2) \quad \text{E6-22}$$

$$j_3 = -Fk_3 (\theta_2 - \theta_3) \quad \text{E6-23}$$

$$j_4 = -Fk_4 (\theta_2 - \theta_3) \quad \text{E6-24}$$

$$j_5 = -Fk_5 \theta_3 \quad \text{E6-25.}$$

The logarithmic ratio is then given by:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{j_3 + j_5}{j_2 + j_4}\right) \\
&= \ln\left(\frac{Fk_3[\theta_2 - \theta_3] + Fk_5\theta_3}{Fk_2[\theta_1 - \theta_2] + Fk_4[\theta_2 - \theta_3]}\right) \\
&= \ln\left(\frac{[k_3/k_2]K_1a_{H^+} + [k_5/k_2]K_1K_2a_{H^+}^2}{1 + [k_4/k_2]K_1a_{H^+}}\right)
\end{aligned}
\tag{E6-26}$$

The logarithmic ratio is still composed of three components. The approximate form at high pH is:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{[k_3/k_2]K_1a_{H^+} + [k_5/k_2]K_1K_2a_{H^+}^2}{1 + [k_4/k_2]K_1a_{H^+}}\right) \\
&\approx \ln\left(\frac{k_3K_1}{k_2}\right) - \frac{pH}{\log e}
\end{aligned}
\tag{E6-27}$$

and that at low pH is:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{[k_3/k_2]K_1a_{H^+} + [k_5/k_2]K_1K_2a_{H^+}^2}{1 + [k_4/k_2]K_1a_{H^+}}\right) \\
&\approx \ln\left(\frac{k_5K_2}{k_4}\right) - \frac{pH}{\log e}
\end{aligned}
\tag{E6-28}$$

Lastly, the transition between the two is:

$$\begin{aligned}
\ln\left(\frac{j_{CO}}{j_f}\right) &= \ln\left(\frac{[k_3/k_2]K_1a_{H^+} + [k_5/k_2]K_1K_2a_{H^+}^2}{1 + [k_4/k_2]K_1a_{H^+}}\right) \\
&\approx \ln\left(\frac{k_3}{k_4}\right)
\end{aligned}
\tag{E6-29}$$

It can be seen that these equations are analogous to those of the previous model with the only difference being the presence of two new variables: K_1 and K_2 . This new model was therefore capable of producing exactly the same plot between the logarithmic product ratios and pH as the previous model was. The parameters for the new model were $k_3K_1/k_2 = 3.5 \times 10^7$, $k_5K_1K_2/k_2 = 1.1 \times 10^{11}$ and $k_4K_1/k_2 = 1.6 \times 10^8$.

The surface coverages were derived similarly by performing a material balance at a steady state:

$$\Gamma \frac{\partial \theta}{\partial t} = \frac{-(j_1 - j_2 - j_3 - j_4 - j_5)}{F} = 0 \quad \text{E6-17.}$$

After substitution and rearranging,

$$\theta_1 = \frac{k_1 a_{CO_2}}{k_1 a_{CO_2} + \frac{k_2 + (k_3 + k_4)K_1 a_{H^+} + k_5 K_1 K_2 a_{H^+}^2}{1 + K_1 a_{H^+} (1 + K_2 a_{H^+})}} \quad \text{E6-30}$$

$$\theta_2 = \frac{\theta_1 K_1 a_{H^+}}{\frac{1}{1 + K_2 a_{H^+}} + K_1 a_{H^+}} \quad \text{E6-31}$$

$$\theta_3 = \frac{\theta_2 K_2 a_{H^+}}{1 + K_2 a_{H^+}} \quad \text{E6-32.}$$

Figure 6-7 and Figure 6-8 show the predicted effects of electrode potential and pH on the partial current densities for formation of both products for the new model with an appropriate set of parameters, which was also set to be analogous to that in the previous model. It can be seen that the large deviations of the predicted partial current densities from the experimental values at high potentials at pH 2.9 were now eliminated with the introduction of K_1 . Though the model still over-predicted the partial current densities at pH 5.9, better agreement was achieved.

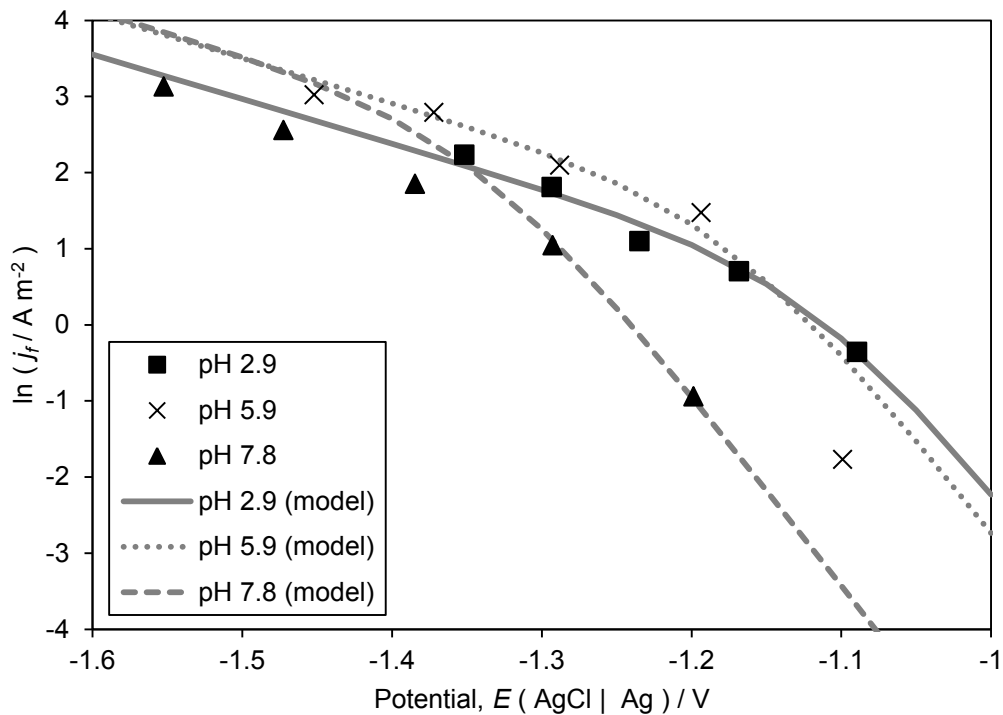


Figure 6-7: Predicted effects of electrode potential and pH on logarithmic partial current densities of formate formation with $k_{1,0} = 9.71 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_1 = 0.15$, $k_{2,0} = 4.00 \times 10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_2 = 0.65$, $K_1 = 1.00 \times 10^6$ and $K_2 = 1.00$

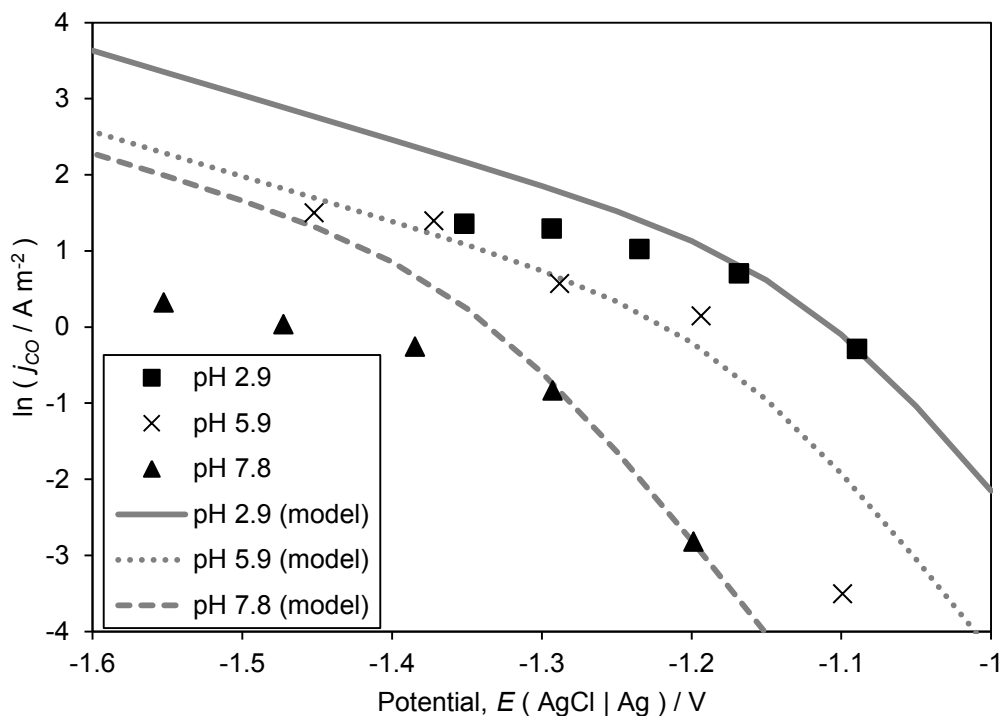


Figure 6-8: Predicted effects of electrode potential and pH on logarithmic partial current densities of CO formation with $k_{1,0} = 9.71 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_1 = 0.15$, $k_{2,0} = 4.00 \times 10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_2 = 0.65$, $K_1 = 1.00 \times 10^6$ and $K_2 = 1.00$

On the other hand, some discrepancies between the predicted partial current densities and the experimental values still existed at low potentials. The pronounced features were the over-predictions of the partial current densities for the formation of CO at pH 2.9 and those for both products at pH 7.8. These disagreements were believed to result from deviations of local proton concentrations from bulk values. The local pHs were expected to be higher than their bulk values as were described earlier in Chapter 5. Consequently, the logarithmic formation ratios of the products were decreased according to equation E6-26, the plot of which against pH is shown in Figure 6-1. The changes in the local pH should have lowered the predicted current densities for the formation of CO at pH 2.9 and also increased those of formate, thereby offering better agreement once incorporated into the model. The higher local pH was also believed to improve the predictions of the current densities for the formation of both products at pH 7.8 by extending the transition region between the two Tafel slopes to cover a larger potential range. There was necessity to develop mass transport models in order to estimate the local pHs for these proposed improvements on the model.

It should be pointed out here that K_2 , the protonation constant for the formation of CO_2H_2^+ , was the only one that was set arbitrarily. Its effect was to decrease the partial current densities of the formation of both products, more pronouncedly at low pH. 2 000 was an approximate threshold of K_2 to cause small changes to the partial current densities at pH 2.9, while those at pH 5.9 were still barely noticeable. However, the effect of K_2 on the partial current densities at pH 2.9 was undesirable as it caused the already accurately predicted partial current densities to deviate from the experimental values. K_2 was therefore set arbitrarily to unity, which was far below the threshold, and was thought to be meaningful only at extremely low pH outside the range studied. The existence of CO_2H_2^+ is debatable as it has never been introduced before. However, if it exists, its likely instability is reflected by the small value of K_2 .

The calculated surface coverages of the intermediates at different pHs from the modified model are shown in Figure 6-9. The trends are more complicated than those observed in Figure 6-5 due to the three levels of protonation but can still be recognised. The total surface coverages of the intermediates, θ_1 , still followed the same behaviour observed in the previous model; the value at a higher pH was

always higher than that at a lower pH. The surface coverages contained larger portions of the protonated intermediates at lower pH; θ_2 at pH 2.9 was almost the same as θ_1 . θ_3 , the surface coverage of $\text{CO}_2\text{H}_2^{+}$, was very small at all three pHs due to the small and arbitrarily set value of K_2 .

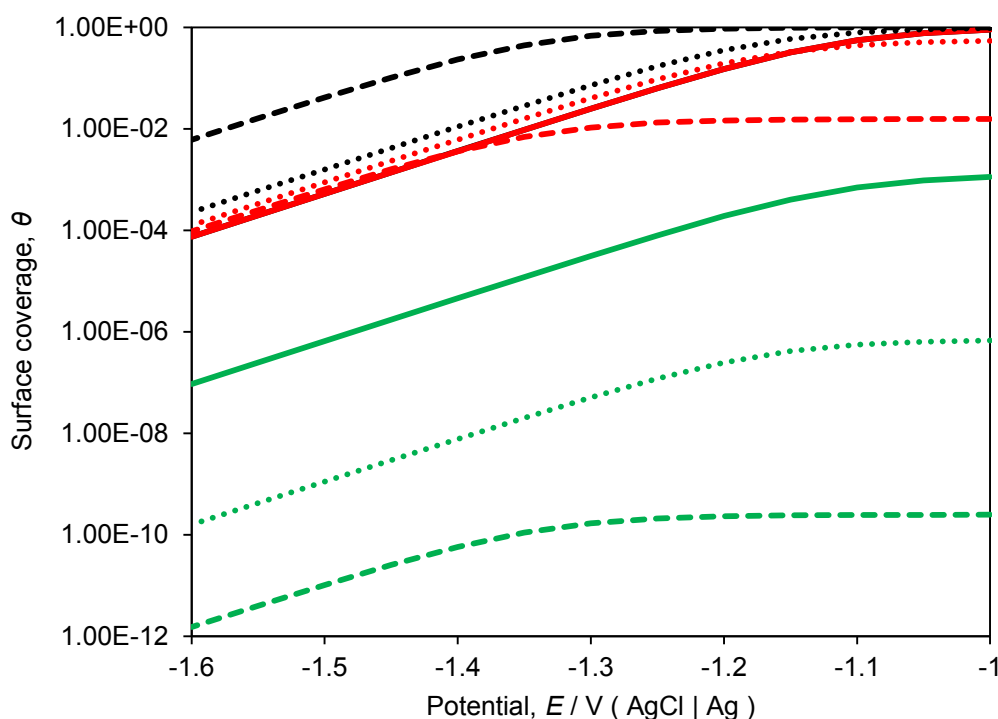


Figure 6-9: Effects of electrode potential and pH on predicted surface coverages of intermediates of CO_2 reduction; black: θ_1 , red: θ_2 , green: θ_3 ; solid lines: pH 2.9, dotted lines: pH 5.9, dashed lines: pH 7.8

6.2 Mass transport model development

The challenge in the development of mass transport models for estimations of local pH lay in the treatment of homogeneous reactions occurring within diffusion layers. The weak acids and their conjugate bases in a buffer solution take part in a number of protonation-deprotonation reactions. Reactions of this kind are often characterised by exceptionally large rate constants reaching 10^{10} s^{-1} (Gibbons & Edsall, 1963). Consequently, accurate measurements of these values are difficult to obtain. Moreover, a system of differential equations describing a system with such fast reactions tends to be stiff. Obtaining a numerical solution from the system can be difficult.

Delacourt et al. (2010) approached this problem by assuming that fast dissociation-recombination reactions are equilibrated. Their paper describes how their

assumption was applied to a carbonate system. The same concept was adopted in this work and also applied to phosphate systems. It was found that the system was easier to describe mathematically and to solve. However, there were also unusual phenomena arising from this assumption, which would be discussed later in this chapter.

The concept of diffusion layers was applied in the model to greatly simplify the systems. Spatial distributions of potential and concentrations were assumed to occur in only one direction so that the systems can be approximated to one-dimensional problems. The physical picture of the model was set as Figure 6-10. x was set to zero at the electrode-electrolyte interface and extends positively to δ , which is the thickness of the diffusion layer determined to be $36.3 \mu\text{m}$ in section 4.4.

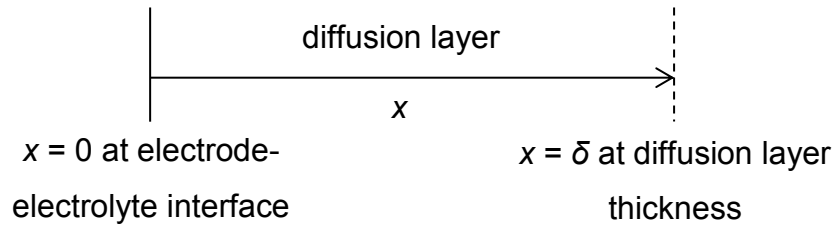


Figure 6-10: Physical picture of diffusion layer

The derivation of a system of equations for each buffer solution started with a material balance at a steady state:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \vec{N}_i + r_i = 0 \quad \text{E6-33.}$$

It follows that:

$$\nabla \cdot \vec{N}_i = r_i \quad \text{E6-34.}$$

It was assumed that diffusion and migration were the only significant modes of transport:

$$\vec{N}_i = -D_i \nabla c_i - z_i u_i c_i F \nabla \phi \quad \text{E6-35.}$$

The Nernst-Einstein equation was also used to relate mechanical mobility of a species to its diffusion coefficient:

$$u_i = \frac{D_i}{RT} \quad \text{E6-36.}$$

Finally, charge neutrality was assumed at any point in the diffusion layer except the thin electrical double layer at the electrode | electrolyte interface:

$$\sum_i Fz_i c_i = 0 \quad \text{E6-37.}$$

Though the condition of charge neutrality is rarely exactly fulfilled, it often results in good approximations of species concentrations in the most part of the diffusion layer, i.e. outside the diffuse layer where significant charge separation occurs.

Mass transport models were developed for these systems: 0.1 M H_3PO_4 /1.0 M NaH_2PO_4 (pH 2.9), 0.02 M H_3PO_4 /0.2 M NaH_2PO_4 (pH 2.9) and 1 atm CO_2 /0.5 M NaOH (pH 7.8). The buffer solutions of 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 5.9) were able to hold local pH close to the bulk value at all potentials studied and therefore did not need a mass transport model.

6.2.1 Mass transport model for buffer solutions at pH 2.9

The main difference between buffer solutions of 0.1 M H_3PO_4 /1.0 M NaH_2PO_4 and 0.02 M H_3PO_4 /0.2 M NaH_2PO_4 was the concentrations of the active species. Therefore, both systems could be described by the same system of equations, but with different initial conditions. The presence of carbonate species resulting from hydration of aqueous CO_2 in the solutions were small at this pH and should not have contributed to pH regulation. Therefore, the entire carbonate system was excluded from the mass transport model for the buffer solutions at pH 2.9. Only the following reactions were assumed to occur in the diffusion layer of both systems:



The material balances of the species took these forms:

$$\nabla \cdot \vec{N}_{\text{H}^+} = r_{\text{H}_3\text{PO}_4} + r_{\text{H}_2\text{PO}_4^-} + r_{\text{HPO}_4^{2-}} + r_{\text{HCOOH}} + r_{\text{H}_2\text{O}} \quad \text{E6-38}$$

$$\nabla \cdot \vec{N}_{\text{H}_3\text{PO}_4} = -r_{\text{H}_3\text{PO}_4} \quad \text{E6-39}$$

$$\nabla \cdot \vec{N}_{\text{H}_2\text{PO}_4^-} = r_{\text{H}_3\text{PO}_4} - r_{\text{H}_2\text{PO}_4^-} \quad \text{E6-40}$$

$$\nabla \cdot \vec{N}_{HPO_4^{2-}} = r_{H_2PO_4^-} - r_{HPO_4^{2-}} \quad E6-41$$

$$\nabla \cdot \vec{N}_{PO_4^{3-}} = r_{HPO_4^{2-}} \quad E6-42$$

$$\nabla \cdot \vec{N}_{HCOOH} = -r_{HCOOH} \quad E6-43$$

$$\nabla \cdot \vec{N}_{HCOO^-} = r_{HCOOH} \quad E6-44$$

$$\nabla \cdot \vec{N}_{OH^-} = r_{H_2O} \quad E6-45$$

$$\nabla \cdot \vec{N}_{H_2O} = -r_{H_2O} \quad E6-46.$$

The subscript of each r refers to the weak acid in one of the dissociation reactions R6-8 to R6-12, the net dissociation rate of which is represented by r .

As mentioned earlier, rates of protonation and deprotonation are exceptionally fast and therefore difficult to model. According to Delacourt et al. (2010)'s procedure, r_i terms could be eliminated by substitution:

$$\nabla \cdot \vec{N}_{H^+} + 3\nabla \cdot \vec{N}_{H_3PO_4} + 2\nabla \cdot \vec{N}_{H_2PO_4^-} + \nabla \cdot \vec{N}_{HPO_4^{2-}} + \nabla \cdot \vec{N}_{HCOOH} + \nabla \cdot \vec{N}_{H_2O} = 0 \quad E6-47$$

$$\nabla \cdot \vec{N}_{H_3PO_4} + \nabla \cdot \vec{N}_{H_2PO_4^-} + \nabla \cdot \vec{N}_{HPO_4^{2-}} + \nabla \cdot \vec{N}_{PO_4^{3-}} = 0 \quad E6-48$$

$$\nabla \cdot \vec{N}_{HCOOH} + \nabla \cdot \vec{N}_{HCOO^-} = 0 \quad E6-49$$

$$\nabla \cdot \vec{N}_{H_2O} + \nabla \cdot \vec{N}_{OH^-} = 0 \quad E6-50.$$

Integration with dx from $x = 0$ to x yielded:

$$\left(N_{H^+} + 3N_{H_3PO_4} + 2N_{H_2PO_4^-} + N_{HPO_4^{2-}} + N_{HCOOH} + N_{H_2O} \right) \Big|_{x=0}^x = 0 \quad E6-51$$

$$\left(N_{H_3PO_4} + N_{H_2PO_4^-} + N_{HPO_4^{2-}} + N_{PO_4^{3-}} \right) \Big|_{x=0}^x = 0 \quad E6-52$$

$$\left(N_{HCOOH} + N_{HCOO^-} \right) \Big|_{x=0}^x = 0 \quad E6-53$$

$$\left(N_{H_2O} + N_{OH^-} \right) \Big|_{x=0}^x = 0 \quad E6-54.$$

At $x = 0$, all fluxes except $N_{H^+} \Big|_{x=0}$ and $N_{HCOO^-} \Big|_{x=0}$ were zero. Therefore,

$$N_{H^+} + 3N_{H_3PO_4} + 2N_{H_2PO_4^-} + N_{HPO_4^{2-}} + N_{HCOOH} + N_{H_2O} = N_{H^+} \Big|_{x=0} \quad E6-55$$

$$N_{H_3PO_4} + N_{H_2PO_4^-} + N_{HPO_4^{2-}} + N_{PO_4^{3-}} = 0 \quad E6-56$$

$$N_{HCOOH} + N_{HCOO^-} = N_{HCOO^-} \Big|_{x=0} \quad E6-57$$

$$N_{H_2O} + N_{OH^-} = 0 \quad \text{E6-58.}$$

The flux of water could be determined independently afterwards. Thereby, it could be eliminated by subtracting E6-58 from E6-55. This gave:

$$N_{H^+} + 3N_{H_3PO_4} + 2N_{H_2PO_4^-} + N_{HPO_4^{2-}} + N_{HCOOH} - N_{OH^-} = N_{H^+} \Big|_{x=0} \quad \text{E6-59.}$$

$N_{H^+} \Big|_{x=0}$ and $N_{HCOO^-} \Big|_{x=0}$, or respectively the consumption rate of protons and the production rate of formate at the electrode, were set explicitly to the values derived from the experimental results rather than determined implicitly in conjunction with the kinetic model. The latter was impossible due to the lack of a precise model for the rates of hydrogen evolution at different pH.

It should also be noted that a mass transport model of this form did not allow specification of the exact proton donors involved in surface reactions at the electrode; production of OH^- ions from water consumption in a surface reaction was treated as equivalent to consumption of H^+ at the electrode due to the assumption of equilibrated reactions. Furthermore, the weak acids are recognised as if they were directly involved in surface reactions. Therefore, the formation of 1 mole of H_2 , formate and CO always required 2 moles, 1 mole and 2 moles of any proton donor, respectively, by the assumption of equilibrated reactions, though the production of some of these species might actually consume specifically water rather than any proton donor. This was also evident mathematically in equation E6-59, where the fluxes of protons and hydroxide ions were present in the same equation.

The flux of each species was related to its concentration through equation E6-35. Substituting this equation for the fluxes in E6-59, E6-56 and E6-57 with the molar conductivities given by equation E6-36 yielded:

$$\begin{aligned} & -D_{H^+} \frac{\partial c_{H^+}}{\partial x} - 3D_{H_3PO_4} \frac{\partial c_{H_3PO_4}}{\partial x} - 2D_{H_2PO_4^-} \frac{\partial c_{H_2PO_4^-}}{\partial x} \\ & - D_{HPO_4^{2-}} \frac{\partial c_{HPO_4^{2-}}}{\partial x} - D_{HCOOH} \frac{\partial c_{HCOOH}}{\partial x} + D_{OH^-} \frac{\partial c_{OH^-}}{\partial x} \\ & - \left(D_{H^+} c_{H^+} - 2D_{H_2PO_4^-} c_{H_2PO_4^-} - 2D_{HPO_4^{2-}} c_{HPO_4^{2-}} + D_{OH^-} c_{OH^-} \right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = N_{H^+} \Big|_{x=0} \end{aligned} \quad \text{E6-60}$$

$$\begin{aligned}
& -D_{H_3PO_4} \frac{\partial c_{H_3PO_4}}{\partial x} - D_{H_2PO_4^-} \frac{\partial c_{H_2PO_4^-}}{\partial x} - D_{HPO_4^{2-}} \frac{\partial c_{HPO_4^{2-}}}{\partial x} - D_{PO_4^{3-}} \frac{\partial c_{PO_4^{3-}}}{\partial x} \\
& - \left(-D_{H_2PO_4^-} c_{H_2PO_4^-} - 2D_{HPO_4^{2-}} c_{HPO_4^{2-}} - 3D_{PO_4^{3-}} c_{PO_4^{3-}} \right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = 0
\end{aligned} \tag{E6-61}$$

$$-D_{HCOOH} \frac{\partial c_{HCOOH}}{\partial x} - D_{HCOO^-} \frac{\partial c_{HCOO^-}}{\partial x} - \left(-D_{HCOO^-} c_{HCOO^-} \right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = N_{HCOO^-} \Big|_{x=0} \tag{E6-62}$$

These three equations, E6-60, E6-61 and E6-62, were the main 3 equations that would be solved for the concentrations of all species. However, there were 9 unknown variables composed of the concentrations of the 8 species and the potential. 6 more equations were required to reduce the degree of freedom to zero. 5 could be derived from the equilibrium relationships amongst species:

$$K_{H_3PO_4} = \frac{c_{H^+} c_{H_2PO_4^-}}{c_{H_3PO_4}} \tag{E6-63}$$

$$K_{H_2PO_4^-} = \frac{c_{H^+} c_{HPO_4^{2-}}}{c_{H_2PO_4^-}} \tag{E6-64}$$

$$K_{HPO_4^{2-}} = \frac{c_{H^+} c_{PO_4^{3-}}}{c_{HPO_4^{2-}}} \tag{E6-65}$$

$$K_{HCOOH} = \frac{c_{H^+} c_{HCOO^-}}{c_{HCOOH}} \tag{E6-66}$$

$$K_{H_2O} = c_{H^+} c_{OH^-} \tag{E6-67}$$

The use of equilibrium relationships was the main concept employed by Delacourt et al. (2010) in their assumption of equilibrated reactions. The last equation to be included was that determining the potential profile. This could be derived from a material balance of Na^+ ions. As they did not take part in any reaction,

$$\nabla \cdot \vec{N}_{Na^+} = 0 \tag{E6-68}$$

Integration with respect to x yielded:

$$\vec{N}_{Na^+} \Big|_{x=0}^x = 0 \tag{E6-69}$$

Na^+ was neither consumed nor produced at the electrode ($x = 0$). Therefore,

$$\vec{N}_{Na^+} = 0 \tag{E6-70}$$

After applying equation E6-35 and E6-36 and rearranging,

$$\frac{\partial \phi}{\partial x} = - \frac{RT}{c_{Na^+} F} \frac{\partial c_{Na^+}}{\partial x} \quad \text{E6-71.}$$

The concentration of Na^+ was inevitably introduced but can be obtained straightforwardly from the assumption of charge neutrality (E6-37). For this system,

$$c_{Na^+} = - (c_{H^+} - c_{H_2PO_4^-} - 2c_{HPO_4^{2-}} - 3c_{PO_4^{3-}} - c_{HCOO^-} - c_{OH^-}) \quad \text{E6-72.}$$

The system of equations at this point was formulated completely. It was further simplified so that only three equations, E6-60, E6-61 and E6-62, needed to be solved simultaneously for the concentrations of three species by appropriate substitution. Once the concentrations of an appropriate set of three species from those involved in the dissociation reactions (R6-8 to R6-12) were specified, the equilibrium relationships and equation E6-71 with the aid of equation E6-72 could be solved explicitly for the concentrations of the other species and the potential. The concentrations of H_3PO_4 , $H_2PO_4^-$ and $HCOOH$ were chosen to be associated with equation E6-60, E6-61 and E6-62, respectively. The dissociation constants and the diffusion coefficients used in the model are listed respectively in Table 3 and Table 4. The three equations were integrated from $x = \delta = 36.3 \mu m$ (Chapter 4), at which the concentrations were identical to those in the bulks and the potential was set arbitrarily to zero, to $x = 0$ with the finite-difference method. Euler's implicit method was employed to cope with the stiff nature of this kind of systems. Codes were developed for trial-and-error solutions with Matlab. The resulting local concentrations of proton are presented in Figure 6-11.

Table 3: Acid dissociation constants used in mass transport model for buffer solutions of pH 2.9

Acid	Dissociation constant, K_a	Reference
H_2O	10^{-14}	Greenwood and Earnshaw (1997)
H_3PO_4	7.11×10^{-3}	Greenwood and Earnshaw (1997)
$H_2PO_4^-$	6.31×10^{-8}	Greenwood and Earnshaw (1997)

HPO_4^{2-}	4.22×10^{-13}	Greenwood and Earnshaw (1997)
HCO_2H	1.84×10^{-4}	Partanen (1996)

Table 4: Diffusion coefficients used in mass transport model for buffer solutions of pH 2.9

Species	Diffusion coefficient, $D/\text{m}^2 \text{ s}^{-1}$	Reference
H^+	9.312×10^{-9}	Newman and Thomas-Alyea (2004)
OH^-	5.26×10^{-9}	Newman and Thomas-Alyea (2004)
H_3PO_4	9.5×10^{-10}	Ruiz-Beviá, Fernández-Sempere and Boluda-Botella (1995)
H_2PO_4^-	1.27×10^{-9}	Mihailescu and Gabor (2011)
HPO_4^{2-}	9.2×10^{-10}	Das and Changdar (1995)
PO_4^{3-}	9.2×10^{-10}	Estimated
HCO_2H	1.4×10^{-9}	Cussler (2008)
HCO_2^-	1.454×10^{-9}	Newman and Thomas-Alyea (2004)

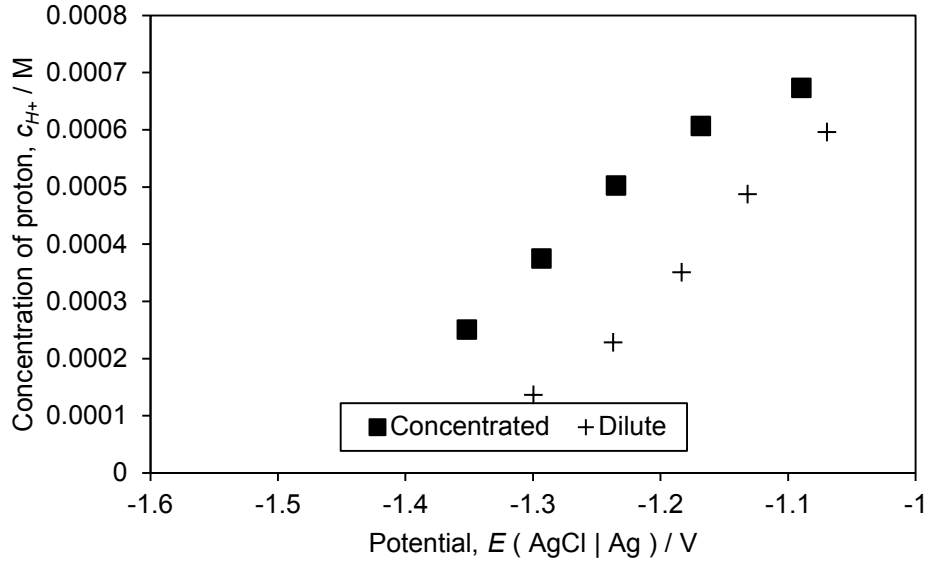


Figure 6-11: Predicted effects of electrode potential and phosphate concentrations on local concentrations of protons at tin electrode in two buffer solutions of different concentrations with bulk pH of 2.9; concentrated: 0.1 M H_3PO_4 /1 M NaH_2PO_4 , dilute: 0.02 M H_3PO_4 /0.2 M NaH_2PO_4

It can be seen that the predicted local proton concentrations in both buffer solutions decreased significantly with increasingly negative potential and those in the dilute buffer solutions were always smaller at the same potential. These trends were expected, but whether the decreased local proton concentrations were significant to improve the model predictions was yet to be confirmed. The validity of this mass transport model would be analysed together with the mass transport model for the buffer solutions of pH 7.8 after its development.

6.2.2 Mass transport model for buffer solutions at pH 7.8

The same procedure was followed for the buffer solutions at pH 7.8, which were obtained by saturating aqueous solutions of 0.5 M NaOH with 1 atm CO_2 . The following reactions were assumed to occur within the diffusion layer:



The material balance of the species resulted in the following equations:

$$\nabla \cdot \vec{N}_{H^+} = r_{H_2CO_3} + r_{HCO_3^-} + r_{HCOOH} + r_{H_2O} \quad E6-73$$

$$\nabla \cdot \vec{N}_{CO_2} = -r_{CO_2} \quad E6-74$$

$$\nabla \cdot \vec{N}_{H_2CO_3} = r_{CO_2} - r_{H_2CO_3} \quad E6-75$$

$$\nabla \cdot \vec{N}_{HCO_3^-} = r_{H_2CO_3} - r_{HCO_3^-} \quad E6-76$$

$$\nabla \cdot \vec{N}_{CO_3^{2-}} = r_{HCO_3^-} \quad E6-77$$

$$\nabla \cdot \vec{N}_{HCOOH} = -r_{HCOOH} \quad E6-43$$

$$\nabla \cdot \vec{N}_{HCOO^-} = r_{HCOOH} \quad E6-44$$

$$\nabla \cdot \vec{N}_{OH^-} = r_{H_2O} \quad E6-45$$

$$\nabla \cdot \vec{N}_{H_2O} = -r_{CO_2} - r_{H_2O} \quad E6-78.$$

Elimination of r_i gave:

$$\nabla \cdot \vec{N}_{H^+} + \nabla \cdot \vec{N}_{CO_2} + 2\nabla \cdot \vec{N}_{H_2CO_3} + \nabla \cdot \vec{N}_{HCO_3^-} + \nabla \cdot \vec{N}_{HCOOH} + \nabla \cdot \vec{N}_{H_2O} = 0 \quad E6-79$$

$$\nabla \cdot \vec{N}_{CO_2} + \nabla \cdot \vec{N}_{H_2CO_3} + \nabla \cdot \vec{N}_{HCO_3^-} + \nabla \cdot \vec{N}_{CO_3^{2-}} = 0 \quad E6-80$$

$$\nabla \cdot \vec{N}_{HCOOH} + \nabla \cdot \vec{N}_{HCOO^-} = 0 \quad E6-49$$

$$\nabla \cdot \vec{N}_{H_2O} - \nabla \cdot \vec{N}_{CO_2} + \nabla \cdot \vec{N}_{OH^-} = 0 \quad E6-81.$$

Integration with respect to x yielded:

$$N_{H^+} + N_{CO_2} + 2N_{H_2CO_3} + N_{HCO_3^-} + N_{HCOOH} + N_{H_2O} = N_{H^+}|_{x=0} + N_{CO_2}|_{x=0} \quad E6-82$$

$$N_{CO_2} + N_{H_2CO_3} + N_{HCO_3^-} + N_{CO_3^{2-}} = N_{CO_2}|_{x=0} \quad E6-83$$

$$N_{HCOOH} + N_{HCOO^-} = N_{HCOO^-}|_{x=0} \quad E6-57$$

$$N_{H_2O} - N_{CO_2} + N_{OH^-} = -N_{CO_2}|_{x=0} \quad E6-84.$$

Subtracting equation E6-84 from equation E6-82 to eliminate the flux of water gave:

$$N_{H^+} + 2N_{CO_2} + 2N_{H_2CO_3} + N_{HCO_3^-} + N_{HCOOH} - N_{OH^-} = N_{H^+}|_{x=0} + 2N_{CO_2}|_{x=0} \quad E6-85.$$

Substituting equation E6-35 for the fluxes in E6-85, E6-83 and E6-57 with the molar conductivities given by equation E6-36 yielded:

$$\begin{aligned}
& -D_{H^+} \frac{\partial c_{H^+}}{\partial x} - 2D_{CO_2} \frac{\partial c_{CO_2}}{\partial x} - 2D_{H_2CO_3} \frac{\partial c_{H_2CO_3}}{\partial x} \\
& -D_{HCO_3^-} \frac{\partial c_{HCO_3^-}}{\partial x} - D_{HCOOH} \frac{\partial c_{HCOOH}}{\partial x} + D_{OH^-} \frac{\partial c_{OH^-}}{\partial x}
\end{aligned} \tag{E6-86}$$

$$-\left(D_{H^+}c_{H^+} - D_{HCO_3^-}c_{HCO_3^-} + D_{OH^-}c_{OH^-}\right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = N_{H^+} \Big|_{x=0} + 2N_{CO_2} \Big|_{x=0}$$

$$\begin{aligned}
& -D_{CO_2} \frac{\partial c_{CO_2}}{\partial x} - D_{H_2CO_3} \frac{\partial c_{H_2CO_3}}{\partial x} - D_{HCO_3^-} \frac{\partial c_{HCO_3^-}}{\partial x} - D_{CO_3^{2-}} \frac{\partial c_{CO_3^{2-}}}{\partial x} \\
& -\left(-D_{HCO_3^-}c_{HCO_3^-} - 2D_{CO_3^{2-}}c_{CO_3^{2-}}\right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = N_{CO_2} \Big|_{x=0}
\end{aligned} \tag{E6-87}$$

$$-D_{HCOOH} \frac{\partial c_{HCOOH}}{\partial x} - D_{HCOO^-} \frac{\partial c_{HCOO^-}}{\partial x} - \left(-D_{HCOO^-}c_{HCOO^-}\right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = N_{HCOO^-} \Big|_{x=0} \tag{E6-62.}$$

The following equilibrium relationships for this system were used:

$$K_{CO_2} = \frac{c_{H_2CO_3}}{c_{CO_2}} \tag{E6-88}$$

$$K_{H_2CO_3} = \frac{c_{H^+}c_{HCO_3^-}}{c_{H_2CO_3}} \tag{E6-89}$$

$$K_{HCO_3^-} = \frac{c_{H^+}c_{CO_3^{2-}}}{c_{HCO_3^-}} \tag{E6-90}$$

$$K_{HCOOH} = \frac{c_{H^+}c_{HCOO^-}}{c_{HCOOH}} \tag{E6-66}$$

$$K_{H_2O} = c_{H^+}c_{OH^-} \tag{E6-67.}$$

The potential was also obtained through a material balance of Na^+ ions. E6-71 still held in this system, but the charge neutrality had a different form:

$$c_{Na^+} = -(c_{H^+} - c_{HCO_3^-} - 2c_{CO_3^{2-}} - c_{HCOO^-} - c_{OH^-}) \tag{E6-91.}$$

The resulting system of equations consisted of three simultaneous equations: E6-86, E6-87 and E6-62. A procedure similar to that used to solve the previous system was employed to solve these equations. The concentrations of CO_2 , HCO_3^- and $HCOOH$ were chosen to be associated with the three equations respectively. The concentrations of the other species and the potential were obtained by solving the explicit equilibrium relationships, equation E6-71 and E6-91. The dissociation constants and the diffusion coefficients used in the model are listed respectively in

Table 5 and Table 6. The predicted effects of electrode potential on the local proton concentrations are shown in Figure 6-12.

Table 5: Acid dissociation constants used in mass transport model for buffer solutions of pH 7.8

Acid	Dissociation constant, K_a	Reference
H ₂ O	10^{-14}	Greenwood and Earnshaw (1997)
CO ₂	1.7×10^{-3}	Greenwood and Earnshaw (1997)
H ₂ CO ₃	2.5×10^{-4}	Greenwood and Earnshaw (1997)
HCO ₃ ⁻	4.84×10^{-11}	Greenwood and Earnshaw (1997)
HCO ₂ H	1.84×10^{-4}	Partanen (1996)

Table 6: Diffusion coefficients used in mass transport model for buffer solutions of pH 7.8

Species	Diffusion coefficient, $D/\text{m}^2 \text{ s}^{-1}$	Reference
H ⁺	9.312×10^{-9}	Newman and Thomas-Alyea (2004)
OH ⁻	5.26×10^{-9}	Newman and Thomas-Alyea (2004)
CO ₂	1.94×10^{-9}	Tamimi, Rinker and Sandall (1994)
H ₂ CO ₃	1×10^{-9}	Estimated
HCO ₃ ⁻	1.105×10^{-9}	Newman and Thomas-Alyea (2004)
CO ₃ ²⁻	9.55×10^{-10}	Tlili et al. (2003)
HCO ₂ H	1.4×10^{-9}	Cussler (2008)
HCO ₂ ⁻	1.454×10^{-9}	Newman and Thomas-Alyea (2004)

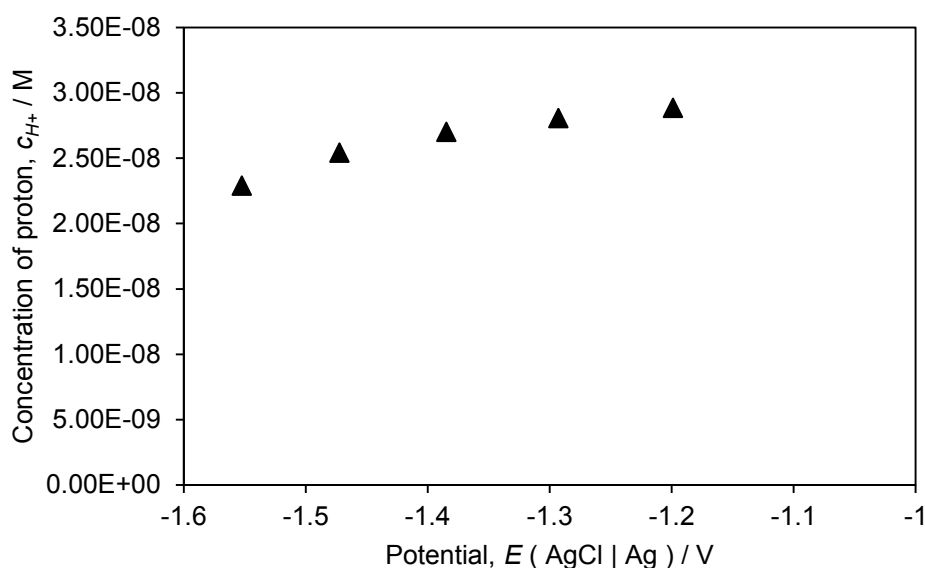


Figure 6-12: Predicted effects of electrode potential on local proton concentrations at tin electrode in buffer solutions with bulk pH of 7.8 prepared by saturating 0.5 M NaOH with 1 atm CO₂

The local proton concentrations also decreased with increasingly negative potential in these buffer solutions, but at rates significantly smaller than those in the buffer solutions of pH 2.9 due to the smaller total current densities. The decreased local proton concentrations in the three buffer solutions would be justified next for their contributions to the accuracy of the model.

