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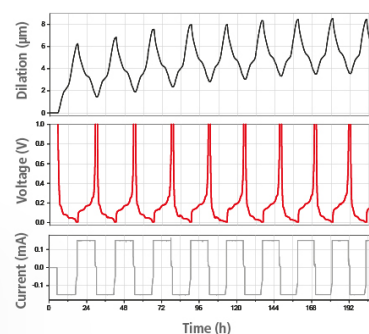
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How to Minimise Hydrogen Evolution on Carbon Based Materials?

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In many electrochemical systems, such as carbon dioxide reduction, batteries and supercapacitors, hydrogen evolution reaction is an undesired competing reaction. Herein, we investigate the factors controlling the hydrogen evolution reaction (HER) on seven different commercial carbon materials commonly found in many of these systems. The electrochemical HER response was determined by rotating disk electrode potential hold measurements in acidic media, and correlated with the physical characteristics of the carbon materials determined nitrogen adsorption/desorption, as well as previous experiments on the same materials. An on-chip electrochemical mass spectrometer was used to probe the gaseous products produced at the electrode in situ, which allowed HER to be distinguished from other competing reaction and the onset of the reaction was established to be -0.38 V vs RHE. The results indicate that carbons with low amount of metal impurities have the lowest H_2 evolution rates.

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There is an urgent need for systematic change in the global chemical industry due to the rise in damaging carbon dioxide emissions.¹ Electrosynthesis utilising renewable sources has garnered interest in recent years as there are many carbon neutral electrochemical processes capable of producing essential chemical, fuels and energy.^{2–6} One example is the electrochemical production of hydrogen which has been researched expansively as it is an energy dense fuel.^{7,8} This interest has driven research into the development of efficiency HER electrocatalysts. However, the hydrogen evolution reaction (HER) is a competing and parasitic reaction in many other promising electrochemical systems such as batteries,^{9,10} supercapacitors,¹¹ and the electrochemical reduction of carbon dioxide^{12–16} and nitrogen.^{17–20}

As hydrogen is a desirable fuel, there has been extensive research into improving the HER; on the other hand, there has been very little research dedicated to suppressing the reaction.²¹ One feature all these sustainable electrochemical systems have in common is the use of carbon black materials. For instance, carbon is used as a high surface conductive catalyst support for carbon dioxide and nitrogen reduction systems²² and as an intercalation material in batteries.¹⁰ In order to improve the selectivity and, therefore, efficiency of these electrochemical systems it is important to understand the influence of these carbon black materials on the system and ultimately minimise the parasitic electrochemical production of hydrogen.

HER has been widely researched to replace the current streams of production such as steam reforming and partial oxidation of fossil fuels. Electrochemical water splitting is favoured over these highly CO_2 emitting processes.⁸ The HER reaction²³ occurs at the cathode in an electrolyser: $H^+ + e^- \rightarrow \frac{1}{2} H_2$. It is a two-electron reaction which proceeds via two steps in acidic media. On metal surfaces, in acid media, the reaction is controlled by the $*H$ binding energy; the most active catalyst should have moderate, thermoneutral $*H$ binding at the equilibrium potential.^{24–26} Nørskov and co-workers provided quantitative proof of this notion by establishing a volcano plot using a density functional theory (DFT) database of the

hydrogen chemisorption energies on close packed surfaces of metals; they observed platinum to be at the top of the volcano.²⁷

Carbon black materials are commonly added in various different well-established and commercialised electrochemical systems such as hydrogen fuel cells and batteries as catalyst supports.^{28–31} They are abundant, low cost, highly conducting and have very high surface areas.^{32,33} Carbon black materials can influence the electrocatalyst through dispersion of the particles and interactions between the catalyst and underlying support.³⁴ Furthermore, they are used as the basis for metal free catalysts which have been an area of interest in electrosynthesis catalysis in recent times as carbon-based materials are abundant compared to costly precious metals such as Pt.^{35–37} Currently, carbon black materials are generally manufactured from petrochemicals by incomplete combustion and impurities are then removed through heat treatment.^{28,29,38} The materials are generally graphitic in nature as they are comprised of small stacks of graphite-like layers that are locally roughly parallel but arranged to form particles that are characteristically spherical with a diameter below 50 nm.³⁹ These primary particles are usually fused to form larger hard aggregates, with varying degrees of aggregation (typically three to hundreds of primary particles, depending on the synthesis method and conditions). The Braunauer-Emmett-Teller (BET) surface area of these typically range from 200–1200 $m^2 g^{-1}$.^{32,40}

There are various active sites with different H-binding on carbon materials that contribute to their electrochemical activity, in acid. The porosity of the carbon materials effects catalytic activity through pore size, shape, connectivity and distribution.⁴¹ A recent study used in situ electrochemical scanning tunnelling microscopy and DFT to calculate the H-binding of various active sites on highly ordered pyrolytic graphite in acidic media. They observed that the most active sites for HER were step-edges and carbon vacancies.⁴² These observations are consistent with previous studies on less well defined surfaces in acid.⁴³ Conversely, in alkaline media³⁶ and non-aqueous battery electrolytes^{10,44} where the hydronium ion is absent, it seems that the need to abstract protons from the proton source (e.g. H_2O or HF) is more important than H binding; in this case, the work function seems to a more relevant descriptor for H_2 evolution.

