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Investigations of ruthenium pyrochlores as bifunctional oxygen electrodes

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Abstract

The lead–ruthenates oxides were synthesized and characterized by X-ray diffraction and thermogravimetric analysis. Compounds in which part of the ruthenium is substituted with iridium were also prepared. The performance of these oxides for oxygen reduction and generation reactions was investigated in porous, gas-fed electrodes. The performance of pyrochlore oxide electrodes was shown to be excellent for oxygen reduction and generation reactions. It was observed that iridium substituted pyrochlores exhibit somewhat better performance for oxygen reduction than the unsubstituted compounds. The anodic corrosion resistance of pyrochlore-based porous electrodes was improved by using two different anionically conducting polymer overlayers, which slow down the diffusion of ruthenates and plumbate out of the electrode. The use of the conducting polymer overlayers resulted in improved performance of these electrodes.

1. Introduction

There has been a considerable interest in the development of bifunctional oxygen electrocatalysts that will reduce as well as generate oxygen for extended periods of time at moderate temperatures (e.g. ≤250 °C). Even the best catalysts, which are presently available such as Pt, show substantial irreversibility with the result that considerable energy is wasted. Interesting examples are the ruthenium pyrochlores. These pyrochlores with metallic conductivity, can be prepared in very high area forms, and also show high electrocatalytic activity for both oxygen reduction and generation [1–8]. In addition, rotating ring-disk electrode measurements provide evidence that the oxygen reduction proceeds by a parallel 4-electron pathway [2, 7]. Owing to the metallic conductivity and high surface area, these ruthenates are also good candidates for self-supported catalysts to avoid the problems associated with carbon oxidation, provided adequate stability can be achieved.

Due to low solubility in concentrated alkali, the transport of oxygen by diffusion through the solution phase at such low concentration is very slow. Consequently, it is necessary to use porous electrodes with gas-filled channels, which provide relatively short paths for oxygen to reach the reaction site on the electrode surface. In order to achieve better transport of oxygen two types of electrodes can be used as oxygen cathodes. These include hydrophilic and semi-hydrophobic type structure. The hydrophilic-type electrode consists of a fine pore layer on the electrolyte side and a coarse layer on the gas side. On the other rear side of the coarse layer an O_2 or air pressure is maintained in order to control the electrolyte meniscus in the region between pore and coarse layer where most of the O_2 reduction occurs. To maintain the gas pressure it is necessary to have a great control over the pore size distribution in the electrode. In addition, very high surface area is required in order to have the oxygen reduction at reasonably high current densities. Therefore, the fabrication of hydrophilic-type electrodes involves the sintered silver particles which make them considerably more expensive especially when the control of pore size distribution is involved. In addition, this electrode structure suffers with the transport problems of oxygen to the active region of the electrode.

In the semihydrophobic electrodes, on the other hand, the electrolyte meniscus in the porous layer is controlled by the contact angle larger than 90°. The preparation of the thin hydrophobic layer which allows the gas to diffuse, but not the electrolyte involves Teflon or Teflon and carbon mixture. The electrolyte side of the electrode contains a wetted high area carbon and the catalyst or in some cases high area catalyst (e.g. ruthenium pyrochlore). The O_2 is transported into the whole active layer primarily through Knudsen diffusion, which involves the gas-filled wicks or capillaries. These gas-filled capillaries or wicks are made up of Teflon particles in chain like clusters that extends into the active layer. The semihydrophobic electrodes were used in the present investigations. This paper will present the electrochemical performance of the gas-fed ruthenate electrodes for O_2 reduction and generation.

2. Experimental details

The lead–ruthenium pyrochlores were synthesized and purified according to the method reported by Horowitz et al. [3]. This method involves an alkaline aqueous solution both as a means of reacting the appropriate metal cations by precipitation and subsequently as a medium for the crystallization of the precipitate in the presence of oxygen. The salts used were $Ru(NO)(NO_3)_3$, 1.5% (w/v) (Strem) and $Pb(CH_3COO)_2 \cdot 3H_2O$ (MCB, reagent grade). The KOH solutions were prepared from low carbonate KOH pellets (Fluka, puriss). The salts were mixed in the appropriate amounts to achieve the desired stoichiometries. The reaction was carried out for 24–72 h, until the supernatant solution was free of detectable amounts of the reactant metal ions. The suspension was filtered and washed with ultrapure water and glacial acetic acid in order to leach out any lead oxide formed during the reaction. The material was then heat-treated at high temperatures (350–750 °C) in air.

