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Nafion®-bonded porous titanium oxide electrodes for oxygen evolution: towards a regenerative fuel cell

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Oxygen evolution on PTFE/Nafion®-bound porous activated XC-72 carbon and on PTFE- and PTFE/Nafion®-bound Ebonex® has been studied, using RuO_2/IrO_2 catalysts. High activity was found for Ebonex®, but carbon, even when coated with Nafion, proved quite unstable.

1. Introduction

Fuel cells based on solid-polymer electrolytes such as Nafion® have been intensively investigated since the original Gemini space programme [1]. Effort has been expended on improvements both in electrocatalysts for the oxygen cathode and on the design of more stable polymer electrolytes [2, 3]. Recently [4], Shukla *et al.* reported very high current densities for SPE®-based fuel cells using porous electrodes which had been fabricated with Nafion® gel. The advantage of these electrodes is that the overall noble-metal loading could be kept extremely low, since all the finely dispersed platinum particles are utilized. Ideally, for space applications, a fuel cell should be regenerable; that is, it should be possible both to use it as a fuel cell and as an electrolyser. SPE®-based electrolysers have been investigated by General Electric; they show high current densities with low loadings of catalyst, but the nature of the anode, in particular, has not been fully disclosed [5]. In this paper we report work carried out in an endeavour to fabricate reversible porous oxygen electrodes.

Although carbon has proved a successful substrate for the reduction of oxygen, its use in regenerable fuel cells is not normally regarded as viable since anodic corrosion tends effectively to strip the electrocatalyst. However, it has been reported recently that vitreous carbon prepared with a fluorocarbon binder shows a substantially enhanced stability for oxygen and ozone evolution [5]. One aim of this work was to test whether porous XC-72 carbon as a substrate material in regenerable fuel cells could be stabilized towards oxygen evolution by coating with Nafion. Catalysts used are platinum and RuO_2/IrO_2 [6], the latter being preferred in this instance, and, as substrates, in addition to porous carbon, particulate Ti_4O_7, the latter being made by grinding the commercial electrode material Ebonex®, supplied by ICI. By using the Nafion®-bonding technique developed earlier [4], very encouraging results have been obtained for the Ti_4O_7, but the XC-72 carbon showed poor stability when used as an anode for oxygen evolution.

2. Experimental details

Commercial Nafion® 117 was boiled in 1 M sulphuric acid for 30 min to convert it to the fully protonated form and then rinsed with distilled water. It was then solubilized by the method of Martin [7] to produce a 5% solution in 1 : 1 ethanol/water. This solution was boiled for several hours to remove organic solvents, then concentrated down to 16%. On cooling this solution, a gel formed that was used in the electrode preparation.

The carbon substrate was Vulcan XC-72, which was activated by heating in a flow of CO_2 at 930° C until a 27% weight-loss was achieved. The Ti_4O_7 substrate was formed by mechanical grinding of commercial Ebonex® in a Specamil vibrational grinder; particle sizes showed a rather wide variation from *ca.* 0.2–2 μm.

Platinum particles were deposited on carbon by suspending the latter in a 3 : 1 mixture of water and *iso*propanol and sonicating for 15 min. The appropriate amount of H_2PtCl_6 solution was then added, followed by the necessary amount of sodium carbonate to neutralize the mixture. The mixture was then boiled for one hour to facilitate the efficient take up of platinum species by the carbon particles. An excess of formaldehyde was then added to reduce the adsorbed metal species to the zero valence state, and the mixture was boiled for a further hour. The resulting mass was filtered, washed with copious amounts of hot distilled water until no more chloride ions were detectable in the washings, and then air dried at 110° C.

The mixed RuO_2/IrO_2 catalyst was dispersed onto carbon by initially dispersing hydrated $RuCl_3$ and $IrCl_3$ (Aldrich) into *iso*propanol by sonicating for 20 min. The carbon powder was then added and the mixture sonicated for a further 30 min. After boiling for one hour, ammonia or Na_2CO_3 was added until the pH reached 12. Aerial oxidation of the adsorbed hydrous oxides to oxidation state (IV) then took place by heating to 400° C. After filtration of the mass, and washing with copious quantities of water, it was dried in air at 110° C.

This catalyst was dispersed on powdered Ti_4O_7 by the following technique; hydrated $RuCl_3$ and $IrCl_3$ were dissolved in *iso*propanol by sonicating for 30 min, powdered Ti_4O_7 added and, after further sonication, the solvent was evaporated slowly to dryness to facilitate adsorption of the catalyst. The impregnated catalyst was dried at 110° C and then heated in air at 400° C for one hour to oxidize the chlorides to the dioxides. The powder was then cooled and washed thoroughly with hot distilled water until no chloride could be detected in the washings. It was finally dried in air at 110° C.