Expansive research by Pumera and co-workers has shown that carbon materials easily attract impurities and it is important to

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consider the elements, particularly metals, that have come in contact with the carbon material as they can easily hinder or catalyse electrochemical activity.^{45,46} For example, Pumera and co-workers observed, in acidic media, that metal impurities on graphite ribbons contributed to an increase in the HER activity of the carbon material.⁴⁷ Furthermore, heteroatom group impurities such as nitrogen, sulfur and oxygen can also affect the catalyst's activity through alteration of acidity and hydrophobicity of the surface of the catalyst.⁴⁸ Some larger oxygen groups such as carboxylic and phenol groups influence the distribution of the metals deposited on the support.³⁴ As these surface chemical characteristics have varying effects on the H-binding, and in-turn the catalytic activity, in acid, it is challenging to identify the exact influence. It is important to elucidate which unique physical characteristics of the carbon black materials are contributing towards the catalytic activity for HER in order to control the reaction, either to favour it or suppress it.

An earlier study, authored by Čolić et al., including one of us, investigated a number of different carbon black materials, in acid, for the competing paths of the oxygen reduction reaction (ORR).⁴⁹ The ORR can proceed via a $4e^-$ pathway to water, the cathodic reaction in a fuel cell, or a $2e^-$ pathway to form hydrogen peroxide, a useful oxidant. The study carried out extensive physical characterisation of the carbon materials. X-ray photoelectron spectroscopy (XPS) was carried out to establish the nitrogen, sulfur and carbon content. Prompt gamma-ray activation/neutron activation analysis (PGA/NAA) was used to determine the total metal content. BET was also employed to obtain the micropore volume and surface area.

The study concluded, on the basis of visual *qualitative* analyses, that aliphatic carbon content rather than graphitic carbon, established by the C1s peak determined by NAA/PGAA and XPS analysis, led to higher H-content and, in-turn, higher faradaic efficiency and partial current density for H_2O_2 production. Furthermore, BET data also supported the conclusion that aliphatic "defect" structures influenced the activity towards H_2O_2 production. However, more sophisticated *quantitative* analyses have been used in the literature to analyse electrocatalytic data for instance, including for oxygen evolution on oxides⁵⁰ and CO_2 reduction on Cu.⁵¹

Herein, we investigate the same seven different carbon black materials as Čolić et al., but for hydrogen evolution reaction activity in acidic electrolytes. The catalytic activity was determined using rotating disk electrode experiments in 0.05 M H_2SO_4 . An on chip electrochemical mass spectrometer with $pmol.s^{-1}$ resolution was used to precisely establish the onset of the reaction. We used statistical analysis of our own data and the earlier study⁴⁹ to establish the factors controlling the hydrogen evolution activity.

Methodology

Electrochemical measurements.—In this study, the following carbons were analysed C-ENERGY Super C-65, ENSACO 350 G (Imerys, Switzerland), YP-80F (Kuraray, Japan) and Vulcan XC72R, PBX51, LITX 200, BP2000, (Cabot, USA). Inks of the carbons were prepared by sonicating in an ultrasonic bath for 40 min (VWR, USA) 9.8 mg of carbon powder in 18.2 MΩ.cm water (Sartorius, Germany), isopropanol and 5% perfluorinated Nafion® resin solution (Sigma Aldrich, USA). The carbon inks were drop cast onto a 0.196 cm², diameter = 0.5 cm, glassy carbon disk (HTW, Germany) and had a loading of 99 $\mu g cm^{-2}_{geo}$. The electrode was left to dry for 30 min in air.

Electrochemical measurements were carried out in a three-electrode system. The working electrode consisted of the glassy carbon disk in a rotating disk electrode (RDE) (Pine Instruments, USA). In order to avoid metal contaminants, graphite foil (Alfa Aesar, USA) was used as a counter electrode and the reference was a leak free Ag/AgCl electrode (Innovative Instruments Inc., USA). A SP-150 potentiostat (Bio-logic, France) was used to carry out electrochemical experiments. Potential electrochemical impedance spectroscopy (PEIS) was used to measure the ohmic resistance between the working and reference electrode at 0 V vs RHE. The

model $R1+Q1/R2+Q3/R3$ was used to fit the data and obtain the high frequency intercept. A typical value of 30 Ohms was observed for the ohmic resistance and the data were corrected manually post experiment using Ohm's law. The electrolyte, 0.05 M sulfuric acid, was prepared from 95% sulfuric acid (Merck Suprapur®, Germany) diluted in ultra-pure water. The electrolyte, 120 ml, was added to the electrochemical cell and purged with high purity argon (N 6.0) for 30 min before measurements began. A PTFE lid was used during purging and measurements to maintain an argon blanket and prevent the competing oxygen reduction reaction (ORR) of atmospheric oxygen.

