Studying the Oxygen reduction and Hydrogen oxidation reactions under realistic fuel cell conditions

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Abstract

A new approach to test fuel cell catalysts under conditions of high mass transport and variable temperature is described. This approach relies upon utilising a 5 μm thick gold grid to act as a catalyst support in contact with a perfluorsulfonicacid (PFSA) membrane in a true three electrode electrochemical configuration. The gold grid has 20 μm ×20 μm sized holes in it which allow the reactant gas to reach the catalyst layer. The high electrical conductivity and low profile of the grid ensure that electrical and mass transport losses are minimal. We have used this configuration to look at the oxygen reduction reaction (*orr*) and the hydrogen oxidation reaction (*hor*) on a platinum-black and platinum on carbon catalyst at a loading of about 10 $\mu\text{g cm}^{-2}$. We find that for the *orr* we can measure kinetic currents over the entire range of relevant fuel cell operating potentials (0.55-1 V). Although platinum-black shows higher specific catalytic activity towards the *orr* than platinum on carbon at high potentials, this performance benefit is reduced at lower potentials. For the *hor* we measure exchange current densities of 0.022 A cm^{-2} and 0.026 A cm^{-2} respectively on the Pt-Black and Pt/C. These values indicate that there does not appear to be a size effect for the *hor*, unlike the *orr*.

Keywords

Oxygen reduction reaction; Hydrogen oxidation; Fuel Cell; Solid-state cell; platinum

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1. Introduction

The electrochemistry of the oxygen reduction reaction (*orr*) and hydrogen oxidation reaction (*hor*) on fuel cell electrocatalysts is usually studied in liquid electrolytes such as sulphuric or perchloric acid under defined mass-transport condition utilising the rotating disk electrode (*rde*) technique. However, the presence of adsorbing anions in liquid electrolytes results in competitive adsorption on the metal catalyst surface¹. In perfluorsulfonic acid (PFSA) electrolytes where anions are not freely mobile, electrode kinetics may differ greatly². It is therefore important to study catalysis at the PFSA interface. Another issue is the relatively low mass transport coefficients achievable at the *rde*. Mass transport limited currents have an upper limit of about 14 mA cm^{-2} for the *orr* and about half that for the *hor* based on a maximum rotation rate of $\sim 10\text{k rpm}$. True limiting currents in well designed fuel cell electrodes may be *at least* 3 orders of magnitude higher when operating on undiluted H_2 or O_2 . A third aspect deals with the presence of water. In aqueous electrolytes, water activity remains more or less constant in a wide range of solution. In contrast, water activity in PSFA electrolytes may vary between 2-20 water molecules/proton due to the combined effect of water evaporation and condensation and water transport through electroosmosis and pressure driven flow³. Finally, there is the increased desire to push fuel cells to operate at higher temperature under which conditions it is not possible to easily perform aqueous electrochemistry.

Attempts have been made to study electrocatalysts directly in fuel cells. It is necessary to pass hydrogen over one of the electrodes (the combined counter/reference electrode) and the reactant of interest over the other test working electrode. Diffusion of hydrogen from the counter electrode to the working electrode will affect the currents measured, especially under low current conditions (hydrogen diffusion across the membrane provides a current of $\sim \text{mA.cm}^{-2}$). Finally there are problems with maintaining uniform reactant, product and water distribution across the electrode.

One of us has previously studied electrochemical reactions such as methanol and hydrogen oxidation⁴ and oxygen reduction^{5,6} at the microdisk electrode/polymer electrolyte interface. But this

approach required that the reactants diffuse through the PFSA electrolyte, leading to limiting currents equivalent to that obtainable with an *rde*.

The goal of this paper is to develop a new approach to test electrocatalysts under realistic fuel cell-like conditions with high mass transport where the temperature and water content can be varied. This is achieved by sandwiching the electrocatalyst between a PFSA membrane and an ultra-fine highly conductive gold grid which gives the reactant gas free access to the catalyst.

2. Experimental

2.1 Chemicals

Nitrogen, oxygen and hydrogen were research grade (99.9999%). High surface area platinum black (**PtB**, HiSPECTM1000, 97%, Johnson Matthey, 27 m²g_{Pt}⁻¹) and platinum on carbon (**Pt/C**, 20 wt%, HiSPECTM3000, Johnson Matthey, 90 m²g_{Pt}⁻¹)⁷ were used as catalysts. Nafion 117 membrane was pretreated by boiling in sulfuric acid (1M) for one hour followed by washing in water.

2.2 Preparation of the electrodes

The PtB or Pt/C catalyst were mixed with water (18 MΩ cm resistivity, Millipore Milli-Q), ethanol, and Nafion solution (20 wt% Aldrich). Then the catalyst was dispersed by ultrasound for 30 minutes. A gold grid (1500 mesh, ϕ 3.05mm, 5µm thickness, Agar Scientific) was used as a gas diffusion layer and current collector. 0.1 µl of the catalyst containing solution was dropped onto the gold mesh and dried in an oven for 2 hours at 100°C leading to a loading of ~10 µg.cm⁻² of geometric area.