The electrodes were fabricated by mixing *ca.* 100 mg of the catalyst-deposited carbon or ebonex with just sufficient water to produce a paste. A 50% suspension of PTFE (ICI-Fluon™-GP2) was then manually mixed into a paste to produce a mixture containing 27% or 40% w/w PTFE. This was followed by Nafion® gel to give the required percentage of Nafion w/w (calculated on the equivalent dehydrated weight of Nafion®). A smooth paste was obtained that could easily be spread onto the current collector. The Nafion® membrane was then rested on top of the paste, and this resulted in three parallel, adjacent discs: first the current collector, then the paste and finally the Nafion® membrane [4]. The electrode was hot-pressed as follows:

(i) a small initial pressure of 5 $kg\,cm^{-2}$ was applied;
(ii) the heaters were switched on, and the press heated to 95° C (3–4 min);
(iii) the compaction pressure was increased to 200 kg cm^{-2} and applied for 5 min;
(iv) the heaters were switched off and the pressure reduced to 5 $kg\,cm^{-2}$;
(v) the electrode is convection cooled to below 50° C before removal;
(vi) the electrode is stored in a moist environment.

Non-Nafion®-bonded carbon electrodes were made in a slightly different way. Sufficient 50% PTFE suspension to give a 27% w/w mixture with the carbon was diluted to 50 cm^3 with distilled water. The catalyst coated carbon was suspended in THF by sonicating for 15 min and the PTFE sol then dripped into the suspension from a burette over a period of one hour with stirring. The resultant suspension was then centrifuged to give a runny paste. This paste was dropped onto the current collector from a Pasteur pipette and excess THF/water removed by a water pump. This mixture was processed in the following way:

(a) a pressure of 350 $kg\,cm^{-2}$ was applied for 5 min;
(b) the resulting pressure was heated at 110° C in an oven for one hour to remove the remainder of the solvent;
(c) it was then heated at 350° C in an oven for 30 min to sinter the electrode.

Electrochemical measurements were carried out in a conventional three-compartment PTFE cell with working, reference ($Hg/Hg_2SO_4/1.0\,M\ H_2SO_4$) and counter (platinum gauze) electrodes. The electrolyte was 2.5 M H_2SO_4, and the reference electrode was connected to the cell by means of a Luggin capillary positioned close to the working electrode surface [8]. Where necessary, correction for *iR* drop was made by the current-interrupt method [9]. All measurements were taken galvanostatically with an Oxsys Micros 68 000-based system capable of controlling eight cells independently, and experiments were carried out at room temperature unless otherwise stated. Electron microscopy was carried out with a JEOL 2000FX microscope in the Chemical Crystallography Department of Oxford University. The catalyst-coated carbon or ebonex was dispersed into carbon tetrachloride and coated onto carbon-covered copper grids. The instrument has a sophisticated X-ray detection system, enabling on-line elemental analysis to be carried out on particles.

3. Results and discussion

3.1. *Oxygen evolution on platinum dispersed on carbon*

Galvanostatic studies at positive potentials for Pt/C show a marked deterioration with time, with a particularly steep decline between the first two runs, followed by a slow and steady deterioration thereafter. This behaviour was particularly marked at higher current densities, and only for the first run was there any evidence of electrocatalysis. In subsequent runs it is likely that a mixture of CO_2 and O_2 is evolved as the carbon is degraded and the catalyst lost. It is clear that the carbon is very susceptible to corrosion, in agreement with TEM studies carried out previously [10, 11]. These studies showed that the electrode structure deteriorates, and the catalyst particles migrate, collide and coalesce, lowering the catalyst area [12]. It has been suggested that the origin of this effect is oxidation of the carbon that can take place at preferred sites such as edges and dislocations, which are also likely to be the reactive sites for catalyst deposition [13]. XC-72 is a turbostratic carbon, and the irregularities in layer separation may also lead to an increased susceptibility to oxidative degradation.

In an effort to retain stability, a platinum-catalysed Nafion®-bonded electrode was tested. However, the results were little better than before, and decay in performance took place rapidly, particularly at elevated temperatures.