Cyclic voltammetry (CV) was used to determine the electrochemical surface area (ECSA) of the carbon materials through double layer capacitance. The RDE was spun at 1600 r.p.m during all electrochemical experiments. A CV was conducted between 0–0.03 V vs RHE at various scan rates including 20 mVs⁻¹, 50 mVs⁻¹, 100 mVs⁻¹, 150 mVs⁻¹ and 200 mVs⁻¹. From these data, the charge or discharge currents at 0.15 V vs RHE were plotted against scan rate and a linear fit was obtained to calculate the value of the double layer capacitance of each carbon material. For more details for calculating see supplementary information.

The hydrogen evolution activity was measured using chronoamperometry. The potential was held for 2 min at intervals of 0.04 V between 0 and –0.8 V vs RHE. The average current was taken for each potential.

BET.— N_2 adsorption at 77k was used to analyse the BET surface area of the carbon materials using a Quantachrome Instruments Autosorb iQ3 surface area and pore size analyser. The samples were degassed at 90 °C for 1 h and then 110 °C for a further 19 h before measurements began. The data were analysed using the iQWin Software and multi-point BET analysis determined the surface area. Barrett–Joyner–Halenda (BJH) method was used to calculate pore volumes.

Electrochemical mass spectrometry.—Electrochemical mass spectrometry (EC-MS) was carried out using specialised system with a membrane chip capable of analysing in situ gas products (Spectroinlets, Denmark). A three electrode system was attached to the EC-MS. The electrodes were identical to the RDE with a graphite foil (Alfa Aesar, USA) as the counter electrode, a leak free Ag/AgCl electrode (Innovative Instruments Inc., USA) as the reference and a stationary glassy carbon insert with the catalyst drop cast on it at a loading of 10 $\mu g cm^{-2}_{geo}$. A detailed description of the EC-MS set up was previously described by by Trimarco et al.⁵² All experiments were carried out in 0.05 M H_2SO_4 , for consistency with the RDE results. The potential was held at two minute intervals between –0.26 V and –0.54 V vs RHE with 2 min potential holds at 0.26 V vs RHE between increasing potential hold. Zillien software was used carry out the EC-MS analysis. Internal calibration assuming 100% Faradaic Efficiency and no competing processes at the highest applied overpotential was used to have comparable baselines for each carbon tested.

Statistical analysis.—JMP statistical software was used to correlate between the electrochemical and physical characteristics of the carbon materials.⁵³ Čolić et al.⁴⁹ previously investigated the same carbon materials for oxygen reduction reaction activity and hydrogen peroxide production, as well as providing extensive physical characterisation of the same carbon black materials. Physical data from their work on the materials, including XPS and PGAA/NAA, combined with BET data from this study was used for comparison in the statistical analysis. Gaussian process regression was used to establish power law relationships between the carbon material characterisation data and the electrochemical data.

Results and Discussion

As often applied in the field, BET analysis was employed to determine physical surface area and pore surface area of the high

Table I. Summary of physical surface area ($\text{m}^2 \text{g}^{-1}$) and pore surface area ($\text{m}^2 \text{g}^{-1}$) from BET analysis. The gravimetric capacitance (F g^{-1}) established using double layer capacitance measurements in Ar-saturated 0.05 M H_2SO_4 , rotation of 1600 r.p.m and a loading of $99 \mu\text{g cm}^{-2}_{\text{geo}}$. CVs were conducted between 0–0.03 V vs RHE at the following scan rates 20 mVs^{-1} , 50 mVs^{-1} , 100 mVs^{-1} , 150 mVs^{-1} and 200 mVs^{-1} and the charge or discharge current at 0.15 V vs RHE were plotted against scan rate and the linear fit was obtained to calculate the double layer capacitance.

Carbon material	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore surface area ($\text{m}^2 \text{g}^{-1}$)	Gravimetric capacitance (F g^{-1})
YP-80F	2244	89	64.9
BP2000	1524	334	20.8
PBX51	1279	344	69.3
ENSACO 350 G	594	197	16.1
VXC72	233	85	9.6
LITX200	143	79	4.9
C-ENERGY 65	39	30	5.5