6.3 Combined model

The local pH predicted from the mass transport models was input to the kinetic model developed in section 6.1.2. A change in the model's parameter was made to obtain better agreement; $k_5 K_1 K_2 / k_2 = 2.0 \times 10^{11}$. Figure 6-13 shows the predicted logarithmic formation ratios of CO to formate together with the experimental results.

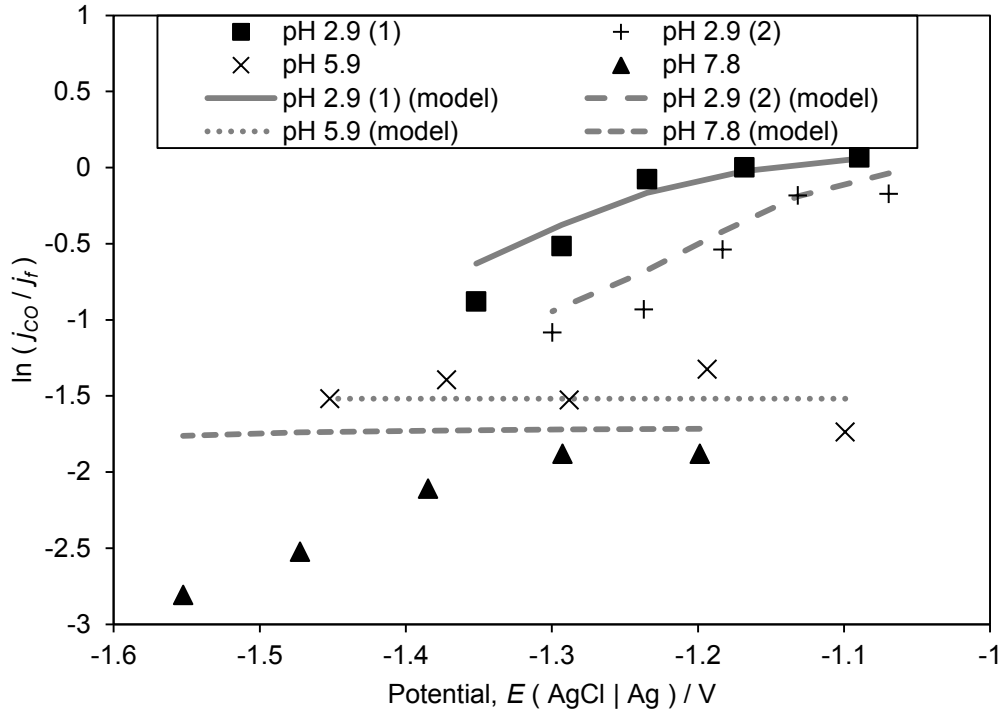


Figure 6-13: Predicted effects of electrode potential and pH on logarithmic formation ratios of CO to formate: (1) 0.1 M H_3PO_4 /1 M NaH_2PO_4 and (2) 0.02 M H_3PO_4 /0.2 M NaH_2PO_4

It can be seen that the model predicted that the logarithmic ratios at pH 2.9 and 7.8 decreased with increasingly negative potential. The predicted logarithmic ratios at pH 2.9 for both concentrations showed that the current densities exceeded the capability of the buffer solutions to hold the local pH. On the other hand, the predicted ratios at pH 7.8 indicated that the predicted local pH did not increase significantly to produce noticeable drops in the ratios at all potentials studied, contradicting the experimental results. This was believed to be caused by a specifically unrealistic assumption of equilibrated reactions in carbonate systems.

The hydration of CO_2 (R6-13) is known to be a slow reaction, for which a rate coefficient of 0.0375 s^{-1} has been reported (Gibbons & Edsall, 1963). Hence, the assumption that all homogeneous reactions in the diffusion layer were equilibrated was unrealistic. However, an easy modification to the model could be made. As the rate coefficients of the slow hydration reaction and the fast dissociation reactions differed by several orders of magnitude, it was assumed that:

$$\nabla \cdot \vec{N}_{CO_2} = -r_{CO_2} \approx 0 \quad \text{E6-92.}$$

Hence, equation E6-85 and E6-83 respectively became:

$$N_{H^+} + 2N_{H_2CO_3} + N_{HCO_3^-} + N_{HCOOH} - N_{OH^-} = N_{H^+} \Big|_{x=0} \quad \text{E6-93}$$

$$N_{H_2CO_3} + N_{HCO_3^-} + N_{CO_3^{2-}} = 0 \quad \text{E6-94.}$$

Substituting E6-35 for the fluxes in E6-93 and E6-94 yielded:

$$\begin{aligned} & -D_{H^+} \frac{\partial c_{H^+}}{\partial x} - 2D_{H_2CO_3} \frac{\partial c_{H_2CO_3}}{\partial x} - D_{HCO_3^-} \frac{\partial c_{HCO_3^-}}{\partial x} - D_{HCOOH} \frac{\partial c_{HCOOH}}{\partial x} \\ & + D_{OH^-} \frac{\partial c_{OH^-}}{\partial x} - \left(D_{H^+} c_{H^+} - D_{HCO_3^-} c_{HCO_3^-} + D_{OH^-} c_{OH^-} \right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = N_{H^+} \Big|_{x=0} \end{aligned} \quad \text{E6-95}$$

$$\begin{aligned} & -D_{H_2CO_3} \frac{\partial c_{H_2CO_3}}{\partial x} - D_{HCO_3^-} \frac{\partial c_{HCO_3^-}}{\partial x} - D_{CO_3^{2-}} \frac{\partial c_{CO_3^{2-}}}{\partial x} \\ & - \left(-D_{HCO_3^-} c_{HCO_3^-} - 2D_{CO_3^{2-}} c_{CO_3^{2-}} \right) \frac{F}{RT} \frac{\partial \phi}{\partial x} = 0 \end{aligned} \quad \text{E6-96.}$$

E6-95, E6-96 and E6-62 were solved with the same procedure to obtain the concentration profiles of all species. The local proton concentrations predicted by the modified mass transport model are presented in Figure 6-14. The logarithmic ratios at pH 7.8 predicted from the modified model are shown in Figure 6-15.

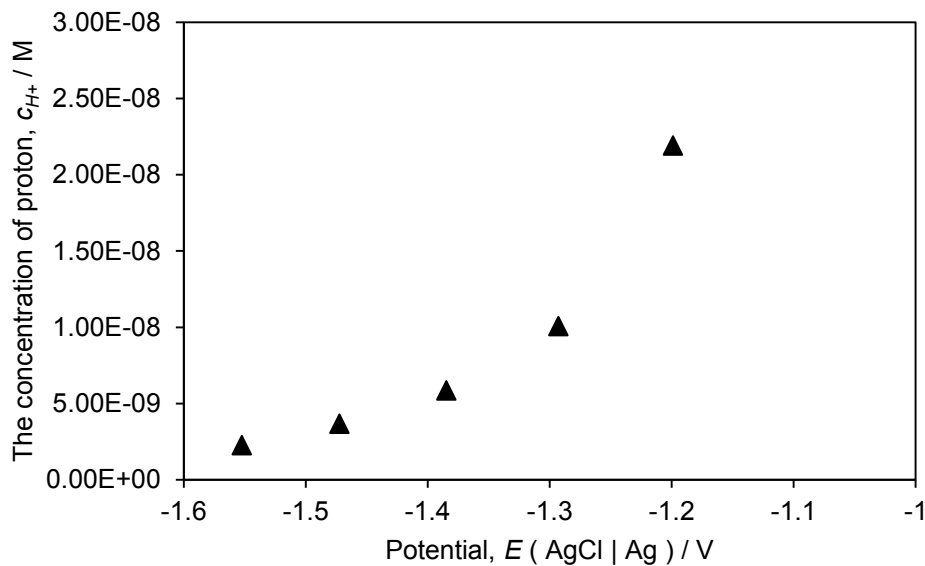


Figure 6-14: Predicted effect of electrode potential on local proton concentrations at tin electrode in buffer solutions with bulk pH of 7.8 prepared by saturating 0.5 M NaOH with 1 atm CO₂

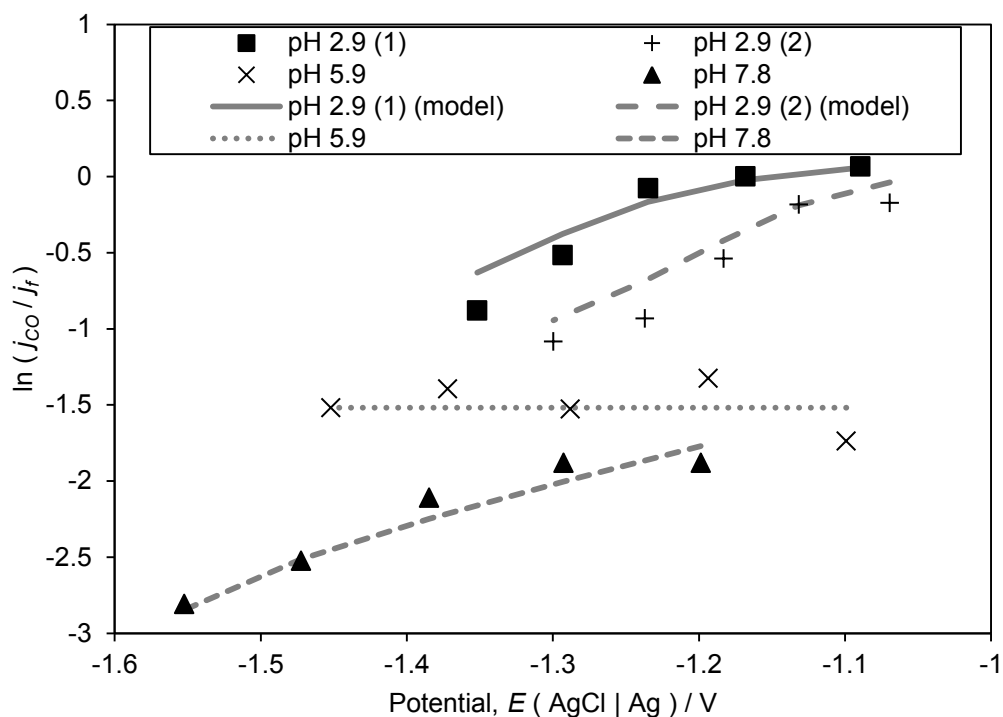


Figure 6-15: Predicted effects of electrode potential and pH on logarithmic formation ratios of CO to formate: (1) 0.1 M H_3PO_4 /1 M NaH_2PO_4 and (2) 0.02 M H_3PO_4 /0.2 M NaH_2PO_4

Significant improvements on the predictions of the ratios at pH 7.8 can be seen. Some minor modifications were also made to the kinetic parameters to obtain better agreement between the model predictions and the experimental data; these changes were: $k_{1,0} = 1.15 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_1 = 0.1$. Figure 6-16 and Figure 6-17 show the predicted effects of electrode potential and pH on the partial current densities for the formation of formate and CO, respectively.

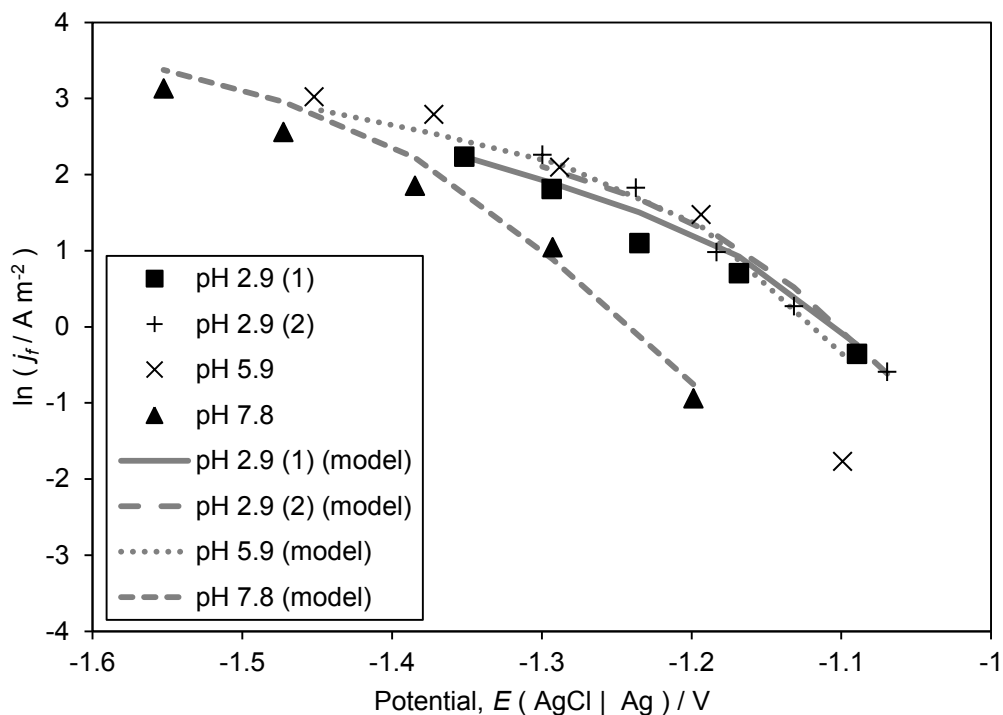


Figure 6-16: Comparison of experimental data with predicted effects of electrode potential and pH on partial current densities of formate formation: (1) 0.1 M H_3PO_4 /1 M NaH_2PO_4 and (2) 0.02 M H_3PO_4 /0.2 M NaH_2PO_4

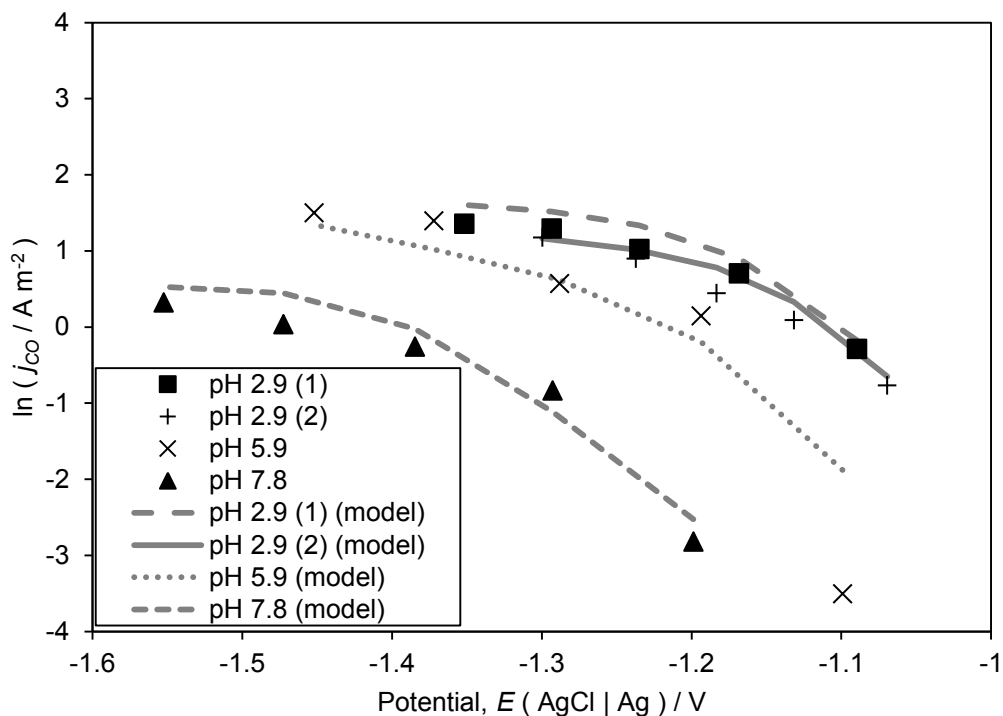


Figure 6-17: Comparison of experimental data with predicted effects of electrode potential and pH on partial current densities of CO formation: (1) 0.1 M H_3PO_4 /1 M NaH_2PO_4 and (2) 0.02 M H_3PO_4 /0.2 M NaH_2PO_4

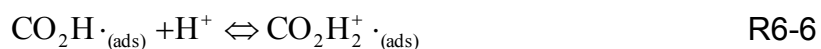
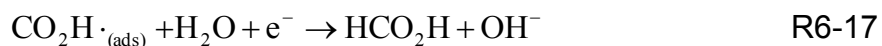
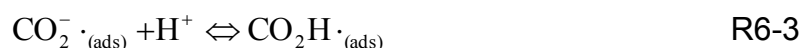
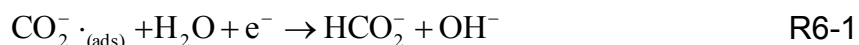
It can be seen that the mass transport model fulfilled its expected role satisfactorily. The combined model was capable of predicting the current densities for the formation of both products over a range of pH with adequate accuracy. The over-predictions of the current densities of the formation of CO at pH 2.9 seen earlier in Figure 6-8 were minimised, and so were those of both products at pH 7.8 previously presented in Figure 6-7 and Figure 6-8. The concept proposed earlier at the end of section 6.1.2 for the effect of changes in local pH appeared to be correct.

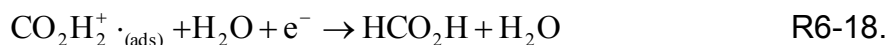
6.4 Additional discussion

6.4.1 Split between CO and formate

Though the reaction scheme introduced in section 6.1.2 represented the system well, it did not offer an insight into the actual cause of the split between CO and formate. Hori et al. (1994) proposed a generalised mechanism for the formation of CO and formate at various metal electrodes based on the adsorption strength between the adsorbed species and the underlying electrode. A similar concept was adopted and expanded to include the effect of pH in an attempt to explain the dependence of the splits between CO and formate on pH.

The results reported in this chapter showed that the pH of the solutions, or rather the local pH, determined the splits between CO and formate by protonating the intermediates, producing different adsorbed species, each of which had a specific production ratio of CO to formate. It was thought that, in addition to the adsorption strength between the adsorbed species and the electrode (C-M), the strength of C-O bonds also played a role in product formation. To illustrate this, a more extensive reaction scheme was proposed:





In this new scheme, the formation of both CO and formate from reduction of the three intermediates were considered. The formation of formate also required adsorbed water molecules as a reactant (Jitaru et al., 1997), probably to allow insertion of H at the C atom of the intermediates, but these more kinetically accurate forms were still equivalent to the previous ones proposed in section 6.1.2. The formation of CO and formate from each intermediate required cleavages of different bonds, as illustrated in Figure 6-18.

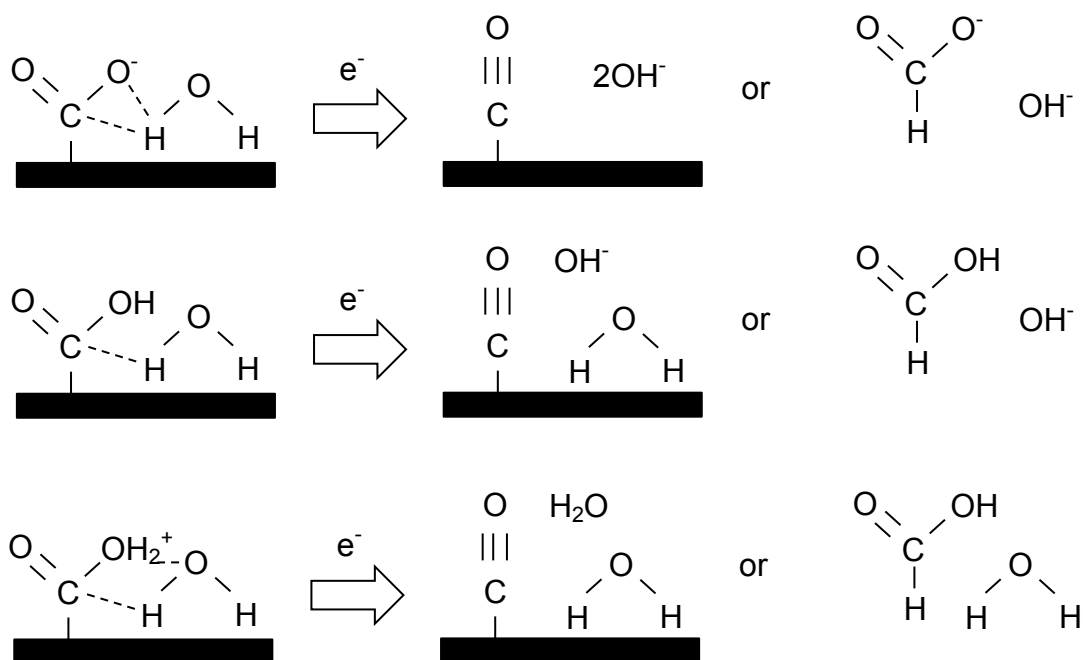


Figure 6-18: Schematic diagram of formation of CO and formate from three intermediates with dashed lines showing possible interactions during electron transfer

Therefore, the strengths of C-O and C-M bonds represent the activation barriers of CO and formate formation, respectively. The formation of O-H bonds in each level of protonation of the intermediates weakens the strength of C-O bonds, favouring the formation of CO. On the other hand, weak C-M bonds promote the formation of C-H bonds, favouring formate formation. The strength of C-M bonds, varying even on the same electrode due to surface inhomogeneity, is strongly dependent on the electrode, but not exclusively as its dependence on protonation was evident from $k_{4,0}$ being larger than $k_{2,0}$; the rate coefficient for the formation of formate from $\text{HCO}_2\cdot$ being larger than that from $\text{CO}_2\cdot^-$ was interpreted as the weakening of C-M bonds by

protonation, which was also believed to be relatively remote as C-M bonds are further from the protonation sites than C-O bonds.

It is thought that the interplay between the strengths of C-O and C-M could be expressed in simpler terms through the strength ratios of C-O to C-M. Following this concept, it was also believed that there is a critical value for the ratios, under which CO is favoured and above which formate forms. Were this ratio plotted, it would appear similar to Figure 6-19.

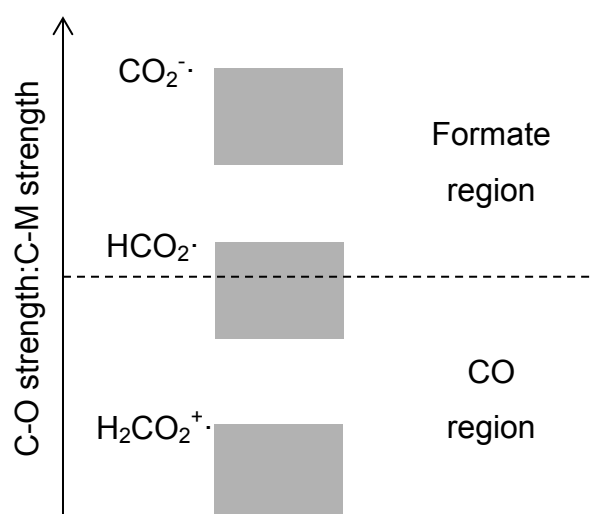


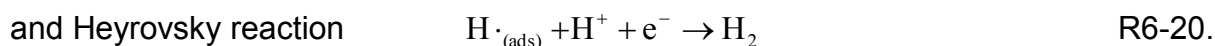
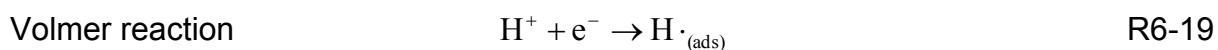
Figure 6-19: Schematic diagram of bond strength ratios of C-O to C-M in three different intermediates in electrochemical reduction of CO_2 with critical ratio represented by dashed line

The strength ratio of each intermediate is shown spreading over a definite range to signify the effect of surface inhomogeneity based on Temkin's approach, which states that the varying adsorption strength of a species at a surface is contained within a maximum and a minimum. Therefore, the intermediates with the strongest C-M bonds are positioned at the bottoms of their grey rectangles and those with the weakest bonds are at the top. The critical ratio is shown passing through the range of the strength ratios of $\text{HCO}_2^{\cdot}$ to be consistent with reaction R6-4 and R6-5, which represent the formation of CO and formate, respectively, from the same intermediate. Hence, the apparent formation rates of CO and formate from each intermediate determined experimentally were the averages over its range of C-M strength.

The effect of pH on product distributions has rarely been reported from any electrode. Pb was shown to produce exclusively formate even at pH 2 (Mahmood et al., 1987). Au and Ag are known to produce only CO. Based on this mechanism, the strengths of C-M bonds on each of these metals were either extremely weak (Pb) or extremely strong (Au and Ag) that the strength ratios were either extremely large or extremely small, respectively, nullifying the effect of pH on product distributions. The unique property of Sn was probably that the strengths of its C-M bonds were moderate that its product preferences could be altered by pH.

6.4.2 Interaction between adsorbed intermediates of hydrogen evolution and CO₂ reduction

An important issue not raised frequently in electrochemical reduction of CO₂ is the interaction between the adsorbed species formed during CO₂ reduction and hydrogen evolution: CO₂^{•-} and H[•]. Both surface species are believed to compete for the same sites and therefore the partial current densities of hydrogen evolution and CO₂ reduction should be suppressed by the presence of one another's adsorbed intermediate. To aid the coming analysis, the mechanism of hydrogen evolution should be introduced; the general mechanism is:



Therefore, the logarithmic current densities of hydrogen evolution are expected to exhibit two Tafel slopes of a larger and a smaller transfer coefficient at high potentials and low potentials, respectively, as a result of the change of the rate-determining step between Volmer and Heyrovsky reaction. The surface coverage of H[•] tends to zero in the region where Volmer reaction is limiting, while it approaches unity when Heyrovsky reaction is the rate-determining step.

An additional series of experiments was conducted to study possible differences in the current densities of hydrogen evolution between the presence and the absence of CO₂. The latter was obtained from electrolyses of N₂-sparged 0.1 M H₃PO₄/1 M NaH₂PO₄, the pH of which was essentially unaffected by the presence of CO₂. The results are plotted in Figure 6-20 together with the partial current densities of hydrogen evolution in the presence of CO₂ at pH 2.9, calculated by subtracting the

partial current densities of CO₂ reduction from their corresponding total current densities. It can be seen that the partial current densities for hydrogen evolution in the presence of CO₂ from both buffer concentrations were consistent at high potentials and deviations were observed only at low potentials, at which mass transport was limiting.

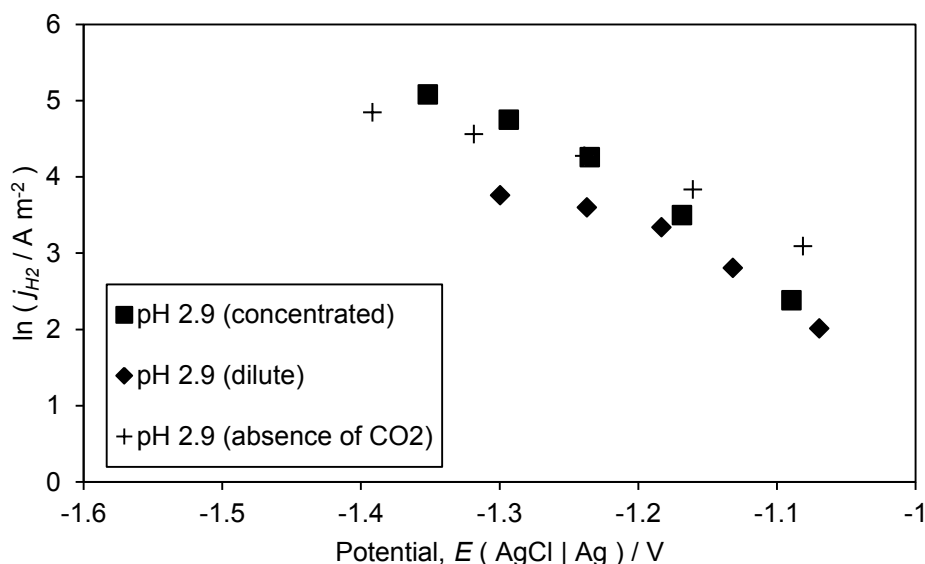


Figure 6-20: Effects of electrode potential and pH on current densities of hydrogen evolution in absence and presence of CO₂

It had been expected that the current densities of hydrogen evolution in the absence of CO₂ would have been larger than those in the presence of CO₂ at the same potential due to the absence of interactions between the adsorbed species. This was in contrast to the results in which the current densities in the absence of CO₂ appeared to be larger only at high potentials and became smaller with increasingly negative potential. The current densities in the presence of CO₂ being larger at low potentials could not be explained with confidence at this point and were rather attributed to unknown causes. If the relatively small differences at lower potentials are neglected and the larger differences at less negative potentials are considered, the results suggest that hydrogen evolution is suppressed significantly only at the latter potentials. This was consistent with the model developed for CO₂ reduction, reflecting that CO₂⁻ intermediates cover a significant portion of the electrode surface in this potential range because reaction R5-1, the transfer of the second electron to the intermediates, was limiting.

On the other hand, it was difficult to assess the effect of hydrogen evolution on the partial current densities of CO₂ reduction experimentally because one cannot simply conduct electrochemical reduction of CO₂ in aqueous solutions without protons when protons are one of the reactants and abundantly available from water. However, with a mathematical model of the reduction of CO₂ in place, a quantitative approach to the matter was attempted, but the model for hydrogen evolution had still been absent and its derivation was required for such analysis. The reaction's dependence on pH was still concerning but hydrogen evolution in the buffer solutions of pH 5.9 could be treated as pH-independent due to the high concentrations. Hence, the analysis was performed for this system and the influence of pH on hydrogen evolution was discarded.

First, the kinetic model for CO₂ reduction was simplified specifically to facilitate this analysis. The various reactions and adsorption steps involved in the second electron transfer were lumped together in a single equation to yield a simplified scheme consisting of only two equations:

$$j_1 = k_1 a_{CO_2} (1 - \theta_{CO_2^-}) \quad E6-97$$

$$\begin{aligned} j_6 &= Fk_{6,0} a_{H^+} \theta_{CO_2^-} \exp\left(\frac{-\alpha_2 FE}{RT}\right) \\ &= Fk_6 a_{H^+} \theta_{CO_2^-} \end{aligned} \quad E6-98.$$

The parameters for the first electron transfer, $k_{1,0} = 1.15 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_1 = 0.1$, were set to be the same as those used in the finalised model introduced at the end of section 6.3. $k_{6,0} = 7.94 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_2 = 0.65$ for the simplified second electron transfer were found to produce a good approximation to the experimental data.

Mathematical expressions for the rates of Volmer and Heyrovsky reactions with Langmuir isotherms are:

$$\begin{aligned} j_V &= -Fk_{V,0} a_{H^+} (1 - \theta_{H\cdot}) \exp\left(\frac{-\alpha_V FE}{RT}\right) \\ &= -Fk_V a_{H^+} (1 - \theta_{H\cdot}) \end{aligned} \quad E6-99$$

and

$$\begin{aligned} j_H &= -Fk_{H,0} a_{H^+} \theta_{H\cdot} \exp\left(\frac{-\alpha_H FE}{RT}\right) \\ &= -Fk_H a_{H^+} \theta_{H\cdot}. \end{aligned} \quad E6-100.$$

Attempts were made to obtain precise kinetic parameters for hydrogen evolution but there were experimental difficulties; this is discussed briefly in Appendix A. Instead, the values of the kinetic parameters for hydrogen evolution would be varied in a few cases to study its influence on the partial current densities of CO₂ reduction.

In order to estimate the kinetic parameters for hydrogen evolution, a high resolution plot of the current densities against electrode potential was required. The potential at which the transition between Volmer and Heyrovsky reaction as the rate-determining steps occurred must also be identified. Therefore, a cyclic voltammetry in the absence of CO₂ was conducted in the cell in one of the buffer solutions of pH 5.9 sparged with N₂. Without influences from changes in local pH and surface interactions, the cyclic voltammogram had been expected to clearly show the transition between the two Tafel slopes, but unrecognised characteristics were observed (Figure 6-21). There were apparently two changes in the slope at circa -1.3 and -1.35 V. Furthermore, it was also marked by hysteresis. Both features were probably caused by the adsorption and the desorption of dihydrogen phosphate, a further discussion of which can be found in Appendix A. Nonetheless, the transition potential remains elusive.

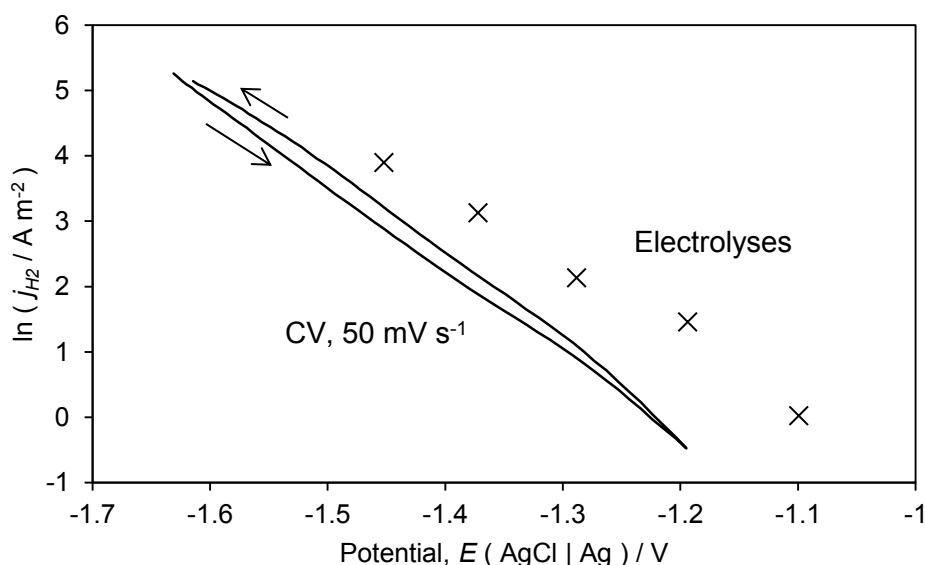


Figure 6-21: Effect of electrode potential on current densities of hydrogen evolution at pH 5.9

Shown along in the figure are the average partial current densities of hydrogen evolution during CO₂ reduction at pH 5.9 for minor discussion. It was unexpected that they were larger than the corresponding current densities obtained from the cyclic voltammetry in the absence of CO₂ at the same potentials. It was thought that

this was caused by unclear time-dependence of current densities. Nevertheless, the plots from the electrolyses retained most of their characteristics including the two transitions in the slope except they were shifted positively along the potential axis.

Despite the failed attempt, the transition potential was first assumed at approximately -1.3 V as possibly suggested by Figure 6-21. $k_{V,0} = 4.12 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_V = 0.24$, $k_{H,0} = 2.88 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_H = 0.39$ were found to adequately approximate the current densities of hydrogen evolution. The surface coverages of $\text{H}\cdot$ and $\text{CO}_2\cdot^-$ were calculated for two hypothetical cases: absence and presence of interactions between the two.

The surface coverages in the absence of interactions were obtained by performing a material balance separately for each intermediate:

$$\theta_{H\cdot} = \frac{k_V}{k_V + k_H} \quad \text{E6-101}$$

$$\theta_{\text{CO}_2\cdot^-} = \frac{k_1 a_{\text{CO}_2}}{k_1 a_{\text{CO}_2} + k_6 a_{\text{H}^+}} \quad \text{E6-102.}$$

On the other hand, the surface coverages in the presence of interactions were obtained with minor modifications to the expressions for the first electron transfer of both hydrogen evolution and CO_2 reduction:

$$j_V = -Fk_V a_{\text{H}^+} (1 - \theta_{H\cdot} - \theta_{\text{CO}_2\cdot^-}) \quad \text{E6-103}$$

$$\text{and} \quad j_1 = -Fk_1 a_{\text{CO}_2} (1 - \theta_{\text{CO}_2\cdot^-} - \theta_{H\cdot}) \quad \text{E6-104.}$$

Slightly more complicated material balances of the adsorbed species yielded:

$$\theta_{H\cdot} = \frac{k_V k_6 a_{\text{H}^+}}{k_H k_1 a_{\text{CO}_2} + k_V k_6 a_{\text{H}^+} + k_H k_6 a_{\text{H}^+}} \quad \text{E6-105}$$

$$\theta_{\text{CO}_2\cdot^-} = \frac{k_H k_1 a_{\text{CO}_2}}{k_V k_6 a_{\text{H}^+} + k_H k_1 a_{\text{CO}_2} + k_H k_6 a_{\text{H}^+}} \quad \text{E6-106.}$$

The surface coverages of $\text{CO}_2\cdot^-$ and $\text{H}\cdot$ are shown in Figure 6-22. It can be seen that the surface interactions were strong at high potentials, at which the intrinsic surface coverages of both intermediates tended to unity, suppressing the coverage of each other significantly. The competition for surface sites was weaker at low potentials, at

which both reactions did not require high surface coverages of their respective intermediates to proceed.

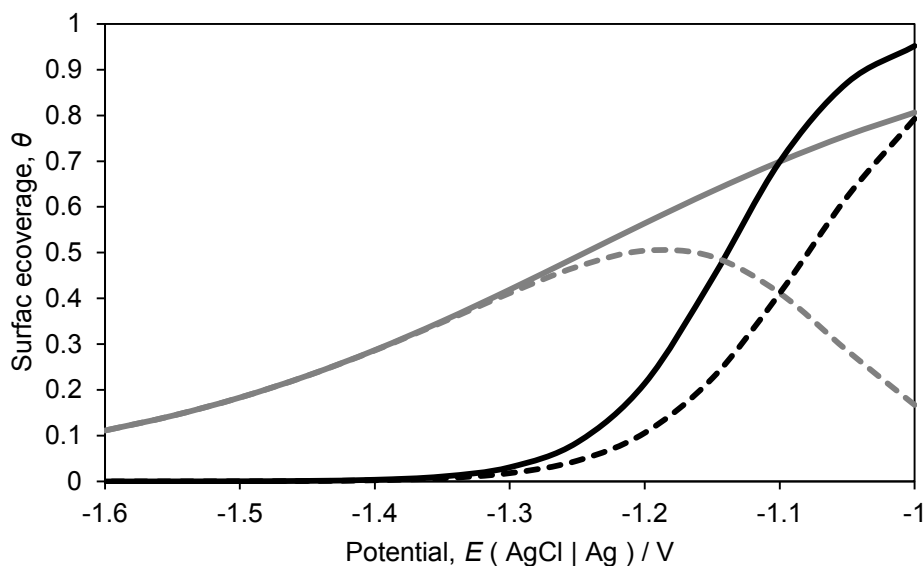


Figure 6-22: Predicted effects of electrode potential on surface coverages; black: CO_2^- , grey: H^- ; solid lines: absence of surface interactions, dashed lines: presence of surface interactions

Furthermore, as equation E6-98 and E6-100 suggest, the partial current densities of both reactions were linearly dependent on their respective surface coverages. Figure 6-23 and Figure 6-24 show respectively the comparison between the suppressed and the unsuppressed partial current densities of hydrogen evolution and CO_2 reduction. While the partial current densities of hydrogen evolution were suppressed only at high potentials, those of CO_2 reduction were inhibited at most of the potentials studied due to its smaller surface coverages at low potentials.