Porous gas-fed electrodes were fabricated as follows. The Teflon T30B suspension was diluted approximately to 2 mg cm^{-3} in water and then slowly added to an aqueous suspension of 38 mg cm^{-3} of the pyrochlore and 35 mg of air-oxidized Shawinigan black (Chevron Chemical, Olefins and Derivatives Div., Houston, TX) which has been partially oxidized for 1 h at 600 °C. The suspension was filtered using a 1 μm filter membrane. The resulting paste was kneaded with a spatula until slightly rubbery, shaped into a 1.75 cm diameter disk in a stainless steel die using hand pressure and then pressed at a pressure of $\sim$100 kg cm^{-2}. The disk was applied to a 0.5 mm thick disk of a Teflon–carbon hydrophobic backing material containing silver-plated nickel mesh (Electromedia, Englewood, NJ). A final pressing was done at $\sim$300 kg cm^{-2} at room temperature and then heat-treated at $\sim$280 °C for 2 h in flowing helium.

In some cases a 1.75 cm diameter disk of a partially fluorinated anion exchange membrane material (Type 4035, RAI, Hauppage) was pressed onto the electrolyte side of the electrode at 200 kg cm^{-2}. In other experiments a mixture of poly(dimethyl-diallyl-ammonium)-chloride (DMDDAC, 15 wt% in aqueous solution, polysciences) and Nafion 117 (5 wt% in alcohol solution, Aldrich) was diluted by a factor of 6 by volume and painted onto the electrolyte side of the porous electrode and allowed to air-dry.

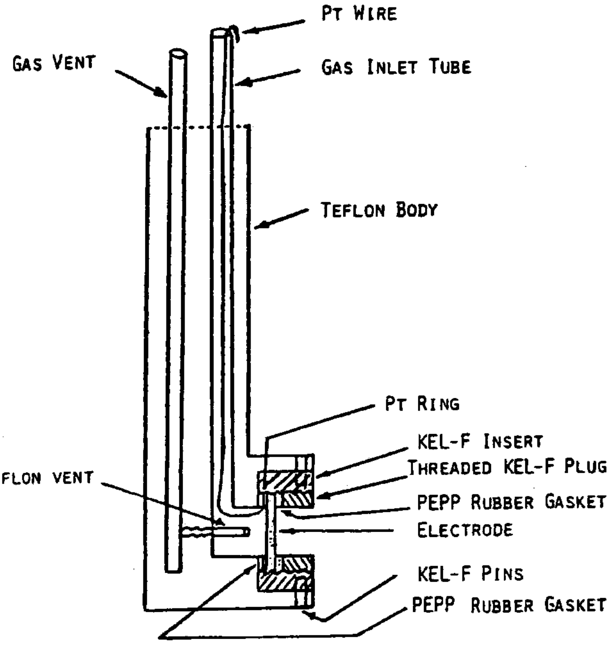

Fig. 1. Schematics of the electrode holder for gas-fed electrode measurements.

The porous gas-fed electrode was placed in a special screw-cap-type Kel-F holder that holds the electrode vertically between a Pt foil current collector on the gas-side and a polyethylene – polypropylene rubber gasket on the electrolyte side (Figure 1). A stream of either air or O_2 was directed at the back of the electrode. The area exposed to the electrolyte was 0.97 cm^2. The O_2 reduction measurements were performed galvanostatically in 5.5 M KOH at 25 °C with a fast-action potentiostat (BC-1200, Stonehart Associates) using the current interruption method to correct for solution-phase IR drop external to the gas-fed electrode.

3. Results and discussion

In porous electrodes gas-filled channels provide relatively short path for oxygen to reach the reaction site on the electrode surface consisting of carbon and the pyrochlore oxide particles. The carbon surface used in these gas-fed electrodes is a catalyst in alkaline solution in its own right to reduce O_2 to HO_2^- by 2-electron reduction. The exchange current densities and the carbon area are sufficiently high so that the electrode potentials prevailing locally within the porous electrode in alkaline electrolytes are expected to follow the Nernst equation for the 2-electron reduction of oxygen to peroxide as suggested by Yeager [9]. The peroxide activity can be depressed to a low value by the use of an additional catalyst, which can eliminate peroxide effectively. The catalysts used in this work as the peroxide decomposer include ruthenium based pyrochlore oxides.