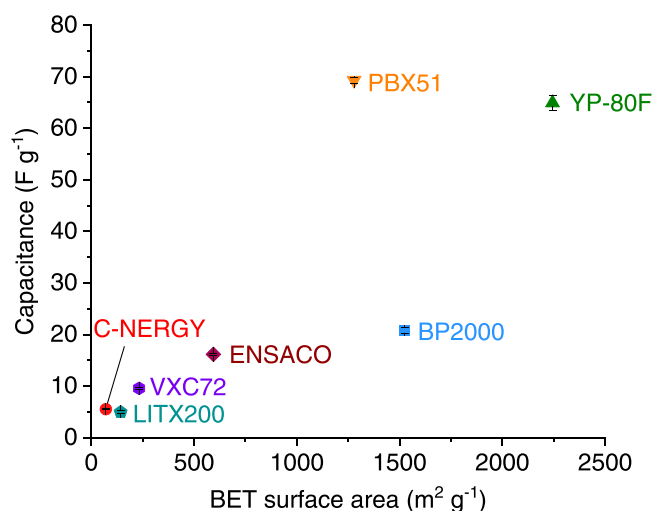


Figure 1. Gravimetric capacitance, F g^{-1} , from electrochemical measurements in Ar-saturated 0.05 M H_2SO_4 and BET surface area ($\text{m}^2 \text{g}^{-1}$). Data taken from Table I. The error bars correspond to standard deviation.

conductivity, graphitised carbon materials. Nitrogen adsorption, indicated a very broad range of results across the different carbon materials studied (Table I). The results range from low surface areas (as low as $39 \text{ m}^2 \text{g}^{-1}$), with associated low pore volumes, for graphitised carbons such as C-ENERGY 65 to high surface area (up to $2244 \text{ m}^2 \text{g}^{-1}$) for activated carbon materials, such as YP-80F.

The gravimetric capacitance, C_g , was established for each carbon material using double layer capacitance measurements by using CVs and scanning the non-faradaic region. The charge and discharge current were taken at 0.15 V vs RHE and plotted against scan rate, Fig. SI1 (available online at stacks.iop.org/JES/169/054516/mmedia). The gradient of this line is equal to the double layer capacitance which was normalised by mass to give the gravimetric capacitance, F g^{-1} (Table I). These values indicate the accessible electrochemical surface area. Although detailed interpretation is complex, depending on the size of the ions and other factors, it is appropriate in these experiments, since the electrolyte is common to both the capacitive and HER measurements.⁵⁴

The relationship between gravimetric capacitance and BET surface area shows a positive correlation (Fig. 1) which is consistent with similar carbons from literature, as the carbon black materials are conductive and the entire surface should be electrochemically active.⁵⁵

Due to the high capacitance of the carbon blacks, the HER activity was not easy to distinguish through CV measurements, however, chronoamperometry identified a clear onset to a reductive current at around -0.4 V vs RHE (Fig. 2); normalised to geometric surface area, the differences between the carbon materials are relatively modest. Electrochemical mass spectroscopy (EC-MS) was used to accurately

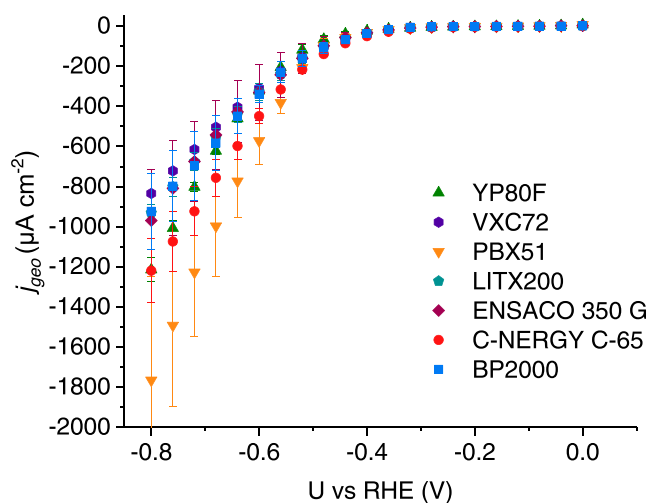


Figure 2. Mean value of the steady state current of the carbon black materials at 0.04 V intervals between 0 and -0.8 V vs RHE in Ar-saturated 0.05M H_2SO_4 with a rotation of 1600 rpm and a loading of $99 \mu\text{g cm}^{-2}_{\text{geo}}$. Each potential was held for two minutes. The current density, $\mu\text{A cm}^{-2}$ is normalised to geometric surface area. The error bars correspond to standard deviation.

establish the nature of the reductive reactions occurring at the cathode. This method allows the in situ detection of both gaseous and volatile intermediates and products during the electrochemical reactions with nanosecond time resolution.⁵² Indeed, our EC-MS measurements showed that our initial RDE experiments, shown in Fig. SI 2, were dominated by the reduction of adventitious O_2 reduction at potentials positive of -0.4 V RHE. This observation highlights the possible errors that may occur, evaluated HER and other reactions, if the reaction products are not directly determined. In the present experiments, the set-up was improved with narrower opening around the RDE shaft to prevent air ingress.