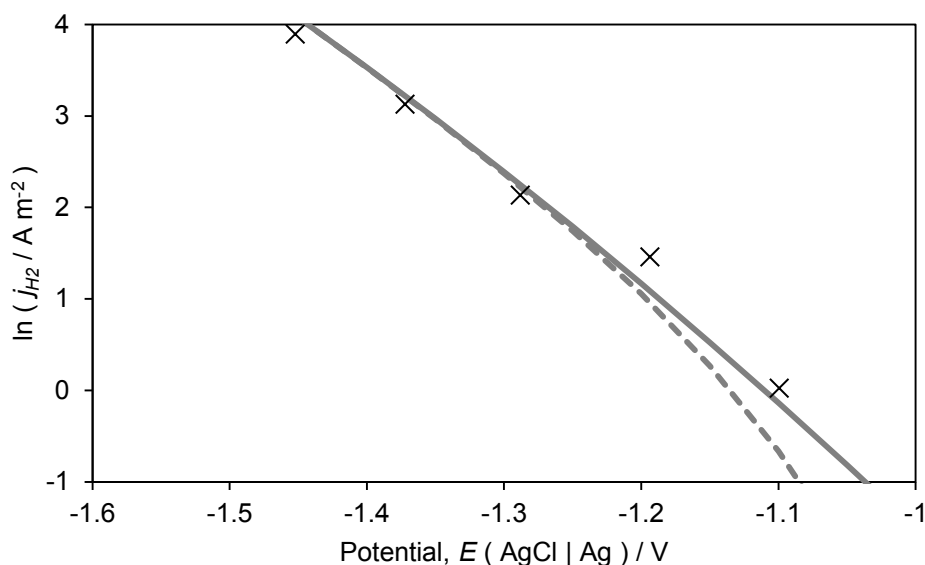


Figure 6-23: Predicted effect of electrode potential on current densities of hydrogen evolution; crosses: experimental values, solid line: absence of surface interactions, dashed line: presence of surface interactions

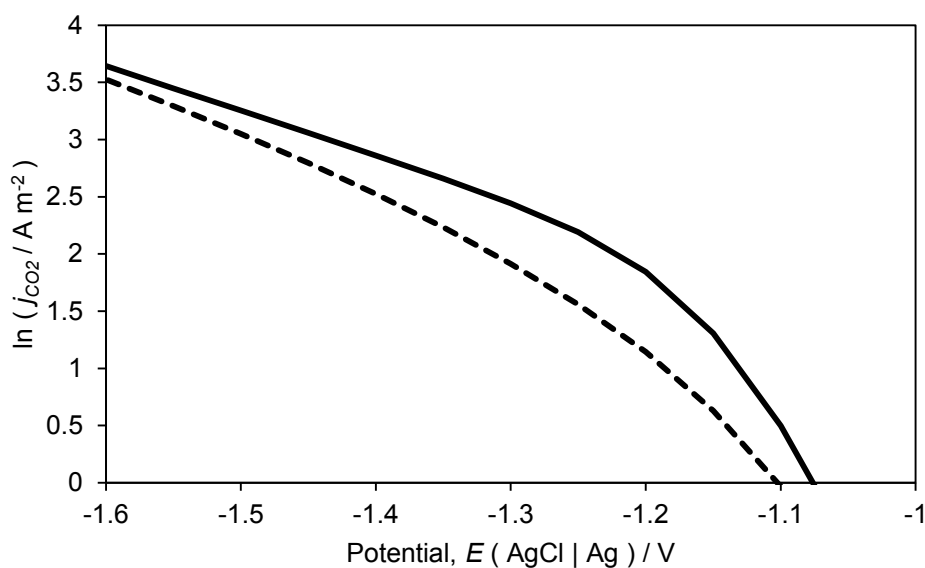


Figure 6-24: Predicted effect of electrode potential on partial current densities of CO₂ reduction; solid line: absence of surface interactions, dashed line: presence of surface interactions

Another set of kinetic parameters for hydrogen evolution could be derived by swapping their corresponding values. It was possible to produce exactly the same current densities of hydrogen evolution in the absence of surface interactions from this new set of kinetic parameters, but the relationship between the surface coverage and electrode potential was reversed, i.e. zero at high potentials and unity at low

potentials. Therefore, the differences were realised only when hydrogen evolution occurred simultaneously with CO₂ reduction.

The surface coverages, the partial current densities of hydrogen evolution and the partial current densities of CO₂ reduction are presented in Figure 6-25, Figure 6-26 and Figure 6-27, respectively. It can be seen that the surface coverages of CO₂^{•-} were decreased significantly at low potentials instead because those of H[•] tended to unity in that potential range. On the other hand, the surface coverages of H[•] were still suppressed by the large surface coverages of CO₂^{•-} only at high potentials. Consequently, while the suppressed partial current densities of hydrogen evolution were still similar to those in the previous surface interaction model, those of CO₂ reduction were highly distorted due to the strong inhibition at low potentials.

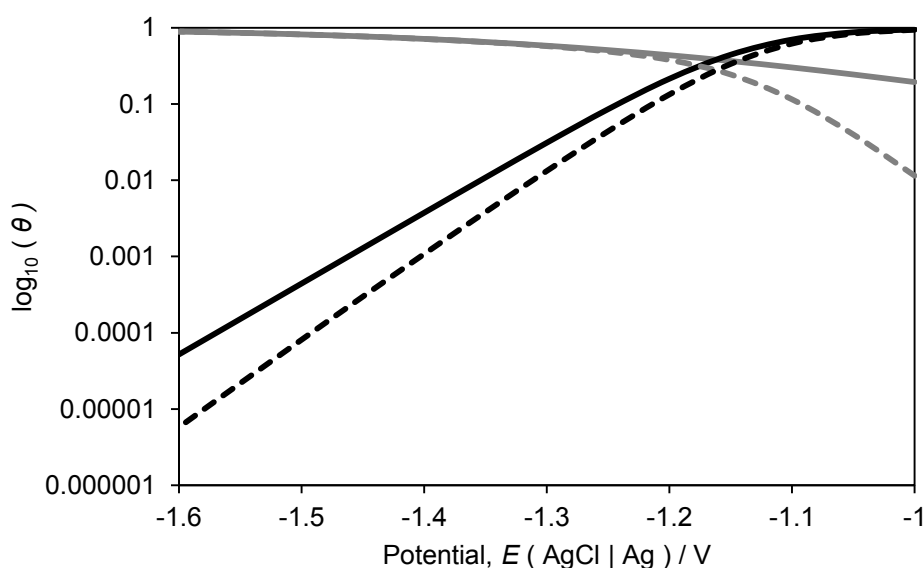


Figure 6-25: Alternative predicted effect of electrode potential on surface coverages; black: CO₂^{•-}, grey: H[•]; solid lines: absence of surface interactions, dashed lines: presence of surface interactions

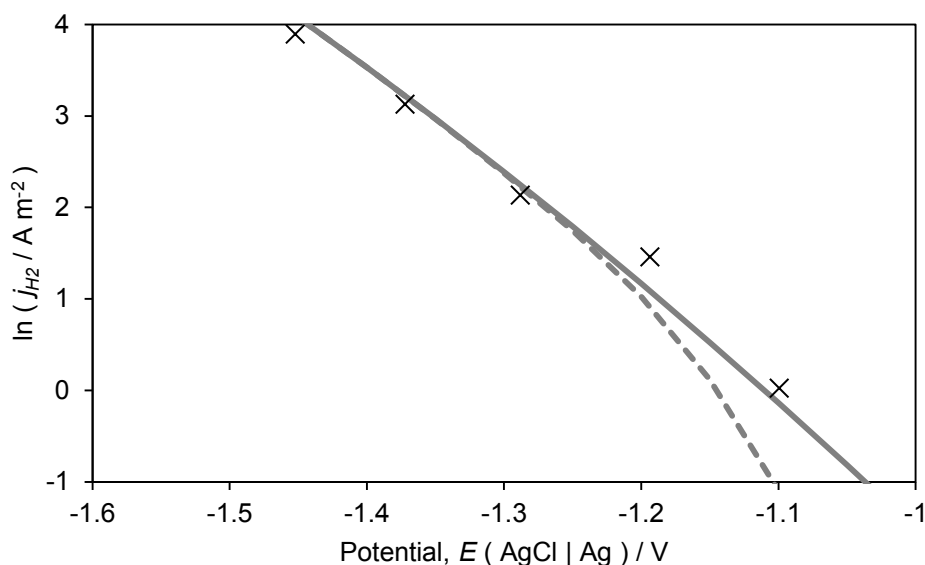


Figure 6-26: Alternative predicted effects of electrode potential on current densities of hydrogen evolution; crosses: experimental values, solid line: absence of surface interactions, dashed line: presence of surface interactions

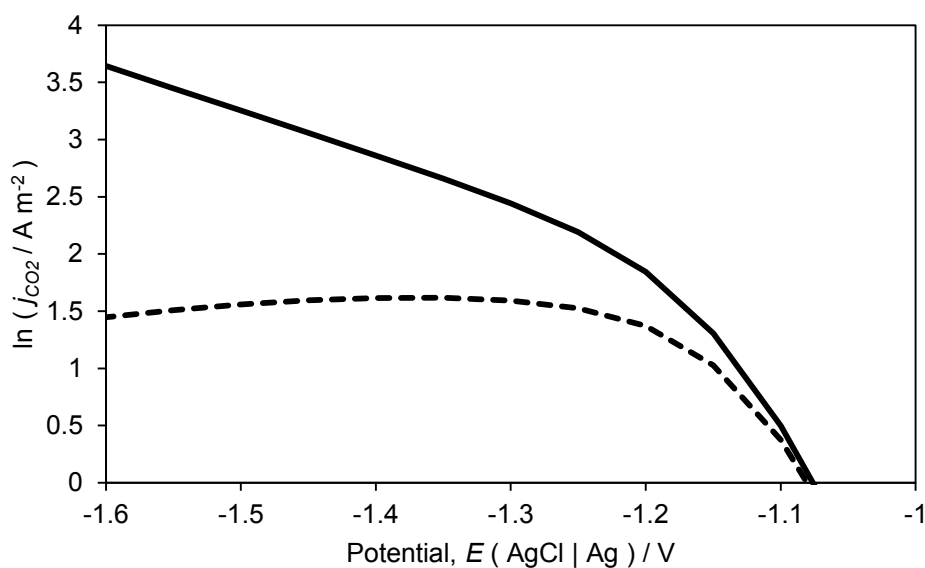


Figure 6-27: Alternative predicted effects of electrode potential on partial current densities of CO₂ reduction; solid line: absence of surface interactions, dashed line: presence of surface interactions

The distorted partial current densities of CO₂ reduction under the influence of surface interactions in both cases suggest that both models for hydrogen evolution were not representative of the system. The transition between the rate-limiting steps of hydrogen evolution was more likely to occur at a potential outside the range of the potentials studied but, whatever it was, the electrode surface should have had

surface coverages of adsorbed hydrogen approaching zero in the range of the potentials studied. A similar assumption was also adopted by Delacourt et al. (2010). Further analysis of surface interactions through electrochemical impedance spectroscopy can be found in Appendix C following a hypothetical case introduced in Appendix B.

6.4.3 Assumption of equilibrated reactions in mass transport models

Though the assumption of equilibrated homogeneous reactions greatly simplified the mass transport equations and offered estimates of local pH, it introduced a few unrealistic phenomena to the systems in which the assumption was applied. Figure 6-28 shows the concentration profiles of protons and phosphoric acid during the electrolysis at -1.30 V (AgCl|Ag) in one of the dilute buffer solutions at pH 2.9, calculated with the assumption of equilibrated reactions. In this system, mathematical analysis showed that diffusion was the main mode of transport. The slopes of the concentration profiles therefore indicated the molar fluxes. The non-zero slopes of the concentration profiles of both species at $x = 0$ suggested that both were consumed at the electrode. The larger gradient of phosphoric acid even suggested that it was the main species being consumed. This contradicts the common acceptance that only protons are reduced at electrodes.

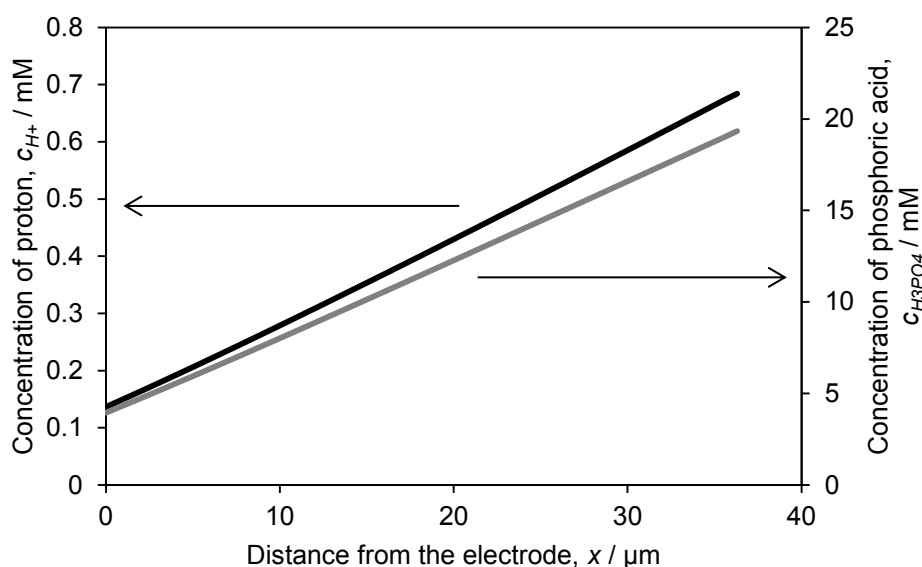


Figure 6-28: Predicted concentration profiles of protons and phosphoric acid in diffusion layer in dilute buffer solution at pH 2.9 (0.02 M H_3PO_4 /0.2 M NaH_2PO_4), calculated with assumption of equilibrated reactions at 55.7 A m^{-2} total current density

Another point not immediately obvious was that protons were being consumed by the conjugate base as they were transported from the bulk to the electrode to regenerate phosphoric acid rather than the opposite. This was known because the calculated divergence of the proton flux was negative at any x , so it followed from equation E6-34 that protons were consumed within the diffusion layer. Consequently, the concentration profiles shown in Figure 6-28 are actually curves, the second derivatives of which are positive for protons and negative for phosphoric acid. This is contrary to what was expected from using buffer agents.

A hypothetical experiment in which protons were consumed at the electrode at $1.75 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ and transported within a $0.363 \text{ }\mu\text{m}$ thick diffusion layer was set to study two approaches to modelling this system: equilibrated reactions and finite reaction rates. The system consisted of only one homogeneous reaction R6-8. The concentration profiles of the species were calculated with the previous procedures for the equilibrium approach. For the finite rate of reaction R6-8, its rate was set to:

$$r_{H_3PO_4} = k_f (a_{H_3PO_4} - a_{H^+} a_{H_2PO_4^-} / K_{H_3PO_4}) \quad \text{E6-107.}$$

Concentration profiles were calculated with arbitrary k_f of 400, 4 000 and 40 000 s^{-1} . Figure 6-29 shows the results of the calculations.

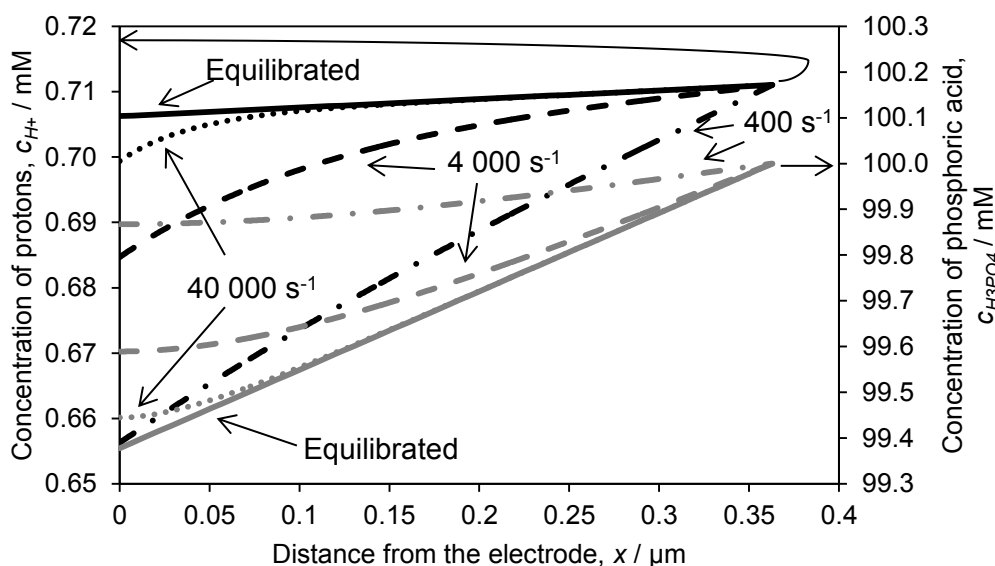


Figure 6-29: Predicted concentration profiles of protons and phosphoric acid in $0.363 \text{ }\mu\text{m}$ thick diffusion layer, calculated for proton consumption rate of $1.75 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$ with assumption of equilibrated reactions and finite reaction rates for dissociation of phosphoric acid

It can be seen that the concentration profiles obtained with the finite-rate assumption better reflected what was expected of the system. The gradients of the proton concentrations at the electrode ($x=0$) were kept constant at all values of k_f and corresponded to the defined proton flux. Those of phosphoric acid, on the other hand, were zero at the electrode, implying that the species was not consumed there.

Despite their unexpected behaviours, the assumption of equilibrated homogeneous reactions was adopted due to its simplicity and the unavailability of the finite rate coefficients. Concentration profiles calculated with this assumption probably offered good estimates for local concentrations, provided that dissociation rates were sufficiently high; as k_f was increased, the concentration profiles calculated with the finite-rate assumption approached those obtained with the assumption of equilibrated reactions. However, even if k_f becomes extremely large, the second derivatives of the concentration profiles of proton and phosphoric acid are still negative and positive, respectively, so that phosphoric acid still fulfils its role of replenishing protons. On the other hand, the results obtained with the assumption of equilibrated reactions did not always follow this behaviour as presented earlier.

6.5 Conclusions

Mathematical models for the kinetics of electrochemical reduction of CO_2 in aqueous solutions at tin were developed. The relationship between the formation ratios of carbon monoxide to formate and pH was successfully expressed mathematically. The partial current densities of the formation of carbon monoxide and formate were also reproduced accurately. A new intermediate, CO_2H_2^+ , was proposed to account for large formation ratios of CO to formate at low pH. The previous deviations of the formation ratios and the partial current densities calculated from the kinetic model alone were essentially eliminated by modifying local proton concentrations with the effect of mass transport limitations. The kinetic model was further expanded qualitatively to gain better understanding of the reaction mechanism and to cover reactions at other metal electrodes. Interactions amongst adsorbed intermediates of CO_2 reduction and hydrogen evolution were explored through simplified models. Minor issues arising from the assumption of equilibrated reactions were also discussed.

7 Electrochemical reduction of CO₂ at tin-plated graphite felt

Graphite felt is a promising material as a conductive but inert structure on which a metal can be deposited to make an electrode with a high surface area, enabling scale-up of superficial current densities relative to those from planar electrodes. However, the physics of 3D electrodes results in spatial distributions of electrolyte and electrode phase potentials, and hence in overpotentials and local current densities in the direction of current flows. This requires their dimensions to be designed specifically for a particular reaction and its operating conditions.

7.1 Equipment

Experiments were conducted in the same three-compartment cell described in Chapter 4 for experiments with the planar electrode, which were replaced by graphite felt with mesh feeder electrodes. A peristaltic pump was used to drive flows of different electrolytes through the working electrode compartment. A schematic diagram of the cell assembly is shown Figure 7-1. The same equipment was used for both deposition of tin on graphite felt and actual experiments on CO₂ reduction. Only formate was analysed in this series of experiments because large amounts of gaseous products were difficult to contain and CO should not have constituted more than 20% of the charges passed to reduce CO₂.

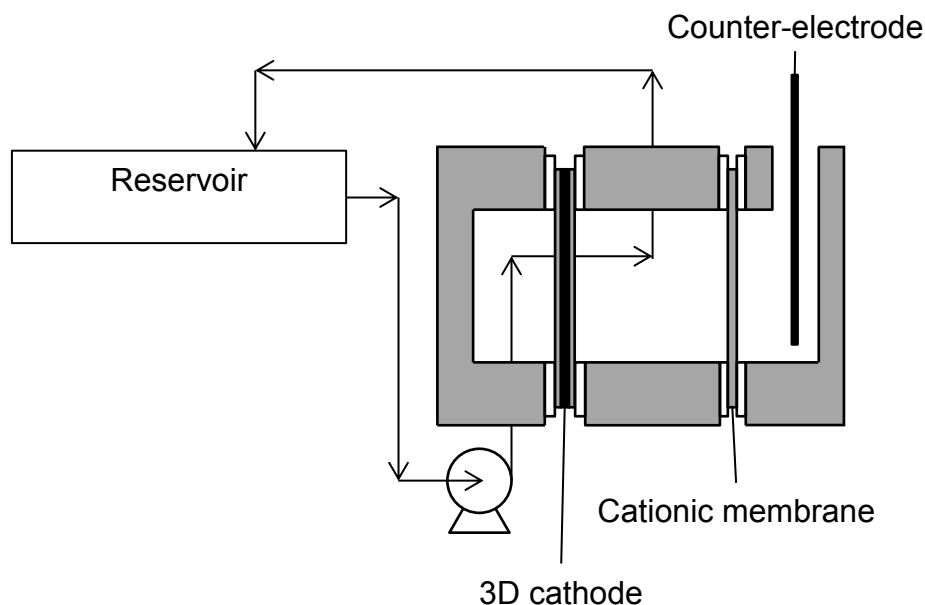


Figure 7-1: Equipment for experiments on electrochemical reduction of CO₂ at 3D tin electrodes

This arrangement of an electrolyte solution flowing along the felt thickness is called a ‘flow-through’ configuration, while an alternative of an electrolyte solution flowing along a felt length is called a ‘flow-by’ configuration. The former was employed because depletion of the reactant, CO₂, along the flow direction was expected to be less severe, whereas the latter, were it to be used, would suppress formate charge yields from the system due to steady decreases in CO₂ concentrations along the flow direction. Flow-by configurations may be more suitable for applications with a purpose of depleting reactants.

7.2 Preliminary experiments

7.2.1 Fabrication of tin-plated graphite felt

An assembly of a 3D electrode was made by first placing a piece of 20×20 mm² graphite felt between two pieces of supporting copper mesh with sizes of 22×22 mm² and 19×19 mm². They were tied together with a silver wire to provide electrical connections throughout the whole assembly. It was held in the cell between two pieces of gaskets by the extra lengths of the larger copper mesh, with the smaller copper mesh facing the counter-electrode. The larger and the smaller copper mesh shall be referred to as the back mesh and the front mesh, respectively. The adjacent

planes of the felt shall be referred to similarly as the back and the front of the electrode. A photograph of one of the assemblies is shown in Figure 7-2.

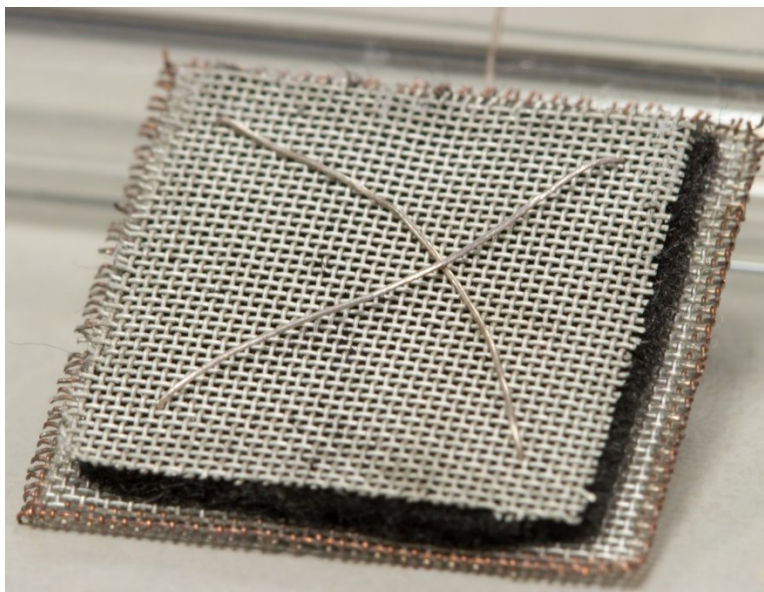


Figure 7-2: Preliminary assembly of 3D electrode

Alkaline solutions of $\text{K}_2[\text{Sn}(\text{OH})_6]$ are widely recommended for electrodeposition of tin with good morphologies (Zhang, 2000) and hence were used in this project. They were prepared from SnCl_4 , which was dissolved in an excess of KOH in the aqueous solutions. The exact composition was adapted from the same reference and consisted of 0.3 M of the precursor and 2.2 M of KOH . A large amount of heat was released during mixing of a KOH solution with a precursor solution that the mixture boiled briefly, indicating a series of exothermic chemical reactions between SnCl_4 and KOH likely to form $[\text{Sn}(\text{OH})_6]^{2-}$ ions and KCl . The final composition was expected to be 0.3 M $\text{K}_2[\text{Sn}(\text{OH})_6]$, 0.4 M KOH and 1.2 M KCl . The last two species also served as supporting electrolytes, high concentrations of which are crucial in minimising potential distributions in 3D electrodes. 4 M KOH was used as the anolyte during deposition to supply K^+ to the plating solution to achieve high conductivities.

Cyclic voltammetry was performed with an assembly of 6 mm thick graphite felt in this solution to study its electrochemical characteristics, resulting in voltammograms shown in Figure 7-3. The two consecutive scans between -1.8 V and 0.2 V started at 0 V and went in the negative direction first.

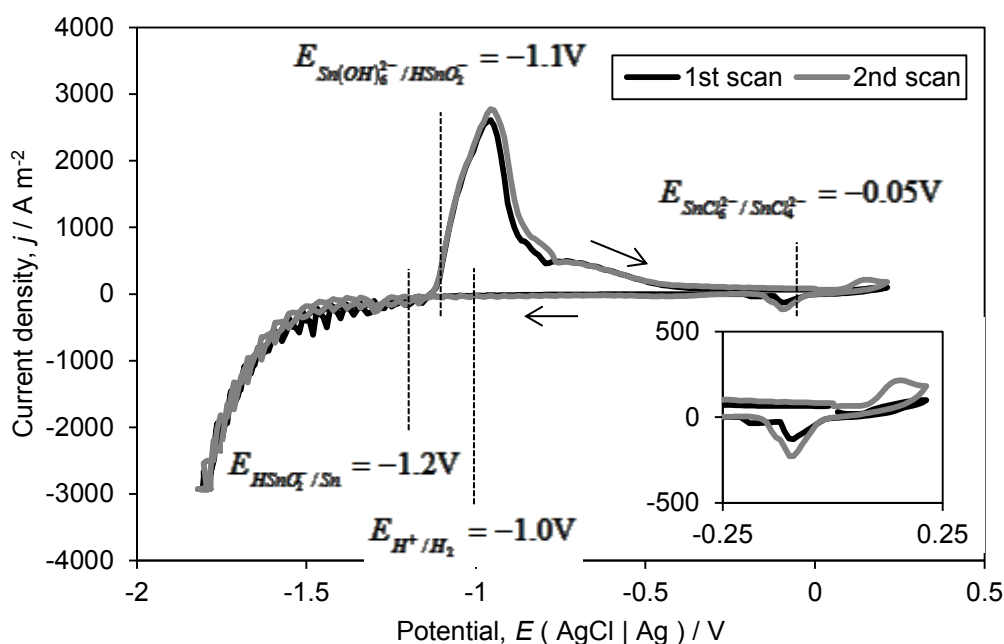


Figure 7-3: Cyclic voltammograms of 6 mm thick graphite felt in quiescent aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH at 0.1 V s^{-1} , with inset magnifying small current peaks between -0.25 and 0.25 V

A negative-going potential scan from 0 V produced a cathodic current peak encountered at ca. 0 V due to reduction of $\text{Sn}^{(\text{IV})}$ to $\text{Sn}^{(\text{II})}$. The next expected but obscured feature was the reduction of $\text{Sn}^{(\text{II})}$ to $\text{Sn}^{(0)}$, or the deposition of tin with probable concomitant hydrogen evolution, evident from the rapid increase in the cathodic current density at the negative limit of the voltammograms. On the subsequent positive-going potential scan, the large anodic current peak at ca. -1 V was due to the oxidation of the previously deposited $\text{Sn}^{(0)}$ to $\text{Sn}^{(\text{II})}$. The last anodic peak at the positive end of the voltammograms was due to the oxidation of $\text{Sn}^{(\text{II})}$ to $\text{Sn}^{(\text{IV})}$, which became obvious only in the second scan cycle after $\text{Sn}^{(\text{II})}$ had accumulated. It should also be pointed out that the presence of the redox current peaks at ca. 0 V suggested that some Sn ions were complexed by chloride ions.

A dense deposit of a metal generally requires slow deposition rates relative to mass transport rates to avoid dendrite formation. However, deposition of a metal on a three-dimensional structure adds another level of complexity: the spatial distributions of current densities and deposition rates due to the distributions of potential in the ionically- and the electronically-conducting phase within the matrix. As ohm's law applies to each phase, the lower the total current densities, i.e. the sum of the partial current densities from the deposition and hydrogen evolution, and the greater the

conductivities of the ionically- and the electronically-conducting phase, the less inhomogeneous will be the potential and the current density distributions. The electronic conductivity of graphite felt was of less concern, as its low initial value should increase sharply once metal is deposited. The voltammograms in Figure 7-3 suggests that potentials below -1.2 V were low enough to activate the deposition of Sn. -1.4 V was chosen as the potential for potentiostatic deposition of Sn, as it enabled adequate deposition rates and acceptable inhomogeneity in the potential distribution.

Preliminary deposition of tin on graphite felt was conducted firstly at -1.4 V for 2 hours with the plating solution flowing through the felt from the back to the front at 132 ml min^{-1} , resulting in the time-dependent current densities shown in Figure 7-4. The cathodic current densities increased rapidly during the first 1 000 seconds, reflecting the time-evolution of the morphology and/or the area, following the initial metallisation of the felt, which would have greatly affected the potential and current distribution. The subsequent steady decreases in the current densities had been thought to be due to depletion of tin in the plating solution, but a calculation showed that only 10% was consumed during the two hours deposition, while the decrease from the maximum current density was ca. 40%; the decreases were not caused by tin depletion but likely to also arise from time-evolution of surface morphologies.

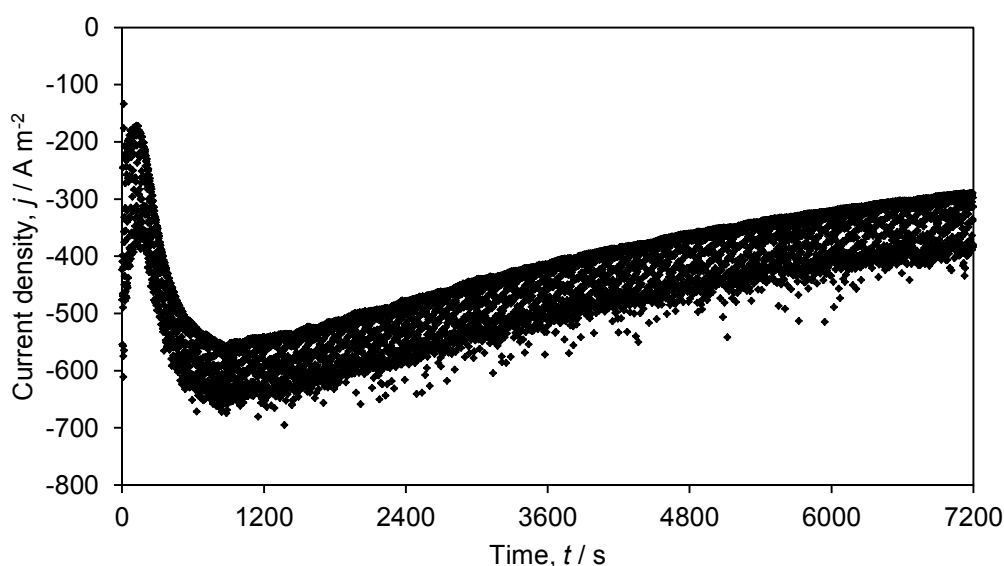


Figure 7-4: Time-dependence of current densities during Sn electrodeposition on 6 mm thick graphite felt at -1.4 V (AgCl|Ag) from aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH flowing at 132 ml min^{-1}

The plated felt was washed with high purity water, dried and sliced in half, exposing the structure shown in Figure 7-5. A slight variation in the amount of deposited tin on the front and the back side of the felt was detected through minute differences in the colour of the plated felt; the slightly lighter colour of the front side suggests thicker deposits. The black area shown in the bottom image probably resulted from air being trapped, resulting in graphite fibres within the volume not contacting the plating solution. The region of bare graphite felt could cause low current densities and low charge yields in subsequent use for CO₂ reduction and therefore should be prevented. Squeezing a piece of graphite felt in high purity water before deposition was found to be effective for expelling air from the felt and was added to the procedure.



Figure 7-5: Images of outside (top) and inside (bottom) of plated felt achieved at -1.4 V (AgCl|Ag) for 2 hours in aqueous solution containing 0.3 M SnCl₄ and 2.2 M KOH flowing at 132 ml min⁻¹

A close-up of the plated felt is shown in Figure 7-6. The scattered dark-grey spots were believed to be cross-sections of bundles of fibres protruding outwards from the felt. A plausible explanation for the darker colour is that the spots contained the black

colour of cross-sections of graphite fibres; this was later confirmed by an SEM micrograph (Figure 7-7). The image also shows that a significant amount of tin deposits was scraped off graphite fibres, but this was likely to have occurred when the plated felt was sliced and handled, as the quality of the deposit underneath was generally better.

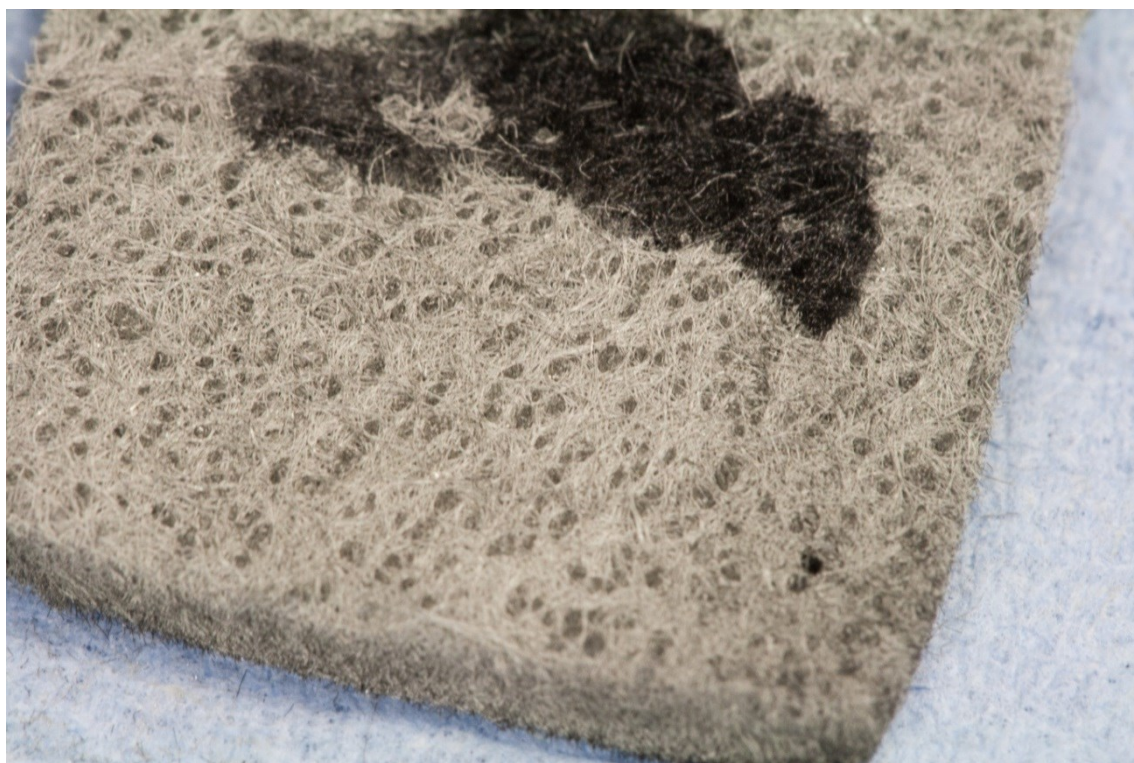


Figure 7-6: Close-up of inside of plated felt achieved at -1.4 V (AgCl|Ag) for 2 hours in aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH flowing at 132 ml min^{-1}

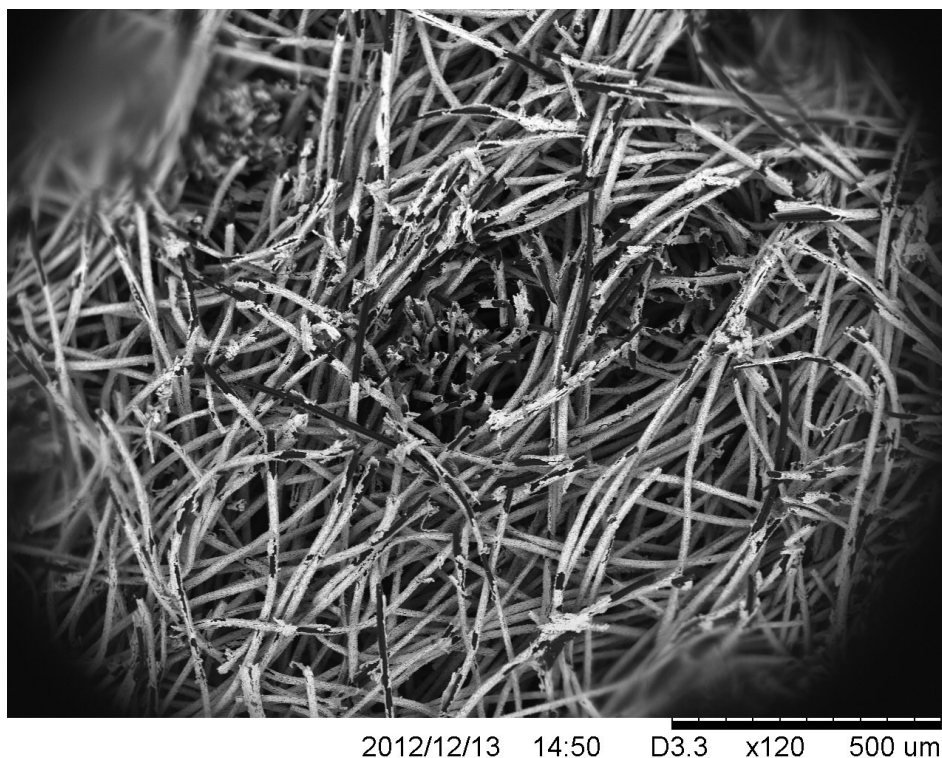


Figure 7-7: SEM micrograph of tin-plated graphite felt achieved at -1.4 V (AgCl|Ag) for 2 hours in aqueous solution containing 0.3 M SnCl₄ and 2.2 M KOH flowing at 132 ml min⁻¹, showing overall quality

Figure 7-8 shows a close-up of a tin-plated fibre of the plated felt with a ca. 1 µm thick tin layer covering the graphite fibre only superficially; the deposit layer formed loosely around each fibre rather than following each groove on the graphite fibre. This should result in a decreased total active surface area but the presence of features like cracks and polycrystallinity could at least partially compensate for the effect or even provide a larger total surface area than that of the bare graphite felt, as implied by the image in Figure 7-9.

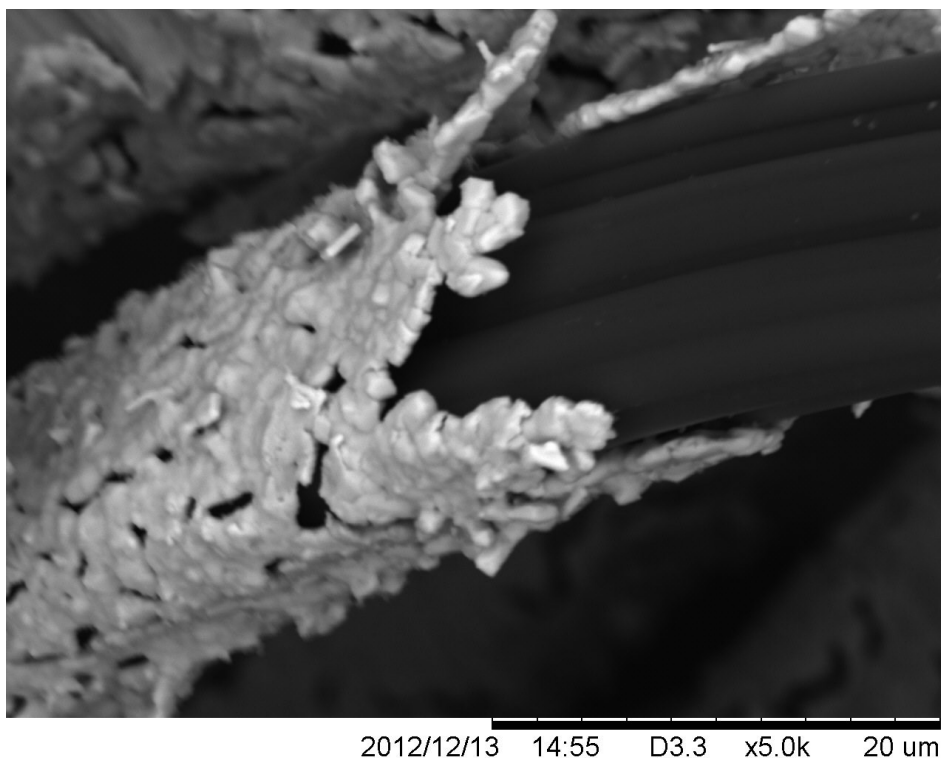


Figure 7-8: SEM micrograph of tin-plated graphite fibre achieved at -1.4 V (AgCl|Ag) for 2 hours in aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH flowing at 132 ml min^{-1}

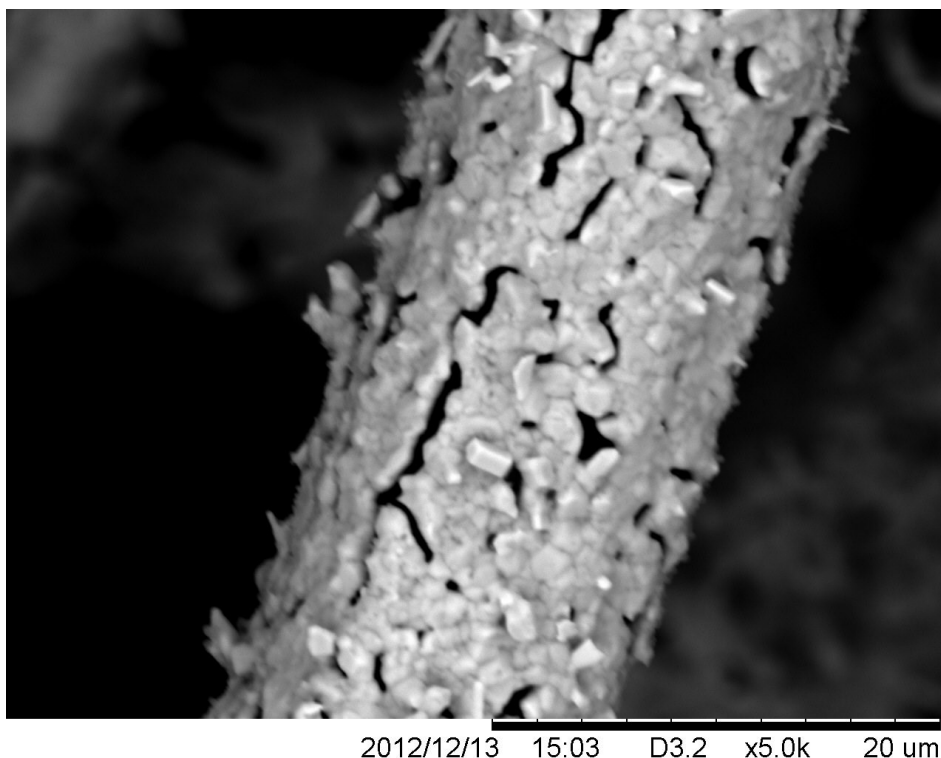


Figure 7-9: SEM micrograph of tin-plated graphite fibre achieved at -1.4 V (AgCl|Ag) for 2 hours in aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH flowing at 132 ml min^{-1} , showing surface morphology

Crystals appeared to have varying sizes with the largest being approximately 2 μm . Some crystals also grew on the existing tin layer, forming scattered ‘buds’. The cracks probably occurred during electrodeposition due to stress accumulation or later when the plated felt was subjected to various harsh treatments: compression and decompression during removal from the supporting meshes, drying and slicing.

