Oxygen electroreduction in perfluorinated sulphonyl imides

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The electroreduction of oxygen in perfluorinated sulphonyl imides has been studied with the emphasis on the identification of alternate acid electrolytes which could replace the presently used phosphoric acid as an electrolyte in H_2–O_2 fuel cells. The activity for oxygen reduction on smooth platinum and gas-fed, high surface area platinum-catalysed electrodes (10% platinum loading on XC-72 carbon support) has been examined. The polarization of the air cathode in the micro-fuel cell in bis(trifluoromethanesulphonyl)imide is 40 mV more positive compared to phosphoric acid at $100\,mA\,cm^{-2}$, presumably due to the increased solubility of oxygen and lower tendency of bis(trifluoromethanesulphonyl)imide to adsorb on the platinum catalyst. The related bis-(fluorosulphonyl)imide is unstable in water and the hydrolysis products adsorb strongly on the catalytic sites, resulting in poor performance.

1. Introduction

The performance of present phosphoric acid fuel cells is severely limited by the relatively high polarization of the air cathode, arising principally because of the slow kinetics of oxygen electroreduction on even high area platinum and platinum alloy catalysts. The possible reasons for the sluggish oxygen reduction reaction in concentrated phosphoric acid are its weak acidity, strong anion adsorption on the catalyst and low oxygen solubility. The polarization of oxygen reduction has been found to be substantially less in various perfluorinated acids such as trifluoromethane sulphonic acid [1–4]. Higher solubility and diffusion coefficient of oxygen and a lower tendency of trifluoromethane sulphonic acid to adsorb on platinum catalyst are believed to be responsible for better performance of the cathode. However, a drawback to using trifluoromethane sulphonic acid in practical fuel cells is that it wets the Teflon-bonded, gas-fed electrodes at higher concentrations ($> 6\,M$) [3, 5]. The conductivity of trifluoromethane sulphonic acid is also low [3, 6] and the resulting kinetic voltage gain due to the increased oxygen solubility is offset by a resistive voltage loss due to the depressed conductivity. Other properties of the acid electrolytes such as electrochemical and thermal stability, low vapour pressure and acid strength are also of critical importance. Identification of alternative acid fuel cell electrolytes exhibiting properties superior to those of phosphoric acid remains a challenge.

The overall objective of the present investigation is to study the role of the nature of the acid electrolytes, particularly concentrated acids, on the oxygen electroreduction. A large number of perfluorinated phosphonic, phosphinic and sulphonyl imide acid electrolytes are being investigated in our laboratory. However, perfluorinated sulphonyl imides, particularly, bis(trifluoromethanesulphonyl)imide

have shown some interesting results. This paper discusses oxygen electroreduction in bis(fluorosulphonyl)imide and bis(trifluoromethanesulphonyl)imide. The behaviour of smooth platinum and the activity for oxygen reduction in these electrolytes have been studied using cyclic voltammetry. The solubilities and diffusion coefficients of oxygen have been determined using a micro-electrode technique [7]. The performance of the air cathode in these electrolytes in the micro fuel cell at 70° C has been examined. The specific conductivities and the wetting characteristics of the electrolytes have also been investigated.

2. Experimental details

Cyclic voltammetry and current–time transients experiments were performed using either a Pine RDE3 or PARC 176 Potentiostat and PARC 175 Universal Programmer, and the i–E and i–t data recorded on a YEW Type 3078 x–y Recorder. For cyclic voltammetry, a smooth platinum disc (area $= 0.07\,cm^2$) sealed in glass was used as the working electrode. The solubilities and diffusion coefficients of oxygen were determined using a platinum micro disc electrode (25 μm in diameter, 99.95% pure platinum, Johnson-Matthey) as the working electrode. The platinum disc electrodes were polished with diamond pastes of different grades, down to 1 μm, and then polished to a mirror finish with 0.05 μm alumina. The electrodes were then cleaned with a 1 : 1 mixture of concentrated nitric and sulphuric acids, followed by a thorough rinsing with distilled water. The counter electrode was a platinum flag. An *in situ* dynamic hydrogen electrode was used as a reference electrode. All voltammetry and transient experiments were carried out at room temperature.