Detailed EC-MS measurements are shown for the materials with the highest (C-ENERGY, Fig. 3a) and lowest (YP-80F, Fig. 3b) HER current densities normalised to surface area and capacitance. Based on the initial RDE experiments, the experiments focused on the onset potential range between -0.26 and -0.54 V vs RHE, gradually stepping to more reducing potentials. Between each voltage step, the potential was held at $+0.26 \text{ V}$ vs RHE, where no HER was expected, to establish a flat mass spectrum baseline. At each voltage step (blue), there is a current transient associated with the electrode capacitance, with a gradually increasing plateau (red), associated with the detection of the mass spectrum signal of hydrogen gas (green), $m/z = 2$. The magnitude of the hydrogen signal increases with more negative potential steps, becoming more noisy as bubble formation sets in. Unlike the CVs or simple RDE experiments, the EC-MS measurement directly identify the onset potential for HER; in this case, the onset was -0.38 V vs RHE, for

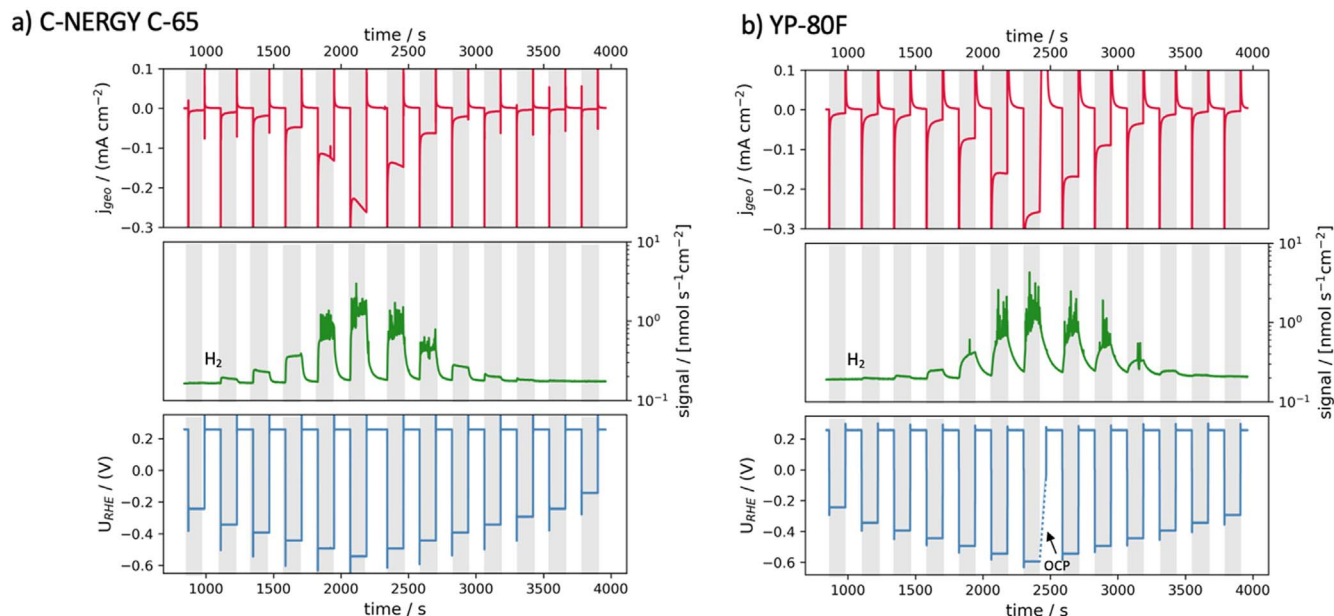


Figure 3. EC-MS data for (a) C-NERGY C-65 (b) YP-80F. The green signal shows the hydrogen production in $\text{nmols}^{-1}\text{cm}^{-2}$, the red line indicates the current in mA and the blue steps indicate the potential applied (V). The grey shading indicates two minute potential hold measurements that are increasing by 0.04 V between 0.26 V and -0.54 V vs RHE and the white background indicates when the potential is at rest for two minutes at 0.26 V vs RHE. The measurements were carried out in He-saturated 0.05 M H_2SO_4 with a loading of $10 \mu\text{g cm}^{-2}_{\text{geo}}$. Internal calibration assuming 100% FE at the highest applied overpotential, assuming no other processes was applied to align the baselines.

both materials, however, C-NERGY C-65 shows higher mass signals for hydrogen than YP-80F at the same potential indicating it is more electrochemically active. These overpotentials are more negative than other metal free carbon catalysts that may be deliberately doped with nitrogen and sulfur to give values as low as -0.26 V vs RHE.^{56,57}

To evaluate the different intrinsic activities between the carbons, the current densities were normalised by both the BET surface area, m g^{-1} , and the gravimetric capacitance, F g^{-1} , as a proxy for electrochemical surface area (Fig. 4). When the current is normalised to the BET surface area or gravimetric capacitance, distinctive differences are observed. YP-80F exhibited low specific activity for HER compared to the other carbons, in both cases, due to its large surface area.

Electrochemical activity normalised by BET surface area shows a stark contrast between C-NERGY C-65 and high surface area materials such as YP-80F or PBX51, which exhibit very low

activity. This suggests C-NERGY C-65 may contain specific active sites or impurities which contribute to higher HER activity. Furthermore it may be that the steady state HER occurs on the outer surface of the primary particles, so none of the small pores contribute to hydrogen production. Even the pores that contribute to the capacitance may not contribute to HER since the protons may not travel inside the primary particles sufficiently quickly. For example it has been observed for OER on NiFeO_xH_y that the most active region is approximately is the top ~ 3 atomic layers rather than the bulk.⁵⁸ It is challenging to establish the difference between the carbon materials activity from the electrochemistry alone.