3.1. *Lead-substituted pyrochlores*

Part of the Ru was substituted with Pb to form a series of 'lead rich' pyrochlores. The performance of gas-fed electrodes based on these compounds such as

$Pb_2[Pb_{0.33}Ru_{1.67}]O_{6.5}$ and $Pb_2[Pb_{0.2}Ru_{1.8}]O_{6.5}$ has been found to be superior to that of the stoichiometric pyrochlore $Pb_2Ru_2O_{6.5}$ This is related to the fact that the lead-rich compounds can be prepared in higher area form [1, 3]. In the present studies, the pyrochlores $Pb_2[Pb_{0.33}Ru_{1.67}]O_{6.5}$ and $Pb_2[Pb_{0.2}Ru_{1.8}]O_{6.5}$ had surface area of 55 m^2 g^{-1} and 44 m^2 g^{-1}, respectively, while stoichiometric pyrochlore $Pb_2Ru_2O_{6.5}$ had a surface area of 35 m^2 g^{-1}. Figures 2 and 3 show the performance of gas-fed electrode made by the ruthenium pyrochlores $Pb_2[Ru_{2-x}Pb_x]O_{6.5}$ for oxygen reduction and generation. In the cathodic mode, the O_2 reduction and carbon oxidation to carbon dioxide or carbonate probably occur via the peroxide mechanism. The linear region in the curves is the Tafel region in which activation control is predominant. At high current densities most of the O_2 reduction polarization curves show significant deviation from linearity. This is due to the fact that at these current densities the potential is controlled not only by the catalyst activity for O_2 reduction but also by other factors such as mass transport problems and ohmic losses within the active layer. It can also be seen from Figure 2 that the pyrochlore with the chemical formula $Pb_{1.67}[Ru_{0.33}Pb_{1.67}]O_{6.5}$ gave the best performance. However, the performance degraded with times especially when the cathodic measurements were taken following the anodic measurements. The loss in the performance is due to dissolution, which occurred during the anodic polarization measurements. The O_2 generation behavior of $Pb_2Ru_2O_{6.5}$ (35 m^2 g^{-1}) behavior was excellent, being one of the best tested (Figure 3). The polarization curves for O_2 reduction may be correlated roughly to the surface area of the individual pyrochlores.

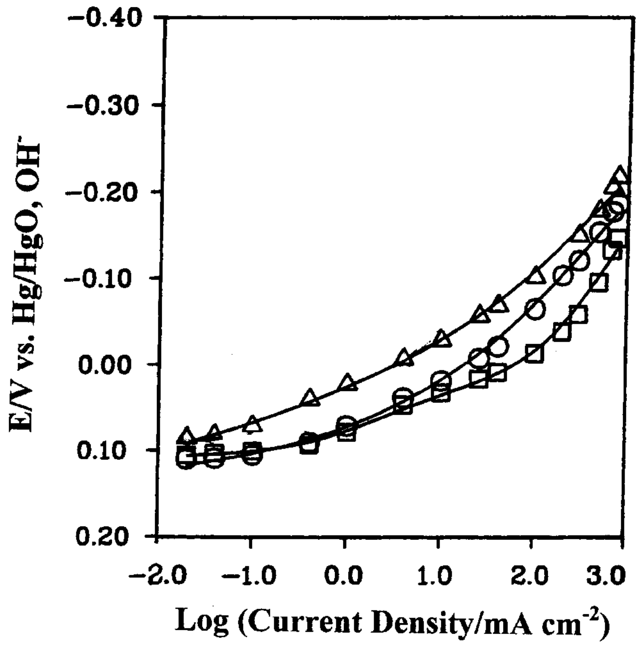

Fig. 2. Polarization curves for O_2 reduction with porous O_2-fed (1 atm) electrodes in 5.5 M KOH at 25 °C. The electrode contained 15.8 mg cm^{-2} pyrochlore, 14.6 mg cm^{-2} air-oxidized Shawinigan black, and 12.2 mg cm^{-2} Teflon T30-B, and was heat treated at 280 °C for 2 h in flowing helium. (○) $Pb_2Ru_2O_{6.5}$; (□) $Pb_2[Ru_{1.67}Pb_{0.33}]O_{6.5}$; (△) $Pb_2[Ru_{1.8}Pb_{0.2}]O_{6.5}$.