The thickness of the felt was set to be 6 mm at first only to allow inspection of the inside by slicing; it had actually been thought to be too thick to be used for CO_2 reduction. Hence the thickness was decreased to 3 mm for subsequent preliminary experiments. Relatively even distributions of the thickness of the tin layer should result because good coverage of the deposited layer had already been achieved with 6 mm felt, for which the potential distribution would have been even less homogeneous. The deposition time was decreased to 1 hour to determine the effect of tin loading and to save experimental time. Figure 7-10 shows the resulting time dependence of the current densities during tin deposition on 3-mm felt at -1.4 V. The resulting plated felt showed similar features to those of the previous sample. The coverages from the two methods showed no distinction despite the thickness of the tin layer being decreased to approximately one-third of that obtained from 2 hours of deposition (Figure 7-11), so 1 hour deposition time was used in subsequent preliminary experiments.

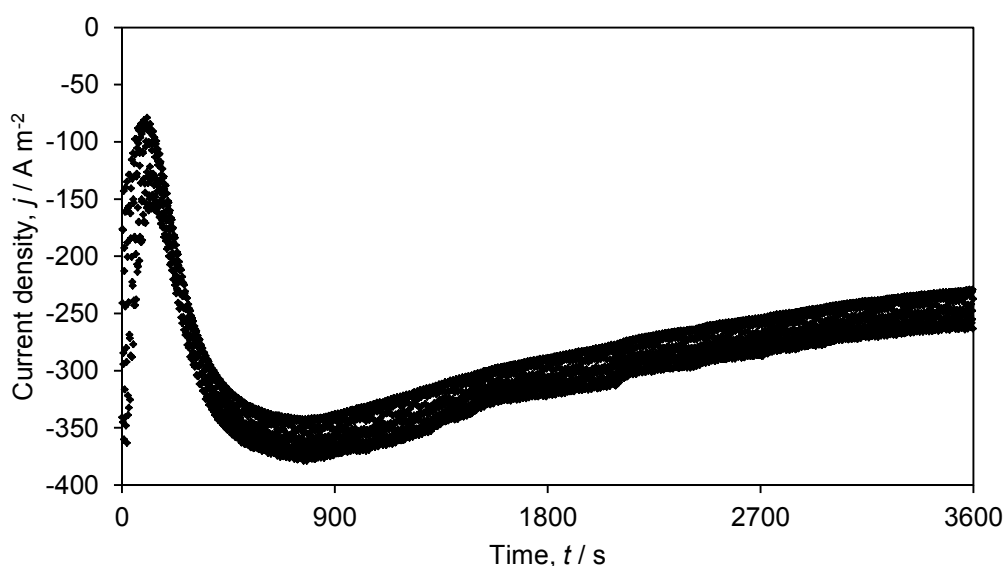


Figure 7-10: Time dependence of current densities during deposition of Sn on 3 mm thick graphite felt at -1.4 V (AgCl|Ag) from aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH flowing at 132 ml min^{-1}

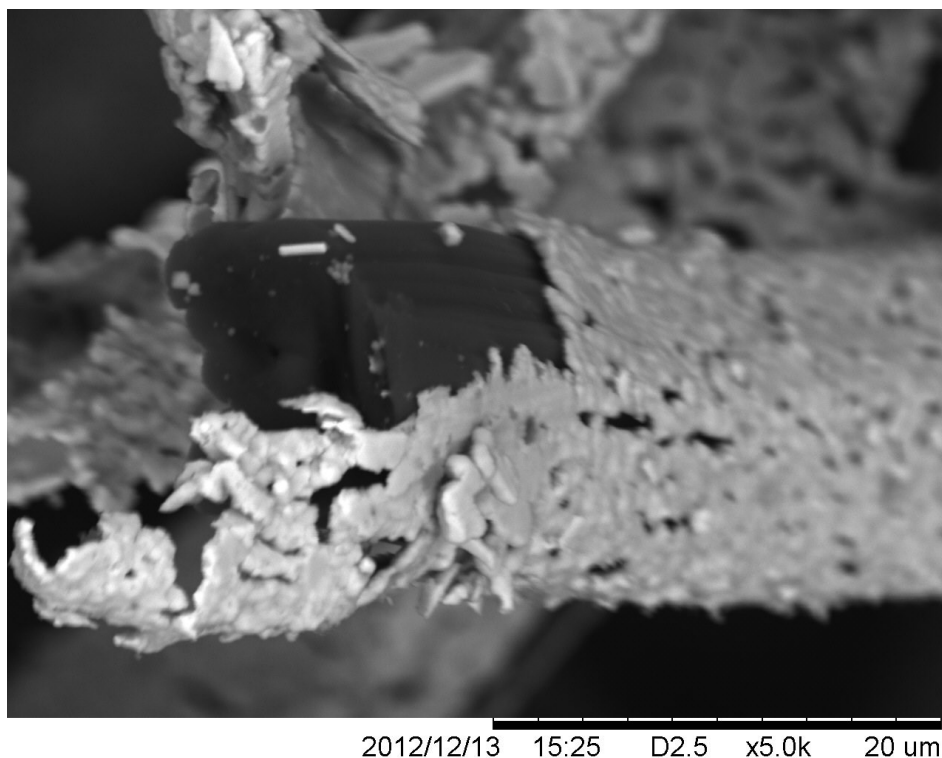


Figure 7-11: SEM micrograph of tin-plated graphite fibre achieved at -1.4 V ($\text{AgCl}|\text{Ag}$) for 1 hour in aqueous solution containing 0.3 M SnCl_4 and 2.2 M KOH flowing at 132 ml min^{-1}

7.2.2 Electrolyses of aqueous solutions containing 0.5 M NaOH saturated with 1 atm CO_2 at tin-plated graphite felt

Freshly prepared tinned graphite felt was used in each experiment. It was removed from the cell after deposition, rinsed thoroughly with high purity water in which it was stored while the cell was cleaned. 100 ml of 0.5 M NaOH was sparged with CO_2 for 15 minutes, during which the 3D electrode was re-assembled in the cleaned cell. The CO_2 -saturated solution was then transferred to a reservoir and circulated between the cell and the reservoir with the peristaltic pump, flowing from the back to the front of the 3D electrode. The cell was shaken to remove bubbles that might have been trapped in the cell. $3\text{ M H}_2\text{SO}_4$ was poured into the counter-electrode compartment as an anolyte. Such a high concentration was used because it provides the highest conductivity for aqueous H_2SO_4 . Electrolyses were conducted for 10 minutes, after which liquid samples were analysed for formate contents.

Figure 7-12 shows the time dependence of the current densities during an electrolysis of a CO_2 -saturated solution at -1.3 V for 10 minutes; the current densities decreased during the first 100 s and then remained constant at ca. 280 A m^{-2} until

around 400 s when fluctuations started and continued until the end of the experiment.

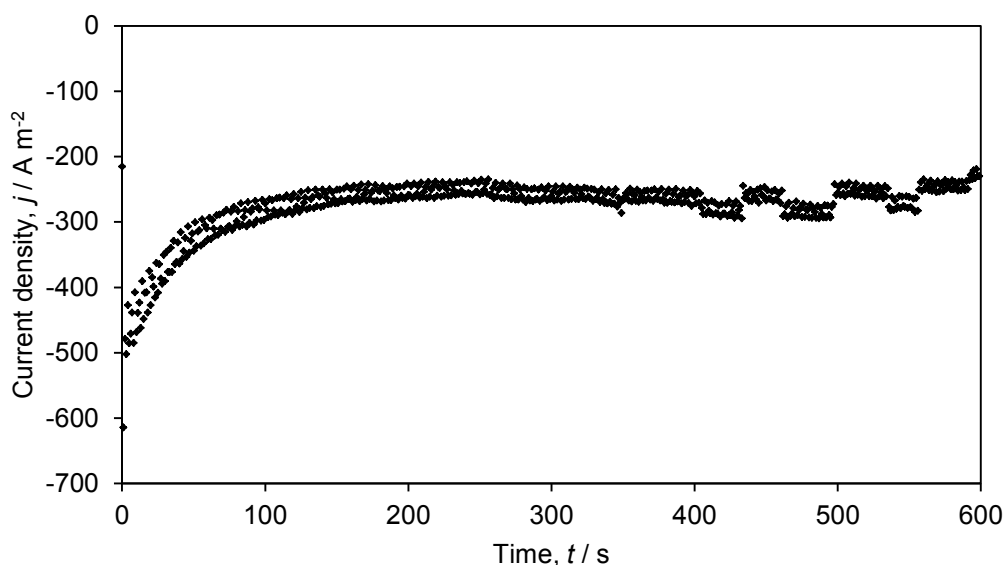


Figure 7-12: Time dependence of current densities during electrolysis at -1.3 V (AgCl|Ag) of aqueous solution containing 0.5 M NaOH saturated with 1 atm CO₂ flowing at 33 ml min⁻¹

Figure 7-13 shows the time dependence of the current densities for a similar experiment, but at -1.5 V, at which the expected larger current densities decayed more rapidly and fluctuations started after ca. 100 s and had larger amplitudes.

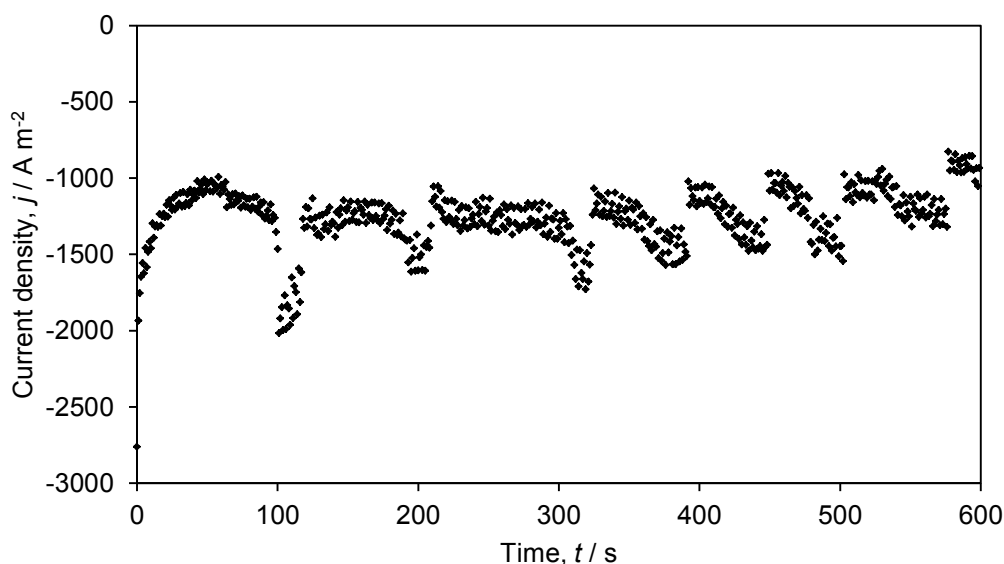


Figure 7-13: Time dependence of current densities during electrolysis at -1.5 V (AgCl|Ag) of aqueous solution containing 0.5 M NaOH saturated with 1 atm CO₂ flowing at 33 ml min⁻¹

These fluctuations were believed to have been caused by gas bubbles; hydrogen was generated constantly from the reduction of protons and water and CO formed as

a minor product of the reduction of CO_2 . The generated gas accumulated gradually within the matrix of the felt, decreasing the conductivity of the electrolyte and/or the contacts between the plated felt and the aqueous solution, causing decreases in the current densities. The bubbles escaped periodically after having accumulated within the plated felt; this renewed the conductivity of the electrolyte, freed the occupied active surfaces and increased the current densities briefly before the process repeated and produced the apparent fluctuations.

Figure 7-14 reports the average current densities and the charge yields of formate from the two experiments. Data for a repeated experiment at -1.3 V is also included to show the good reproducibility of the system. Despite the massive increase in the current densities when potential was decreased from -1.3 V to -1.5 V, the low charge yields did not change significantly, probably because of inadequate mass transport rates of CO_2 ; hence the flow rate of the electrolyte solution was increased to 110 ml min^{-1} to enhance the mass transport.

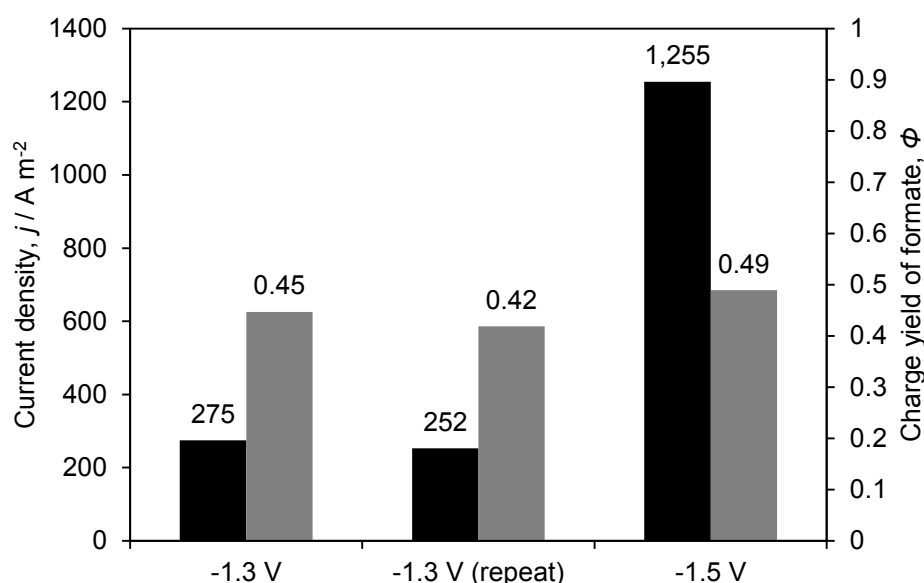


Figure 7-14: Current densities (black) and charge yields of formate (grey) from electrolyses of aqueous solutions containing 0.5 M NaOH saturated with 1 atm CO_2 flowing at 33 ml min^{-1} for 600 s

Figure 7-15 reports results for the electrolyses at -1.3 V at two flow rates, together with data for the repeated experiment at 110 ml min^{-1} . The current densities and the charge yields of formate unexpectedly decreased with the increased flow rates. It was believed that this abnormal behaviour was caused by the physical arrangement of the 3D cathodes within the reactor.

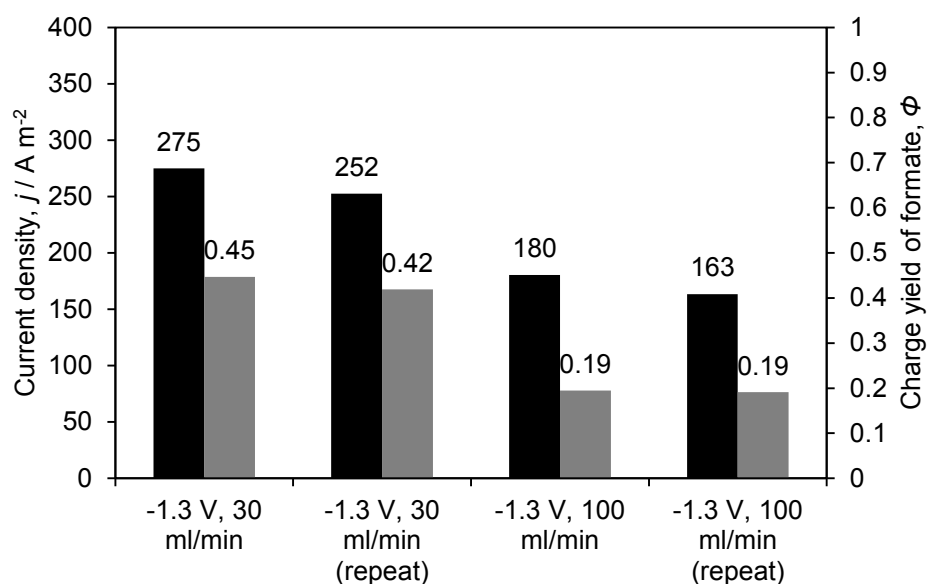


Figure 7-15: Current densities (black) and charge yields of formate (grey) from electrolyses of aqueous solutions containing 0.5 M NaOH saturated with 1 atm CO_2 for 600 s at -1.3 V (AgCl|Ag) and two different flow rates

The proposed flaw of the physical arrangement of the 3D electrodes is shown schematically in Figure 7-16. Electrons could be transferred to the felt from both supporting meshes, but a larger portion was believed to go through the rear mesh because of its better electrical contacts with the wire. At low flow rates, the contacts between the felt and the two meshes were firm, facilitating electron transfer between the meshes and the felt. As the flow rate of the electrolyte solutions was increased, a larger pressure drop and skin friction imposed on the felt pressed the felt cathode against the front mesh with a stronger force, weakening the pressure exerted by the felt on the back mesh, resulting in looser rear contacts, diminishing the main path of electron transfer. A better assembly was developed specifically to address this problem.

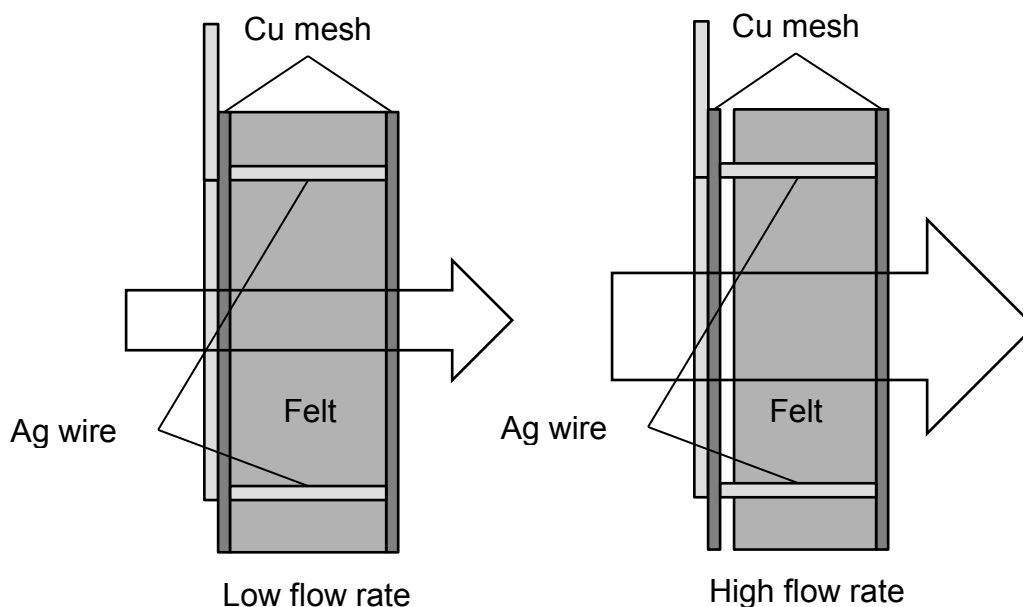


Figure 7-16: Schematic cross-sectional view of 3D electrode assembly at low and high flow rates

7.3 Improved experiments

7.3.1 Fabrication of tin-plated graphite felt

A new assembly for 3D electrodes was made with emphasis on good electrical contacts throughout. Two 50×25 mm² copper meshes were used as supporting meshes. Both ends of each piece were soldered to wires to minimise contact resistances. A piece of 1.5 mm thick gaskets were attached to each side of the back mesh in the middle with silicone sealant to form seals. Silicone sealant was applied to the front mesh to form seals where it was expected to contact the front gasket of the back mesh. The gasket between the two pieces of mesh also served as a spacer. The thickness of graphite felt for subsequent experiments was also reduced to 1.5 mm to be consistent with the thickness of the gasket. A photograph of this new assembly is shown in Figure 7-17. Compression of felt was introduced as a means to improve good electrical contacts between felt and the supporting meshes, achieved by tightening the reactor until the spacer gasket and the felt were compressed to 1.2 mm.

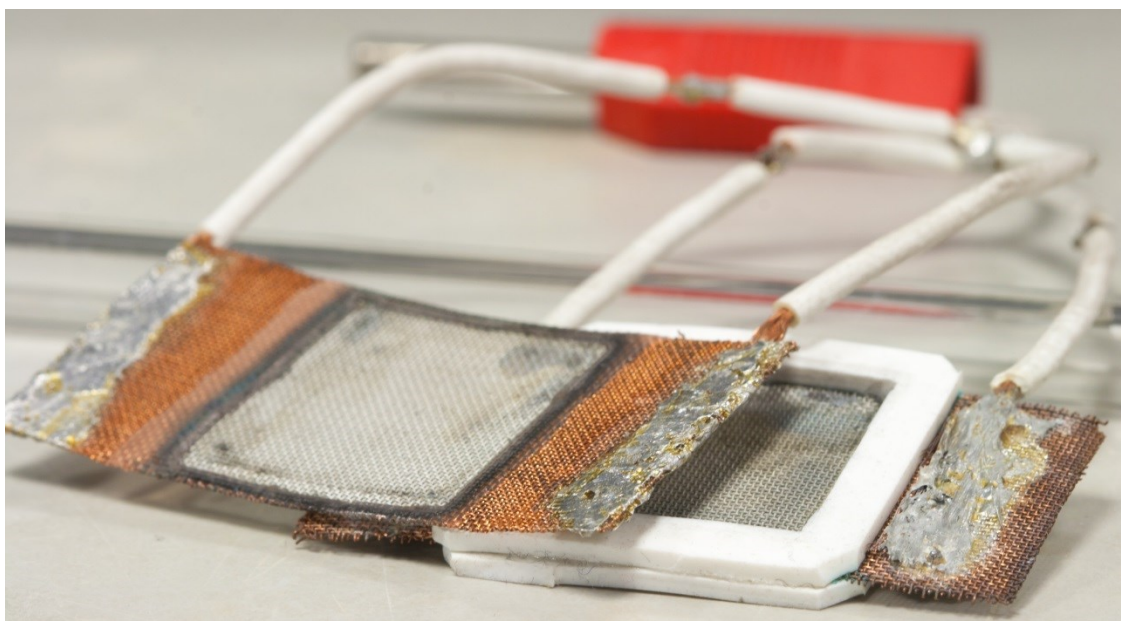


Figure 7-17: Improved assembly for 3D electrodes

Potential drops in the ionically-conducting phase across the thickness of the felt were also recorded in this series of experiments with a second reference electrode (SCE) positioned at a point in the inlet tube close to the inlet port of the cell. The long distance between the back of a 3D electrode and the tip of the second reference electrode should not have caused any significant additional potential drop because it was not a part of the electrical pathway between the anode and the cathode.

$\text{K}_2[\text{Sn}(\text{OH})_6]$, the precursor of tin in the plating solutions, was used rather than being prepared from SnCl_4 . The plating solutions were first prepared to mimic the expected final composition of those derived from SnCl_4 : 0.3 M $\text{K}_2[\text{Sn}(\text{OH})_6]$, 0.4 M KOH and 1.2 M KCl. However, this was found to result in unreliable plating performance. At the same potential, tin could be deposited at a higher current density from a solution aged overnight but not from a freshly prepared solution (Figure 7-18). The presence of Cl^- in the solutions was believed to replace some OH^- in $[\text{Sn}(\text{OH})_6]^{2-}$ via a series of slow reactions, causing a distributed speciation of $[\text{SnCl}_n(\text{OH})_{6-n}]^{2-}$ where n is an integer ranging from 0 to 6. $\text{Sn}^{(\text{IV})}$ with Cl^- ligands seemed to be reduced more easily than stannate and therefore offered higher current densities during deposition at the same potential.

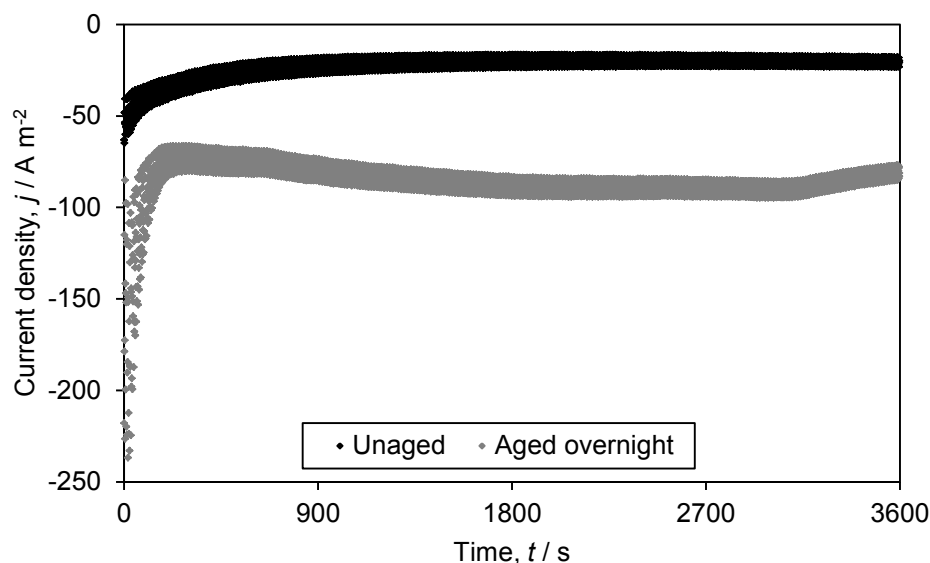
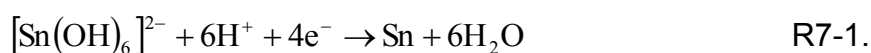


Figure 7-18: Time dependence of current densities during deposition of tin on 1.2-mm-thick graphite felt at -1.45 V (AgCl|Ag) from aqueous solution containing 0.3 M $K_2[Sn(OH)_6]$, 0.4 M KOH and 1.2 M KCl flowing at 132 ml min^{-1}

Therefore, the absence of Cl^- was crucial to the stability of plating solutions, but a replacement was required to maintain a high conductivity, which was increased by increasing the concentration of KOH to 2.2 M. However, the deposition rate was decreased greatly by this approach and best demonstrated through Figure 7-19 and Figure 7-20, in which the deposition profiles from plating solutions with 2.2 M KOH and 0.4 M KOH are shown, respectively. K_3PO_4 was also added to the latter to increase the conductivity. The electrode potential required to achieve 125 A m^{-2} in the solution with 2.2 M KOH was between -1.8 and -2.0 V, whereas only -1.7 V was sufficient to attain current densities larger than 200 A m^{-2} in the solution with 0.4 M KOH. The deposition of tin from $[Sn(OH)_6]^{2-}$ seemed to be dependent on pH and required protons to remove OH^- ligands via the overall reaction:



Having a pH higher than 14, a solution with 2.2 M KOH should have significantly limited the current densities of this reaction. The new plating condition was therefore set to -1.7 V in an aqueous solution of 0.3 M $K_2[Sn(OH)_6]$, 0.4 M KOH and 0.5 M K_3PO_4 flowing at 132 ml min^{-1} . As the current densities from this deposition method on 1.2 mm felt were comparable to those from the preliminary deposition method on 3 mm felt, 1 hour of deposition was thought to produce even thicker layers of deposit.

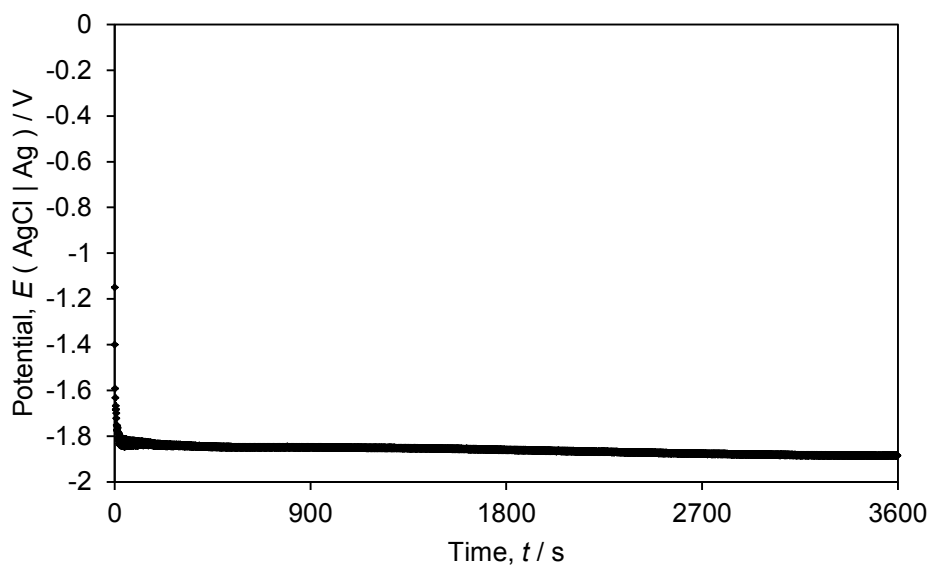


Figure 7-19: Time dependence of electrode potential during deposition of tin on 1.2 mm thick graphite felt at 125 A m^{-2} from aqueous solution containing $0.3 \text{ M K}_2[\text{Sn}(\text{OH})_6]$ and 2.2 M KOH flowing at 132 ml min^{-1}

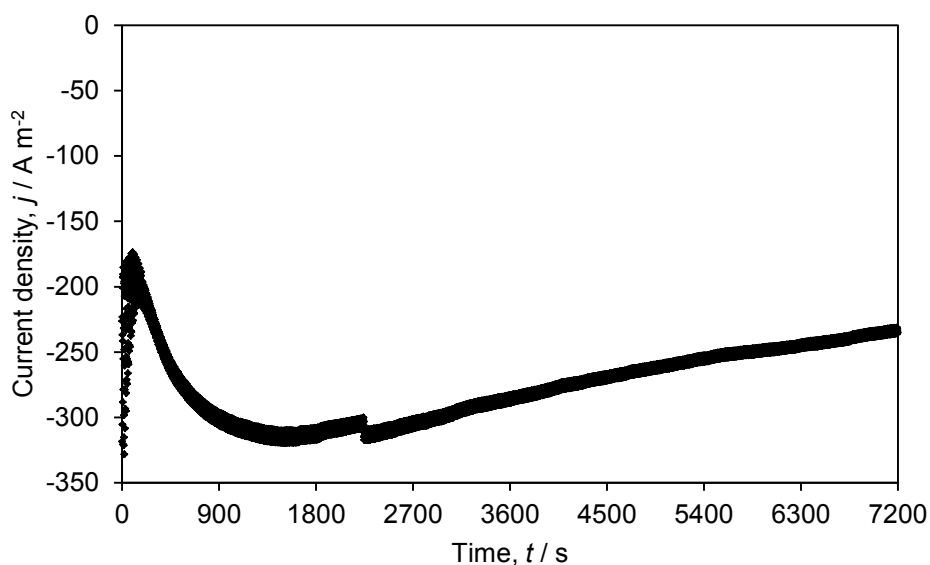


Figure 7-20: Time dependence of current densities during deposition of tin on 1.2 mm thick graphite felt at -1.7 V (AgCl|Ag) from aqueous solution containing $0.3 \text{ M K}_2[\text{Sn}(\text{OH})_6]$, 0.4 M KOH and $0.5 \text{ M K}_3\text{PO}_4$ flowing at 132 ml min^{-1}

A piece of graphite felt plated by this method was used as a cathode to electrolyse a solution containing 0.5 M NaOH and 1 M NaClO_4 saturated with 1 atm CO_2 at -1.3 V for 10 minutes to test its performance. NaClO_4 was added in this and subsequent experiments to increase solution conductivities, decreasing ohmic potential losses and inhomogeneities in the potential distributions in felt. The resulting charge yield of formate was only 0.34, significantly smaller than 0.45 obtained in the preliminary

experiment at the same potential (Figure 7-14). Another piece of tinned felt was fabricated with 2-hour deposition time and used as a cathode to reduce CO_2 under the same conditions. Figure 7-21 reports the results together with those from the felt electroplated for 1 hour. Though the current densities were comparable, the charge yield of formate obtained from the felt electroplated with tin for 2 hours was significantly larger, probably because 1 hour was insufficient to completely cover graphite fibres with tin from the new deposition solutions through currently unknown causes. The exposed graphite surfaces were not active for CO_2 reduction and therefore decreased overall charge yields of formate. The deposition time was hence increased to 2 hours for subsequent deposition.

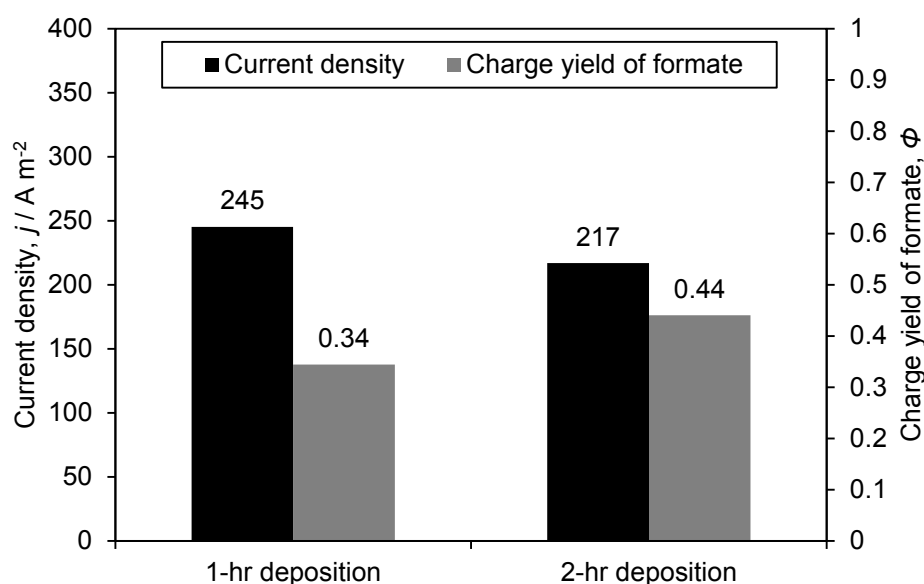


Figure 7-21: Effects of deposition time on current densities and charge yields of formate from electrolyses at -1.3 V ($\text{AgCl}|\text{Ag}$) of aqueous solutions containing 0.5 M NaOH and 1 M NaClO_4 saturated with 1 atm CO_2 flowing at 33 ml min^{-1}

Figure 7-22 shows a SEM photomicrograph of the resulting graphite felt plated with tin at -1.7 V from $0.3 \text{ M K}_2[\text{Sn}(\text{OH})_6]$, 0.4 M KOH and $0.5 \text{ M K}_3\text{PO}_4$ for 2 hours. The overall quality of the deposit was mostly similar to that shown in Figure 7-7 for preliminary plated felt, except the edges of the plated fibres in Figure 7-22 appeared to be more blurred, indicating rougher surfaces. The regions of partially exposed graphite surfaces were localised more on the top and the external surfaces of the sample that were subject to handling damage, as had been observed in the felt used in preliminary experiments. Figure 7-23 shows that the deposited tin layer was thicker from this deposition method, ca. $2.5 \mu\text{m}$ and covering the graphite felt almost

completely. Figure 7-24 reveals that the morphology of the tin layer is clearly different from that of preliminary plated felt and more complete coverage was achieved. The localised 'buds' seen in Figure 7-9 were now enlarged and populated the surfaces more densely, becoming a generic feature from this deposition method. The seemingly rougher surfaces were expected to increase the current densities during CO₂ reduction.

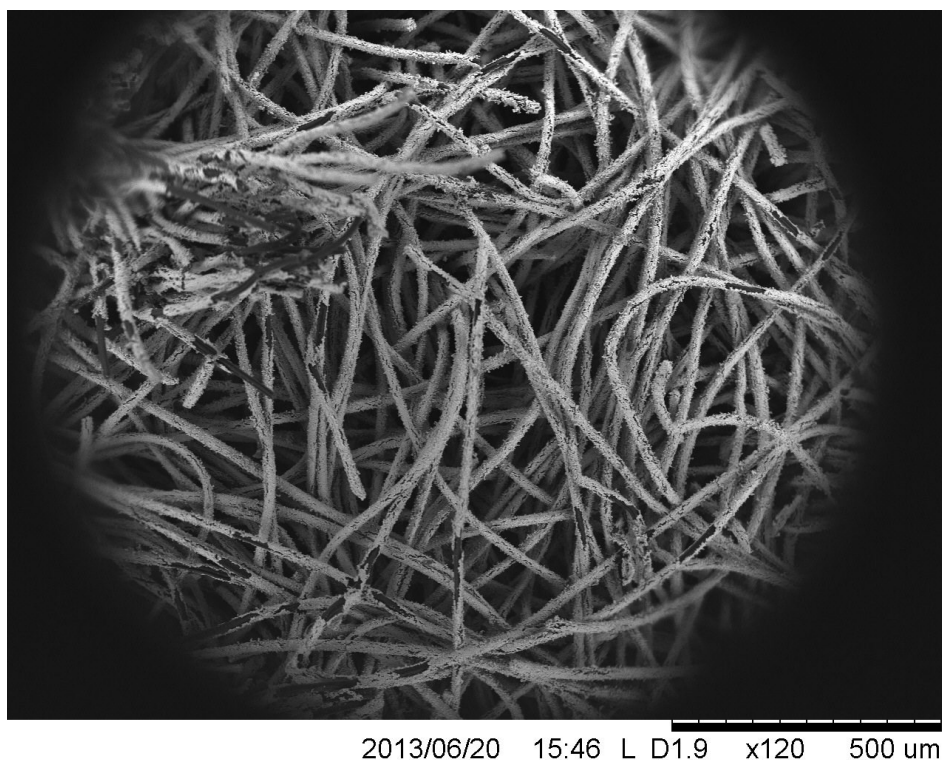


Figure 7-22: SEM micrograph of tin-plated graphite felt achieved at -1.7 V (AgCl|Ag) for 2 hours in aqueous solution containing 0.3 M K₂[Sn(OH)₆], 0.4 M KOH and 0.5 M K₃PO₄ flowing at 132 ml min⁻¹, showing overall quality

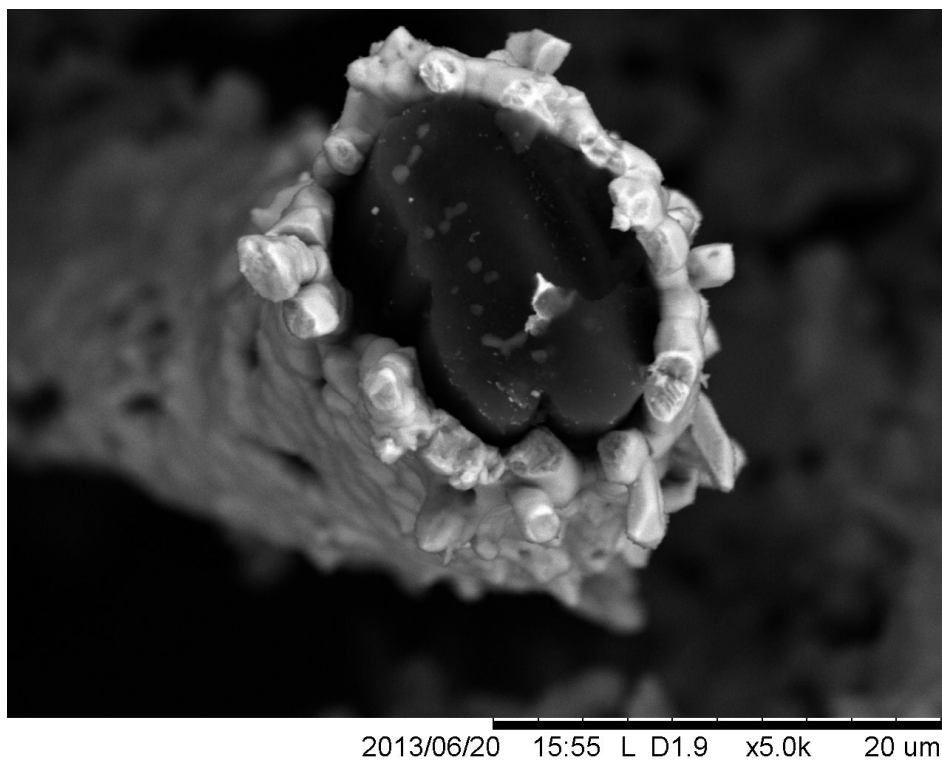


Figure 7-23: SEM micrograph of tin-plated graphite fibre achieved at -1.7 V (AgCl|Ag) for 2 hours in aqueous solution containing $0.3\text{ M K}_2[\text{Sn}(\text{OH})_6]$, 0.4 M KOH and $0.5\text{ M K}_3\text{PO}_4$ flowing at 132 ml min^{-1}

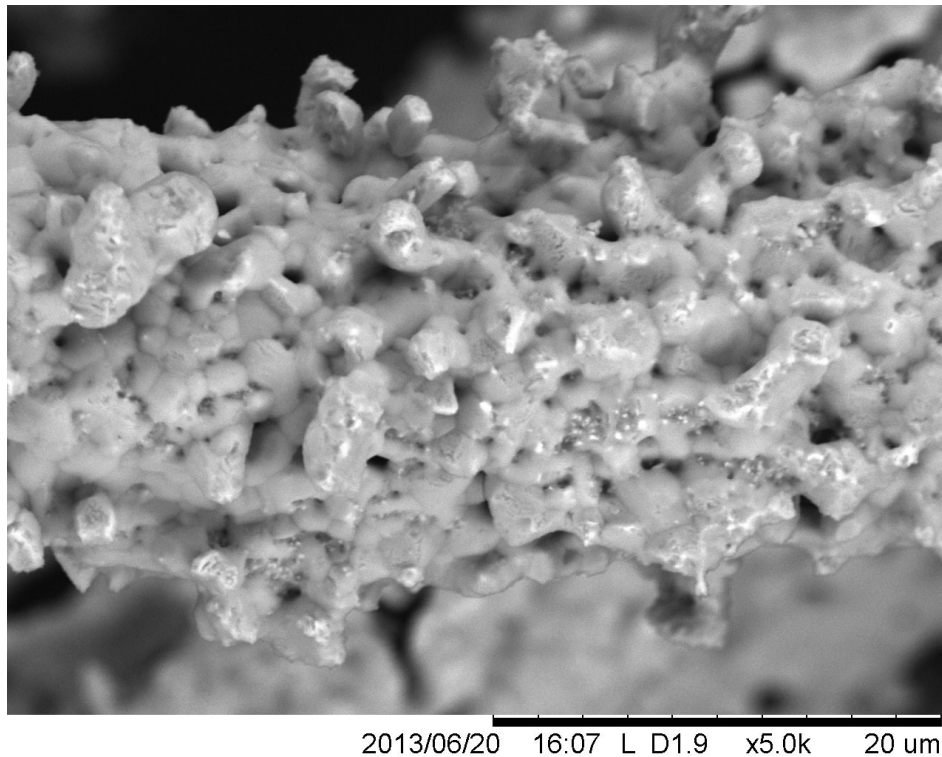


Figure 7-24: SEM micrograph of tin-plated graphite fibre achieved at -1.7 V (AgCl|Ag) for 2 hours in aqueous solution containing $0.3\text{ M K}_2[\text{Sn}(\text{OH})_6]$, 0.4 M KOH and $0.5\text{ M K}_3\text{PO}_4$ flowing at 132 ml min^{-1}

The accumulation of bubbles generated from hydrogen and CO evolution within felt could significantly affect performances of tinned graphite felt during CO₂ reduction. Figure 7-25 shows a peculiar relationship between the current densities and the potential drops across the felt thickness during the electrolysis at -1.3 V of an aqueous solution containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂ flowing at 33 ml min⁻¹. They were actually from the same experiment the results of which are shown on the right in Figure 7-21. The gradual and periodic decreases in the current densities before sudden increases were accompanied by gradual increases in the potential drops across felt thickness, which was actually expected to decrease when the current densities decreased. A sound explanation for the observed behaviour was that bubbles gradually displaced the aqueous solution within the felt as they accumulated, reducing its superficial conductivity, increasing the potential drops and decreasing the current densities simultaneously. Release of trapped bubbles in large bulks occurred periodically and restored both the current densities and the potential drops in the process.