To understand the differences in HER activity, a comparison between electrochemical and physical data was required. From the EC-MS data it was shown that at potentials negative of -0.38 V vs RHE HER is the dominating reaction and so the current density at -0.52 V vs RHE was chosen to represent the HER activity of each carbon for comparison with the physical characterisation data.

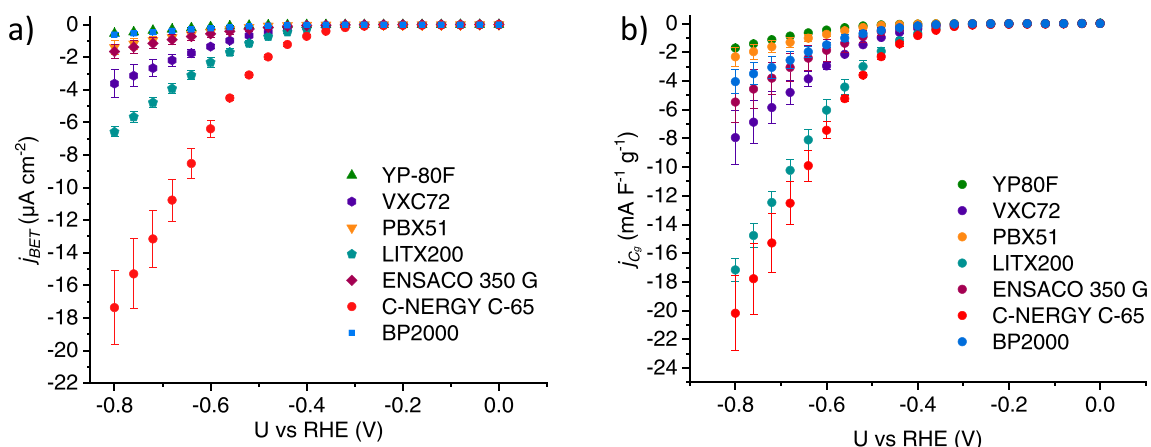


Figure 4. Chronoamperometry measurements between 0 and -0.8 V vs RHE at 0.04 V intervals normalised to (a) BET surface area ($\mu\text{A cm}^{-2}$) (b) the gravimetric capacitance ($\mu\text{A F}^{-1} \text{g}^{-1}$) of the carbon black materials. The potential was held for two minutes and the average current recorded. The measurements were carried out in Ar-saturated 0.05 M H_2SO_4 with a rotation of 1600 rpm and a loading of $99 \mu\text{g cm}^{-2}_{\text{geo}}$. The error bars correspond to standard deviation.

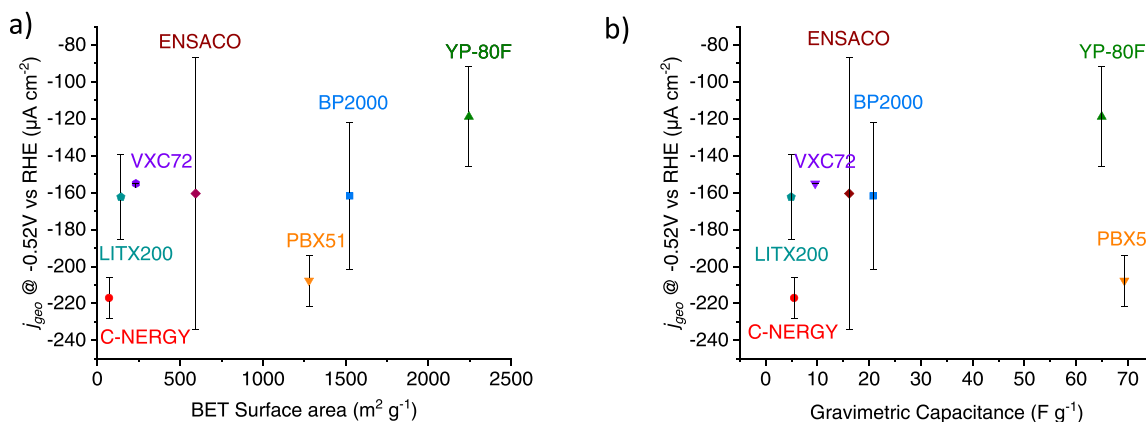


Figure 5. Comparison of the geometric current density at -0.52 V vs RHE ($\mu A cm^{-2}$) with (a) BET ($m^2 g^{-1}$) (b) gravimetric capacitance ($F g^{-1}$). Conditions were 1600 rpm rotation speed, Ar-saturated 0.05 M H_2SO_4 as electrolyte and a catalyst loading of $99 \mu g cm^{-2}_{geo}$. The error bars correspond to standard deviation.