2.3 Electrochemical cell

The electrochemical cell is displayed in Figure 1 and is composed of a glass tube, needle, membrane, and platinum plate for counter electrode^{2, 4}. A reversible hydrogen electrode (RHE) composed of a capillary glass tube containing a platinum wire, a bubble of hydrogen gas and 1 mol dm⁻³ H₂SO₄ was placed in contact with the membrane <5 mm laterally offset from the working

electrode. Measurement of the uncompensated resistance by electrochemically impedance spectroscopy both under load and in the absence of load confirmed that the reference electrode potential was not being disturbed by the secondary current distribution. Furthermore, results did not vary with placement of the reference electrode. The glass tube ($\varnothing$ 3 mm o.d., 1 mm i.d.) was used to support the gold grid and provide the reactant flow channel. A hypodermic needle placed concentrically within the tube allows gas flow towards the electrode, and the gas was then discharged out of the free end of the glass tube. The outside of the glass tube was gold plated to provide electrical contact to the gold mesh. The mesh with catalyst was pressed onto the membrane for 10 minutes at 50 °C. Then the glass tube was pressed against the gold mesh and configured as shown in figure 1. Nitrogen, oxygen, and hydrogen were prehumidified by passing them through temperature controlled bubblers operating at the same temperature as the experiment. A flow rate of 5 ml min⁻¹ was used. Measurements were performed using an Autolab potentiostat (Ecochemie, Netherlands).

3. Results and Discussion

Figure 2 shows a voltammogram in the test cell of a gold grid with 0.1 μg **PtB** (12.7 $\mu\text{g}\cdot\text{cm}^{-2}$ loading) deposited on it. Even with such a low loading of platinum, we can clearly distinguish the features of platinum electrochemistry. A slight distortion or ‘slope’ of the voltammogram is due to residual oxygen ($\sim 10\text{ppm}$) in the system which is very difficult to remove. For comparison, we also display on the same plot (but different axes) voltammograms of the gold grid without any catalyst under N₂ and under O₂. It can be seen that under nitrogen there is only a very small background current. Under oxygen reduction is seen at potentials less than 0.3 V. This current is at least 10000 times smaller than the current for oxygen reduction on our platinum catalyst at this potential.

Figure 3 shows oxygen reduction curves for both **PtB** and **Pt/C** electrodes utilising a scan rate of 5 mV s⁻¹. Both forward and reverse sweeps are shown, and there is little hysteresis. Specific current densities were calculated by dividing the experimental current by the electrochemical hydrogen

adsorption surface areas under nitrogen gas. Specific current densities reach about $-100 \text{ mA} \cdot \text{cm}^{-2}$ (i.e. a turnover frequency of about 120 s^{-1} , calculated by dividing the specific current density by the charge associated with the oxidation of one monolayer of oxygen – $4 \times 210 \text{ } \mu\text{C cm}^{-2}$) at 0.4V due to the fast transport of oxygen. Typical cathodes for air breathing fuel cells have roughness factors (i.e. the ratio of real to geometric area) of ~ 200 . Translating this performance to that of a real fuel cell electrode would imply an operating current density of 20 A cm^{-2} . We also display the limiting current achievable on a Pt *rde* for the *orr* reaction at 1600 rpm⁸. As the diffusion limited current for the *orr* on an *rde* is reached at a potential of $\sim 0.75 \text{ V}$ it is clear that using our new technique allows us to determine the electrocatalytic performance of catalysts at potentials more relevant to fuel cell operation. Displayed inset into this diagram is an expansion of the potential region in the range 0.85-1.0 V. We have assessed the “kinetic specific current density” at 0.90 V. For this new experimental method, the mass transport limited current density is very large –corresponding to specific current densities of ca. 1 A cm^{-2} based upon the limiting current for the *hor* (below). We find that there is no need to correct our data for mass transport limitations as this correction makes $<5\%$ difference to the currents at $E > 0.55 \text{ V}$. Hence the data displayed in figure 3 are effectively kinetic currents at $E > 0.55 \text{ V}$ – i.e. we have a measure of kinetic current over the important range of potentials over which fuel cells operate.

At a temperature of 50°C , we find values for the kinetic current of $80 \text{ } \mu\text{A cm}^{-2}$ for **Pt/C** and $830 \text{ } \mu\text{A} \cdot \text{cm}^{-2}$ for the **PtB** catalyst. These values are close to those reported by Gasteiger et al under similar conditions⁸. Although the kinetic current is greater for **PtB** than **Pt/C** catalyst at 0.90 V, at potentials less than 0.6 V the **Pt/C** catalyst “catches up”. Indeed, the 10-fold specific activity benefit which **PtB** has over **Pt/C** at 0.9 V decreases to a four-fold benefit at 0.75 V, a potential more relevant to fuel cell operation. This result almost certainly is associated with greater oxide coverage on **Pt/C** at 0.90 V.