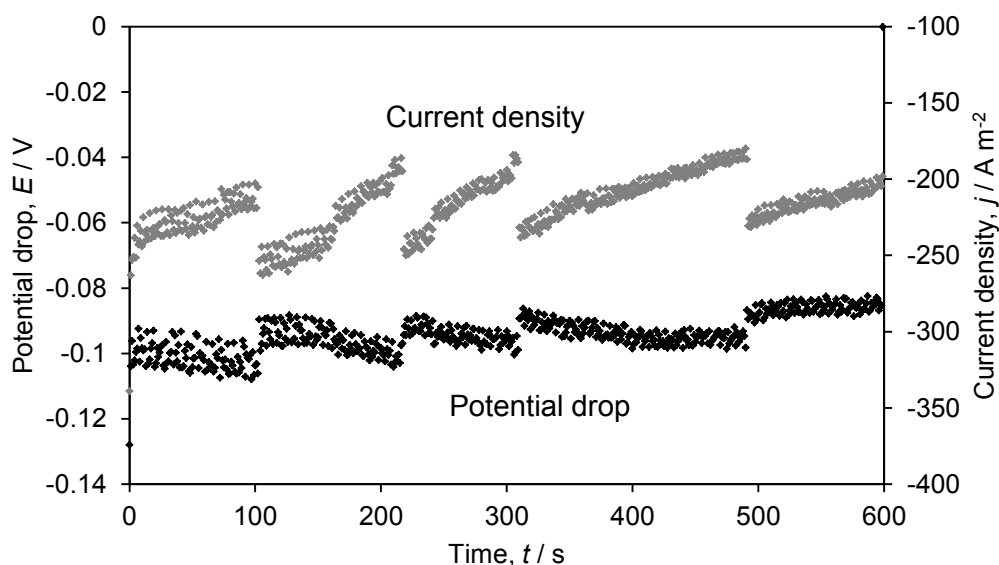


Figure 7-25: Current densities and potential drops across felt thickness from electrolysis at -1.3 V (AgCl|Ag) of aqueous solution containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂ flowing at 33 ml min⁻¹

Increasing electrolyte flow rates should reduce bubble accumulation, but this solution may lead to detachment of felt from the back mesh occurred in preliminary experiments. Extra caution was exercised by decreasing the flow rate of the plating solutions during deposition so that tin-plated felt became stiff due to the deposits in a

more expanded state and could withstand higher flow rates during CO₂ reduction without losing the firm contacts with the back mesh. Two experiments were conducted to determine whether a slower flow rate of the plating solution decreased the performance of 3D electrodes. Two pieces of felt tinned at flow rates of 132 and 33 ml min⁻¹ were used for CO₂ reduction at -1.5 V for 10 minutes with CO₂-saturated solutions flowing at 33 ml min⁻¹. The current densities and charge yields of formate are shown in Figure 7-26. Only subtle differences between the two sets of results were detected and likely to be statistical deviations. It was concluded from these results that 33 ml min⁻¹ was a sufficient flow rate not to impede electrodeposition of tin and so was used in subsequent tin electrodeposition.

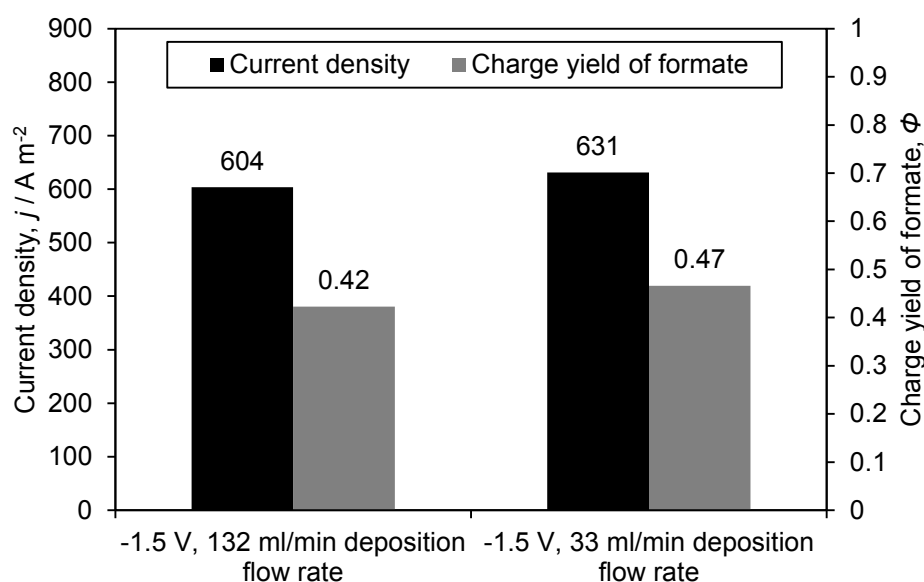


Figure 7-26: Effect of flow rates of plating solutions during electrodeposition of Sn on graphite felt on current densities and charge yields of formate from electrolyses at -1.5 V (AgCl|Ag) of aqueous solution containing 0.5 M NaOH and 1 M NaClO₄ saturated with CO₂ flowing at 33 ml min⁻¹

7.3.2 Electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with CO₂ at tin-plated graphite felt

Freshly prepared tinned graphite felt was used in each experiment. To minimise disturbance to the electrode assembly, the cell was kept assembled after the deposition and flushed with 500 ml of high purity water flowing at 33 ml min⁻¹ to rinse both the cell and the tinned graphite felt. 100 ml of an aqueous solution containing 0.5 M NaOH and 1 M NaClO₄ was sparged with CO₂ for 15 minutes, during which

the cell was drained. The rest of the procedure was similar to that followed in the preliminary experiments.

The resistances between the Luggin probe and the front plane of a 3D electrode were also measured with electrochemical impedance spectroscopy to quantify the potential drops between the two points, which could be significant even at less negative potentials due to large current densities expected from 3D electrodes. However, the required values cannot be obtained with EIS performed directly on a working 3D electrode; had the measurement been made, the resulting resistances would have included portions of the resistances within the structure. Therefore, the needed values were measured with only the front mesh assembled in the cell. The resistances obtained in this way contained the values between the Luggin probe and the front plane of the front mesh plus portions of those within the thickness of the mesh; i.e., they were better estimates of the values actually required.

Figure 7-27 shows the current densities and the charge yields of formate from CO₂ reduction at tinned graphite felt conducted at different potentials and flow rates. As expected, decreasing electrode potential increased the current densities but its effect on the charge yields of formate was mixed. The charge yield of formate at -1.27 V was very close to the value of 0.42 obtained in the experiment with the planar tin electrode in Chapter 5 (Figure 5-5), while the values at -1.52 V and -1.50 V were significantly smaller than their counterpart of 0.61. The highest charge yield of formate observed in this series of experiments was 0.58 at -1.62 V with a flow rate of 99 ml min⁻¹ and was close to the analogous value of 0.63 from the experiment on the 2D electrode. Charge yields being able to approach corresponding values from the planar electrode also suggested that good tin coverage on graphite fibres was achieved from this deposition method.

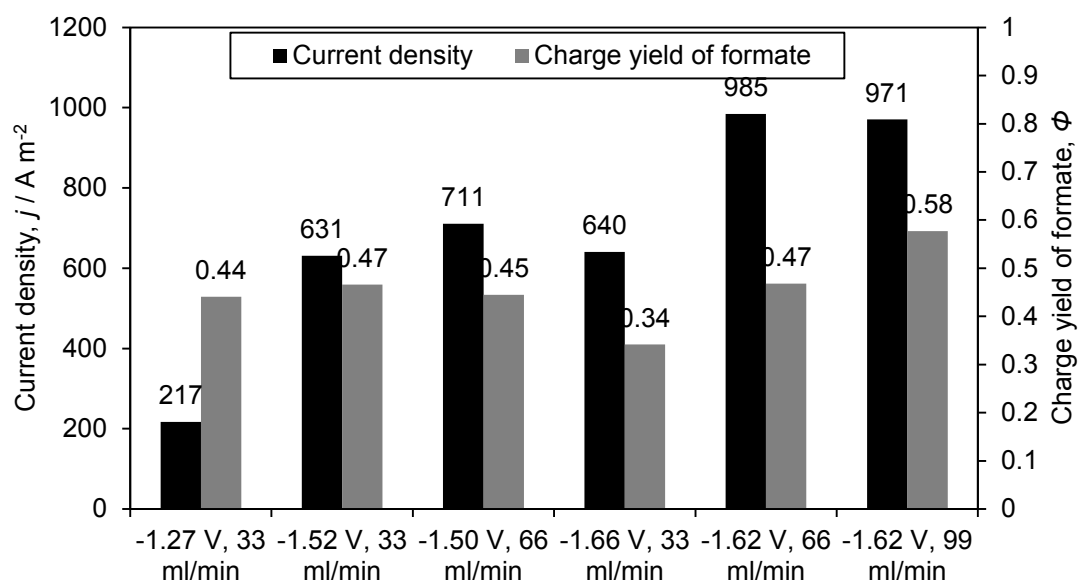


Figure 7-27: Effects of electrode potential and flow rates on current densities and charge yields of formate from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

At the same potential, a higher flow rate tended to increase both the current density and the charge yield. A higher flow rate was thought to purge bubbles from a felt matrix at a higher rate, decreasing the total volume occupied by gases in the aqueous phase, increasing the superficial conductivity of the solution, decreasing the potential drop across the felt thickness, and thereby increasing the current density. As shown in Figure 7-28, the potential drops across the felt thickness seemed to follow the trend described.

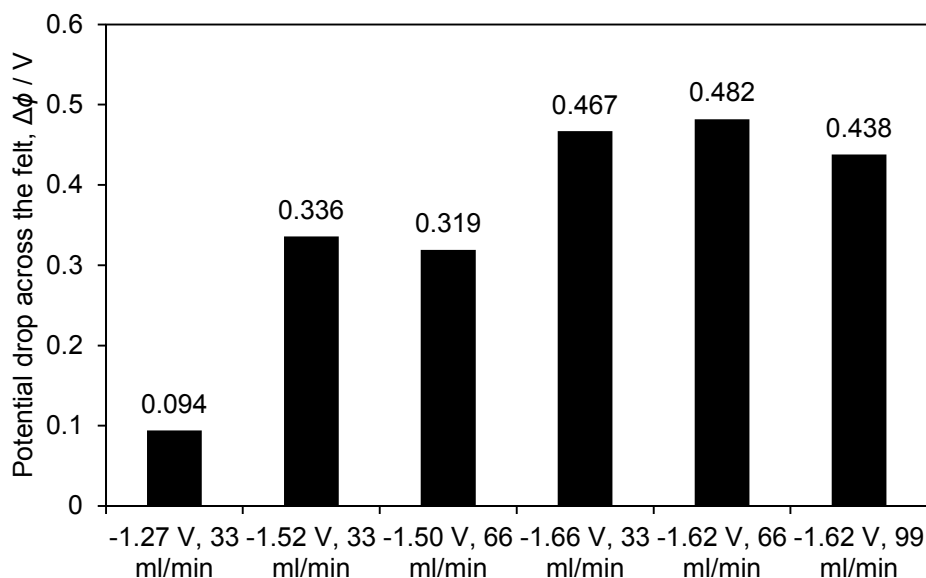


Figure 7-28: Effects of electrode potential and flow rates on potential drops across felt thickness during electrolyses of aqueous solution containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

The concern left unanswered in preliminary experiments whether mass transport of CO₂ was rate-limiting at 33 ml min⁻¹ was re-examined. At -1.5 V, both the current densities and the charge yields at the flow rates of 33 and 66 ml min⁻¹ were comparable, indicating an insignificant effect of flow rates on the performances of 3D electrodes. The partial current density for formate formation, obtained by multiplying a current density by its charge yield, increased by 8 per cent from 296 to 320 A m⁻² despite the flow rate being doubled, suggesting that mass transport of CO₂ was rather independent of electrolyte flow rates and probably not limiting.

Despite that, the partial current density of formate formation at -1.6 V and 33 ml min⁻¹ of 218 A m⁻², which was smaller than the values at -1.5 V, indicated that mass transport of CO₂ was suppressed at this potential by an additional mechanism. This behaviour is uncommon as, at a planar electrode with an electrolyte flowing at a constant rate, the partial current density of an electrochemical reaction is not expected to become smaller after overpotential is increased unless there is an additional suppressing process. Such mechanism was thought to involve the accumulation of bubbles within felt matrices. If this is true, the unexpectedly small potential drop at -1.6 V and 33 ml min⁻¹ simply reflects the peculiarly small total current density resulting from the suppressed partial current density of CO₂ reduction. Although it has been described elsewhere that the mass transport of a

reactant is enhanced by bubble formation at planar electrodes (Vogt, 1983), it was hypothesised here that it could actually be suppressed by the presence of overwhelming bubbles within 3D electrodes.

7.4 Conclusions

Graphite felt electrodes plated with tin were fabricated and used as three-dimensional cathodes for electrochemical reduction of CO₂. The deposition of tin on graphite fibres was explored and optimum deposition conditions were developed. It was found that firm electrical contacts were crucial to minimising their resistances and consequently to achieving adequate performance of 3D electrodes. The unconventional relationship between electrode potential and the current densities in the experiments was explained qualitatively by the accumulation of gas bubbles within felt matrices.

8 Modelling of three-dimensional tin-plated graphite felt cathodes

The relationship between superficial current densities and electrode potential in a 3D electrode can be complicated and may not follow a simple exponential function mainly due to the spatial distribution of electrode potential within the electrode. The main purpose of developing a mathematical model for 3D electrodes was to approximate the profiles of electrode potential, so that the rates of electrochemical reactions at each point could be estimated and integrated to predict superficial current densities. The concept of bubble accumulation introduced in the previous chapter in order to explain the effect of electrolyte flow rates was also incorporated into the model. The complete model was expected to relate the three measured variables: current densities, charge yields of formate and potential drops within 3D electrodes to the two independent variables: electrode potential and electrolyte flow rates.

8.1 Model development

Potential of both the electronically- and the ionically-conducting phase within a three-dimensional electrode is related to current density in their respective phases according to:

$$\kappa_s \nabla \phi = -\vec{j}_s \quad \text{E8-1.}$$

Significant variations of potential in both phases are expected if both phases have comparable superficial conductivities. However, metals are often exceedingly more conductive than aqueous solutions, probably possessing only a slight and negligible variation in potential even when used as a 3D electrode. The mathematical model will be greatly simplified if the potential in the electronically-conducting phase is assumed to be constant.

The superficial conductivity of graphite felt tinned with the last method described in Chapter 7 was estimated to determine whether such an assumption is justified. The structure of tin covering graphite fibres could be modelled as two resistances connected in parallel: one of the graphite fibres and the other of the tin layer. As the

conductivity of tin is almost 2 orders of magnitude larger than that of graphite and the cross-sectional areas of graphite fibres and tin layers were comparable (Figure 7-23), most of an electrical current passing through tinned graphite felt would pass through tin. Thereby, the conductivity of tinned graphite felt was estimated with only the parameters of the tin layers through the Bruggeman equation:

$$\kappa_s = \kappa(1 - \varepsilon)^{1.5} \quad \text{E8-2.}$$

Whereas the conductivity of tin could be obtained easily, volumetric fractions of the tin layers had to be estimated. Physical characteristics of a piece of plated graphite felt were approximated from the SEM micrographs and the current densities during deposition. Firstly, the volume of deposited tin was calculated from the total charge passed with an assumption of unity charge yield:

$$V_{Sn} = \frac{QM}{\nu_e F \rho} \quad \text{E8-3.}$$

The volumetric fraction of tin was obtained by dividing the volume of tin by the superficial volume of a piece of plated graphite felt:

$$\varepsilon_{Sn} = \frac{V_{Sn}}{V_f} \quad \text{E8-4.}$$

Additional physical characteristics can also be estimated if the deposited tin layer was assumed to form a tubular sheath with a constant inner and outer diameter along the entire length of graphite fibres, which could be approximated from the volume of tin and the diameters read from the SEM micrographs from:

$$V_{Sn} = \frac{\pi}{4} (d_o^2 - d_i^2) L \quad \text{E8-5.}$$

The total geometrical surface area of a piece of tinned graphite felt can be obtained from:

$$A = \pi d_o L \quad \text{E8-6.}$$

Specific fibre lengths and specific geometrical surface areas could be obtained by deviding total fibre lengths and total geometrical surface areas by superfical volumes of graphite felt.

The estimated physical characteristics of tinned graphite felt fabricated with the three methods are shown in Table 7. The 1.2 mm felt was the one that had been used in

the last series of experiments in Chapter 7 and would be modelled in this chapter. The values of the other felt electrodes are presented for comparison.

Specific fibre lengths should not be altered by deposition of tin and so should remain the same for any piece of graphite felt produced from the same manufacturer with the same method. The estimated values that were similar for all felt tinned with the three methods reflected the consistency of the estimated characteristics. It should also be noted that 1.2 mm felt was compressed from its uncompressed thickness of 1.5 mm, so its specific fibre length and specific geometrical surface area were larger than the rest.

Table 7: Estimated physical characteristics of tinned graphite felt

	6 mm felt, 2 hour	3 mm felt, 1 hour	1.2 mm felt, 2 hour
Outer diameter of tin layers, $d_o/\mu\text{m}$	17.0	16.0	20.0
Inner diameter of tin layers, $d_i/\mu\text{m}$	15.0	14.5	15.0
Volumetric fraction of tin, ε_{sn}	0.023	0.015	0.069
Superficial felt conductivity, $\kappa_s/\text{S m}^{-1}$	3.10E+04	1.60E+04	1.66E+05
Specific fibre length, L/m^{-2}	4.5E+08	4.0E+08	5.0E+08
Specific geometrical surface area, a/m^{-1}	2.4E+04	2.0E+04	3.1E+04
Void fraction of the plated felt, ε_f	0.90	0.92	0.84

In order to approximate the largest possible potential drop within felt, an assumption was made that the largest current density, 985 A m⁻² in Figure 7-27, was passed through a piece of 1.2 mm thick tinned graphite felt from the front to the back. A potential drop of 7.1 μV was obtained from an estimated effective felt conductivity of 1.66×10⁵ S m⁻¹. This insignificant potential drop was also supported experimentally when the same current density was actually passed through a piece of 1.2 mm thick felt and an undetectable potential drop was measured. Therefore, it was concluded that it was reasonable to assume that potential within the electronically-conducting phase was essentially independent of position.

The superficial current density in equation E8-1 is related to the true current density at tinned surfaces of graphite fibres through a charge balance at a steady state:

$$\nabla \cdot \vec{j}_s = \nu_e F a j \quad \text{E8-7.}$$

Electrode potential determining rates of the true current density, j , also varies along the direction of current flows, thus leading to varying reaction rates across a felt thickness. Figure 8-1 shows schematic profiles of various potentials in a 3D electrode during a cathodic operation with the assumption of flat potential distributions in the electronically-conducting phase. The potential of the electrolyte was expected to decrease from the front to the back of the 3D electrode with diminishing rates of decrease, eventually having a zero gradient at the back of the electrode due to zero superficial current density. The potential of a reference electrode would exhibit similar decreases and maintain a constant difference from the potential of the electrolyte were it possible to move one freely inside the felt electrode. It should also be pointed out here that the main reference electrode was placed near the front plane of 3D electrodes. Hence, electrode potentials measured by the potentiostat during electrolyses were the differences between ϕ_m and ϕ_{ref} at the front plane.

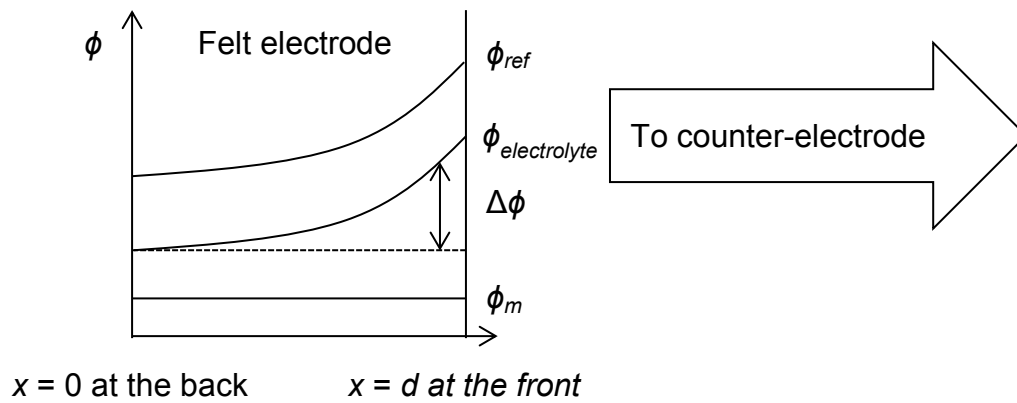


Figure 8-1: Schematic profiles of potential distributions in felt electrode with flat distribution of potential in electronically-conducting phase

Therefore, electrode potential must be corrected for the varying potentials:

$$\begin{aligned}
 E &= \phi_m - \phi_{ref} \\
 &= (\phi_m - \phi_{electrolyte}) - (\phi_{ref} - \phi_{electrolyte}) \\
 &= \left\{ \phi_m \Big|_{x=0} - (\phi_{electrolyte} \Big|_{x=0} + \Delta\phi) \right\} - \left\{ \phi_{ref} \Big|_{x=0} - \phi_{electrolyte} \Big|_{x=0} \right\} \\
 &= E \Big|_{x=0} - \Delta\phi
 \end{aligned}
 \tag{E8-8}$$

$\Delta\phi$ is also related to the superficial current density in a 3D electrode by an equation similar to E8-1:

$$\kappa_s \nabla(\Delta\phi) = -\vec{j}_s \quad \text{E8-9.}$$

The superficial conductivities of the ionically-conducting phase were estimated with a modified version of the Bruggeman equation E8-2:

$$\kappa_s = \kappa (1 - \varepsilon_f)^{1.5} (1 - \varepsilon_b)^{1.5} \quad \text{E8-10;}$$

volumetric fractions of the ionically-conducting phase were firstly set to equal the void fraction of tinned felt presented in Table 7, further reduced by the presence of H_2 and CO bubbles in terms of volumetric fractions of bubbles in the ionically-conducting phase.

The derivation of a bubble fraction at a point along the thickness of a 3D electrode started with a mole balance of gases produced during an electrolysis at a steady state:

$$0 = -\nabla \cdot \vec{N}_g + \frac{a|j_g|}{|v_e|F} \quad \text{E8-11.}$$

Bubbles were assumed to move only in the same direction as the liquid, i.e. from the back to the front of 3D electrodes. They gained velocities from two sources: gas generation and drag from electrolyte flows. The first generated velocities for the bubbles due to direct displacement of itself and was already taken into account in equation E8-11, whereas the latter occurred through momentum transfer, which is a complicated mechanism and was modelled simply by assuming that bubbles travelled at the same interstitial velocities as the liquid.

Therefore, interstitial velocities of liquid flows must be estimated. They could be related approximately to superficial velocities of electrolyte flows, which were simply the volumetric flow rates of the liquid divided by the superficial surface area of felt, with the aid of the void fraction of the felt and bubble fractions:

$$\bar{v}_{l,i} = \frac{\bar{v}_{l,s}}{\varepsilon_f (1 - \varepsilon_b)} \quad \text{E8-12.}$$

Interstitial velocities of the bubbles were then set to equal those of the liquid:

$$\bar{v}_{g,i} = \bar{v}_{l,i} = \frac{\bar{v}_{l,s}}{\varepsilon_f(1 - \varepsilon_b)} \quad \text{E8-13.}$$

Superficial velocities of the bubbles could be obtained with the aid of the felt void fraction and bubble fractions:

$$\bar{v}_{g,s} = \bar{v}_{g,i} \varepsilon_b \varepsilon_f = \frac{\bar{v}_{l,s} \varepsilon_b \varepsilon_f}{\varepsilon_f(1 - \varepsilon_b)} = \frac{\bar{v}_{l,s} \varepsilon_b}{(1 - \varepsilon_b)} \quad \text{E8-14.}$$

The molar flux of the gases was then readily derived with the assumption of ideal gas:

$$\bar{N}_g = \frac{\bar{v}_{g,s} P}{RT} = \frac{\bar{v}_{l,s} \varepsilon_b P}{(1 - \varepsilon_b) RT} \quad \text{E8-15.}$$

Therefore, bubble fractions were:

$$\varepsilon_b = \frac{\bar{N}_g}{\frac{\bar{v}_{l,s} P}{RT} + \bar{N}_g} \quad \text{E8-16.}$$

Mass transport will add another level of complexity to the model if it is included. Therefore, it was useful to know whether the limiting current densities at all flow rates used in this project were sufficiently large that mass transport limitations could be neglected. An experiment was carried out to determine mass transfer coefficients in a tinned graphite felt electrode at different flow rates through the reduction of ferricyanide. However, the experiment was unsuccessful because the aqueous solution of ferricyanide lost its yellow colour gradually as soon as it was pumped through the cell even before an electrical current was passed. It was thought that ferricyanide was reduced spontaneously by the tin deposited on the graphite felt, so that reaction could not be used for this purpose. Another chemical that is frequently used to study mass transport is bromine, but this strong oxidising agent is even more likely to spontaneously oxidise tin and hence cannot be used. The last option was to estimate mass transfer coefficients from the literature, though there was a concern whether values reported for bare graphite felt were applicable to tinned graphite felt possessing apparently larger surface areas.

There are many reports on mass transport in graphite felt electrodes in flow-by configurations, but only a few in flow-through configurations. Furthermore, there

seems to be different definitions of flow-through and flow-by arrangements. Kinoshita and Leach (1982), for example, published a study of mass transport in graphite felt electrodes under flow-through configurations, whereas their described experiments indicated flow-by configurations under the definition adopted in this project. It is important to know exactly under which configuration a mass transfer coefficient was derived because of different characteristics of mass transport between the two configurations; under a mass transport controlled regime and the same flow velocity, flow-by configurations tend to completely deplete the active species as an electrolyte flows through the length of a 3D electrode, whereas the reactant is consumed to a significantly smaller extent under flow-through configurations. This was implied by the mass transfer coefficients reported by Kinoshita and Leach (1982) being smaller by different orders of magnitude than those reported by Delanghe, Tellier and Astruc (1990), who published one of only a few papers describing mass transport in graphite felt electrodes under a 'true' flow-through configuration, at the same flow velocities.

The latter group studied mass transport through the reduction of ferricyanide at different flow rates and proposed an empirical correlation between mass transfer coefficients and flow rates in a flow-through configuration:

$$k_m = 0.022v^{0.36} \quad \text{E8-17.}$$

The units are fixed in this correlation: mass transfer coefficient in cm s^{-1} and flow velocity in cm s^{-1} . A k_m of 0.011 cm s^{-1} results from this correlation with a flow rate of 33 ml min^{-1} . The corresponding thickness of the diffusion layer is $6.8 \text{ }\mu\text{m}$ with $7.28 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Eroğlu et al., 2011) as the diffusion coefficient of ferricyanide. A limiting superficial current density of CO_2 reduction at this flow rate is $70\,000 \text{ A m}^{-2}$ calculated with $1.94 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Tamimi et al., 1994) as the diffusion coefficient of CO_2 and the physical characteristics of 1.2 mm felt in Table 7. The actual limiting superficial current density should even be larger than the calculated value because of the rough plated surfaces, which result in a larger true specific surface area. As the limiting current density at this flow rate already exceeded the largest current density measured from a 3D electrode in this project by more than an order of magnitude, it was reasonable to simplify the model by not including effects of CO_2 mass transport.

On the other hand, the mass transport of protons was of great concern because of their low concentrations. Though the 6.8 μm diffusion layer thickness was about a fifth of that in the experiments with the planar electrode, local pH can still be significantly higher than bulk values, suppressing partial current densities of CO_2 reduction. However, the range of potentials that produced total current densities large enough to cause large variations in local pH was within the range in which the rate-limiting step of CO_2 reduction is the pH-independent transfer of the first electron and therefore the rates of CO_2 reduction in this potential range would have been only slightly affected by increases in local pH. Hence, the effect of proton mass transport was also neglected.

The last kinetic model of CO_2 reduction presented in Chapter 6 was simplified to remove certain parts of the equations that were significant only at low pH. Equation E6-25, which is the equation for the formation rate of CO from CO_2H_2^+ , was removed, leaving only four equations for CO_2 reduction:

$$j_1 = Fk_1a_{\text{CO}_2}(1 - \theta_1) \quad \text{E6-21}$$

$$j_2 = Fk_2(\theta_1 - \theta_2) \quad \text{E6-22}$$

$$j_3 = Fk_3(\theta_2 - \theta_3) \quad \text{E6-23}$$

$$j_4 = Fk_4(\theta_2 - \theta_3) \quad \text{E6-24.}$$

θ_3 was set to zero and K_2 was also reduced accordingly to zero. Equation E6-30 and E6-31 were modified accordingly:

$$\theta_1 = \frac{k_1a_{\text{CO}_2}}{k_1a_{\text{CO}_2} + \frac{k_2 + (k_3 + k_4)K_1a_{\text{H}^+}}{1 + K_1a_{\text{H}^+}}} \quad \text{E8-18}$$

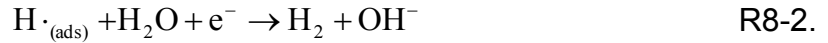
$$\theta_2 = \frac{\theta_1 K_1 a_{\text{H}^+}}{1 + K_1 a_{\text{H}^+}} \quad \text{E8-19.}$$

The model for 3D electrodes also required a mathematical expression for total current densities from both CO_2 reduction and hydrogen evolution at ranges of electrode potentials expected to vary across the 3D electrode thickness. The kinetic model of hydrogen evolution was still based on the Volmer-Heyrovsky mechanism:





However, current densities of hydrogen evolution at pH 7.8 appeared to be affected by changes in local pH, as evident in Figure 8-2 from the apparently low Tafel slope at more negative potentials with a small transfer coefficient of 0.14. Furthermore, the apparent transfer coefficient of 0.7 at less negative potentials being larger than a reported value of 0.26 (Appleby et al., 1982) probably reflected the diminishing suppressing effect on hydrogen evolution rates by adsorbed intermediates of CO₂ reduction as potential was decreased. The kinetics of hydrogen evolution were probably most complicated at pHs near this value due to comparable rates of hydrogen evolution from both protons and water:



It is even possible that the adsorbed intermediate was formed from water in the Volmer reaction, but consumed with protons in the Heyrovsky reaction, and vice versa. Therefore, the exact dependence of current densities on pH was difficult to model in the absence of the kinetic parameters. A simple model for hydrogen evolution at pH 7.8 was developed based on the two-step electron transfer:

$$\begin{aligned} j_V &= -Fk_{V,0}a_{\text{H}^+}(1-\theta_{\text{H}\cdot})\exp\left(\frac{-\alpha_V FE}{RT}\right) \\ &= -Fk'_V(1-\theta_{\text{H}\cdot}) \end{aligned} \quad \text{E8-20}$$

and

$$\begin{aligned} j_H &= -Fk_{H,0}a_{\text{H}^+}\theta_{\text{H}\cdot}\exp\left(\frac{-\alpha_H FE}{RT}\right) \\ &= -Fk'_H\theta_{\text{H}\cdot}. \end{aligned} \quad \text{E8-21.}$$

Figure 8-2 shows the effect of electrode potential on the predicted current densities for hydrogen evolution, calculated with values of the kinetic parameters that were kinetically unrealistic, but employed knowingly to simulate deviations of local pH from bulk values and interactions amongst adsorbed intermediates.

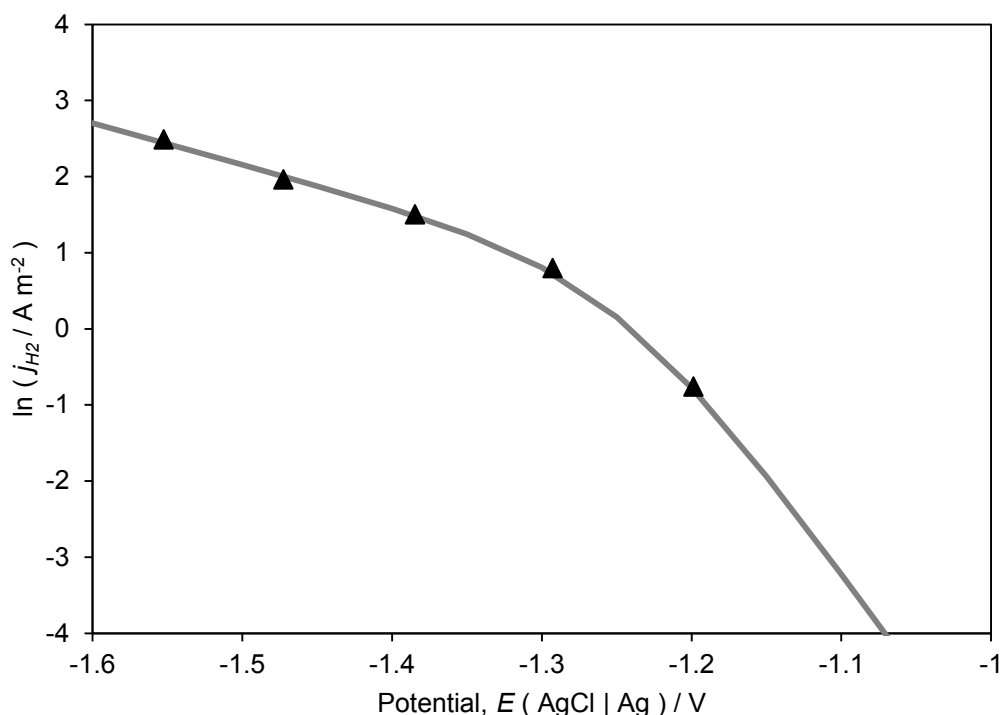


Figure 8-2: Effect of electrode potential on logarithmic partial current densities of hydrogen evolution at planar tin electrode at pH 7.8 obtained by saturating aqueous solutions of 0.5 M NaOH with CO₂; triangles: experimental data, line: model with $k'_V = 1.26 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$, $\alpha_V = 0.14$, $k'_H = 2.07 \times 10^{-20} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_H = 0.7$

With the mathematical equations for hydrogen evolution rates derived, it was possible to study the effect of electrode potential on charge yields of formate in the absence of limitations on CO₂ mass transport. Figure 8-3 predicts a maximum charge yield at ca. -1.45 V, which was greater than that determined experimentally as reported in Chapter 5. This was caused mainly by differences in the partial current densities of formate between the experimental data and model predictions produced with the kinetic parameters that were generalised for a range of pH rather than derived specifically for this system.

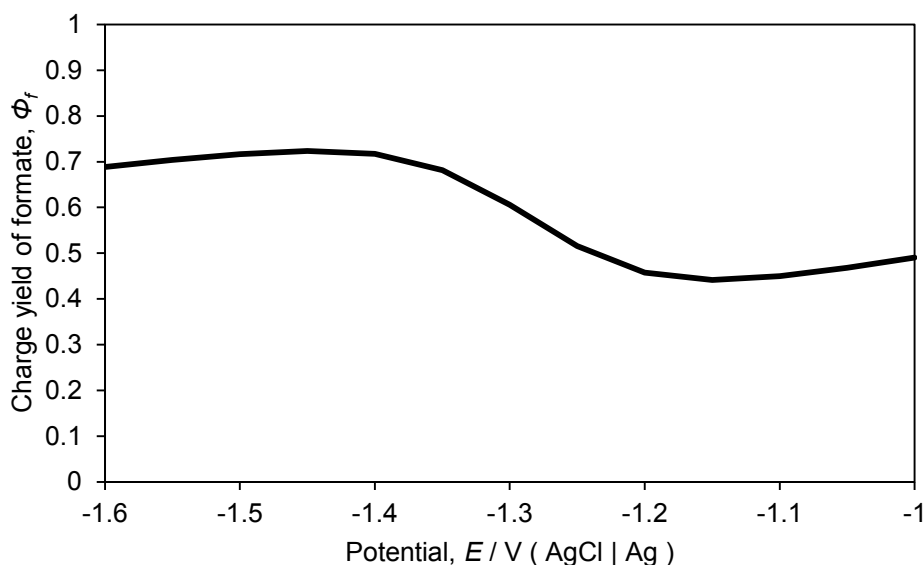


Figure 8-3: Predicted effect of electrode potential on charge yields of formate in aqueous solutions of pH 7.8 prepared by saturating 0.5 M NaOH with 1 atm CO₂

A system of coordinates was set as shown previously in Figure 8-1. The origin was placed at the centre of the back of 3D electrodes, with the x axis extending positively through the front plane of 3D electrodes. Plug flows were assumed, so that variations in potential and partial current densities along the y and z directions could be neglected.

The main differential equations of this model were equation E8-7 and E8-9, which were solved numerically with Euler's implicit method for superficial current densities and potential differences, $\Delta\phi$, of the ionically-conducting phase. The calculations for the finite-difference method started from the back of 3D electrodes, $x = 0$, where the gradient of potential difference, the superficial current density and the bubble fraction were zero, to the front, $x = d$. Trial and error was performed on the electrode potential at the back of a 3D electrode so that the calculated electrode potential at the front matched the value set experimentally for each combination of electrode potential and a flow rate. Electrode potential was adjusted according to equation E8-8 and used to calculate true electrochemical reaction rates. The true conductivity of the electrolyte, which consisted of 0.5 M NaOH and 1 M NaClO₄ and was saturated with CO₂, was measured as 9.36 S m⁻¹. Bubble fractions were calculated with equation E8-16 and input to the modified Bruggeman equation E8-10 to calculate superficial ionic conductivities. The only adjustable parameters of this model were the specific surface area of 3D electrodes and the power number of Bruggeman

equation E8-10. However, the latter was retained because, though being a constant in an empirical correlation, the value was supported experimentally. Therefore, the specific surface area of 3D electrodes was the only model parameter and was set to $31\,000\text{ m}^{-1}$ following the calculations presented in Table 7.

8.2 Results and discussion

The current densities, the charge yields of formate and the potential drops at different potentials at the front plane and flow rates are shown in Figure 8-4, Figure 8-5 and Figure 8-6, respectively, together with corresponding model predictions. The current densities were mostly significantly over-predicted even though the specific surface area was set to the calculated geometrical value, which was very likely to be smaller than the actual value of the rough surfaces. The calculated charge yields were also larger than the experimental values. In contrast, the potential drops were highly under-predicted.

