Electrochemical reduction of oxygen on mesoporous platinum microelectrodes

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The electrochemical reduction of oxygen is studied using electrochemically deposited mesoporous platinum microelectrodes, which exhibit efficient mass transfer of material to the electrode surface and accelerated reduction kinetics when compared to polished microelectrodes.

The reduction of molecular oxygen at the surface of an electrode is of considerable importance to many fields of research. Specific areas of interest include the quantitative analysis of oxygen concentration, the monitoring of enzymatic reactions and the conversion of chemical to electrical energy within a fuel cell. The mechanism for the reduction of molecular oxygen is known to be complex and dependent on the substrate employed.[1] In particular, two groups of substrates can be identified, those reducing oxygen to hydrogen peroxide through a 2 electron pathway[2,3] and those reducing oxygen to water through a 4 electron pathway.[4] In many instances it is desirable that the 4-electron pathway be selected. As an example, the reduction of molecular oxygen within a fuel cell is commonly achieved by a platinum-loaded high surface area cathode.[5] This choice is governed by platinum's superior catalytic activity. However, the performance of the platinum cathode is still limited at high potentials due to the formation of adsorbed species on the surface of the platinum metal.[1,6,7] These species inhibit oxygen reduction and reduce the operating potential of the electrode to around 0.8 V *vs.* RHE instead of the theoretical performance 1.229 V *vs.* RHE.[6,8] This limitation imposes a significant loss in the overall performance of the fuel cell, which has as yet to be fully addressed. It is reported here, for the first time, that Pt mesoporous modified microelectrodes have significantly altered oxygen reduction kinetics when compared to polished platinum microelectrodes of the same dimensions within the same solution.

Attard *et al.* first reported the use of a 'true liquid crystal templating technique' for the synthesis of mesoporous platinum powders (H_I-Pt) *via* the reduction of hexachloroplatinic acid (HCPA).[9]

Attard *et al.* also showed that it was possible to electrochemically produce mesoporous electrode materials and modified electrodes with a variety of nanostructures, for example, either hexagonal (H_I-ePt) or cubic (V_I-ePt) and that the dimensions of the mesoporosity could be finely tuned by varying the deposition conditions.[10–13]

Here we report the results of a study where the thickness of the mesoporous deposit is increased by controlling the deposition charge density. The results presented here are representative of a larger number of H_I-ePt modified microelectrodes studied. The subsequent effect on the mass transfer characteristics of the microelectrodes and electroreduction of molecular oxygen are now reported.

Electrodeposition was performed on a number of polished 25 μm diameter Pt microelectrodes sealed in glass. The platinum metal was deposited potentiostatically at a potential of −0.1 V *vs.* SCE from a template solution described previously.[10,12] Monitoring the charge passed during the deposition process enabled the amount of platinum metal deposited to be controlled. The control of the deposition conditions and charge enables the characteristics of the deposit to be chosen. Cyclic voltammograms of the H_I-ePt modified microelectrodes in 2 mol dm^{-3} sulfuric acid were performed and showed polycrystalline Pt characteristics as shown previously.[10,12] These voltammograms demonstrated that as the charge density is increased the surface area of the microelectrodes increases as expected. The voltammograms can be used to gain an estimate of the effective surface area of the Pt deposit by analysis of hydrogen UPD onto the surface.[10,13] Table 1 gives a summary of the effective surface roughness, R_f, of the deposit as a function of deposition charge within the template mixture. It can be seen that the surface area of the metal deposit scales approximately linearly with the charge density of the deposition process.