The micro fuel cell used for obtaining the galvanostatic i–E curves was made of Kel-F. The cathode and the anode were high surface area Prototech standard gas diffusion electrodes (10% platinum loading on Vulcan XC-72). The electrodes were of circular shape with one surface (catalyst) exposed to the electrolyte. The gas was fed to the catalytic sites by diffusion through the pores of the Teflon backing. The apparant

surface exposed to the electrolyte was 1.1 cm^2. The gap between the cathode and the anode was 3 mm. The reference electrode compartment was separated by a Luggin, placed at a distance of 1 mm from the cathode. The total volume of the electrolyte in the micro fuel cell was 0.6 cm^3. Pure oxygen and hydrogen were circulated at 1.0 atm pressure at the rear of the cathode and the anode respectively. The fuel cell was operated under temperature control in an air thermostat (temperature controlled drying oven). The galvanostatic current–potential curves were recorded using a Stonehart Associate BC 1200 Potentiostat and a Hi-Teck PPR1 Waveform Generator.

Analar grade phosphoric acid was used and it was further purified using the procedure described elsewhere [8]. The perfluorinated sulphonyl imides were prepared by a literature method [9, 10]. Aqueous solutions were prepared using distilled water obtained from a reverse osmosis-distillation system.

3. Results and discussion

3.1. *Voltammetry*

Adsorbable impurities in the electrolytes adversely effect the oxygen reduction kinetics. It is therefore essential that the electrolytes be free from impurities. As a preliminary qualitative check on the purity level and the adsorption characteristics of the electrolytes, voltammograms on smooth platinum electrodes were recorded. To conserve the electrolytes, voltammetry experiments were performed in dilute solutions (0.1 M); voltammetry is regarded as sensitive to the adsorbable impurities at a 10^{-3} M level (at a potential sweep rate of 100 mV s^{-1}) and, therefore, it is anticipated that even in 0.1 M solution, voltammetry would provide sufficient information about the impurity levels in the electrolytes. Although voltammetry of platinum in both dilute and 85% phosphoric acid is known [8, 11, 12], the voltammetry of platinum in 0.1 M phosphoric acid has been included here for comparison. Fig. 1 shows the voltammograms of platinum in 0.1 M solutions of phosphoric acid, bis-(fluorosulphonyl)imide and bis(trifluorome-
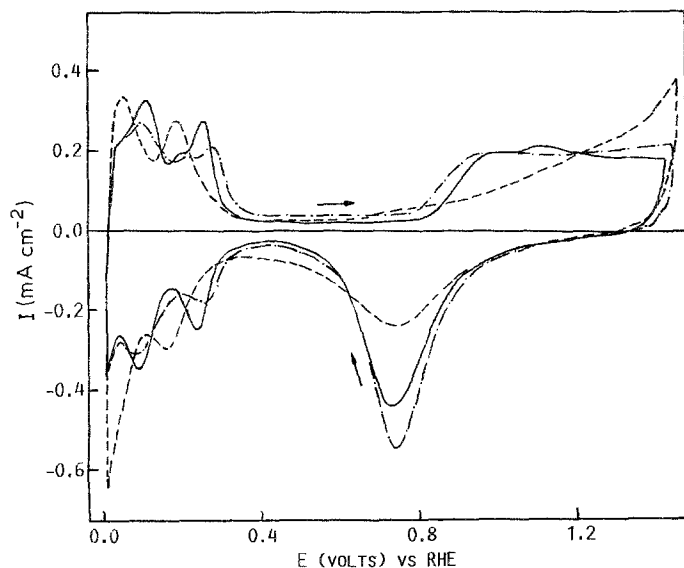
Fig. 1. Voltammograms of smooth platinum in 0.1 M solution saturated with nitrogen: H_3PO_4 (——); $(FSO_2)_2NH$ (— — —); $(CF_3SO_2)_2NH$ (— · — · —). Sweep rate, 100 mV s^{-1}; T, 20° C.

thanesulphonyl)imide, all saturated with nitrogen. The voltammograms were recorded after cycling the potential between 0.01 V and 1.4 V vs RHE until a steady-state behaviour was obtained. The voltammogram of platinum in phosphoric acid is similar to that reported in the literature and shows a well-characterized oxide formation region and reduction of the oxide and very symmetrical hydrogen adsorption–desorption peaks which indicate that the solution is relatively free from residual impurities.