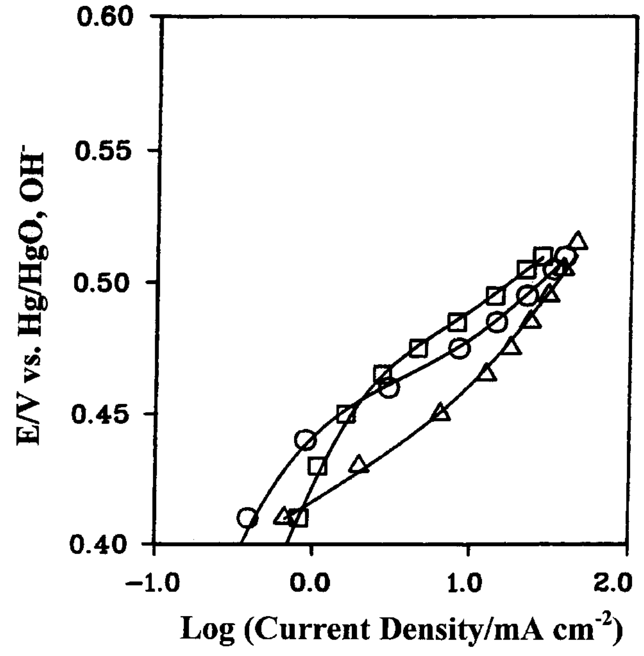

Fig. 3. Polarization curves for O_2 generation with the porous electrodes with an O_2-fed (1 atm) electrode in 5.5 M KOH at 25 °C. The electrode preparation was the same as described in Figure 1. (○) $Pb_2[Ru_{1.8}Pb_{0.2}]O_{6.5}$; (□) $Pb_2[Ru_{1.67}Pb_{0.33}]O_{6.5}$; (△) $Pb_2Ru_2O_{6.5}$.

3.2. *Iridium-substituted pyrochlores*

The electrochemical behavior, including the O_2 reduction and generation activity, as well as the stability in the anodic mode, can be modified by substituting a part of either the Pb or Ru with other metals. One such type of substitution, which was examined, is that of Ir for Ru in the B site of the pyrochlore structure. It is expected to be more resistant to anodic dissolution than Ru [10]. The ionic radii are very similar [11–12] and the lattice parameters for $Pb_2Ru_2O_{6.5}$ are very similar [13]. Thus there is probably a continuous range of solid solutions possible. Horowitz et al. [3] mentioned that it is possible to prepare such compounds using the alkaline solution technique. Two compounds were prepared and the X-ray diffraction indicates a single pyrochlore phase. Although the effects on the O_2 reduction are slight, they are encouraging (Figure 4). The effects on the oxygen generation were also slight (Figure 5). However, these iridium-substituted pyrochlores showed significantly higher stability in the anodic mode than their unsubstituted counterparts. It is not clear at present to what extent these effects might be due to changes in the wetted catalyst area. With iridium in the pyrochlore structure ($Pb_2Ru_xIr_{1-x}O_{6.5}$), mixed with air oxidized Shawinigan black shows somewhat better performance for O_2 reduction (Figure 4). However, no direct correlation was found between the catalytic activity for O_2

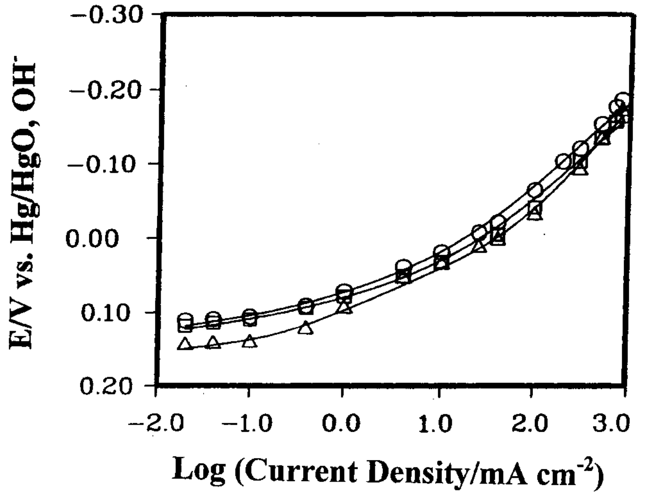

Fig. 4. Polarization curves for O_2 reduction with porous O_2-fed (1 atm) iridium substituted pyrochlore electrodes in 5.5 M KOH at 25 °C. The electrode contained 15.8 mg cm^{-2} Ir-substituted pyrochlore, 14.6 mg cm^{-2} air-oxidized Shawinigan black, and 12.2 mg cm^{-2} Teflon T30-B, and was heat treated at 280 °C for 2 h in flowing helium. (○) $Pb_2Ru_2O_{6.5}$; (□) $Pb_2Ru_{1.2}Ir_{0.8}O_{6.5}$; (△) $Pb_2Ru_{1.5}Ir_{0.5}O_{6.5}$.

reduction (Figure 4) and generation (Figure 5) and x in the above formula.