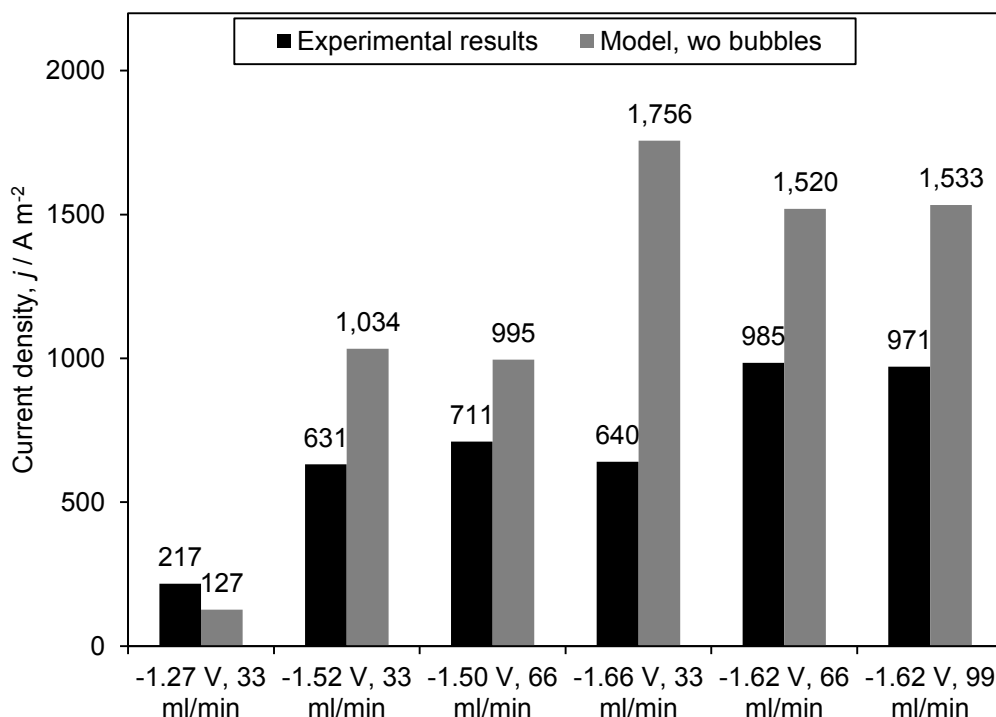


Figure 8-4: Predicted effects of electrode potential and flow rates on current densities from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

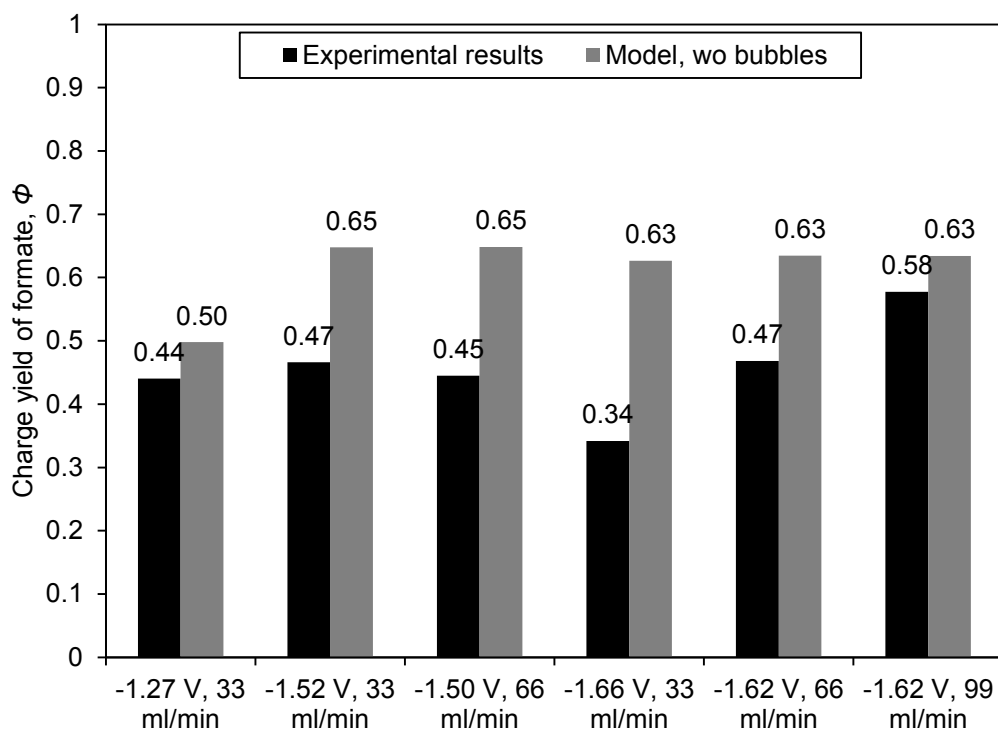


Figure 8-5: Predicted effects of electrode potential and flow rates on charge yields of formate from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

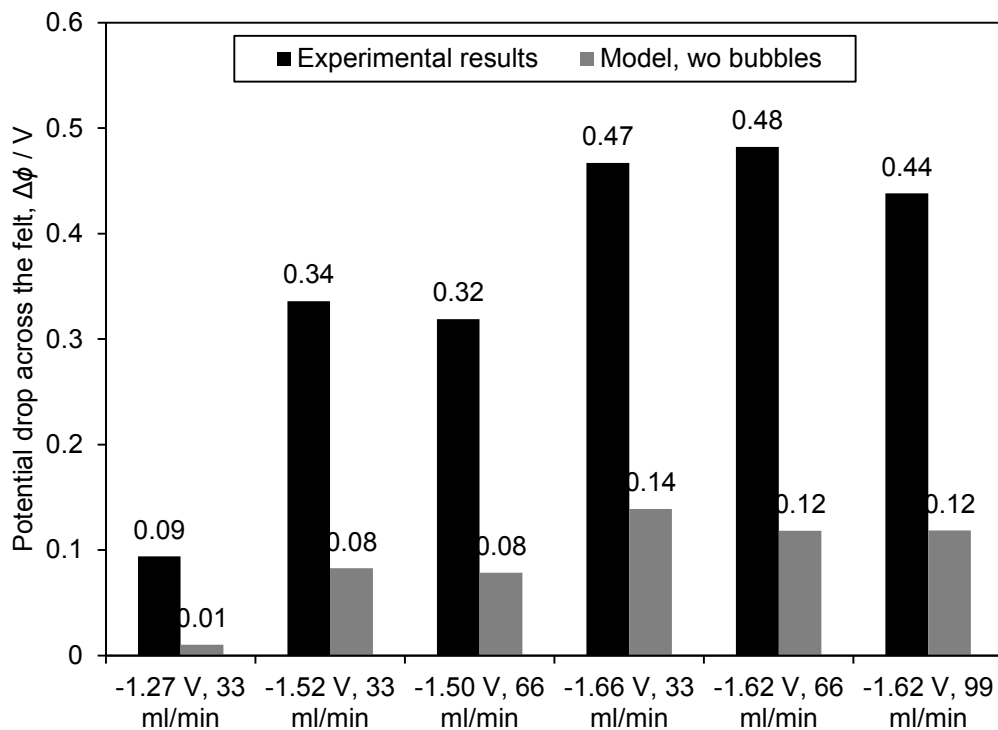


Figure 8-6: Predicted effect of electrode potential and flow rates on potential drops across felt thickness from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

The trend of the predicted current densities in Figure 8-4 as a function of electrolyte flow rates was also the reverse of what was determined experimentally. As the flow rate was increased, the current densities were actually expected to increase because a higher flow rate should have resulted in a smaller bubble fraction and therefore a larger overpotential at any point behind the front of the electrode. The experimental results agreed with this hypothesis except the last set of data at -1.6 V and 99 ml min⁻¹, which had a slightly smaller current density as the flow rate was increased from 66 ml min⁻¹. The model still consistently produced an opposing trend at this potential and flow rate by predicting a slight increase in the current densities.

It was found later that the cause of the unrealistic predicted trend in the current densities was that, at the same nominal electrode potential, the overpotential at the front mesh at 33 ml min⁻¹ was larger than that at higher flow rates. The smaller current densities obtained from the experiments at this flow rate resulted in smaller potential drops between the Luggin probe and the front plane of the 3D electrode, thereby lowering the electrode potentials at the front plane. The weak but expected current-density-suppressing effect of a low flow rate in this model was simply overwhelmed by the stronger influence of the increased overpotentials.

The over-predicted charge yields of formate also exhibited a different trend to that of the experimental results. The highest charge yield of 0.65 was predicted at -1.5 V, whereas 0.58 at -1.6 V was the highest value determined experimentally. The model also predicted only a small effect of flow rates on the charge yields at -1.6 V, while the experimental results suggested a strong relationship between the two. The predicted potential drops across the felt thickness were also essentially unaffected by flow rates, whereas they were expected to become smaller with increasing flow rates.

Figure 8-7 shows the predicted profiles of the potential differences in the ionically-conducting phase and the ionic current densities cumulated from the back to the front of 3D electrodes. The potential differences in the ionically-conducting phase decreased from the front to the back of 3D electrodes. The gradients of the potential differences were largest at exactly the front plane, becoming smaller towards the back and being zero at exactly the back plane. The ionic current densities followed a similar trend according to equation E8-1, being largest at the front plane as the entire ionic current densities entered the matrix here. They were consumed as they

travelled towards the back, becoming smaller and eventually being zero at exactly the back plane of the electrode. Strong relationships between the cumulative ionic current densities and the respective potential differences in the ionically-conducting phase can also be seen.

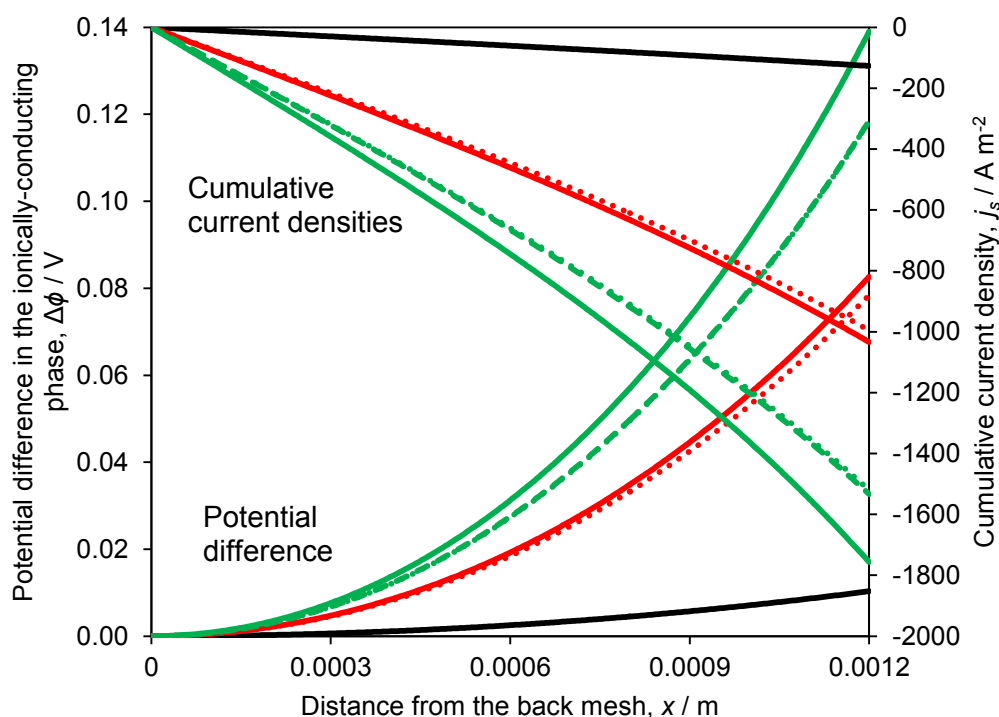


Figure 8-7: Predicted profiles of cumulative ionic current densities and potential differences in ionically-conducting phase at different electrode potentials at front plane and flow rates; black: -1.3 V, red: -1.5 V, green: -1.6 V; solid lines: 33 ml min⁻¹, dotted lines: 66 ml min⁻¹, dashed lines: 99 ml min⁻¹

Figure 8-8 shows the predicted profiles of the cumulative bubble fractions and the cumulative charge yields of formate. The bubble fractions increased from the back to the front of the 3D electrode as the bubbles generated in the matrices were carried by electrolytes flowing in the same direction. The bubble fractions predicted by this model were smaller than 0.06, explaining why electrolyte flow rates affected the predicted performances only weakly. The cumulative charge yields of formate decreased from the back to the front of the electrode, except at -1.3 V and 33 ml min⁻¹, at which the formate charge yields increased slightly. The decreasing charge yields at potentials ≥ -1.5 V indicated that the values were already beyond the potential of the highest charge yield, being consistent with Figure 8-3 showing the predicted effect of electrode potential on the charge yields.

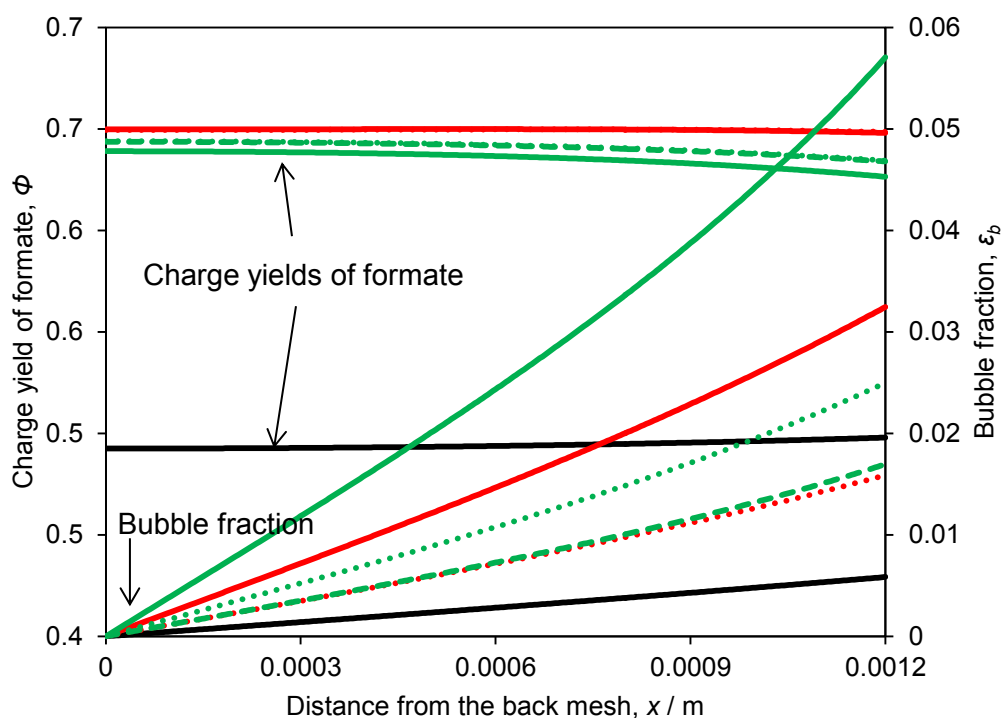


Figure 8-8: Predicted profiles of cumulative charge yields of formate and cumulative volumetric bubble fractions at different potentials of the front plane and flow rates; black: -1.3 V, red: -1.5 V, green: -1.6 V; solid lines: 33 ml min^{-1} , dotted lines: 66 ml min^{-1} , dashed lines: 99 ml min^{-1}

With only one parameter, this model could never be adjusted to predict the three measurable variables accurately. If the specific surface area of graphite felt were increased, the predicted potential drops would also be increased but so would the current densities, most of which were already highly over-predicted. Similarly, no improvements could be gained by decreasing the specific surface area. It is worth mentioning that Ateya and El-Anadouli (1991) also experienced similar under-predicted potential drops in the ionically-conducting phase across the thickness of their porous electrode in modelling hydrogen evolution at copper wool through a similar modelling approach. They also applied the assumption of no slip between the flows of electrolytes and bubbles and eventually attributed differences between their experimental results and their predictions to the effect of unaccounted trapped gas bubbles. No further solution was given. Clearly, an additional model parameter was needed; one affecting the motion of gas bubbles relative to that of flowing electrolytes was thought to be promising.

Few papers on modelling of 3D electrodes have incorporated effects of electrogenerated gas bubbles. Shah, Al-Fetlawi and Walsh (2010) claimed that the

motion of hydrogen bubbles generated in carbon felt electrodes in a redox flow battery could be simulated through a balance of forces acting on a bubble;

$$\frac{1}{2} \rho_l C_D |\bar{v}_{slip}| \bar{v}_{slip} = \frac{V_b}{A_b} \nabla P \quad \text{E8-22,}$$

where $\bar{v}_{slip} = \bar{v}_{g,s} - \bar{v}_{l,s}$ E8-23.

The drag coefficient was related to the Reynolds number of bubble flows:

$$C_D = \frac{24}{\text{Re}_b} \quad \text{E8-24,}$$

where $\text{Re}_b = \frac{d_b \rho_l |\bar{v}_{slip}|}{\mu_l}$ E8-25.

It readily follows that $\bar{v}_{slip} = \frac{d_b^2}{18\mu_l} \nabla P$ E8-26.

The pressure gradient was related to the superficial flow velocity of the liquid through Darcy's law modified with the Kozeny-Carman equation:

$$\bar{v}_{l,s} = -\frac{d_f^2}{K_f \mu_l} \frac{\varepsilon_f^3 (1 - \varepsilon_b)^3}{(1 - \varepsilon_f (1 - \varepsilon_b))^2} \nabla P \quad \text{E8-27.}$$

At a liquid flow rate of 33 ml min^{-1} , or 0.0014 m s^{-1} , these correlations yield a slip velocity of $-2.81 \times 10^{-5} \text{ m s}^{-1}$ with $d_f = 200 \text{ }\mu\text{m}$, $d_b = 172 \text{ }\mu\text{m}$, $K_f = 5.55$, $\mu_l = 0.001 \text{ Pa s}$, $\varepsilon_f = 0.84$ and $\varepsilon_b = 0.06$; i.e., the bubbles were travelling at 98 per cent of the electrolyte flow velocity. Such relative motion had been approximated in the model by assuming that the velocities of gas bubbles were equal to those of the liquid but proved not representative of the observed behaviour of this system.

It was believed that bubbles actually travelled at velocities significantly smaller than those of the liquid due to: i) them adhering to electrode surfaces, ii) their paths being obstructed by felt matrices and/or iii) them being physically trapped after coalescing into large bubbles in large pores with smaller entrances and exits. These physical phenomena had not been taken into account before but would be loosely expressed here by assuming that the interstitial velocities of gas bubbles were only fractions (f) of the interstitial velocities of the liquid. Equation E8-13 was modified:

$$\bar{v}_{g,i} = f\bar{v}_{l,i} = \frac{f\bar{v}_{l,s}}{\varepsilon_f(1-\varepsilon_b)} \quad \text{E8-28.}$$

It followed that

$$\bar{v}_{g,s} = \bar{v}_{g,i}\varepsilon_b\varepsilon_f = \frac{f\bar{v}_{l,s}\varepsilon_b\varepsilon_f}{\varepsilon_f(1-\varepsilon_b)} = \frac{f\bar{v}_{l,s}\varepsilon_b}{(1-\varepsilon_b)} \quad \text{E8-29.}$$

The molar flux of the gases with the ideal gas assumption was then:

$$\bar{N}_g = \frac{\bar{v}_{g,s}P}{RT} = \frac{f\bar{v}_{l,s}\varepsilon_bP}{(1-\varepsilon_b)RT} \quad \text{E8-30.}$$

Lastly, bubble fractions were:

$$\varepsilon_b = \frac{\bar{N}_g}{\frac{f\bar{v}_{l,s}P}{RT} + \bar{N}_g} \quad \text{E8-31.}$$

This approach to the model offered two adjustable parameters: the specific surface area of 3D electrodes and the relative velocity factor, f . 180 000 m⁻¹ and 0.0016 for the first and the latter, respectively, were found to be optimal for generating fairly accurate predictions of the experimental results. The current densities, the charge yields of formate and the potential drops at different electrode potentials at the front plane and flow rates are shown in Figure 8-9, Figure 8-10 and Figure 8-11, respectively, together with the corresponding predictions from this modified model. In general, the modified model was capable of reproducing the performances of 3D electrodes more accurately. The predicted current densities were closer to the experimental values and their stronger dependence on flow rates was evident from the disappearance of the peculiarly large values at 33 ml min⁻¹ due to increased overpotentials, which were previously evident in Figure 8-4. The predicted charge yields of formate were now not as high as predicted by the previous model (Figure 8-5) although still did not vary with flow rates as strongly as did the experimental results. The predicted potential drops still followed the expected behaviour but had better accuracy.

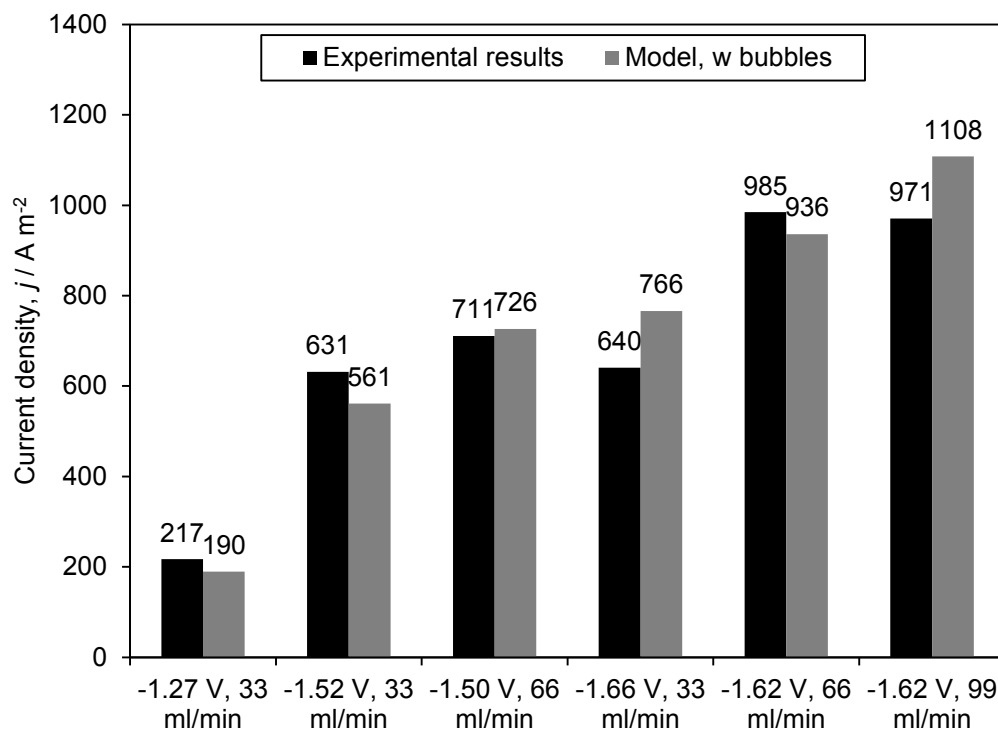


Figure 8-9: Improved predicted effect of electrode potential and flow rates on current densities from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

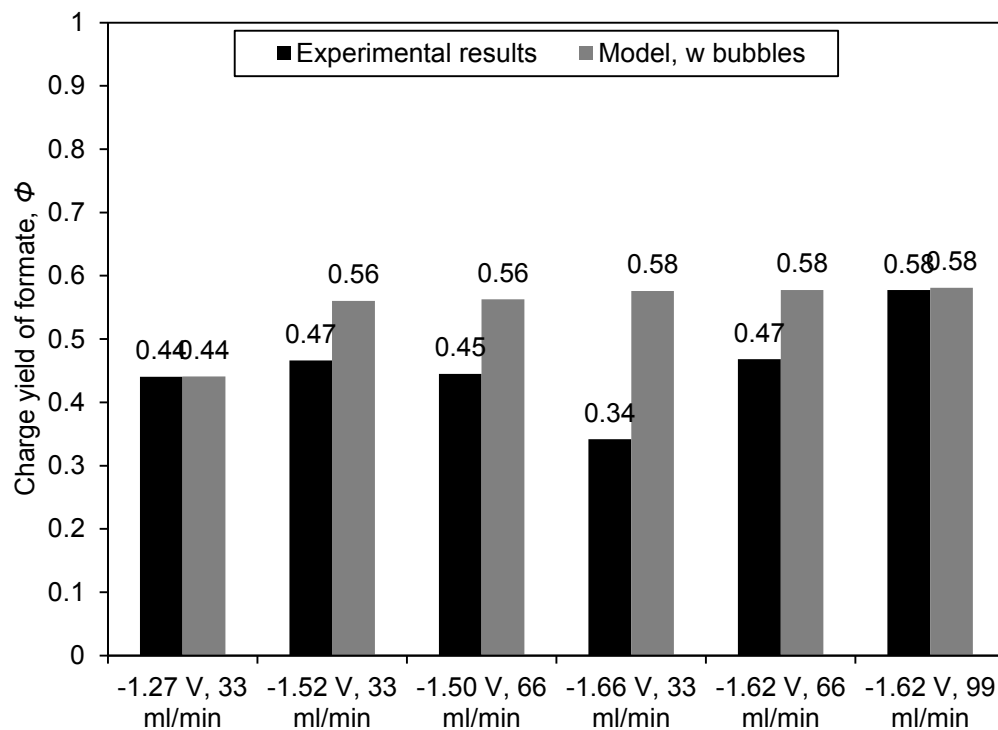


Figure 8-10: Improved predicted effect of electrode potential and flow rates on charge yields of formate from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

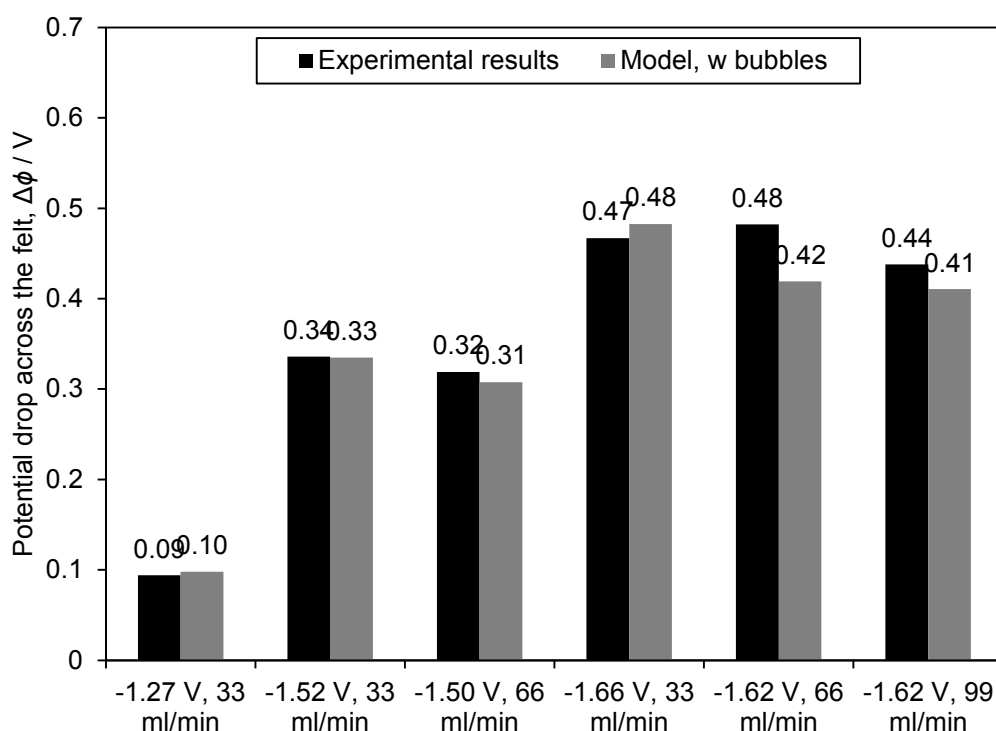


Figure 8-11: Improved predicted effect of electrode potential and flow rates on potential drops across felt thickness from electrolyses of aqueous solutions containing 0.5 M NaOH and 1 M NaClO₄ saturated with 1 atm CO₂

Figure 8-12 shows the predicted profiles of the cumulative ionic current densities and the potential differences in the ionically-conducting phase, exhibiting similar behaviours to the predictions from the previous model, but now with heavily skewed nature, especially at high current densities. The poor distributions of the current densities along the thickness of 3D electrodes were predicted to lead to ineffective use of cathode surface areas. At -1.3 V and 33 ml min⁻¹, half of the 190 A m⁻² was generated within 0.3 mm from the front of the electrode, while half of the 766 A m⁻² at -1.6 V and 33 ml min⁻¹ was generated in only 0.06 mm into the electrode.

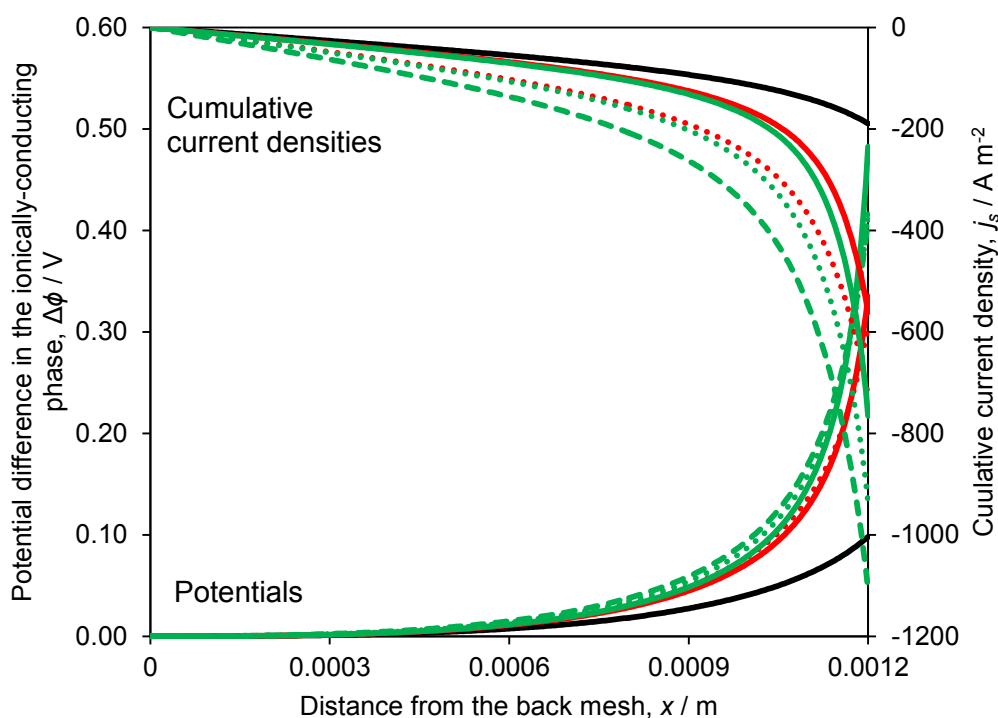


Figure 8-12: Predicted profiles of cumulative ionic current densities and potentials in the ionically-conducting phase at different electrode potentials at front plane and flow rates; black: -1.3 V, red: -1.5 V, green: -1.6 V; solid lines: 33 ml min⁻¹, dotted lines: 66 ml min⁻¹, dashed lines: 99 ml min⁻¹

Figure 8-13 shows the predicted cumulative bubble fractions and the cumulative charge yields of formate. The bubble fractions at the front of 3D electrodes were predicted to accumulate above 0.9, significantly larger than those below 0.06 in the previous model, because they were predicted to travel at velocities much lower than those of the liquid in this modified model. These extremely large bubble fractions were predicted to decrease the superficial conductivities of the ionically-conducting phase greatly. Equation E8-2 suggests that a bubble fraction of 0.9 decreases the superficial conductivity of the electrolyte to only 3 per cent of its bulk phase value. A direct consequence of this is that the potential differences in the ionically-conducting phase decreased steeply near the front of electrodes (Figure 8-12) in order to support the large current densities. As the charge yields of formate depend on electrode potential, they increased to appreciable values only near the front of the felt where electrode potentials were sufficiently low. Ateya and El-Shakre (1984) also reported comparable bubble fractions back-calculated by the Bruggeman equation from potential drops measured across the electrode thickness in their study of hydrogen evolution at metal wool electrodes.

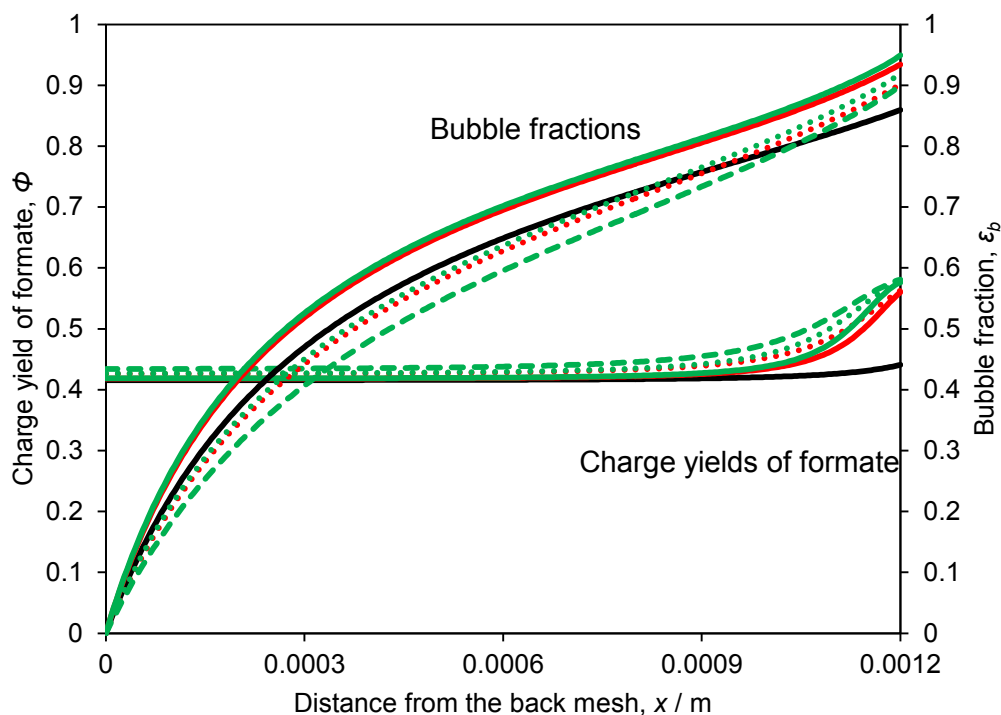


Figure 8-13: Predicted profiles of cumulative charge yields of formate and cumulative volumetric bubble fractions at different potentials at front plane and flow rates; black: -1.3 V, red: -1.5 V, green: -1.6 V; solid lines: 33 ml min⁻¹, dotted lines: 66 ml min⁻¹, dashed lines: 99 ml min⁻¹

The issue of bubble accumulation is discussed here. However, there seems to be no acknowledged study of the effect of bubbles on mass transport in 3D electrodes, whereas there is extensive literature on the topic for planar electrodes. According to Vogt (1983), the formation of bubbles at a two-dimensional electrode enhances mass transfer through three mechanisms:

1. The expansion of a bubble anchoring on the electrode surface pushes the liquid electrolyte radially, creating flows of the electrolyte near the electrode surface.
2. An individual bubble departing from the electrode surface transfers some of its momentum to the liquid, creating small electrolyte circulation near the surface.
3. The swarm of bubbles travelling relatively further from the electrode induces circulation in the bulk of the electrolyte.

The effects of bubbles on mass transport at planar electrodes under flowing electrolytes were also published (Eigeldinger & Vogt, 2000, Balzer & Vogt, 2003).

The low value of the relative velocity factor, f , used in the model suggested that the majority of bubbles were physically trapped and/or adhered to electrode matrices, rather than simply obstructed along their paths due to the felt tortuosity. If this is the case, mechanism 3 is probably suppressed to a large extent. Furthermore, a trapped bubble obstructed an electrolyte flow, redirecting the liquid around an entire fibre bunch in which the bubble was trapped. The concept is also illustrated in Figure 8-14. The thin liquid films between the fibres and the trapped gas bubble were relatively stagnant and therefore dissolved CO_2 might not be adequately supplied. Even if mechanism 1 and 2 are still active, the local concentrations of CO_2 at the fibre surfaces facing inwards tend to be lower than those facing outwards because the bulk concentrations of CO_2 within the dead zones are already significantly lower than those outside the bunch. Although a higher flow rate around the fibre bunch could be expected due to a smaller liquid fraction, true partial current densities of CO_2 reduction were not enhanced any further due to the already exceedingly large mass transfer coefficients in the absence of bubbles calculated earlier in section 8.1 and having led to the neglect of CO_2 mass transport. Therefore, enhancements to mass transport by bubble motion were ineffective in this instance. The generally over-predicted charge yields of formate in Figure 8-10 were probably a consequence of the absence of such suppressing mechanism in the modified model.

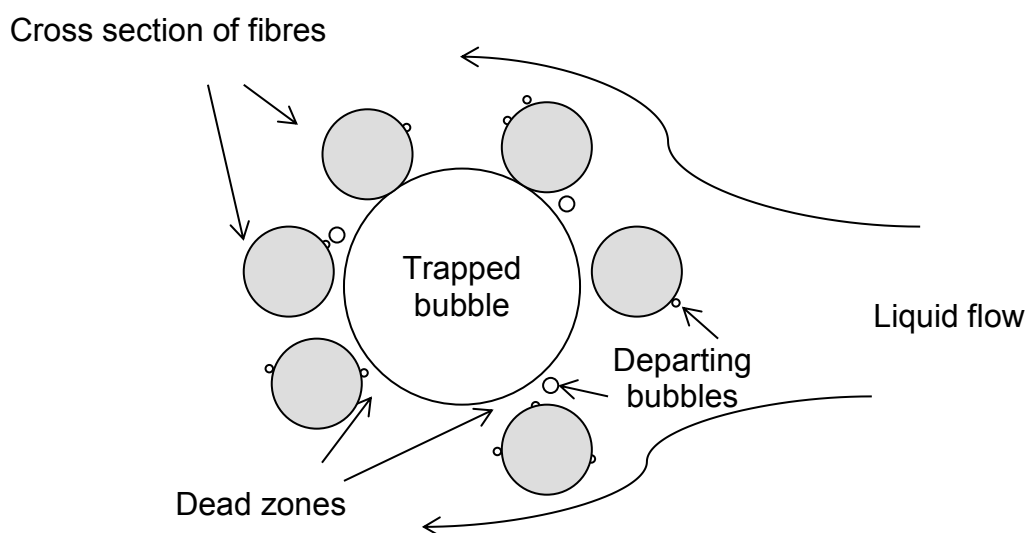


Figure 8-14: Schematic diagram of bubble trapped within bunch of graphite fibres

Another aspect of the relative motion factor, f , is that it could actually be a function of bubble fractions. The value could be significantly larger at a smaller bubble fraction

due to higher bubble mobility. As bubbles coalesced to larger sizes in a felt matrix, a larger portion was trapped and had lower mobility, thus reducing the value of the relative velocity factor. Consequently, the factor should actually have decreased from the back to the front of 3D electrodes. However, such relationship has not been established and therefore a single average value was employed in the modified model.

Despite the more accurate predictions from the modified model, the specific surface area of 3D electrodes had to be set to a number approximately 6 times larger than the calculated geometrical value shown in Table 7. The large value might reflect the rough surfaces having a larger true surface area than the calculated geometrical value. Nevertheless, an even larger number should be expected because surface blockages due to bubbles adhering to tinned fibres were yet to be taken into account, compensating for the unavailable surfaces.

Amongst a number of electrodes with increased surface areas developed by various research groups presented in section 2.3.1, the packed-bed electrodes of tin particles by Li and Oloman (2007) in particular shared certain similarities with this system. They also showed that different forms of tin particles used as packed-bed cathodes yielded different formate charge yields ranging from 0.20 to 0.75 at the same electrolysis conditions. The tin granules with the highest formate charge yield of 0.75 were then employed in their reactor for CO₂ reduction, offering a charge yield of 0.6 at a current density as high as 3 000 A m⁻², which were better than the results achieved from graphite felt electrodes in this project, despite a specific surface area of only 17 000 m² m⁻³. Although the authors did not discuss the potential distributions within their packed beds, the better results were believed here to be due to the higher formate charge yields from the tin granules, which led to smaller gas production rates in their 3D electrodes, less severe bubble accumulation, thus the better performance. Hence, bubble accumulation was thought to be one of the main factors limiting current densities from a 3D electrode.

8.3 Energy consumption during CO₂ reduction

The calculations of the energy consumption require cell voltages, which depend on the configuration of the whole cell including the types of both the anode and the cathode, the conductivities of both the anolyte and the catholyte and the dimensions

of the assembly. The electrochemical cell used in this project was designed to facilitate product analysis and the versatility for 2D and 3D electrodes, rather than being designed to minimise energy losses. However, the available data enabled calculation of cell potential differences and estimations of specific energy consumptions.

The values based on the performances of the reduction of CO₂ at tinned graphite felt electrodes in Figure 7-27 and Figure 7-28 are tabulated in Table 8. The electrode potential of the anode, which was a RuO₂-coated titanium mesh, was obtained from another experiment to determine the relationship between electrode potential and currents. The ohmic potential drops in electrolytes were calculated with the conductivities of 82.5 S m⁻¹ for the anolyte and 9.36 S m⁻¹ for the catholyte. The Gibbs energy yields of formate were calculated on the basis of 236 kJ mol⁻¹, which is the change in the Gibbs energy of converting 1 atm CO₂ to 1 M formate at pH 7.8.