The voltammogram of platinum in bis(fluorosulphonyl)imide, however, does not show a well-defined oxide formation region and the oxide reduction current is low, which indicates that the oxide formation has been suppressed. The hydrogen adsorption–desorption peaks are distorted and shifted to more negative potentials relative to phosphoric acid. This electrolyte hydrolyses in water to hydrogen fluoride and ammonium sulphate [9] and the depressed oxide formation reaction and distortion of the hydrogen adsorption–desorption peaks could be due to strong adsorption of the acid and/or the hydrolysis products on platinum.

The voltammogram of platinum in bis(trifluoromethanesulphonyl)imide shows a well-characterized oxide formation region and reduction of the oxide and symmetrical hydrogen adsorption–desorption peaks. The slightly higher current in the oxide formation region

(beyond 1.2 V vs RHE) is probably due to some minor impurities in the electrolyte. The impurity effect is more prominent in the voltammogram recorded at a potential sweep rate of 10 mV s^{-1} (Fig. 2). However, the impurity level is low and it has no appreciable effect on the oxide formation and hydrogen adsorption–desorption reactions. The strong anion adsorption on platinum displaces the oxide formation potential to a more positive value and the hydrogen adsorption region to a more negative value [4, 13]. The voltammogram of platinum in bis(trifluoromethanesulphonyl)imide shows a noticeable anodic shift in the hydrogen adsorption region and a cathodic shift in the oxide formation region, which suggests that the adsorption of bis(trifluoromethanesulphonyl)imide is weaker compared to that of bis(fluorosulphonyl)imide and phosphoric acid.

Fig. 3 shows the voltammograms for oxygen reduction on platinum in 0.1 M phosphoric acid, bis(fluorosulphonyl)imide and bis(trifluoromethanesulphonyl)imide solutions saturated with oxygen. A single irreversible wave corresponding to oxygen reduction is observed prior to the hydrogen adsorption peaks. The peak current density for oxygen is higher in bis(trifluoromethanesulphonyl)imide, but it is lower in bis(fluorosulphonyl)imide compared to the current density observed in phosphoric acid (see Table 1). The half-wave potential ($E_{1/2}$) for oxygen reduc-
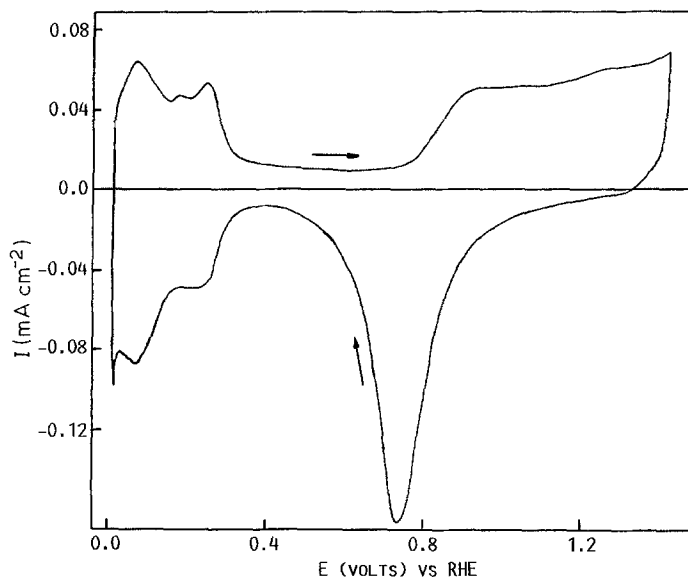
Fig. 2. Voltammogram of platinum in 0.1 M solution of $(CF_3SO_2)_2NH$ saturated with nitrogen. Sweep rate, $10\,mV\,s^{-1}$; T, $20°\,C$.

tion in bis(trifluoromethanesulphonyl)imide is 30 mV more positive and in bis(fluorosulpho-nyl)imide it is 160 mV more negative compared to the $E_{1/2}$ observed in phosphoric acid (Table 1). The lower current density and high overpotential for oxygen reduction in bis(fluorosulpho-nyl)imide suggest that the active sites on the electrode have been occupied by the impurities and/or by the acid itself which slow down the oxygen reduction kinetics. On the other hand,

high current density and lower overpotential in bis(trifluoromethanesulphonyl)imide   indicate that the electrolyte is relatively free from residual impurities and that it does not adsorb strongly on the platinum electrode.