3.2. *Oxygen evolution on RuO_2/IrO_2 dispersed on carbon*

The deterioration of the platinum-catalysed carbon electrodes revealed above was thought to be due to the relatively poor catalysis of oxygen evolution by platinum. Far better catalysts are those based on RuO_2, though this material cannot be used by itself as it is oxidized slowly to RuO_4 at the anodic potentials required to drive the oxygen evolution reaction [14–16]. However, it has been found that alloying the RuO_2 with IrO_2 stabilizes the Ru [17], a result explained on

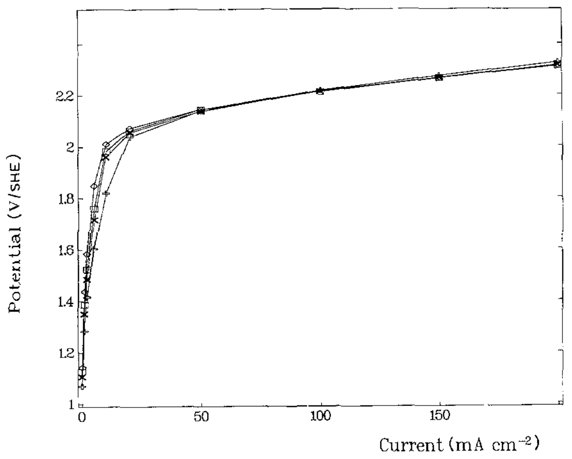

Fig. 1. Oxygen evolution on a PTFE-bonded XC-72 porous-carbon electrode without Nafion® present as additional binder. Potential V/SHE); electrolyte is 2.5 M H_2SO_4, temperature 25° C. (+): Run 1; (×): Run 2; (□): Run 3; (◇): Run 4.

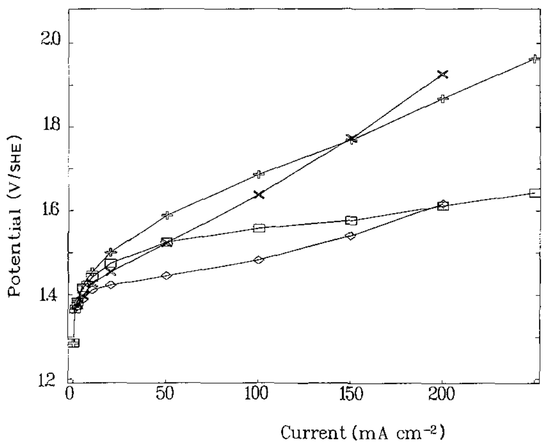

Fig. 3. Oxygen evolution on a PTFE-bonded Ebonex® electrode with Nafion® added as described in the text. Conditions as for Fig. 1. (+): 27% PTFE; (×): 27% PTFE/17% Nafion®; (□): 27% PTFE, *iR* corrected; (◇): 27% PTFE/17% Nafion, *iR* corrected.

the basis of shifted oxidation potentials and lack of surface segregation of the catalysts [18, 19].

Carbon electrodes with dispersed RuO_2/IrO_2 were fabricated as described above. The mean size of the catalyst particles, as revealed by electron microscopy, was 3.5–5.3 nm, though occasional much larger aggregates were found, which microprobe analysis revealed to be primarily either IrO_2 or RuO_2 that had segregated. The polarization behaviour of a typical electrode is shown in Fig. 1, which shows that for non-Nafion®-bound electrodes, a very rapid loss of activity takes place between the first and second runs, with subsequent runs reflecting very little improvement over platinum. Even for a Nafion®-bound electrode, however, the XC-72 carbon is not stable, and deterioration takes place over a series of runs, as shown in Fig. 2. Lifetime tests confirm this loss of activity: at 100 mA cm^{-2}, the Nafion®-bonded RuO_2/IrO_2 electrode deteriorated over a period of a few hours to a polarization of 2.4 V (η = 1.2 V), and slowly thereafter to 2.5 V after 100 h.

It is evident that Nafion® does have some beneficial effect; one possibility is that the electrodes are rather more robust when Nafion® bound, and visual inspection does confirm that they show fewer signs of catastrophic failure typical of those electrodes without Nafion®. It is also likely that Nafion® can inhibit, at least to some extent, oxidation of edge and dislocation sites that are the main nucleation centres for the catalyst particles. However, it is also clear that turbostratic carbons such as XC-72 are intrinsically unstable at very high potentials, and a usable system must concentrate on other substrates.

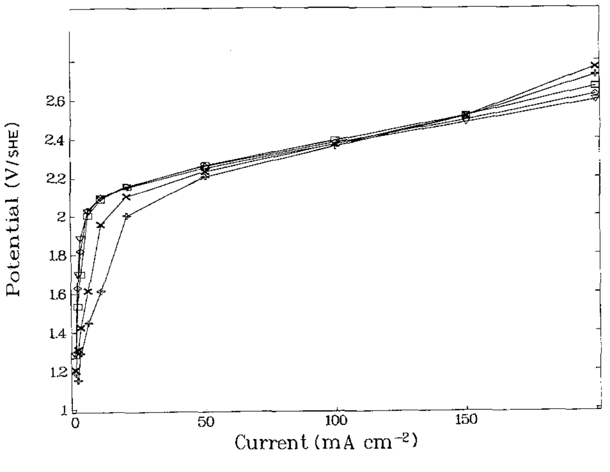

Fig. 2. Oxygen evolution on a PTFE-bonded XC-72 porous-carbon electrode with Nafion® binder. Conditions as Fig. 1 (+): Run 1; (×): Run 2; (□): Run 3; (◇): Run 4; (▽): Run 5.