Microelectrodes were chosen for this project due to their unique properties which are related to their size.[14] Clearly as the electrodeposition proceeds the geometric characteristics could be altered by the H_I-ePt deposited. In order to test this we cycled the microelectrodes in a solution containing a suitable redox species. Fig. 1 shows the voltammetry of a series of microelectrodes within a solution containing $[Fe(CN)_6]^{3-}$ [16] and demonstrates that as the electrodeposition charge density was increased in the range 0 to 37.9 C cm^{-2} the reduction current for the redox species also increased. This indicates that the geometric area of the 25 μm Pt microelectrode has been effectively enlarged by the modification procedure. Further evidence for this change in geometric area is shown by the SEM image of one of the H_I-ePt modified microelectrodes (see insert in Fig. 1). This image shows that the deposit has spread over the surface of the glass insulator effectively increasing the geometric surface area. The SEM image also shows that the deposit is largely uniform and attached rigidly to the substrate surface. It is possible to calibrate the geometric surface area of the modified electrodes by comparing the average steady state current at −0.1 V *vs.* SCE for the electroreduction of $[Fe(CN)_6]^{3-}$ at a polished 25 μm Pt microelectrode and comparing this with the signal recorded with the H_I-ePt

Table 1 Measured parameters for the 25 μm diameter Pt microelectrodes investigated

Electrode	Deposition charge/μC	Real surface area/10^{-3} cm^2	R_f[a]	Effective diameter[a]/μm	$E_{1/2}$ O_2/mV[b]	n_{app}[c]
Polished (A)	—	0.01242	2.53	25	−422	2.36
H_I-ePt (B)	31	1.38	281	25.8	−219	3.82
H_I-ePt (C)	93	3.57	727	31.8	*ca.* −222	3.95
H_I-ePt (D)	186	5.69	1160	36.5	*ca.* −231	4.4

[a] R_f calculated by dividing the real surface area by the geometric area prior to modification. [b] vs. Hg/Hg_2SO_4. [c] The apparent number of electrons involved in the reduction of molecular oxygen, n_{app} was calculated from the current recorded at a potential of −0.5 V *vs.* Hg/Hg_2SO_4 for the H_I-ePt microelectrodes and −0.7 V *vs.* Hg/Hg_2SO_4 for the polished microelectrode (see Fig. 2).

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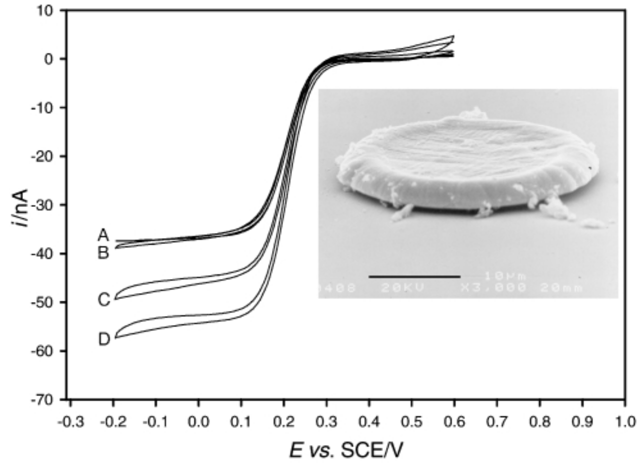

Fig. 1 Plot showing cyclic voltammograms recorded for a series of 25 µm Pt microelectrodes recorded at 2 mV s^{-1} in a solution containing 10 mmol dm^{-3} $K_3[Fe(CN)_6]$ in $Sr(NO_3)_2$ at 25 °C under anaerobic conditions; A, B, C, D as in Table 1. The insert in the figure shows a SEM image of the 93 µC H_I-ePt modified microelectrode recorded after the experiments were performed. The scale bar on the SEM represents 10 µm.

modified microelectrodes. This calibration shows that the effective geometric diameter changes in the range 25–37 µm for the thinnest and thickest film respectively. The actual values are shown in Table 1.