3.2. Specific conductivity measurements

Hydrogen–oxygen fuel cells are usually operated at moderately high temperatures (> 190° C). In order to achieve such high operating temperatures the activity of water in the acid electrolytes must be low. This can be achieved by minimizing the water content in the acid electrolytes. However, very concentrated perfluorinated acids have poor conductivities [3] due to lack of a hydrogen-bonded network, and the conduction occurs only through the migration of protons in a highly viscous medium (in contrast to the Grotthus-type conduction mechanism operative in concentrated phosphoric acid). In the present study, attempts were made to use highly con-
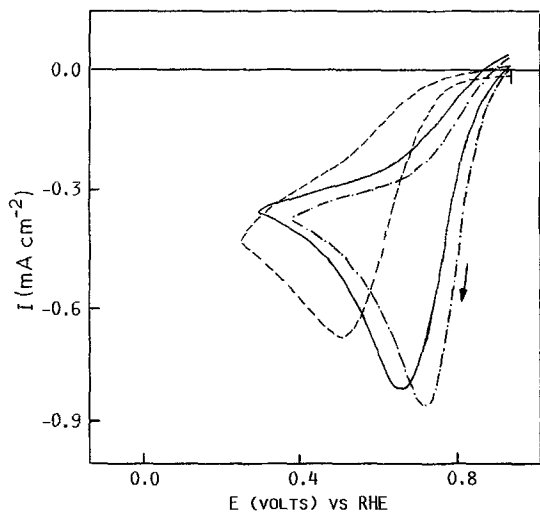

Fig. 3. Voltammograms for oxygen reduction at a smooth platinum electrode in 0.1 M solution saturated with oxygen: H_3PO_4 (———); $(FSO_2)_2NH$ (– – –); $(CF_3SO_2)_2NH$ (–·–·–·–). Sweep rate, $10\,mV\,s^{-1}$; T, $20°\,C$.

Table 1. Voltammetry data for oxygen reduction on platinum in 0.1 M solutions saturated with oxygen, T = 20° C

Electrolyte	i_p (mA cm^{-2})	$E_{1/2}$ (V) vs RHE
H_3PO_4	0.83	0.73
$(FSO_2)_2NH$	0.63	0.57
$(CF_3SO_2)_2NH$	0.85	0.77
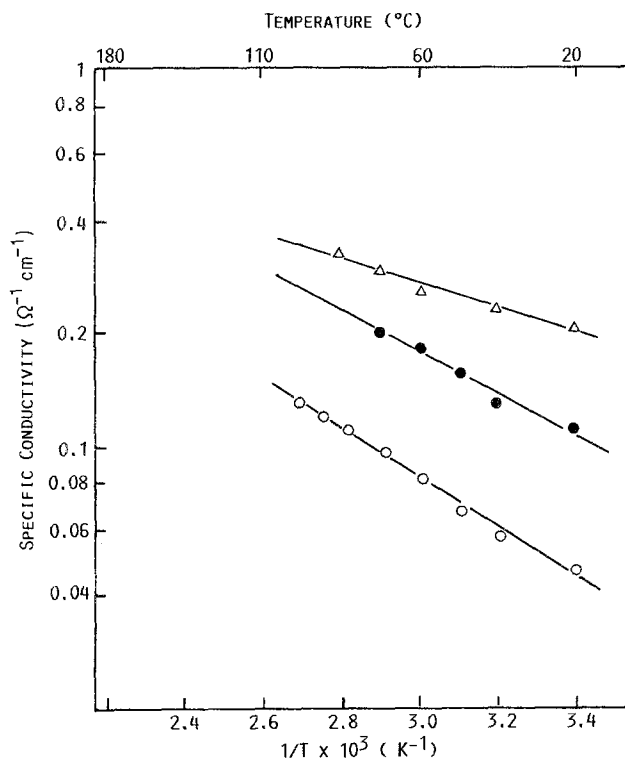
Fig. 4. Specific conductance of the acids $(M_{H_2O}/M_{H^+} = 3)$ as a function of the reciprocal temperature. $\triangle$, H_3PO_4; $\bigcirc$, $(FSO_2)NH$; $\bullet$, $(CF_3SO_2)_2NH$.