3.3. *Oxygen evolution on Nafion®-bound Ti_4O_7 powder*

The suboxides of titanium form an extensive series, whose properties have been tabulated by Goodenough and Hamnett [20]. A composite material, of formula approximating to Ti_4O_7 has been marketed under the trade name Ebonex®, and this shows good corrosion resistance in strongly acidic and weakly basic solutions [21]. It is also a metallic conductor [22, 23]. There are extensive reports of Strong-Metal-Support-Interaction (SMSI), particularly for noble metals on Ti_4O_7 [21, 24, 25], which have been ascribed to interaction between the d_π-orbitals on the titanium and the noble metal. This SMSI is illustrated graphically by the electron-microscopic examination of the Ti_4O_7-supported RuO_2/IrO_2 electrodes fabricated as above. This shows that the Ti_4O_7 particles are uniformly coated with the catalyst, and that there are no large aggregates of segregated catalyst, in marked contrast to the behaviour of carbon.

Electrodes containing 27% PTFE-bonded Ebonex® particles with an RuO_2/IrO_2 catalyst were found to be far more stable that their carbon-substrate counterparts, particularly at low current densities. Polarization behaviour for a typical electrode is shown in Fig. 3, and the effect of adding Nafion® is clearly to improve the performance slightly, particularly at low current densities. This is clearer from the iR-corrected data, also shown in Fig. 3, though it is also clear from these data that the effect of added Nafion® was slightly to increase the overall resistance of the electrodes

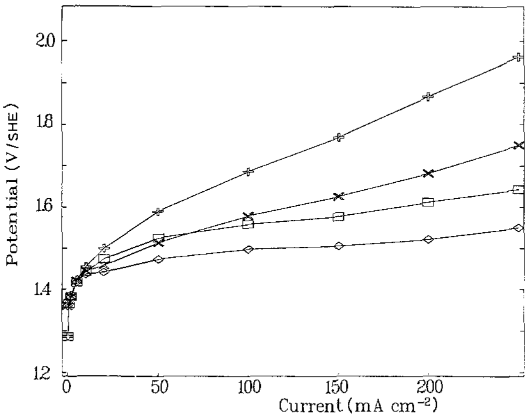

Fig. 4. Oxygen evolution on Ebonex® electrodes bonded with 27% and 40% PTFE but without Nafion®. Conditions as for Fig. 1. (+): 27% PTFE; (×): 40% PTFE; (□) 27% PTFE, *iR* corrected; (◇) 40% PTFE, *iR* corrected.

fabricated. Lifetime tests for the PTFE-bound electrode without Nafion® were carried out, and the electrode proved completely stable in operation at 100 mA cm^{-2} for 300 h, the longest run made.

The 27% PTFE-bound Ebonex® electrodes were, however, found to be rather less stable at current densities above $\sim$150 mA cm^{-2}, but the stability could be markedly improved by increasing the PTFE content to 40%. Figure 4 shows the results of a polarization run of such an electrode compared to the 27% electrode; not only is the stability improved, but the performance at higher current densities is also considerably better. Unfortunately, it did not prove possible, using the techniques described above, to fabricate 40% PTFE-bonded Ebonex® electrodes containing Nafion® without encountering rather high internal resistances.

The behaviour of these electrodes as oxygen *reduction* electrodes has been investigated at a preliminary level. The RuO_2/IrO_2 catalyst is not active for oxygen reduction, but platinum was used as an electrocatalyst and deposited on Ebonex® in a similar manner to that used for carbon. Initial results suggest that whilst a reasonable open-circuit potential can be obtained ($\sim$0.9 V), the current drawn is severely restricted by electrode design problems on which we are working at the moment.

4. Conclusions

It is evident that turbostratic carbons such as XC-72 do not provide sufficiently stable substrates for oxygen evolution, even with such active catalysts as RuO_2/IrO_2. By contrast, Ebonex®-based substrates are far more stable at all current densities explored. At lower current densities, addition of Nafion® appears to improve the performance of the Ebonex® electrodes, but performance at high current densities appears to be enhanced by incorporating a higher PTFE-content; these electrodes are not improved by addition of Nafion®. The best results obtained on these electrodes compare well with the electrolysers currently available, and for lower current densities, the combination of Nafion® and PTFE confers both longevity and ease of engineering.

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