Turning to the activity of the H_I-ePt modified microelectrodes for oxygen electroreduction, a series of voltammograms were recorded in air-saturated pH 7 phosphate buffer. Fig. 2 shows the voltammetry recorded at 2 mV s^{-1} between +0.1 and −0.7 V *vs.* Hg/Hg_2SO_4. For comparison the electroreduction of oxygen under the same conditions on a polished 25 µm Pt microelectrode is included. A marked difference between the polished microelectrode and the H_I-ePt can clearly be seen. First, the plateau current for the H_I-ePt modified microelectrodes is consistently higher than at the polished microelectrode. It is possible to calculate the effective number of electrons involved in the reduction of oxygen on the polished Pt microelectrode as *ca.* 2 assuming an oxygen concentration[17] of 0.24 mmol dm^{-3} and a value for the diffusion coefficient of oxygen, D,[18] of 2.29×10^{-5} cm^2 s^{-1}. This is unusual for Pt, as normally the mechanism for electroreduction of molecular oxygen is stated as a 4 electron process. However, under the conditions employed in this study a consistent value of 2.36 electrons was obtained. The reason for this change is unclear but it is known that adsorption of ions[1,19,20] and high rates of mass transfer[18] can force the number of apparent electrons to fall below 4. Nevertheless the reduction of molecular oxygen on the H_I-ePt modified microelectrodes was associated with an increase in the plateau current to a value close to 4 electrons. Fig. 2 also shows that as the surface area of the deposit increased, the voltammogram became less well defined. This leads to some difficulty in accurately measuring the apparent number of electrons involved in the reaction for the thicker films studied. This distortion was attributed to the rising background signal associated with surface reactions on the increasingly large Pt surface. The anodic current supports the distortion, presumably due to oxide formation, above 0.0 V *vs.* Hg/Hg_2SO_4 for the larger surface area microelectrodes. Cyclic voltammograms (not shown) in the absence of oxygen also support these findings. Second, the reduction of molecular oxygen at the H_I-ePt proceeds at a considerably more positive potential *ca.* −219 mV *vs.* Hg/Hg_2SO_4 for the 31 µC H_I-ePt modified microelectrode compared to *ca.* −422 mV *vs.* Hg/Hg_2SO_4 for the polished microelectrode. However, increasing the surface area of the deposit further by increasing the deposition charge did not significantly shift the reduction wave to more positive potentials. In these cases the inhibition of oxygen reduction by adsorbed species is presumably still the predominant factor and increasing the surface area further has no beneficial kinetic effect. However, the increase in apparent number of electrons involved in the reaction and the improved kinetics of oxygen reduction, point to these materials being of potential use in either analytical chemistry or fuel cell technology. It is important to remember that these materials are electrodeposited onto the surface and as such are adherent and mechanically robust. Additionally the current densities, due to the unique mass transfer characteristics of microelectrodes, are of the order of 1.95 mA cm^{-2} for a catalyst loading calculated to be 1.29 mg cm^{-2} at 25 °C under stagnant conditions. This calculation assumed a maximum deposition efficiency of *ca.* 43%.[12]

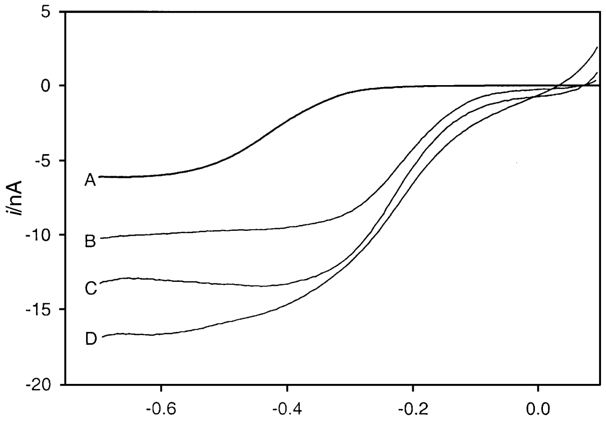

Fig. 2 Plot showing voltammograms recorded for a series of 25 µm Pt microelectrodes recorded at 2 mV s^{-1} in 0.2 mol dm^{-3} pH 7 phosphate at 25 °C under aerobic conditions; A, B, C, D as in Table 1.

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