centrated acids in the fuel cell experiments with reasonable conductivities. The concentration of the perfluorinated sulphonyl imides was chosen such that for each available proton from the acid, three water molecules were added $(M_{H_2O}/M_{H^+} = 3)$. This ratio of water to proton was chosen in order to solvate the protons to obtain reasonable conductivity without diluting the acids too much.

The specific conductivities of the acids as a function of reciprocal temperature in the range between 20 and 80° C are shown in Fig. 4. The specific conductivity of each acid increases with temperature. However, the specific conductance versus $1/T$ curves for bis(fluorosulphonyl)imide and bis(trifluoromethanesulphonyl)imide are steeper compared to the curve for phosphoric acid, which shows that the activation energy for the ionization of phosphoric acid is greater than that for the imides. The specific conductivity of phosphoric acid at 80° C is higher than bis(fluorosulphonyl)imide and bis(trifluoromethanesulphonyl)imide by a factor of 2 to 3, but due to the difference in the activation energy of ionization of phosphoric acid and the imides, the conductivities of the imides at temperatures

$> 180°$ C will approach (within a factor of 1 to 2) the conductivity of phosphoric acid (see Fig. 4).

3.3. Contact angle with Teflon

A severe restriction imposed on fuel cell electrolytes for use with Teflon-type, gas-fed electrodes (e.g. Prototech) is that they can not wet Teflon; on wetting, the gas supply channels are blocked and the gas supply to the catalyst is severely hampered and occurs only through diffusion. It must be emphasized that the wetting characteristics of the electrolytes are related to the total water content; the electrolytes with high water content do not wet Teflon. The simplest method of studying the wetting ability of the electrolytes is by placing a drop of the electrolyte on a Teflon plate and observing visually whether the drop forms a spherical bead or spreads out; the electrolytes that form spherical beads are considered as non-wetting, whereas the electrolytes that spread out are considered as wetting electrolytes. The wetting properties of bis(fluorosulphonyl)imide and bis(trifluoromethanesulphonyl)imide were studied by placing a drop of the acid $(M_{H_2O}/M_{H^+} = 3)$
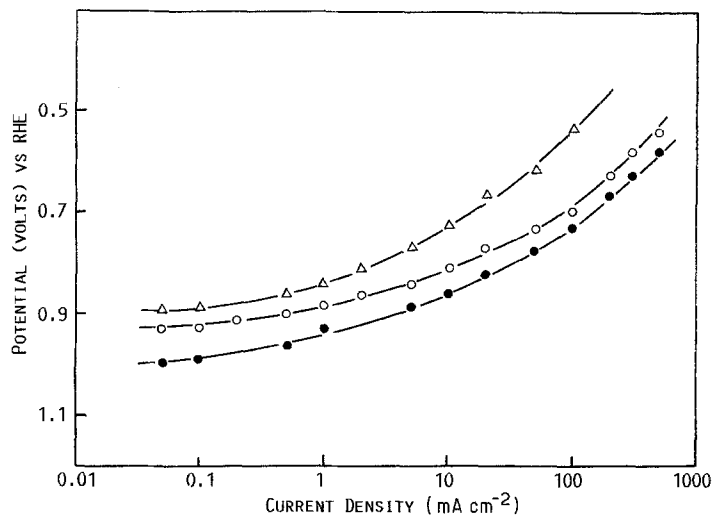
Fig. 5. Polarization curves of oxygen reduction at high surface area Proto-tech Standard Gas Diffusion Electrode (10% platinum loading on XC-72 carbon support) at 70°C. ○, H_3PO_4; △, $(FSO_2)_2NH$ and ●, $(CF_3SO_2)_2NH$. Acid concentration $M_{H_2O}/M_{H^+} = 3$.

on a Teflon-bonded, gas-fed electrode at 20°C. The electrolyte drops formed spherical beads which indicated that the electrolytes do not wet Teflon (at this particular water to proton ratio).