Atypically for electrocatalysis, there is no clear correlation between HER activity and BET surface area or gravimetric capacitance, as shown in Fig. 5; if active sites were uniformly distributed, there should be a positive correlation. The smallest surface area material, C-ENERGY C-65, has the highest current density on geometric basis, whereas YP-80F, which has the highest surface area, had the lowest current density on a geometric basis; this observation may suggest that certain active sites or impurities are influencing the hydrogen production on the carbons.

To explore the possibility of active heteroatoms, the activity was compared statistically with data measured previously for these carbons:⁴⁹ from XPS, the nitrogen, sulfur and carbon content; from PGA/NAA, the metal content and hydrogen content; and from BET, the micropore volume. These data were used in combination with the pore radius, pore surface area and BET surface area determined in this study. JMP software was used to establish statistically which physical characteristics were the most influential on the hydrogen evolution activity. A heatmap, using Pearson correlation coefficients (Fig. 6), was used to establish any linear correlations between pairs of variables indicated by a scale from 1 to -1 . If the correlation coefficient is close to 1, shown in red, it indicates a positive correlation. Whereas if the correlation value is -1 , shown in blue, it represents a negative correlation and if the value is close to zero, indicated by paler colours, there is no correlation.⁵⁹

The electrochemical activity was represented by the geometric current density at -0.52 V vs RHE and plotted against various physical characteristics of the carbon (Fig. 6). The heatmap reveals that pore radius, gravimetric capacitance and pore surface area are uncorrelated with activity. On the other hand, C1s 284.6/285.7 eV peak ratio and particle size (measured from TEM) have a positive correlation. From XPS, the C1s peak with a binding energy of (BE) 285.7 eV peak corresponds to sp^3 aliphatic carbons, and the C1s with BE 284.6 eV relate to aromatic, graphitic sp^2 carbons. Higher C1s 284.6/285.7 peak ratio indicates the carbon is more graphitic in nature. The positive correlation with primary particle size rules out a dependence on simple external surface. Surprisingly, the micropore volume and BET surface area have a negative correlation with the geometric current density, suggesting that high surface carbons lack some feature or impurities relevant to HER.

Furthermore, the correlation heatmap shows total metal content, which includes Fe, Ni, Co, Cr, V, Al, Ti, Mn and W has a strong linear positive correlation activity. Sulfur, oxygen, hydrogen and nitrogen content show very little correlation to HER activity implying they do not contribute to the electrochemical activity. The degree of graphiticity, C1s 284.6/285.7 eV peak ratio, is positively correlated with metal content and negatively correlated with non-metallic heteroatoms; higher temperature carbon production can be expected to drive off light non-metallic elements, and may even concentrate less volatile

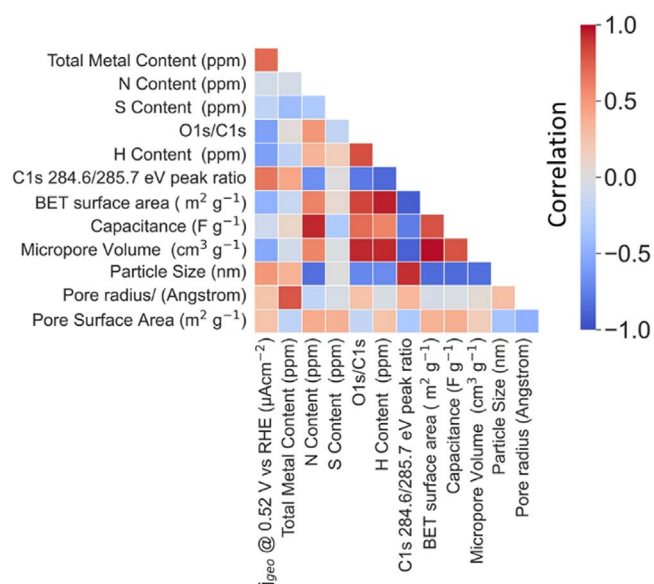


Figure 6. Heatmap indicating Pearson correlation between the physical characteristic analysis and the geometric current density at -0.52 V vs RHE the Pearson coefficient is 1 or close to one it has a positive correlation and is indicated in red. If the coefficient is -1 or close to it, there is a negative correlation shown in blue. If the value is close to zero there is no correlation and it is indicated in light grey.

metals if more carbon is volatilised with the light heteroatoms or directly burnt as fuel.⁶⁰

In order to consider the significance of possibly interacting descriptor variables, gaussian process regression was used. The method was used to establish any correlation between the geometric current density at -0.52 V vs RHE and the physical data. The characteristics that had the largest absolute correlation coefficients (closest to 1 and -1) from the Pearson correlation analysis, were examined to elucidate any significant relationships between them and the HER activity. It is striking that there is a mildly negative correlation between the geometric current density and either measure of surface area, i.e. capacitance or BET surface area.