Table 8: Estimations of cell voltages and various energetic values

	-1.27 V, 33 ml min ⁻¹	-1.52 V, 33 ml min ⁻¹	-1.50 V, 66 ml min ⁻¹	-1.66 V, 33 ml min ⁻¹	-1.62 V, 33 ml min ⁻¹	-1.62 V, 99 ml min ⁻¹
Current density, j /A m ⁻²	217	631	711	640	984	970
Potential of the anode, E_a (AgCl Ag)/V	1.41	1.48	1.49	1.48	1.53	1.52
Ohmic drop in the anolyte, V_a /V	0.03	0.08	0.09	0.08	0.12	0.12
Ohmic drop in the catholyte, V_c /V	0.51	1.48	1.67	1.50	2.31	2.28
Potential of the cathode, E_c (AgCl Ag)/V	-1.27	-1.52	-1.5	-1.66	-1.62	-1.62
Cell voltage, U_{cell} /V	3.22	4.56	4.75	4.72	5.58	5.54
Charge yield of formate, Φ_f	0.44	0.47	0.44	0.34	0.47	0.58
Specific electrical energy consumption, w_p /kW h tonne ⁻¹	8707	11556	12852	16543	14147	11373
Gibbs energy yield of formate, $\Phi_{G,f}$	0.17	0.13	0.11	0.09	0.10	0.13

The ohmic potential drops in the catholyte constituted large portions of the cell potential differences, especially at high current densities. This was due to the limited conductivity of the catholyte and the 22 mm long current path between the membrane and the front plane of 3D cathodes. The conductivity of the catholyte at 9.36 S m^{-1} was achieved by addition of 1 M NaClO_4 and so was difficult to increase further. On the other hand, the distance between the front plane of electrodes and the membrane could be reduced in a well-designed reactor.

An interesting point is that the highest Gibbs energy yield of formate was obtained at -1.27 V and the flow rate of 33 ml min^{-1} , and did not necessarily coincide at the same conditions that produced the highest charge yield. This resulted because Gibbs energy yield is strongly affected by two variables: charge yields and energy loss through overpotentials and ohmic potential losses. A relatively large value can still be obtained even at a low charge yield as long as energy loss is small; this is the case for the highest value in the table. At the other extreme, a high charge yield can compensate for a high energy loss to maintain a high Gibbs energy yield.

Gibbs energy yields may be even more important than charge yields when CO_2 reduction is employed specifically for energy storage. If the system is advanced enough in the future that the charge yields approaches unity, the Gibbs energy yields will probably remain the only concern between the two. It will be reduced only by minimising energy losses through overpotentials and ohmic potential drops. Operations at small overpotentials will be favourable but the expected small current densities will probably call for electrodes with high surface areas or three-dimensional ones to reduce reactor sizes and hence costs.

8.4 Conclusions

The performances of tin-plated graphite felt electrodes used for electrochemical reduction of CO_2 were modelled with adequate accuracy. Bubbles were found to be trapped in felt matrices rather than to be carried away easily by liquid flows. Their accumulation was found to inhibit the performances of this system heavily by decreasing superficial conductivities of electrolytes, leading to inhomogeneous potential and current density distributions and impeding sufficient mass transport of CO_2 .

9 Conclusions

Electrochemical reduction of aqueous CO₂ at tin cathodes produced carbon monoxide, formate and hydrogen, their rates depending on electrode potential and pH, with carbon monoxide favoured at lower pH and formate at higher pH. Tin was chosen as cathode material, inter alia, as its kinetics of hydrogen evolution are well known to be slow, though increased with decreasing pH. The partial current densities for CO₂ reduction appeared to follow the generally accepted mechanism of two-step electron transfer and were modelled accordingly. Increasing the protonation state of the adsorbed intermediate ($H_nCO_2^{(1-n)-}_{ads}$; $0 \leq n \leq 2$) was assumed to increase its tendency to produce carbon monoxide, so pH affected the CO : HCO₂⁻ product molar ratio. The mathematical model based on this concept was shown to predict that ratio satisfactorily.

As partial current densities for CO₂ reduction were limited to 25 A m⁻², electrodeposition of tin onto graphite felt cathodes with a geometrical specific surface area of ca 31 000 m² m⁻³ was investigated as a structure for subsequent scale-up. The physics of such 3D electrodes resulted in spatial distributions of potential and current density, so careful design was required, limiting the dimension to a few mms in the direction of current flow. Electrochemical reduction of CO₂ was found to be sensitive to flow rates of electrolyte solutions, in addition to feeder electrode potential. This was due to accumulation of H₂ and CO bubbles within the voids of the felt, decreasing the effective electrolyte conductivity, so making the potential distribution more inhomogeneous, and impeding CO₂ mass transport to cathode surfaces.

The highest superficial (cross-sectional) current density was 971 A m⁻², with a fractional charge yield for formate of 0.58, at a front feeder cathode potential of -1.62 V (AgCl|Ag) and an electrolyte flow rate of 99 ml min⁻¹. A mathematical model incorporating empirically the effect of bubble accumulation on the superficial conductivities of the ionically-conducting phase was developed and successfully tuned to reproduce the experimental results with moderate accuracy. However, the influence of bubbles on mass transport of CO₂ was complex so could not be

included; consequently, the charge yields of formate were over-predicted for some of the experimental conditions.

10 Suggestions for future work

The kinetic model for electrochemical reduction of CO_2 had been developed without consideration of the interaction between the intermediates of CO_2 reduction and hydrogen evolution due to the lack of a kinetically accurate model for hydrogen evolution. However, it was shown that, for the range of electrode potentials studied, rates of CO_2 reduction were unlikely to be affected by the rates of hydrogen evolution. The validity of the model for CO_2 reduction could be extended to a larger range of potentials if an accurate model for hydrogen evolution could be developed. However, the kinetics of hydrogen evolution can be different at the same electrode material supplied from different sources. What is probably more important than a kinetic model is an easy but reliable means to obtain the kinetic parameters. With such procedure in place, a model for hydrogen evolution can be derived individually for each electrode.

The electrochemical reduction of CO_2 at 3D electrodes proved to be suppressed by bubble accumulation, which impeded the process via two mechanisms: reducing the superficial conductivities of the ionically-conducting phases and inhibiting CO_2 mass transport. However, the empirical equation introduced accounted only for the relatively simple effect of the former. A more theoretical approach should be formulated to enable mass transport effects to be included.

The generation of gaseous products was a source of many problems encountered in the reduction of CO_2 at 3D electrodes, which need to be better engineered. Optimising their void dimensions with respect to bubble diameters should enable improved bubble disengagement while minimising pressure drop and hence pumping costs.

11 References

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Appendix A Search for kinetic parameters of hydrogen evolution

The interaction between the adsorbed intermediates of CO₂ reduction and hydrogen evolution was actually considered even before the experiments on the reduction of CO₂ were conducted. Obtaining a complete set of the kinetic parameters of hydrogen evolution from proton and water was the first part of the original plan for the study of the kinetics of CO₂ reduction. The strategy was to examine hydrogen evolution from water in an aqueous solution at high pH first. The kinetics of proton reduction in aqueous solutions at lower pH was then studied. Cyclic voltammograms were obtained with a rotating tin disc electrode and modelled with the Volmer-Heyrovsky mechanism. Two Tafel regions corresponding to the two elementary steps of hydrogen evolution were expected. The kinetic parameters were re-checked by reproducing the results from electrochemical impedance spectroscopy (EIS).

Theoretically, EIS can reaffirm the two Tafel regions because the spectra from the two regions are different and this can be shown mathematically. The current densities of the elementary steps of hydrogen evolution as described by the Volmer-Heyrovsky mechanism are:

$$j_V = -Fk_V a_{H^+} (1 - \theta_H) \quad \text{E6-99}$$

and
$$j_H = -Fk_H a_{H^+} \theta_H. \quad \text{E6-100.}$$

The sum of the two is therefore the current density of hydrogen evolution. Differentiating this current density with respect to electrode potential yields the reciprocal of the Faradaic impedance of hydrogen evolution:

$$\begin{aligned}
\frac{1}{Z_F} &= \frac{\partial(j_V + j_H)}{\partial E} \\
&= -Fa_{H^+} \left(\frac{\partial k_V(1 - \theta_{H.})}{\partial E} + \frac{\partial k_H \theta_{H.}}{\partial E} \right) \\
&= -Fa_{H^+} \left\{ \begin{aligned} &-k_V \frac{\partial \theta_{H.}}{\partial E} + k_V(1 - \theta_{H.}) \left(\frac{-\alpha_V F}{RT} \right) \\ &+ k_H \frac{\partial \theta_{H.}}{\partial E} + k_H \theta_{H.} \left(\frac{-\alpha_H F}{RT} \right) \end{aligned} \right\} \\
&\approx -Fa_{H^+} \left\{ \begin{aligned} &-k_V \frac{\partial \theta_{H.}}{\partial E} + k_V(1 - \bar{\theta}_{H.}) \left(\frac{-\alpha_V F}{RT} \right) \\ &+ k_H \frac{\partial \theta_{H.}}{\partial E} + k_H \bar{\theta}_{H.} \left(\frac{-\alpha_H F}{RT} \right) \end{aligned} \right\}
\end{aligned} \tag{EA-1.}$$

An equation for the dependence of the surface coverage on electrode potential could be developed through a mass balance of the adsorbed species:

$$\Gamma \frac{\partial \theta_{H.}}{\partial t} = k_V a_{H^+} (1 - \theta_{H.}) - k_H a_{H^+} \theta_{H.} \tag{EA-2.}$$

At steady states, accumulation rates of the adsorbed species are zero:

$$\begin{aligned}
\Gamma \frac{\partial \theta_{H.}}{\partial t} &= 0 = k_V a_{H^+} (1 - \bar{\theta}_{H.}) - k_H a_{H^+} \bar{\theta}_{H.} \\
\bar{\theta}_{H.} &= \frac{k_V}{k_V + k_H}
\end{aligned} \tag{EA-3.}$$

Equation EA-2 could be simplified to the first derivative of its Taylor series:

$$\begin{aligned}
\Gamma \frac{\partial \theta_{H.}}{\partial t} &= \frac{\partial \{k_V a_{H^+} (1 - \theta_{H.}) - k_H a_{H^+} \theta_{H.}\}}{\partial E} \Delta E \\
&= \left\{ \begin{aligned} &-k_V a_{H^+} \frac{\partial \theta_{H.}}{\partial E} + k_V a_{H^+} (1 - \bar{\theta}_{H.}) \left(\frac{-\alpha_V F}{RT} \right) \\ &-k_H a_{H^+} \frac{\partial \theta_{H.}}{\partial E} - k_H a_{H^+} \bar{\theta}_{H.} \left(\frac{-\alpha_H F}{RT} \right) \end{aligned} \right\} \Delta E
\end{aligned} \tag{EA-4.}$$

The ΔE could be obtained from the sinusoidal input of electrode potential;

$$\begin{aligned}
E &= \bar{E} + \tilde{E} \exp(i\omega t) \\
\Delta E &= \tilde{E} \exp(i\omega t)
\end{aligned} \tag{EA-5.}$$

Differentiating ΔE with respect to time gave:

$$\frac{\partial \Delta E}{\partial t} = \frac{\partial E}{\partial t} = i\omega \tilde{E} \exp(i\omega t) \quad \text{EA-6.}$$

Dividing equation EA-4 by equation EA-6 yielded:

$$\begin{aligned} i\omega\Gamma \frac{\partial \theta_{H.}}{\partial E} &= -k_V a_{H^+} \frac{\partial \bar{\theta}_{H.}}{\partial E} + k_V a_{H^+} \left(1 - \bar{\theta}_{H.}\right) \left(\frac{-\alpha_V F}{RT}\right) \\ &\quad - k_H a_{H^+} \frac{\partial \bar{\theta}_{H.}}{\partial E} - k_H a_{H^+} \bar{\theta}_{H.} \left(\frac{-\alpha_H F}{RT}\right) \\ \frac{\partial \theta_{H.}}{\partial E} &= \frac{k_V a_{H^+} \left(1 - \bar{\theta}_{H.}\right) \left(\frac{-\alpha_V F}{RT}\right) - k_H a_{H^+} \bar{\theta}_{H.} \left(\frac{-\alpha_H F}{RT}\right)}{k_V a_{H^+} + k_H a_{H^+} + i\omega\Gamma} \end{aligned} \quad \text{EA-7.}$$

Substituting equation EA-7 for $\frac{\partial \theta_{H.}}{\partial E}$ in equation EA-1 and rearranging resulted in

$$\frac{1}{Z_F} = \frac{1}{R_{ct}} + \frac{1}{R_{ad} + i\omega L_{ad}} \quad \text{EA-8,}$$

where

$$R_{ct} = \frac{(k_V + k_H)RT}{k_V k_H a_{H^+} F^2 (\alpha_V + \alpha_H)} \quad \text{EA-9,}$$

$$R_{ad} = \frac{(k_V + k_H)^2 RT}{k_V k_H a_{H^+} (k_V - k_H)(\alpha_H - \alpha_V) F^2} \quad \text{EA-10,}$$

and

$$L_{ad} = \frac{\Gamma(k_V + k_H)RT}{k_V k_H a_{H^+}^2 (k_V - k_H)(\alpha_H - \alpha_V) F^2} \quad \text{EA-11.}$$

It follows that R_{ad} and L_{ad} are simultaneously positive or negative. Furthermore, as electrode potential is decreased, both are always positive in the first Tafel region and negative in the second regardless of which is the rate-determining step in each region. Consequently, an impedance in the first Tafel region possesses an inductive component and that in the second has a capacitive component. Both are generally located at the low-frequency end of an impedance spectrum. These features could be useful in determining the potential at which the rate determining step changes from one to the other in case the voltammogram is obscure.

The total electrochemical impedance of an electrode can be obtained by adding appropriately the impedances of the electrical double layer and the solution between the Luggin probe and the working electrode to the Faradaic impedance:

$$\begin{aligned}
Z &= R_s + \frac{1}{\frac{1}{Z_F} + \frac{1}{Z_{dl}}} \\
&= R_s + \frac{1}{\frac{1}{R_{ct}} + \frac{1}{R_{ad} + i\omega L_{ad}} + i\omega C_{dl}}
\end{aligned}
\tag{EA-12.}$$

However, the experimental results were masked with unexpected features that conceal the characteristics of the impedance spectra as will be shown.

A.1 Experimental details

Experiments were carried out both with the planar tin electrode and with a rotating disc electrode. The preparation of the former was similar to the procedure followed in Chapter 5 except the gas for sparging was nitrogen. The disc electrode was a tin disc with a diameter of 5 mm and a length of 4 mm, cut from a 6 mm diameter tin rod (Puratronic, 99.9985%, Alfa Aesar). The disc electrode was embedded in a PTFE cup so that only the circular area was exposed. It was electropolished in 70% perchloric acid according to the procedure in Chapter 5 prior to each measurement.

Both cyclic voltammetry and EIS with the planar electrode were conducted in the same cell used in Chapter 5. The solutions were stirred at the same rate. Experiments with the rotating disc electrode was conducted in a large three-compartment cell containing aqueous buffer solutions constantly sparged with nitrogen to minimise oxygen contamination. The resistances of the electrolyte between the electrode and the Luggin probe were estimated from the taken electrochemical impedance spectra and used to determine the actual electrode potentials.

A.2 Results and discussion

Figure A-1 shows a cyclic voltammogram obtained with the rotating disc electrode in an aqueous solution of 1 M NaOH. A positive-going potential scan was started from the negative potential limit and reversed at the positive potential limit. The non-linear plot was probably caused by the rate-determining step changing from one to the other, so EIS was performed at different electrode potentials to clarify this. However, the spectra exhibited large fluctuations, especially at low frequencies, at which the decisive features were expected. The spectrum shown in Figure A-2 was obtained at the lowest potential, below which spectra were extremely noisy, especially at low

frequencies; though still retaining their semi-circular shapes, they could not provide useful information.

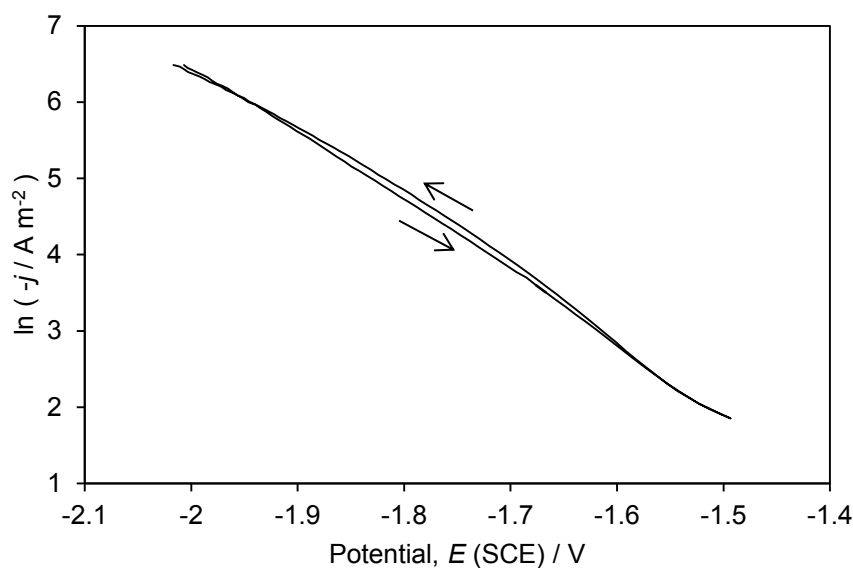


Figure A-1: Cyclic voltammogram of tin disc electrode rotating at 2000 rpm in 1 M NaOH at 0.01 V s^{-1} scan rate

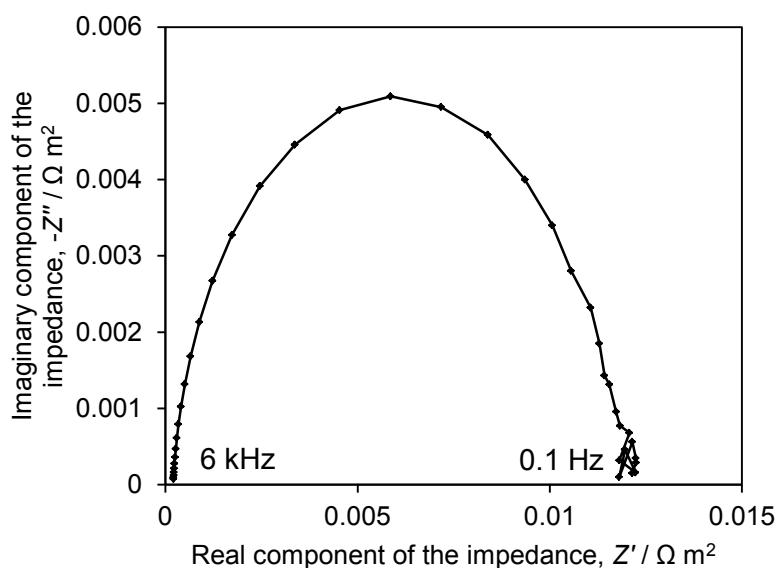


Figure A-2: Electrochemical impedance spectrum of tin disc electrode rotating at 2000 rpm at -1.6 V (SCE) in 1 M NaOH

Figure A-3 shows a cyclic voltammogram obtained in an aqueous buffer solution of pH 5.9 containing 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 . The positive-going scan was started at -1.0 V (SCE) , swept to the positive end, then to the negative potential limit, before being returned to -1.0 V (SCE) . The current densities at potentials above -1.2 V (SCE) were caused by the limiting current density of oxygen evolution and so

should be ignored. The apparent change in the Tafel slope in the negative scan at approximately -1.35 V (SCE) might be a result of the change in the rate-determining step from one to the other although this was not evident on the positive-going scan. This was again checked with electrochemical impedance spectra taken at -1.25 V (SCE) and -1.4 V (SCE).

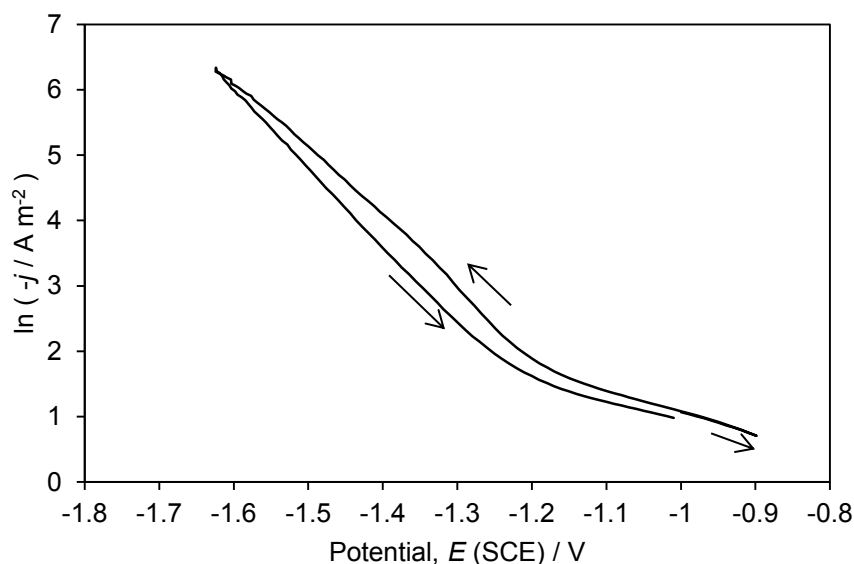


Figure A-3: Cyclic voltammogram of tin disc electrode rotating at 2000 rpm in 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 5.9) at 0.01 V s^{-1} scan rate

The spectrum measured at -1.25 V (SCE) (Figure A-4) showed a minute characteristic of an inductive component at low frequencies, at which the fluctuations were of comparable magnitude. The low-frequency end of that taken at -1.4 V (SCE) (Figure A-5) was obscured even more by fluctuations and unrecognisable features. Therefore, the cause of the apparent change in the Tafel slope was still inconclusive.

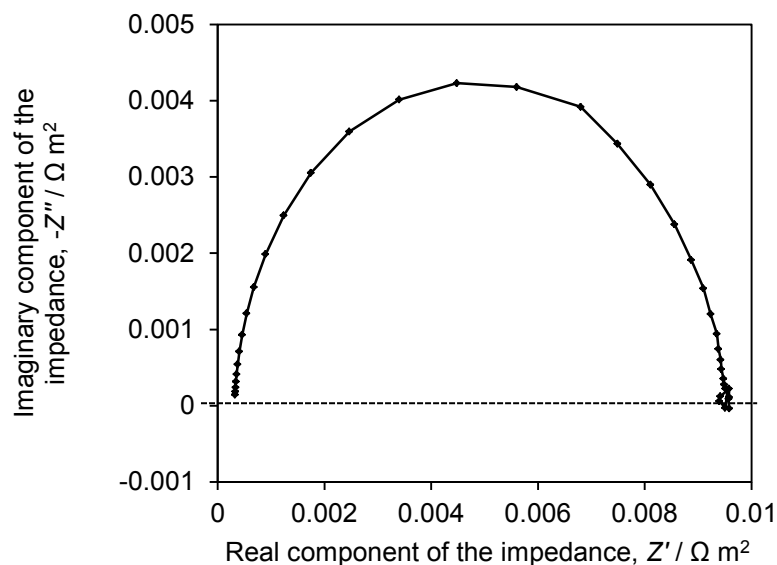


Figure A-4: Electrochemical impedance spectrum at -1.25 V (SCE) from tin disc electrode rotating at 2000 rpm in 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 5.9)

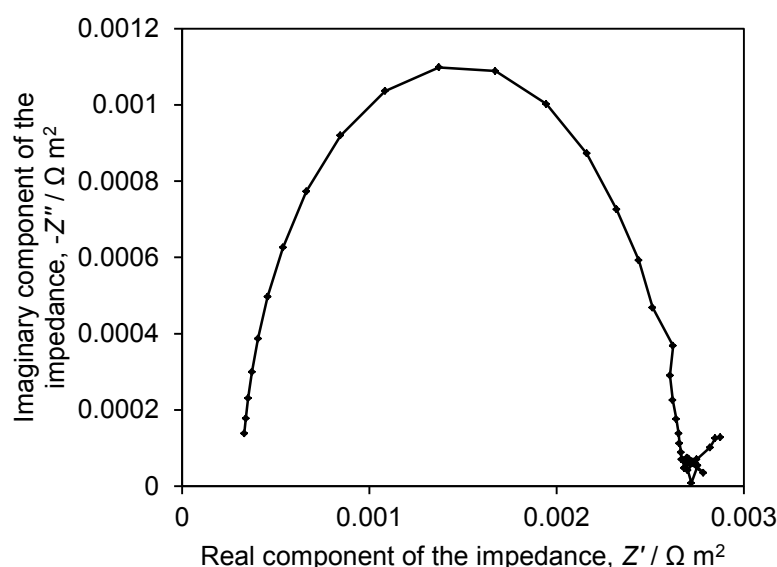


Figure A-5: Electrochemical impedance spectrum at -1.4 V (SCE) from tin disc electrode rotating at 2000 rpm in 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 5.9)

The voltammogram shown in Figure A-3 was also marked by pronounced hysteresis. This feature was not observed in the voltammogram obtained in the 1 M NaOH solution (Figure A-1) and so was believe to have been due to the presence of dihydrogen phosphate. As shown in Figure A-6, similar hysteresis was still evident in cyclic voltammograms of tin in an aqueous solution of pH 6.5 containing 0.4 M NaH_2PO_4 /0.4 M Na_2HPO_4 . The scans were started from the negative potential limit, swept to the positive end first and returned to the start point. It can be seen that the

extent of the hysteresis depended on the less negative potential limit of each scan; the hysteresis became more obvious as that limit was increased. It was believed that this phenomenon was caused by the specific adsorption of dihydrogen phosphate. The presence of specifically adsorbed anions lowered the potential of the inner Helmholtz plane and therefore the outer Helmholtz plane, increasing the current density of hydrogen evolution according to equation E1-17. With increasingly positive electrode potential, the anion adsorption became more favourable. However, the process appeared to be slow that more anions were adsorbed progressively at high potentials, resulting in the increased current densities in the subsequent negative-going potential scans.

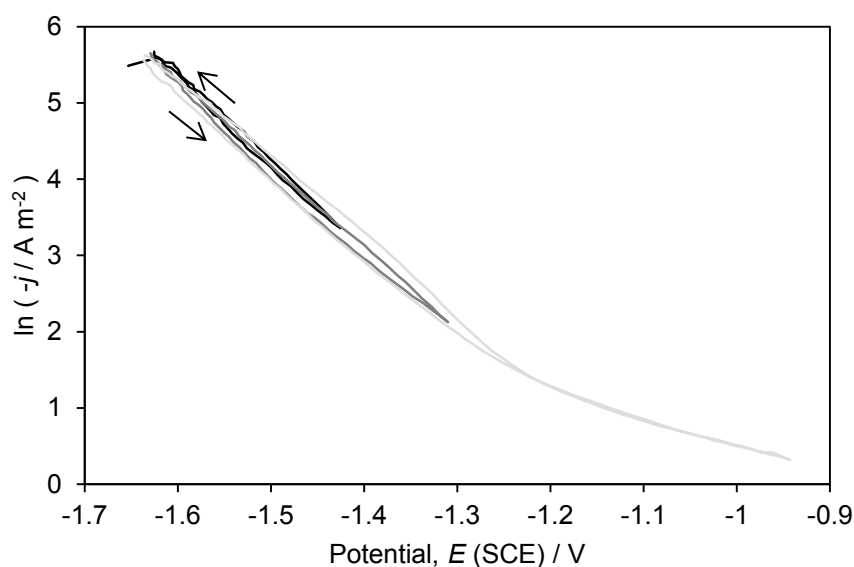


Figure A-6: Cyclic voltammogram of tin disc electrode rotating at 2000 rpm in 0.4 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 6.5) at 0.01 V s^{-1} scan rate

Appendix B Electrochemical reduction of *CO₂* at very low electrode potentials

Vassiliev et al. (1985)'s paper is one of a few that show plots of logarithmic partial current densities of CO₂ reduction at very low electrode potentials (Figure B-1). Their experiments were conducted with disc electrodes rotating at 2000 rpm so that dissolved CO₂ was adequately transferred to the electrode. However, all partial current densities of CO₂ reduction appeared to be limited at some point and even decreased as electrode potential was decreased. Even if the transport of CO₂ were limiting, the decreases in the partial current densities should not be expected without additional suppressing mechanism. This feature was addressed only briefly by the authors of the paper and attributed to decreases in adsorbed CO₂ molecules at highly negative potentials below potentials of zero charge, but was believed here to be caused by either 1) the suppression of the partial current densities of CO₂ reduction by adsorbed H[•] or 2) the suppression of the current densities by adhering bubbles.

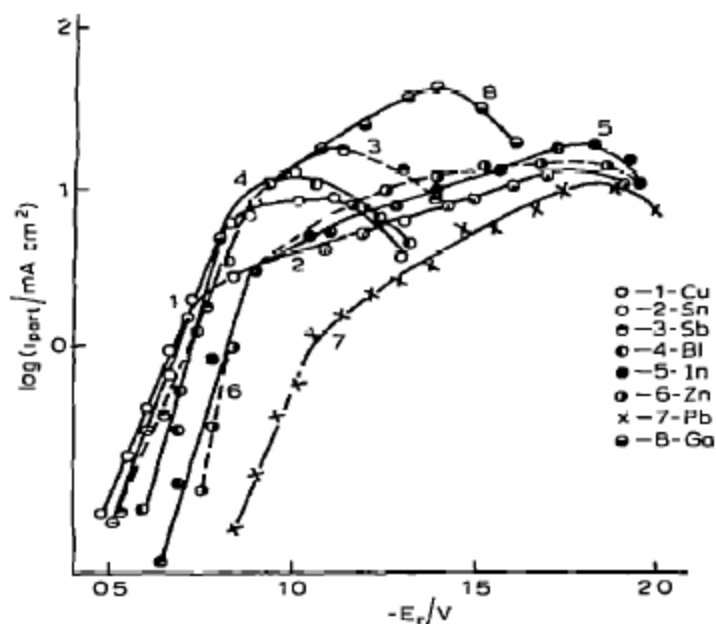


Figure B-1: Effects of electrode potential and cathode material on logarithmic partial current densities of CO₂ reduction in buffer solutions of pH 5.5 (Vassiliev et al., 1985)

If the first is the case, it then follows that the transition between the Volmer and Heyrovsky reaction as the rate-limiting steps occurs around the potential where the

partial current densities of CO_2 reach the maximum limits and that the fractional surface coverage of $\text{H}\cdot$ increases from a low to a high value as electrode potential was decreased. This situation can also be shown mathematically through a similar model developed in section 6.4.2. $k_{V,0} = 2.47 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_V = 0.24$ were set to simulate the experimental results from electrolyses at pH 5.9 shown in Figure 6-21, while $k_{H,0} = 4.12 \times 10^2 \text{ mol m}^{-2} \text{ s}^{-1}$ and $\alpha_H = 0.04$ were set arbitrarily. The surface coverages of the intermediates of hydrogen evolution and CO_2 reduction calculated with and without surface interactions are presented in Figure B-2. It can be seen that the surface coverages of $\text{CO}_2\cdot^-$ in both cases started from unity at high potentials and then diminished gradually to low values at low potentials, but distinctions between the two cases were clear at low potentials. On the other hand, the surface coverages by $\text{H}\cdot$ increased to unity with increasingly negative potential. While that calculated under the influence of CO_2 reduction still did similarly, it started with a smaller value. The suppression seemed to be stronger on the intermediate that tended to have smaller surface coverage, while the one with a significantly larger surface coverage was virtually unaffected.

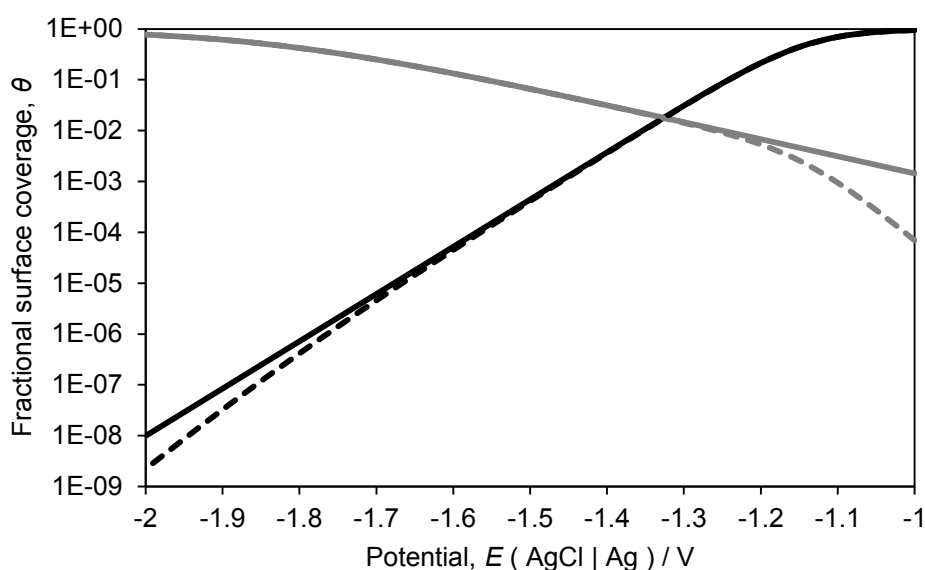


Figure B-2: Predicted effect of electrode potential on surface coverages of $\text{H}\cdot$ and $\text{CO}_2\cdot^-$; black: $\text{CO}_2\cdot^-$, grey: $\text{H}\cdot$; solid lines: absence of surface interactions, dashed lines: presence of surface interactions

As the relationship between surface coverages and partial current densities is linear, the plots indicated that the partial current densities of hydrogen evolution were suppressed only at high potentials, while those of CO_2 reduction were only at very

low potentials. The calculated partial current densities of hydrogen evolution and CO₂ reduction are shown respectively in Figure B-3 and Figure B-4. It can be seen that the simple model of the surface interaction could reproduce the suppression of the partial current densities of both reactions rather satisfactorily; the inhibited partial current densities of hydrogen evolution at high potentials were achieved, although under-predicted, and the decreased partial current densities of CO₂ reduction at very low potentials could also be simulated.

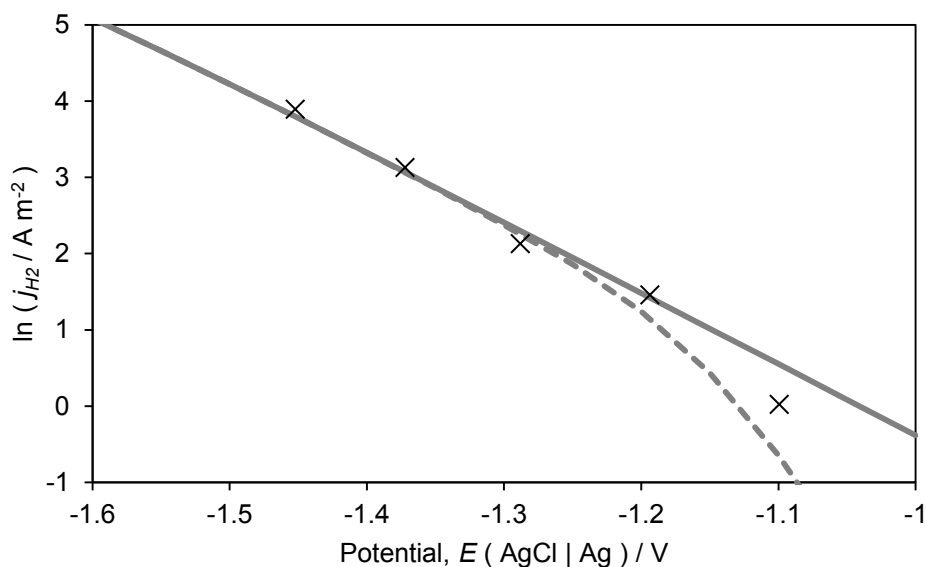


Figure B-3: Predicted effect of electrode potential on logarithmic partial current densities of hydrogen evolution at planar tin electrode in buffer solutions of pH 5.9; crosses: experimental, solid line: absence of surface interactions, dashed line: presence of surface interactions

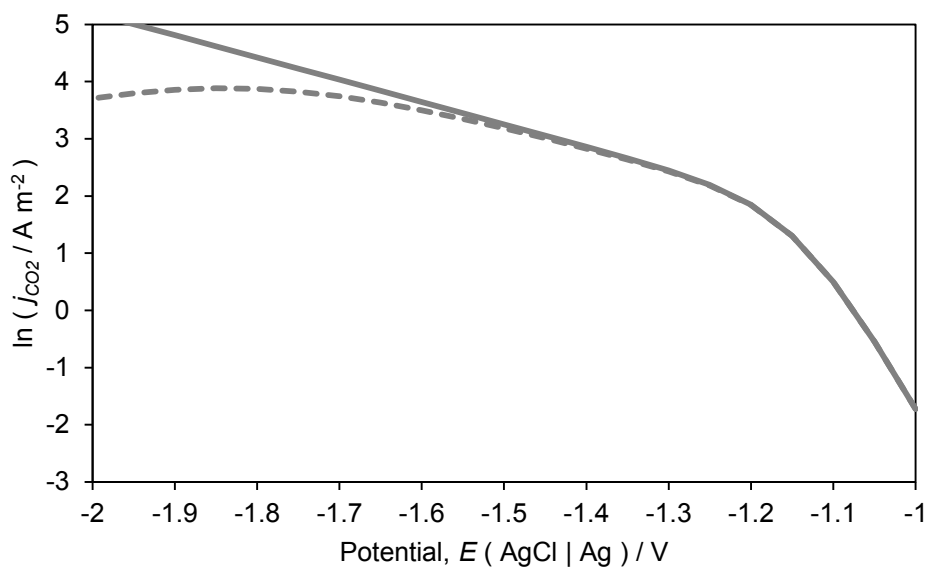


Figure B-4: Predicted effect of electrode potential on logarithmic partial current densities of CO₂ reduction at tin in buffer solutions of pH 5.9; solid line: absence of surface interactions, dashed line: presence of surface interactions

However, the latter possibility that the decreases in the partial current densities of CO₂ reduction at low potentials were caused by adhering bubbles has yet to be ruled out. The effects of bubbles were complicated and so not included here. The analysis of the interactions between the adsorbed species was merely a suggestion and therefore should not be considered as conclusive.

Appendix C Study of interaction between adsorbed intermediates through electrochemical impedance spectroscopy

Some EIS experiments were also conducted in the presence of CO₂ with intending to confirm that hydrogen evolution and CO₂ reduction share the same surface sites. If this is the case, a mathematical description of the impedance spectra of such system suggests some unique features in the spectra. The derivation of the equations was based on the simultaneous reactions introduced in section 6.4.2. The procedure was similar to that presented in the Appendix A but significantly longer. Eventually, these expressions resulted:

$$\frac{1}{Z_F} \approx -F \left\{ \begin{aligned} & a_{H^+} k_V \left(-\frac{\partial \theta_{H^+}}{\partial E} - \frac{\partial \theta_{CO_2^-}}{\partial E} \right) + a_{H^+} k_V \left(1 - \bar{\theta}_{H^+} - \bar{\theta}_{CO_2^-} \right) \left(\frac{-\alpha_V F}{RT} \right) \\ & + a_{H^+} k_H \frac{\partial \theta_{H^+}}{\partial E} + a_{H^+} k_H \bar{\theta}_{H^+} \left(\frac{-\alpha_H F}{RT} \right) \\ & + a_{CO_2} k_1 \left(-\frac{\partial \theta_{H^+}}{\partial E} - \frac{\partial \theta_{CO_2^-}}{\partial E} \right) + a_{CO_2} k_1 \left(1 - \bar{\theta}_{H^+} - \bar{\theta}_{CO_2^-} \right) \left(\frac{-\alpha_1 F}{RT} \right) \\ & + a_{H^+} k_6 \frac{\partial \theta_{CO_2^-}}{\partial E} + a_{H^+} k_6 \bar{\theta}_{CO_2^-} \left(\frac{-\alpha_2 F}{RT} \right) \end{aligned} \right\} \quad \text{EC-1,}$$

$$\bar{\theta}_{H^+} = \frac{k_V k_6 a_{H^+}}{k_H k_1 a_{CO_2} + k_V k_6 a_{H^+} + k_H k_6 a_{H^+}} \quad \text{EC-2,}$$

$$\bar{\theta}_{CO_2^-} = \frac{k_H k_1 a_{CO_2}}{k_V k_6 a_{H^+} + k_H k_1 a_{CO_2} + k_H k_6 a_{H^+}} \quad \text{EC-3,}$$

$$\frac{\partial \theta_{H^+}}{\partial E} = \left\{ \begin{aligned} & -a_{H^+}k_V \frac{\left[a_{CO_2}k_1 \left(1 - \bar{\theta}_{H^+} - \bar{\theta}_{CO_2^-} \right) \left(\frac{-\alpha_1 F}{RT} \right) - a_{H^+}k_6 \bar{\theta}_{CO_2^-} \left(\frac{-\alpha_2 F}{RT} \right) \right]}{a_{CO_2}k_1 + a_{H^+}k_6 + i\omega\Gamma} \\ & + a_{H^+}k_V \left(1 - \bar{\theta}_{H^+} - \bar{\theta}_{CO_2^-} \right) \left(\frac{-\alpha_1 F}{RT} \right) - a_{H^+}k_H \bar{\theta}_{H^+} \left(\frac{-\alpha_H F}{RT} \right) \end{aligned} \right\} \quad \text{EC-4,}$$

$$\times \frac{(a_{CO_2}k_1 + a_{H^+}k_6 + i\omega\Gamma)}{\{(a_{H^+}k_V + a_{H^+}k_H + i\omega\Gamma)(a_{CO_2}k_1 + a_{H^+}k_6 + i\omega\Gamma) - a_{H^+}a_{CO_2}k_Vk_1\}}$$

$$\frac{\partial \theta_{CO_2^-}}{\partial E} = \left\{ \begin{aligned} & -a_{CO_2}k_1 \frac{\left[a_{H^+}k_V \left(1 - \bar{\theta}_{H^+} - \bar{\theta}_{CO_2^-} \right) \left(\frac{-\alpha_V F}{RT} \right) - a_{H^+}k_H \bar{\theta}_{H^+} \left(\frac{-\alpha_H F}{RT} \right) \right]}{a_{H^+}k_V + a_{H^+}k_H + i\omega\Gamma} \\ & + a_{CO_2}k_1 \left(1 - \bar{\theta}_{H^+} - \bar{\theta}_{CO_2^-} \right) \left(\frac{-\alpha_1 F}{RT} \right) - a_{H^+}k_6 \bar{\theta}_{CO_2^-} \left(\frac{-\alpha_2 F}{RT} \right) \end{aligned} \right\} \quad \text{EC-5.}$$

$$\times \frac{(a_{H^+}k_V + a_{H^+}k_H + i\omega\Gamma)}{\{(a_{H^+}k_V + a_{H^+}k_H + i\omega\Gamma)(a_{CO_2}k_1 + a_{H^+}k_6 + i\omega\Gamma) - a_{H^+}a_{CO_2}k_Vk_1\}}$$

Figure C-1 shows a spectrum for a tin disc electrode rotating at 2200 rpm in 0.5 M NaOH saturated with CO₂, together with a simulated curve calculated with the simplified model of the simultaneous reactions introduced in section 6.4.2 at pH 5.9. The kinetic parameters of hydrogen evolution were assumed to be the same as those used in the previous appendix. The experimental spectrum exhibited both a capacitive and an inductive component probably resulting from the simultaneous reactions of hydrogen evolution and CO₂ reduction. The simulated spectrum also showed similar features although the size was clearly smaller due to the larger current density expected from the lower pH. Nevertheless, the mathematical model of the impedance spectrum being able to reproduce the observed characteristics suggested that hydrogen evolution and CO₂ reduction shared the same surface sites.