3.4. Performance of perfluorinated sulphonyl imides in the fuel cell

The galvanostatic polarization curves for oxygen reduction at an oxygen-fed Prototech standard gas diffusion electrode (10% platinum loading on Vulcan XC-72 carbon support) in phosphoric acid, bis(fluorosulphonyl)imide and bis(trifluoromethanesulphonyl)imide ($M_{H_2O}/M_{H^+} = 3$) at 70°C are shown in Fig. 5. The i–E curves have been corrected for the iR drop using the current interupter method [14]. The i–E curves were recorded by the point by point method. The electrode was polarized in both directions, but no appreciable hysteresis was observed. The performance of the cathode was found to improve after each cycle of polarization and after three to four cycles a steady-state behaviour was observed. This is probably due to the wetting of the active sites with time. The polarization curves shown in Fig. 5 were recorded after the fourth cycle.

The polarization curve in bis(fluorosulpho-nyl)imide is about 40 mV more negative in the lower current density range and numerically increases to 150 mV at 100 mA cm⁻², compared to the polarization observed in phosphoric acid

(Fig. 5). Above 100 mA cm⁻² the polarization increases rapidly. High polarization of the platinum-catalysed cathode is often associated with either the flooding of the gas supply channels or due to the strong adsorption of the electrolyte and/or the impurities on the catalyst. At the end of the experiment the electrodes were examined to check whether the electrolyte had wet the Teflon backing (gas supply channels) during the time scale of the experiment and the backing was found to be completely dry. Therefore, the high polarization can not be considered due to the flooding of the backing layer. This does not preclude the possibility of flooding of the gas-filled channels in the active layer. The more likely source of the high polarization, however, is that it is predominantly due to the strong interaction of the electrolyte, particularly the hydrolysis product, with the catalyst sites. Indeed, after obtaining the polarization curve, some white crystalline material, probably ammonium sulphate, was found in the fuel cell.

The polarization curve in bis(trifluorome-thanesulphonyl)imide is 70 mV more positive in the lower current density range than for phosphoric acid with the difference decreasing to 40 mV at 100 mA cm⁻², and with the polarization always being lower in bis(trifluorome-thanesulphonyl)imide than in phosphoric acid to the highest current density (500 mA cm⁻²) studied. This provides evidence that the oxygen reduction kinetics are faster in bis(trifluorome-
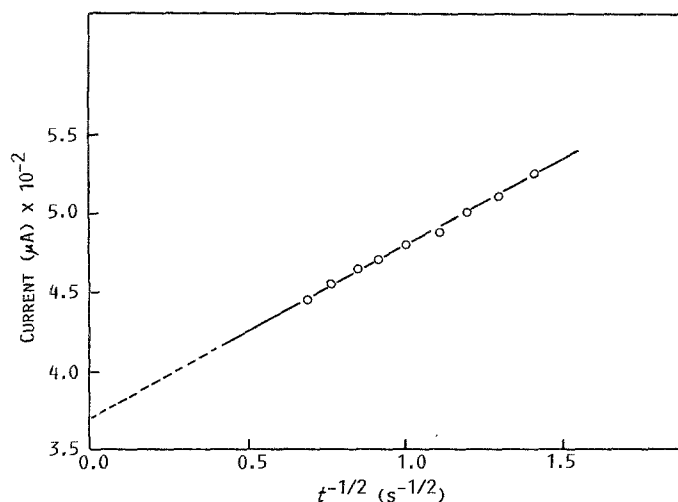
Fig. 6. Plot of i versus $1/t^{1/2}$ for oxygen reduction in 84% $(CF_3SO_2)_2NH$ at 25°C.

thanesulphonyl)imide. The catalytic sites do not appear to be blocked by the adsorption of bis(trifluoromethanesulphonyl)imide.