Using Gaussian process regression, we established that total metal content and geometric current density were correlated; the analysis predicted the mean and uncertainty of the power law relation between geometric current density and total metal content.⁶¹ The gradient of the mean was calculated to be $\frac{d \log J}{d \log c_m} = 0.077 \pm 0.01$, which was found to be equal to the result of liner regression. (Figure 7) The

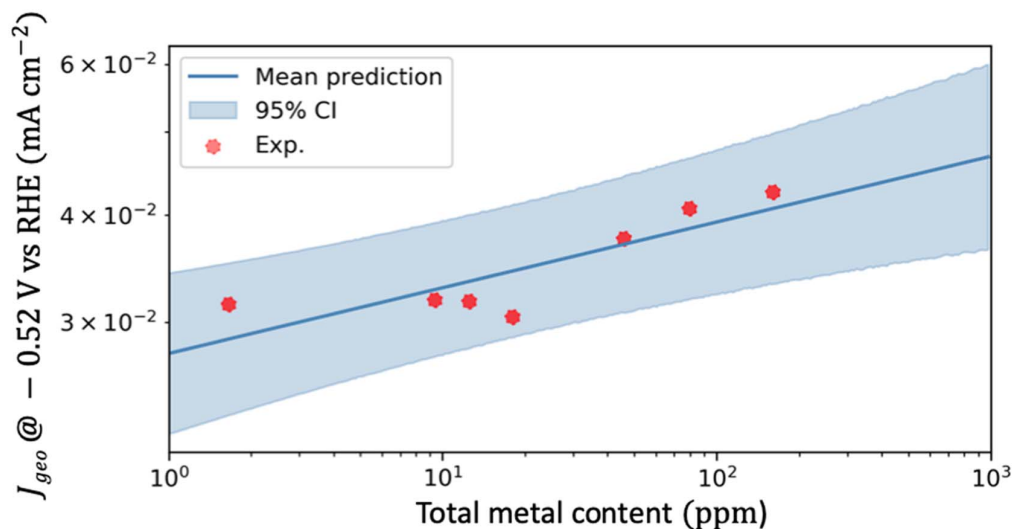


Figure 7. Mean prediction of the power law relationship between geometric current density at -0.52 V vs RHE and total metal content. The mean prediction line is shown in blue and the red symbols show the experimental data. The blue shading represents 95% confidence intervals. The apparent mean square error (MSE) was calculated to 0.003.

geometric current density and total metal content are related by the following equation, where k_0 is an apparent rate constant:

$$j_{geo} = k_0 \cdot \text{Total metal content}^{0.1}$$

The positive effect of metal impurities on HER activity is unsurprising, and consistent with previous studies; for example tungsten impurities have contributed to HER activity on graphene nanoribbons.^{45,47} Similarly, for hydrogen peroxide production on carbon nanotubes metal impurities as low as 10–100 ppm have influence on the activity.⁴⁶ However, the low value of the exponent, at 0.1, suggests a complex relationship between the total metal content in the bulk and the catalytic activity. A more simple first order dependence could be conceivable, for instance if (i) there were a direct linear correlation between bulk and surface concentration of metal impurities and (ii) if the electrochemically accessible surface area were constant between the different carbons. How

The lack of correlation with light heteroatoms is perhaps most surprising, given theoretical and experimental results in HER.⁴⁰ Nitrogen-doped carbons have been an area in recent for electrocatalysis particularly for ORR where they have high catalytic activity.⁶² However, numerous studies suggest the specific local structure surrounding the N is important;⁴² the highly active configurations of N on C may be absent on the carbons. Controlled heat treatments or leaching experiments on these carbons could help to confirm the effects observed. In addition, it might be possible to design syntheses to deliberately leverage these effects. For example, the removal of heteroatoms from graphene was shown to increase defect concentration and hence electrochemical activity for alkaline HER.³⁶

Conclusions

This study surveys the HER activity, under acid conditions, of seven archetypical carbon black materials often used in electrochemical electrodes. The use of electrochemical mass spectroscopy techniques provided useful confirmation of the HER activity and onset potential, and to avoid experimental artefacts, for example associated with adventitious oxygen. In rotating disk experiments, the HER activity correlated with neither BET nor the capacitance, both of which are measures of the microscopic surface area. Statistical analysis of the HER performance compared to a range of physiochemical parameters, in fact, highlighted a negative correlation with the BET and the capacitance; this relationship is beneficial for catalyst support applications, as it suggests that a high surface area material, which maximises dispersal of catalyst nanoparticles, does not necessarily result in higher

rates for undesired hydrogen evolution. Perhaps surprisingly, the analysis showed heteroatom content such as sulfur, nitrogen and oxygen had minimal influence on the HER activity. The statistical model showed a power law relation between the HER activity and metal content, indicating that metal impurities in the 100 ppm range are likely the dominant effect. Further investigation into localised activity would need to be carried out to elucidate more details on the active sites within the carbon materials. Therefore, electrochemical systems which need to minimise HER, such as carbon dioxide or nitrogen reduction, should use carbon black materials which have low metal content, or take steps to actively remove unwanted metals.

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