3.3. *Cobalt-doped pyrochlores*

Cobalt is often a constituent of O_2 reduction and generation catalysts. Attempts were made to synthesize the pyrochlore oxides in which small amount of Co (2–5%) was doped within the pyrochlore structure. The gas-fed electrode performance of two such electrodes is shown for O_2 reduction and generation reactions in Figures 6 and 7. The polarization curves for $Pb_2Ru_2O_{6.5}$ are also shown in the figures for comparison purposes. It can be seen from these figures that O_2 reduction and generation activity of these compounds is poorer than that of $Pb_2Ru_2O_{6.5}$. This is due to a number of reasons that include the low surface area of these compounds expected from the 950 °C synthesis temperature, change in the oxygen deficiency and effect of decrease in the Pb ratio in the pyrochlore composition.

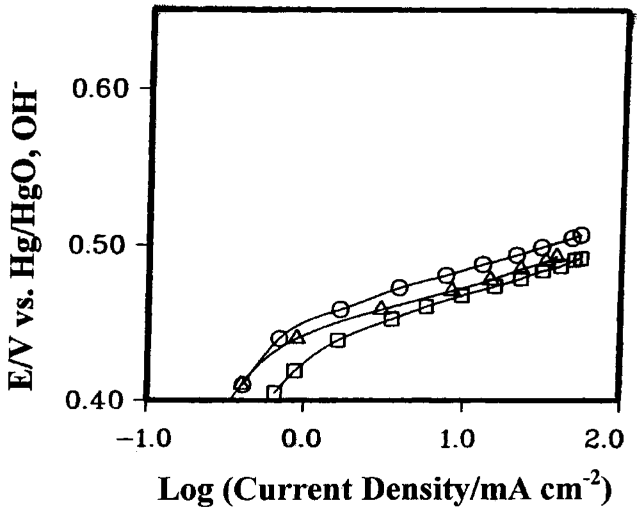

Fig. 5. Polarization curves for O_2 generation with the porous electrodes with an O_2-fed (1 atm) Ir-substituted pyrochlore electrodes in 5.5 M KOH at 25 °C. The electrode preparation was the same as described in Figure 3. (○) $Pb_2Ru_{1.5}Ir_{0.5}O_{6.5}$; (□) $Pb_2Ru_{1.2}Ir_{0.8}O_{6.5}$; (△) $Pb_2Ru_2O_{6.5}$.

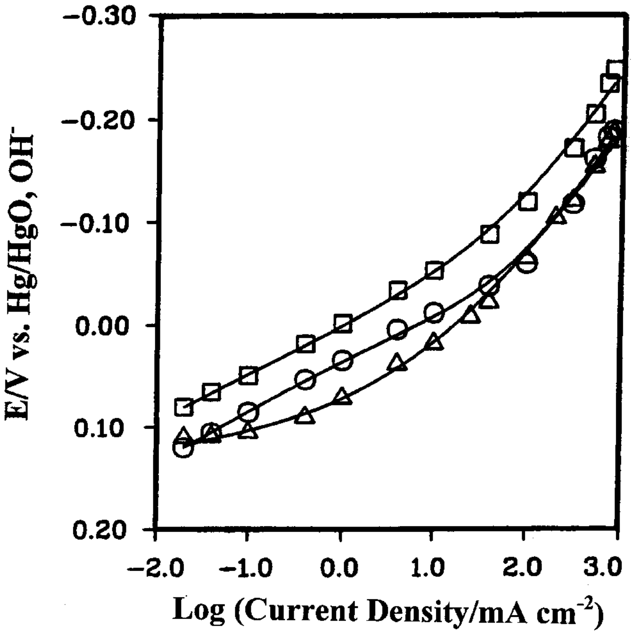

Fig. 6. Polarization curves for O_2 reduction with porous O_2-fed (1 atm) Co-doped ruthenium pyrochlore electrodes in 5.5 M KOH at 25 °C. The electrode contained 15.8 mg cm^{-2} Co-doped ruthenium pyrochlore, 14.6 mg cm^{-2} air-oxidized Shawinigan black, and 12.2 mg cm^{-2} Teflon T30-B, and was heat treated at 280 °C for 2 h in flowing helium. (○) $Pb_{1.5}Co_{0.5}Ru_{0.2}O_{6.5}$, (□) $Bi_{1.5}Co_{0.5}RuIr_{6.5}$; (△) $Pb_2Ru_2O_{6.5}$.