3.5. Measurements of oxygen solubility and diffusivity

The difference in oxygen reduction rate in various electrolytes is generally believed to be due to the differences in the degree of adsorption of the anion on platinum and the solubility and diffusivity of oxygen [4, 15, 16]. In order to understand which of these factors are important, the solubilities and diffusion coefficients of oxygen in 85% phosphoric acid and 84% bis-(trifluoromethanesulphonyl)imide were determined using a micro-electrode technique [7]. Before recording the i–t data, the platinum micro-electrode was pretreated by stepping the potential between 1.4 to 0.4 V (three times) and the i–t transients were then recorded by stepping the potential from 1.0 V, where the oxygen reduction is negligible, to 0.4 V, where oxygen reduction is assumed to be under diffusion control. From the intercept and the slope of i versus $1/t^{1/2}$ plots, the solubility (C_{O_2}) and diffusion coefficients (D_{O_2}) were calculated by using equations given by Winlove et al. [7],

$$C_{O_2} = B^2/nFAa^3 \qquad (1)$$

$$D_{O_2} = a^2A^2/\pi B^2 \qquad (2)$$

where A is the intercept, B is the slope, a is

the radius of the platinum micro disc, n is the number of electrons transferred and F is the Faraday constant. A typical i versus $1/t^{1/2}$ plot for oxygen reduction in 84% bis(trifluoromethanesulphonyl)imide is shown in Fig. 6. The values of the solubility and diffusion coefficient calculated by using equations 1 and 2 are $3.8 \times 10^{-3}\,mol\,l^{-1}$ and $6.53 \times 10^{-6}\,cm^2\,s^{-1}$, respectively. The solubility of oxygen in bis(trifluoromethanesulphonyl)imide is over an order of magnitude higher than in phosphoric acid. The diffusion coefficient in bis(trifluoromethanesulphonyl)imide is a factor of 5.4 higher than in phosphoric acid (see Table 2). Due to the unstability of bis(fluorosulphonyl)imide in water, no solubility and diffusivity data were obtained in this electrolyte.

4. Conclusions

The voltammetry curves and the relatively high polarization with gas-fed electrodes provide evidence that bis(fluorosulphonyl)imide adsorbs strongly on the electrode surface and the oxygen

Table 2. Solubilities and diffusion coefficients of oxygen in phosphoric acid and bis(trifluoromethanesulphonyl)imide

Electrolyte	Solubility (mole l^{-1})	Diffusion coefficient (cm² s⁻¹)
85% H_3PO_4	3.3×10^{-4}	1.21×10^{-6}
84% $(CF_3SO_2)_2NH$	3.8×10^{-3}	6.53×10^{-6}

reduction kinetics in this electrolyte are slow. Furthermore, bis(fluorosulphonyl)imide appears to hydrolyse and consequently is not suitable for fuel cell applications. The bis(trifluoromethane-sulphonyl)imide, however, appears to be relatively stable and free from adsorbable impurities. The voltammetry of smooth platinum (Fig. 1) suggests that this electrolyte does not adsorb strongly on platinum. The solubility and diffusion coefficient of oxygen in this electrolyte are considerably higher than in phosphoric acid. Therefore, it is proposed that the relatively low polarization with gas-fed electrodes in bis-(trifluoromethanesulphonyl)imide is due to the relatively weak adsorption on platinum and higher solubility of oxygen. The difference between the polarization curves for bis(trifluoro-methanesulphonyl)imide and phosphoric acid decreases with increasing current density. This suggests that the difference in diffusion coefficients is not a major factor since diffusion is more important at higher current densities. At a water to proton ratio of 3, this electrolyte does not wet Teflon and has a conductivity comparable to that of phosphoric acid at temperatures $> 180°$ C. This suggests that this electrolyte is a potential candidate for fuel cell applications. However, more studies, particularly concerning the performance of the cathode in the fuel cell in highly concentrated bis(trifluoromethane-sulphonyl)imide ($> 90\%$ by weight) at elevated temperature ($> 200°$ C) over extended periods (several hundreds of thousands of hours), would be necessary before claiming the superiority of this electrolyte over phosphoric acid.

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