In figure 4 we show the *hor* on both catalysts. Typically, measurements of the *hor* on an *rde* quickly reach mass transport limitations, and kinetic information is difficult to obtain. This has led

to a wide scatter in the values of the exchange current density (j_0) for the *hor* on platinum: many of the values are spuriously low⁹. For both catalysts we find limiting currents, with specific limiting current densities of 0.206 A cm⁻² for the **PtB** and 0.247 A cm⁻² for the **Pt/C** catalyst based on the mean values for the forward and reverse sweeps. The difference in limiting currents on the forward and reverse sweeps point to properties of the system being history dependent – most likely due to changes in water hydration near the catalyst. The slight difference in the limiting currents between the **PtB** and **Pt/C** curves is because of differences in loading and specific surface area of the catalysts on the gold grids. Inset into Figure 4 is an expansion of the micropolarisation region showing the forward and reverse scans. The **PtB** and **Pt/C** curves superimpose over each other, but have been offset horizontally by 5 mV so that they can be better compared. The currents measured in the micropolarisation region are a significant proportion of the limiting current, and so the linearised form of the Butler-Volmer equation needs to be modified to include a term associated with this limiting current⁹:

$$j = \frac{\frac{2F}{RT}\eta}{\frac{1}{j_{dl}} + \frac{1}{j_0}} \quad (1)$$

j is the specific current density and η the overpotential. The j_0 values measured are quite similar on the two catalysts, **PtB**: $j_0 = 0.022$ A cm⁻²; **Pt/C**: $j_0 = 0.026$ A cm⁻². These values are close to those values previously determined for the *hor* on small single platinum particles in sulfuric acid⁹.

The high performance of these catalysts towards the *hor* is shown by the fact that the electrodes are able to sustain a specific current density of around 20 mA cm⁻² with only a 10 mV overpotential – i.e. a turnover frequency of about 50 s⁻¹.

4. Conclusion

In this paper a new method to test fuel cells under relevant fuel cell conditions has been presented. The benefit of this approach is that it allows measurement of oxygen reduction and hydrogen oxidation under conditions of minimal mass transport losses, and so we can measure electrokinetics

of reactions at fuel cell relevant potentials rather than having to extrapolate performance from *rde* measurements made at potentials where mass transport effects are not too severe. Oxygen reduction measurements show 10-fold higher specific performance for **PtB** at 0.90 V compared to **Pt/C** as has been previously reported in the literature. However, this significant benefit of **PtB** is shown to rapidly decrease when the potential is shifted to lower, more fuel cell relevant potentials. At 0.75 V, the specific activity of **PtB** is only four times that of **Pt/C**. We see no difference in the activity of the two catalysts towards the *hor*. Exchange current densities of 0.022 A cm⁻² and 0.026 A cm⁻² are measured for the **PtB** and **Pt/C** respectively.

This approach should allow study of electrocatalysis under fuel cell relevant conditions for next-generation fuel cell systems – i.e. hot (T > 100°C) and dry conditions – environments that are not amenable to current aqueous electrolyte electrochemical measurements.

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1. Figures

Figure 1. Diagram of the experimental configuration for measuring the electrocatalytic activity of fuel cell electrocatalysts. The catalyst loaded gold grid is placed on a Nafion 117 membrane. A gold plated glass tube is placed in contact with the mesh. A needle within the glass tube allows pre-humidified gas to flow over the gold grid. A platinum foil counter electrode is placed on the other side of the Nafion membrane and a reversible hydrogen electrode is contacted with Nafion 117 membrane for use as a reference electrode.

Figure 2 Cyclic voltammogram of the gold mesh in contact with the Nafion 117 electrolyte under N_2 (—) and O_2 (.....) gas at a scan rate of 5 mV s^{-1} (left hand scale). Superimposed is the cyclic voltammogram of a mesh with $12.7 \mu\text{g cm}^{-2}$ of platinum black deposited on it in contact with a Nafion 117 membrane under N_2 gas (- - -) at a scan rate of 0.5 V s^{-1} (right hand scale).

Figure 3 Oxygen reduction at composite electrodes composed of Pt-Black (—) or Pt/Carbon (- -) dispersed on an Au grid in contact with Nafion 117 membrane at a temperature of 50°C, 5 mV s⁻¹ scan rate. Currents are presented as specific current densities (i.e. ratioed to the electrochemical surface area of the catalyst). Also displayed is the background current density of an Au grid in contact with the Nafion membrane, and the limiting oxygen reduction current on an rde electrode at 1600rpm (....). Inset is an expansion of the plot over the potential range 0.85-1.0V.

Figure 4 Hydrogen oxidation reaction at composite electrodes composed of Pt-Black (—) or Pt/Carbon (- - -) dispersed on an Au grid in contact with Nafion 117 membrane at a temperature of 50°C, 5 mV s⁻¹ scan rate. Currents are presented as specific current densities (i.e. ratioed to the electrochemical surface area of the catalyst). Inset diagram shows the micropolarisation region with the results for Pt/C and Pt-Black offset horizontally by 5 mV from each other to enhance visibility.