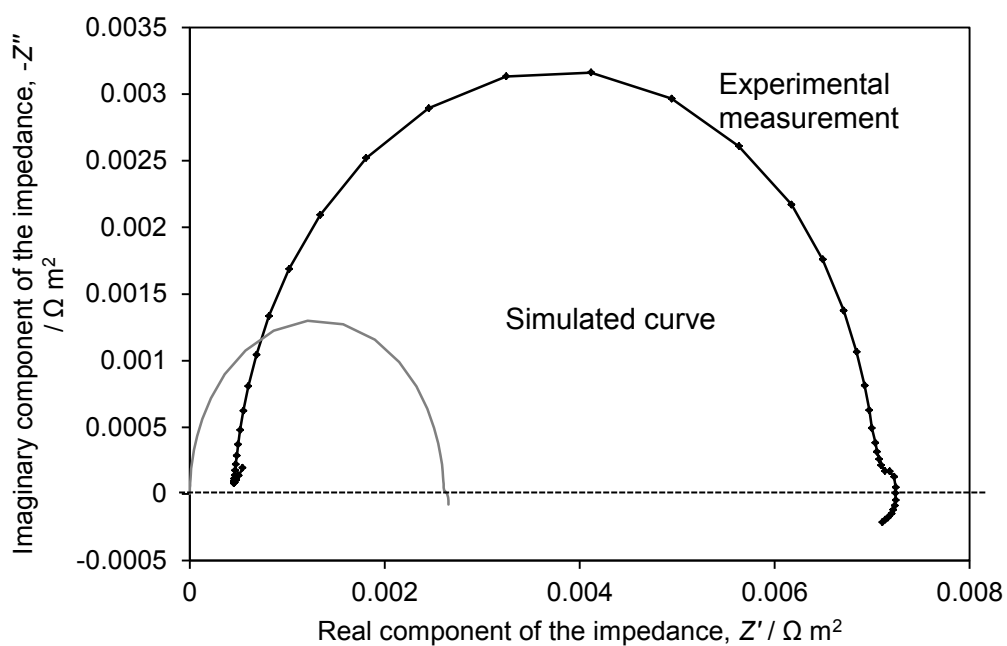


Figure C-1: Electrochemical impedance spectrum at -1.4 V (SCE) from tin disc electrode rotating at 2200 rpm in aqueous solution of 0.5 M NaOH saturated with CO_2 (pH 7.8) and curve simulated at -1.5 V (AgCl|Ag) and pH 5.9 with $\Gamma = 0.15 \text{ mol m}^{-2}$ and $C_{dl} = 0.43 \text{ F}$

Appendix D Electrochemical reduction of CO₂ at gas-diffusion electrodes

The scale-up of an electrochemical reactor for CO₂ reduction had also been studied with gas-diffusion electrodes. The development involved a number of electrode configurations. Preliminary experiments were conducted on cathodes made of metal meshes pressed against ionic membranes. The concept was considered feasible following detectable formate formation. Finely structured GDEs were fabricated afterwards through spraying of catalyst suspensions on ionic membranes. However, this method did not offer good control over the thicknesses of the catalyst layers. The GDEs were eventually fabricated with doctor-blading. The integrity of the MEAs was enhanced by hot pressing.

D.1 Experimental details

D.1.1 Fabrication of GDEs

The catalyst suspensions for the doctor-blading consisted of 0.73 g of Sn powders, 0.3 g of solubilised ionic membrane and 0.018 g of NH₄HCO₃, the amounts of which were tuned following several experiments. Anionic membranes were used according to the reasons described in the literature survey and therefore Fumatech FAA-3 was chosen. The membrane solution, Fumion FAA-3 was also obtained from the same supplier. NH₄HCO₃ was added as a pore former (Zhao et al., 2007). The catalyst suspension was applied on a piece of 30×30 mm² carbon cloth by doctor-blading. The resulting catalyst-coated cloth was dried at room temperatures for 15 minutes and then in an oven at 130 °C overnight. The dried assembly was fused with a piece of 30×30 cm² Fumatech FAA-3 by hot-pressing at 120 °C and 43.6 M Pa for 5 minutes.

D.1.2 Electrolyses

A freshly prepared MEA was assembled in a 2-compartment glass cell. The anolyte was 40 ml of 0.5 M NaOH, in which an SCE was placed as a reference electrode. The MEA was pre-treated by electrolysis at -2.0 V (SCE) for 30 minutes with N₂ flowing across the surface of the MEA in the liquid-less cathode compartment. The gas was changed to CO₂ afterwards and electrolysis was performed at different

electrode potentials for 3 hours. The anolyte was sampled and analysed with an HPLC for the concentration of formate.

D.2 Results and discussion

Figure D-1 shows photomicrographs of cross sections of an MEA. Three distinct layers of the carbon cloth, the catalyst layer and the anionic membrane are presented. Three-phase boundaries can also be seen in the close-up micrograph. The general structure appeared to be rather coarse. The quality of the electrical contacts was a concern as poor contacts amongst tin particles could cause large ohmic potential losses within the electronically-conducting phase as an electrical current travelled from the carbon cloth to the interfaces between the membrane and the tin particles. Similarly, poor connections between the solidified solubilised membrane and the actual membrane layer could lead to significant potential drops within the ionically-conducting phase.

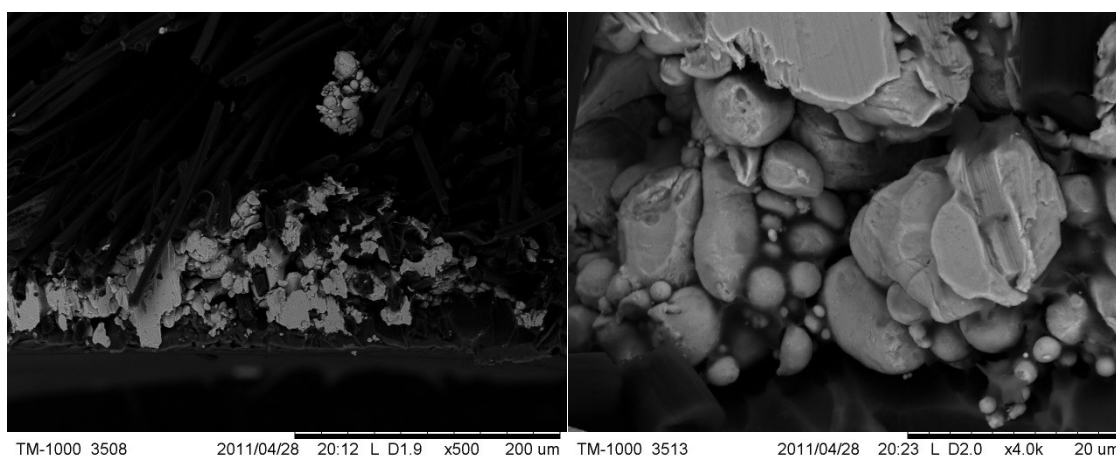


Figure D-1: Cross-sectional views of MEA

The electrolyses were performed at -1.5, -2.0, and -2.5 V (SCE) and the results are presented in Figure D-2. It can be seen that both the total current densities and the charge yields of formate increased as electrode potential was decreased. However, the performances did not seem to be significantly enhanced, as the current densities were comparable to what can be obtained from planar electrodes. Furthermore, the charge yields failed to reach 0.5 despite the unusually low electrode potentials. This was thought to be caused by the described significant potential drops within both the electronically-conducting and the ionically-conducting phases of the MEAs. As the structure of the MEAs seemed to be complicated and difficult to control, this project was eventually discontinued.

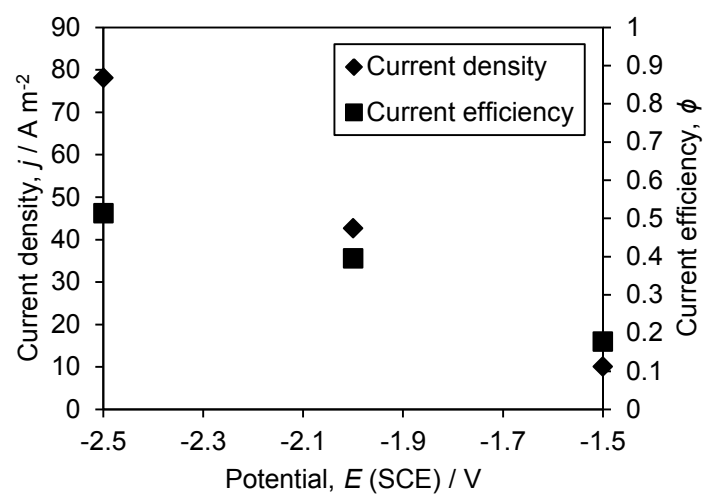


Figure D-2: Effect of electrode potential on total current densities and current efficiencies of CO_2 reduction at GDEs

Appendix E Raw measurement data

E.1 Calibration curves for HPLC and GC analyses

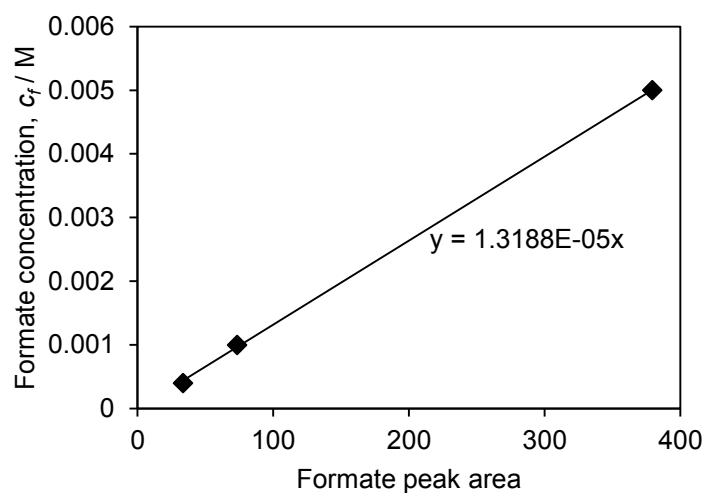


Figure E-1: Relationship between formate peak areas and formate concentrations

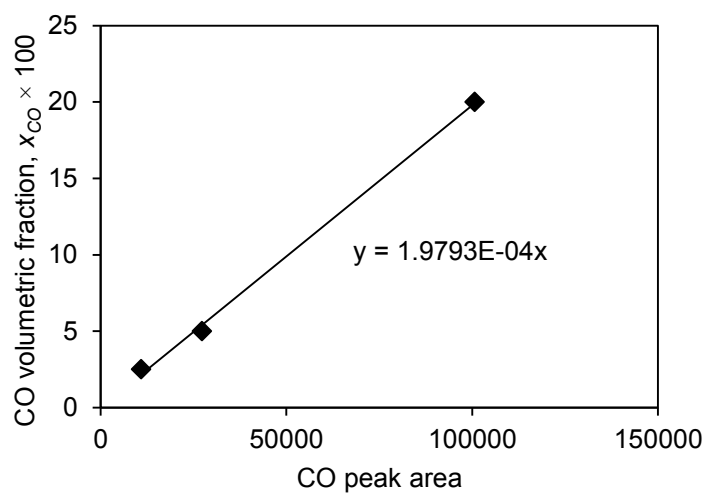


Figure E-2: Relationship between CO peak areas and CO volumetric fractions

E.2 Experiments with planar electrode

E.2.1 Electropolishing of tin electrode

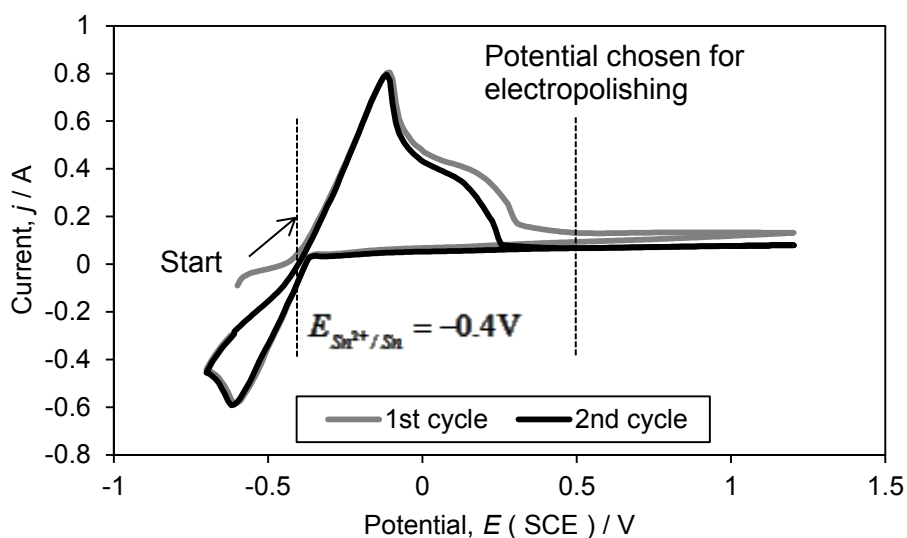


Figure E-3: Two consecutive voltammograms of planar tin electrode in 70% HClO_4 with 0.1 V s^{-1} scan rate

E.2.2 Determination of solution resistances between Luggin probe and working electrode

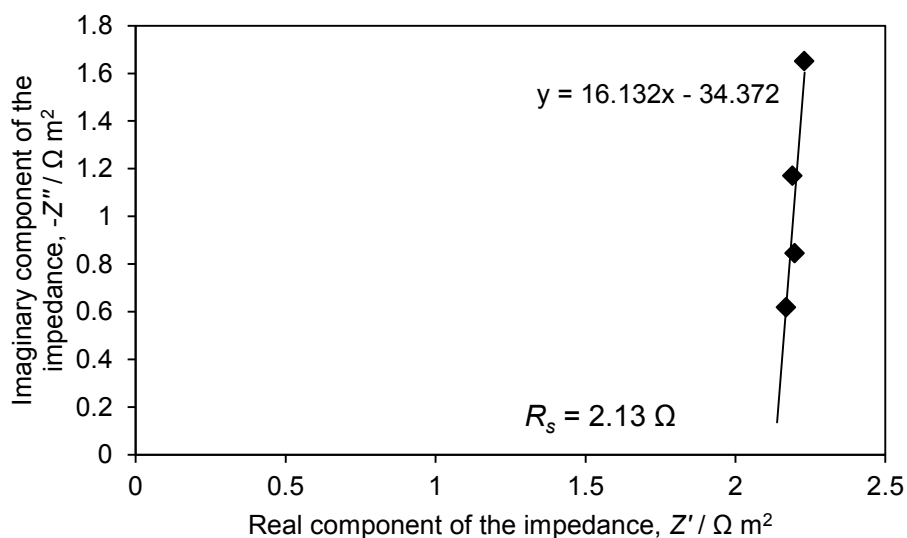


Figure E-4: Electrochemical impedance spectrum of planar tin electrode at -0.9 V ($\text{AgCl}|\text{Ag}$) in aqueous solution containing $0.1 \text{ M H}_3\text{PO}_4/1 \text{ M NaH}_2\text{PO}_4$ ($\text{pH } 2.9$), showing values measured at $6\,000$, $4\,160$, $2\,884$ and $2\,000 \text{ Hz}$ from bottom to top

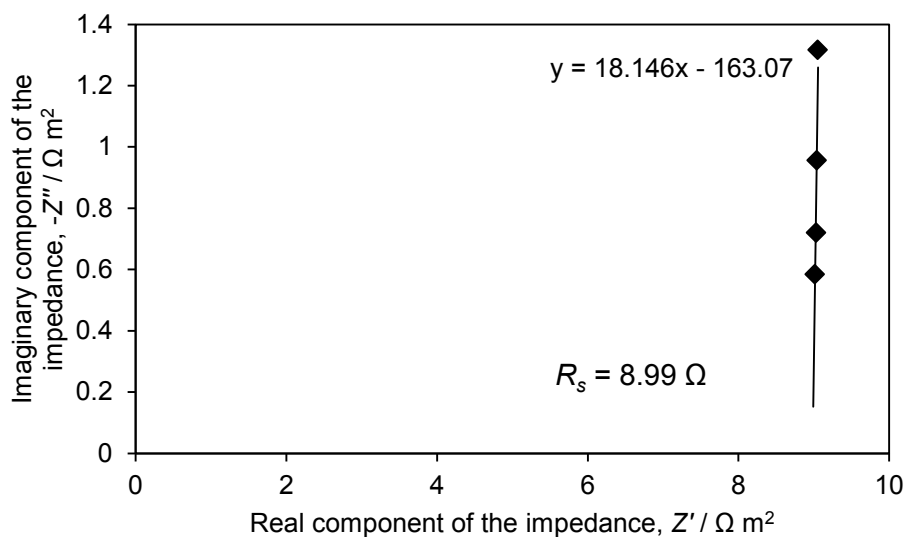


Figure E-5: Electrochemical impedance spectrum of planar tin electrode at -0.9 V (AgCl|Ag) in aqueous solution containing 0.02 M H_3PO_4 /0.2 M NaH_2PO_4 (pH 2.9), showing values measured at 6 000, 4 160, 2 884 and 2 000 Hz from bottom to top

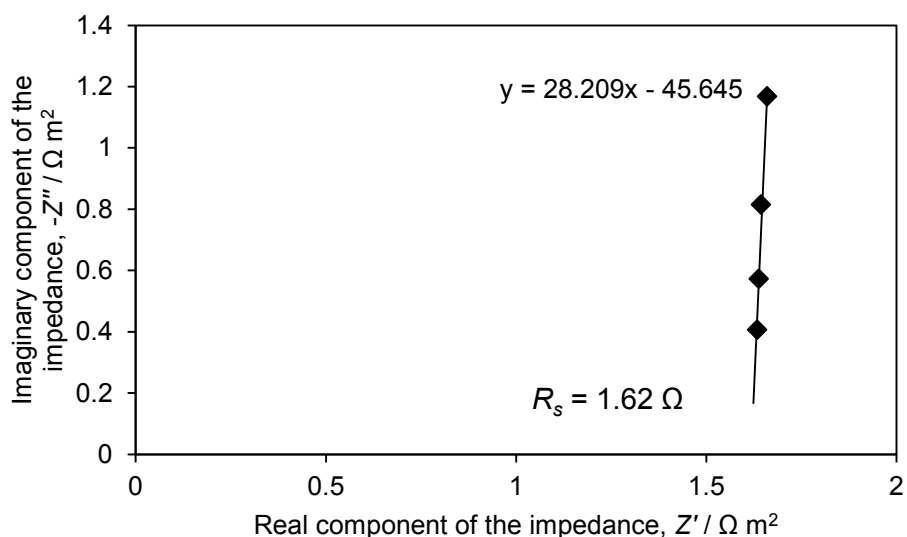


Figure E-6: Electrochemical impedance spectrum of planar tin electrode at -1.0 V (AgCl|Ag) in aqueous solution containing 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 5.9), showing values measured at 6 000, 4 160, 2 884 and 2 000 Hz from bottom to top

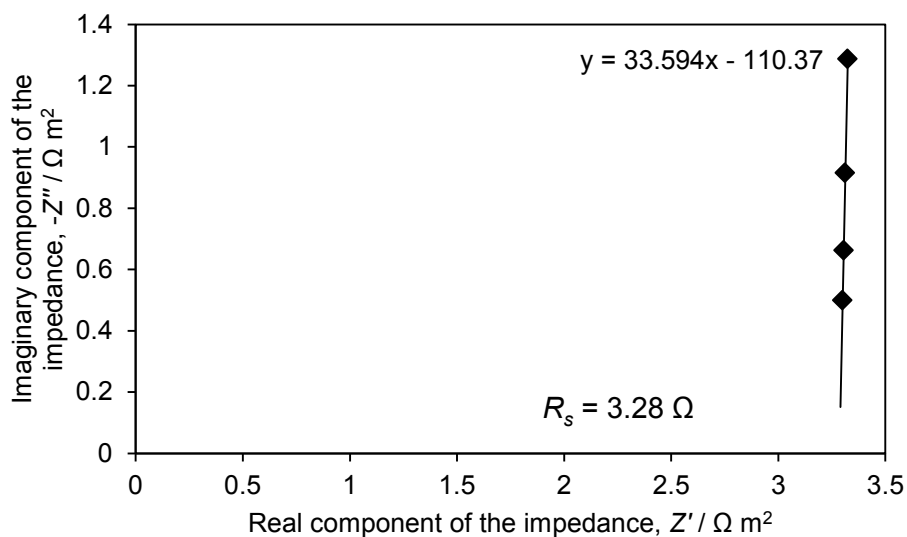


Figure E-7: Electrochemical impedance spectrum of planar tin electrode at -1.1 V (AgCl|Ag) in aqueous solution containing 0.5 M NaOH saturated with 1 atm CO₂ (pH 7.8), showing values measured at 6 000, 4 160, 2 884 and 2 000 Hz from bottom to top

E.2.3 Electrolyses with planar electrode

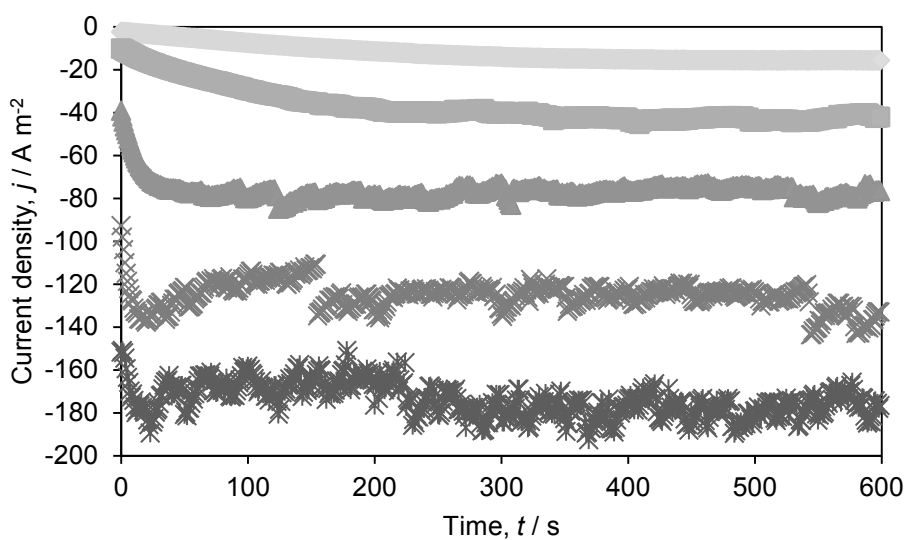


Figure E-8: Time dependence of total current densities during electrolyses of 0.1 M H₃PO₄/1 M NaH₂PO₄ (pH 2.9) at, from top to bottom, -1.1, -1.2, -1.3, -1.4 and -1.5 V (uncorrected)

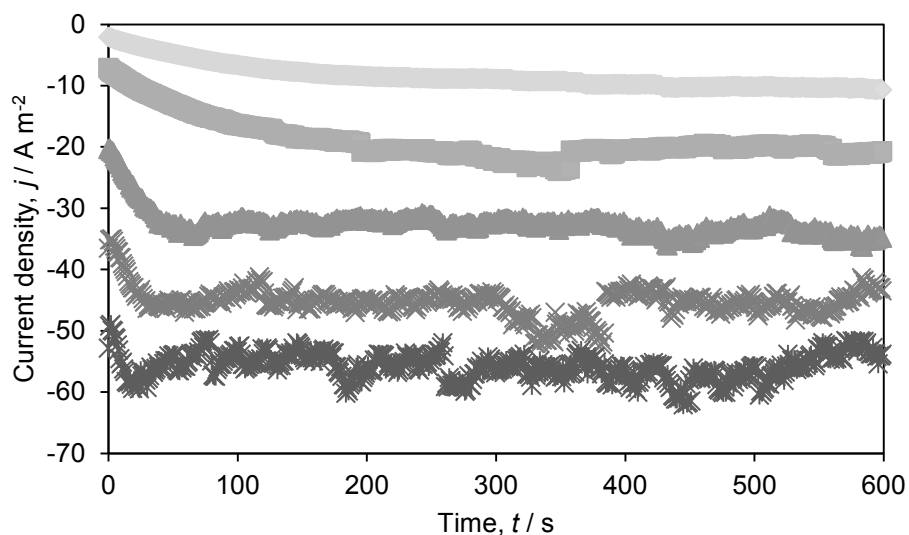


Figure E-9: Time dependence of total current densities during electrolyses of 0.02 M H_3PO_4 /0.2 M NaH_2PO_4 (pH 2.9) at, from top to bottom, -1.1, -1.2, -1.3, -1.4 and -1.5 V (uncorrected)

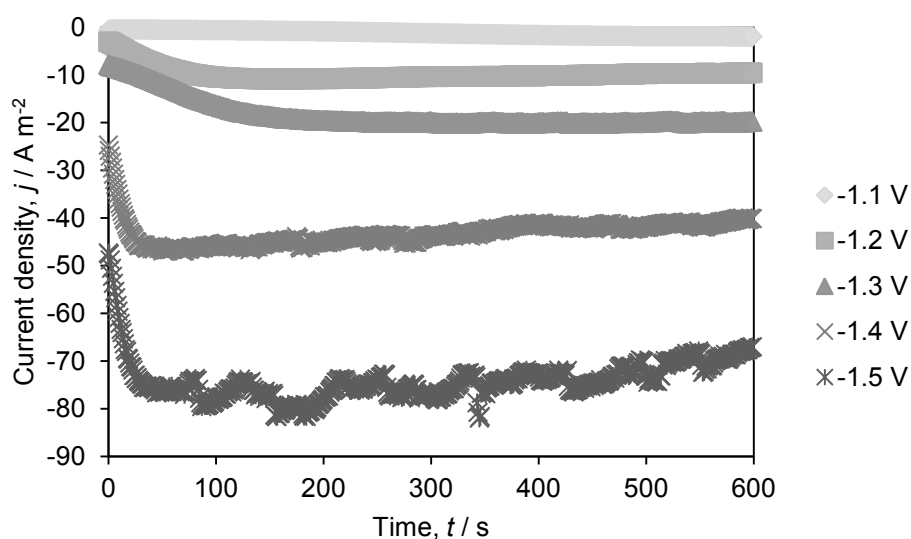


Figure E-10: Time dependence of total current densities during electrolyses of 1 M NaH_2PO_4 /0.4 M Na_2HPO_4 (pH 5.9) at, from top to bottom, -1.1, -1.2, -1.3, -1.4 and -1.5 V (uncorrected)

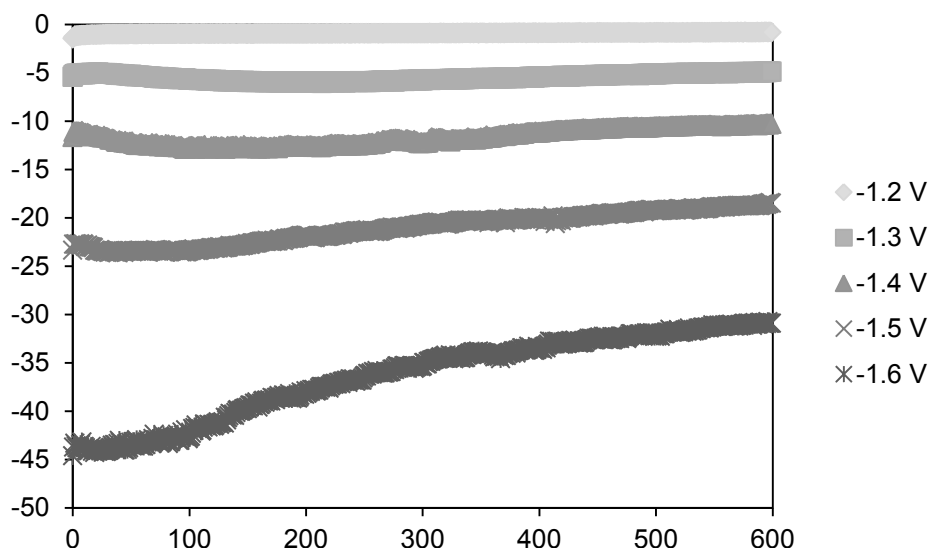


Figure E-11: Time dependence of total current densities during electrolyses of 0.5 M NaOH saturated with 1 atm CO₂ (pH 7.8) at, from top to bottom, -1.2, -1.3, -1.4, -1.5 and -1.6 V (uncorrected)

E.3 Experiments with 3D electrodes

E.3.1 Determination of solution resistance between Luggin probe and working electrode

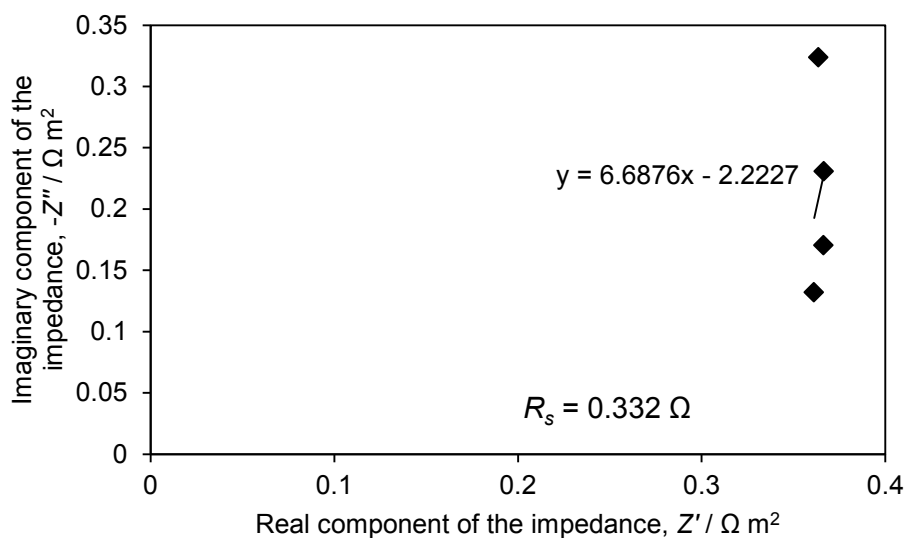


Figure E-12: Electrochemical impedance spectrum of copper mesh electrode at -1.1 V (AgCl|Ag) in aqueous solution containing 0.5 M NaOH saturated with 1 atm CO₂ (pH 7.8), showing values measured at 6 000, 4 160, 2 884 and 2 000 Hz from bottom to top

E.3.2 Electrolyses with 3D electrodes

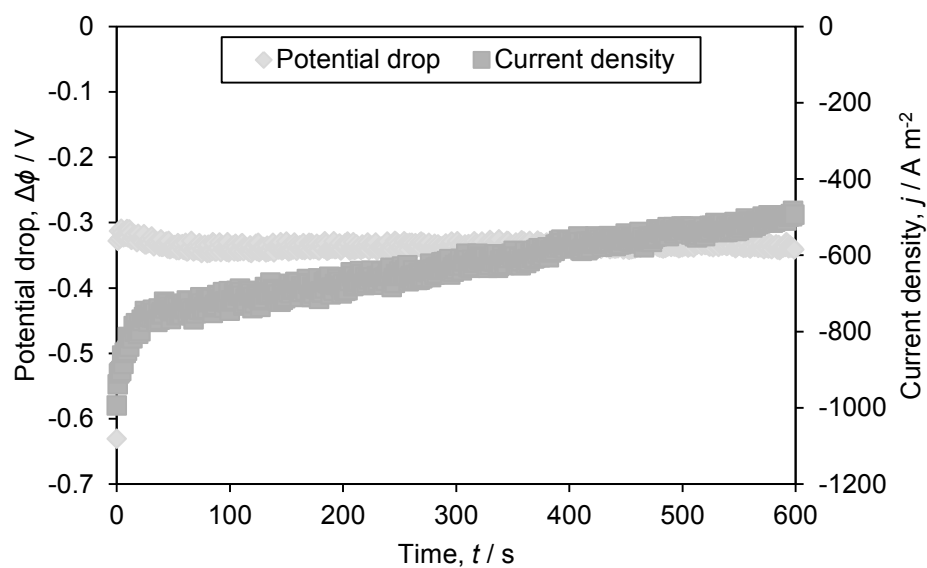


Figure E-13: Time dependence of total superficial current densities and potential drops during electrolyses of 0.5 M NaOH saturated with 1 atm CO₂ at -1.6 V (uncorrected) and 33 ml min⁻¹ with 3D electrode

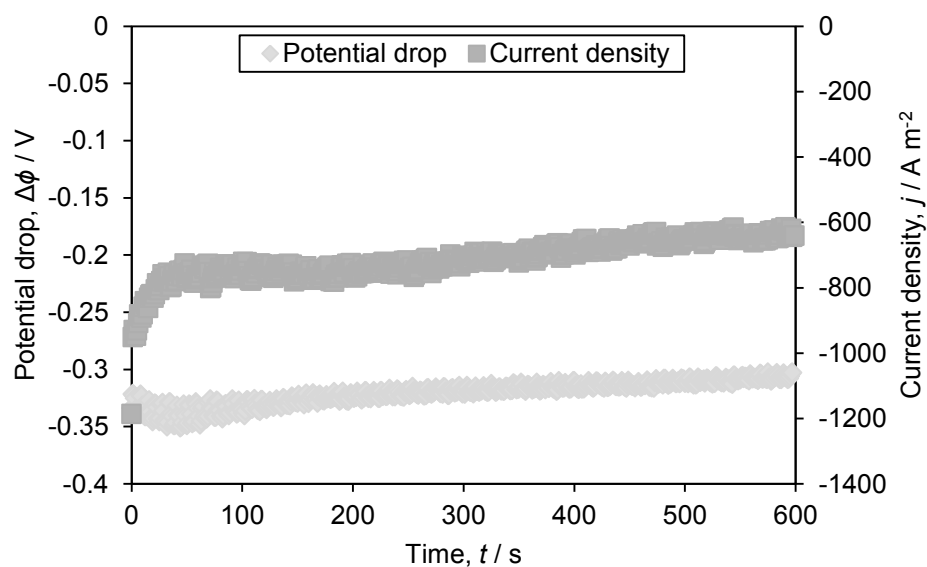


Figure E-14: Time dependence of total superficial current densities and potential drops during electrolyses of 0.5 M NaOH saturated with 1 atm CO₂ at -1.6 V (uncorrected) and 66 ml min⁻¹ with 3D electrode

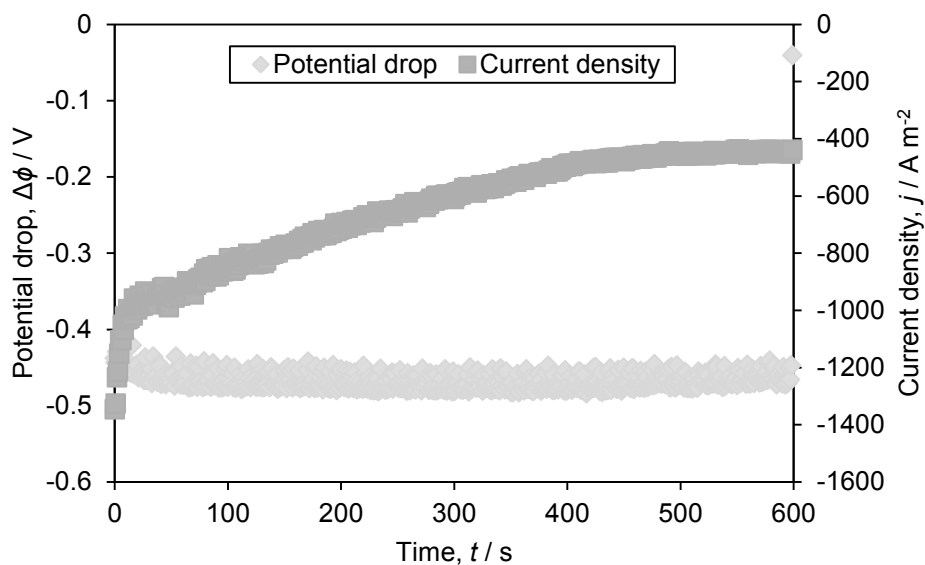


Figure E-15: Time dependence of total superficial current densities and potential drops during electrolyses of 0.5 M NaOH saturated with 1 atm CO₂ at -1.75 V (uncorrected) and 33 ml min⁻¹ with 3D electrode

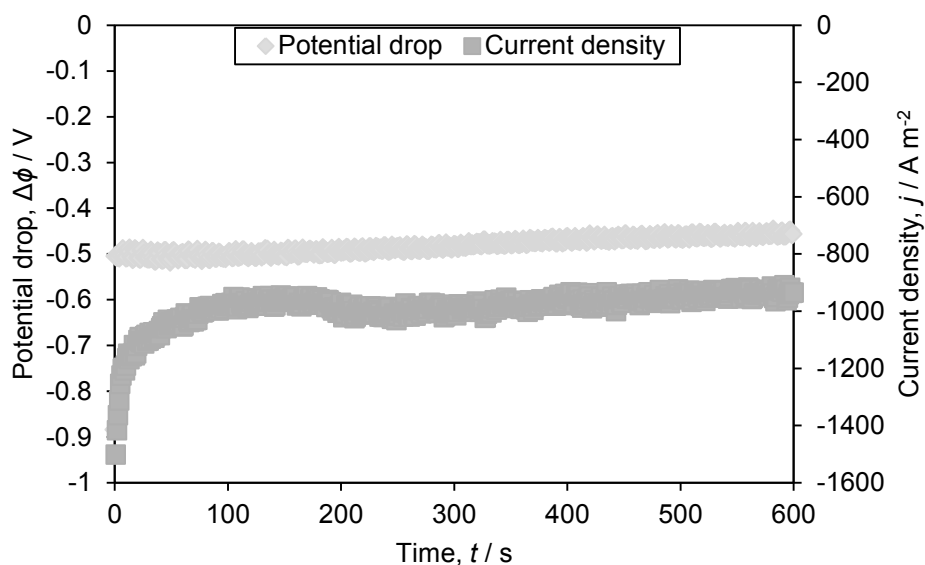


Figure E-16: Time dependence of total superficial current densities and potential drops during electrolyses of 0.5 M NaOH saturated with 1 atm CO₂ at -1.75 V (uncorrected) and 66 ml min⁻¹ with 3D electrode

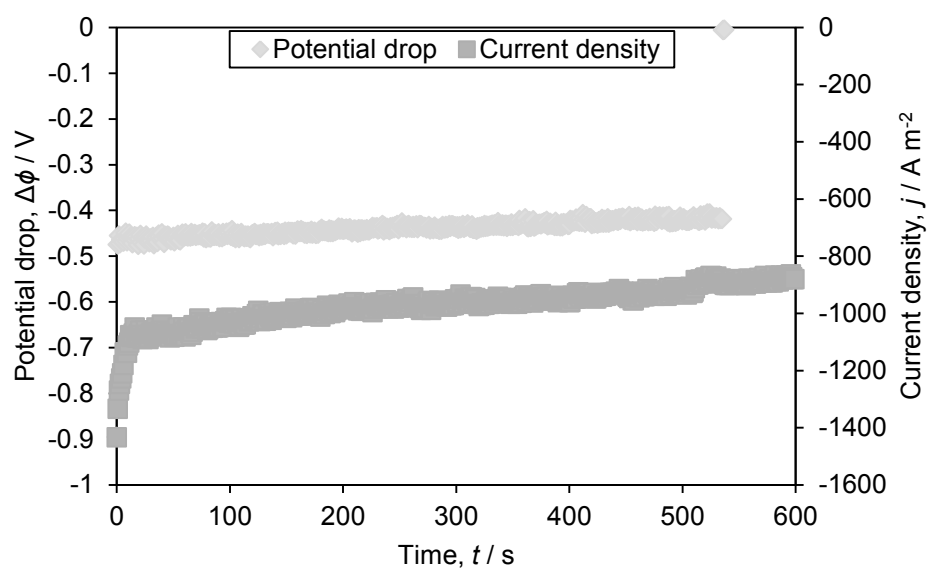


Figure E-17: Time dependence of total superficial current densities and potential drops during electrolyses of 0.5 M NaOH saturated with 1 atm CO₂ at -1.75 V (uncorrected) and 132 ml min⁻¹ with 3D electrode