3.4. *Use of ionically conducting polymers*

At the potential involved in the anodic mode the ruthenate pyrochlores have substantial equilibrium solubility in concentrated alkaline electrolyte. This results in the loss of catalyst into the bulk solution and a decline in catalytic activity. Furthermore, the hydrogen generation counter electrode may become contaminated with reduction products from the pyrochlores. To solve this problem it may be necessary to use ionically conductive solid polymer or an anion exchange membrane to immobilize the pyrochlore catalyst within this polymer.

Due to susceptibility of many of these compounds to anodic dissolution, it would be desirable to prevent soluble species from leaving the porous electrode. A possible approach is to use a conducting solid ionomer either as a replacement for the liquid electrolyte within the porous O_2 cathode or as an overlayer on the electrolyte side of the electrode. For bulk alkaline electrolytes, an anion exchange polymer is needed with a transference number close to unity for the OH^- ion. Such a membrane may not completely block the transport of the lead and ruthenium, which are expected

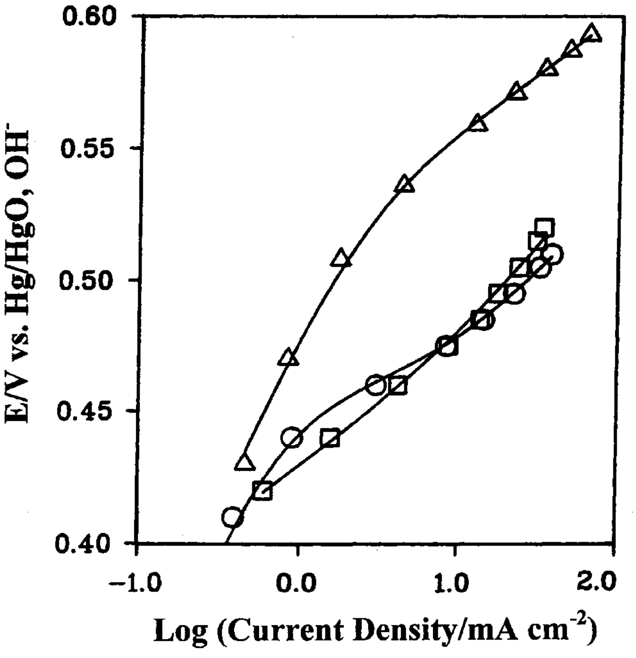

Fig. 7. Polarization curves for O_2 generation with the porous electrodes with an O_2-fed (1 atm) Co-doped ruthenium pyrochlore electrodes in 5.5 M KOH at 25 °C. The electrode preparation was the same as described in Figure 5. (○) $Pb_{1.5}Co_{0.5}Ru_{0.2}O_{6.5}$; (□) $Bi_{1.5}Co_{0.5}RuIr_{6.5}$; (△) $Pb_2Ru_2O_{6.5}$.

to be in complex anionic form. Even though the dissolved species are ionic, (RuO_4^{2-}, $HPbO_2^-$, PbO_3^{2-}), they should diffuse relatively slowly in such ionomers due to size and electrostatic effects. Two types of ionomers were used in this work. The first was a partially fluorinated anion exchange membrane (RAI 4035) as an overlayer. The second was a hydrogel coating, which consisted of a mixture of poly(dimethyl-diallyl-ammonium)chloride (DMDDAC), and Nafion [14]. The hydrogel coating becomes an ingredient of the active layer and fills the volume normally occupied by the liquid electrolyte and possibly improve the performance through an increase in the O_2 concentration associated with the polymer fluorocarbon backbone. The effect of these membranes on the performance in O_2 reduction and generation is shown in Figures 8 and 9. It can be seen from Figure 8 that the effect of these membranes in O_2 reduction mode is negligible in the Tafel region. However, with both ionomers there is an improvement in the O_2 generation performance (Figure 9). The RAI membrane exhibited a definite effect in slowing down the release of ruthenates into the solution when an electrode made from $Pb_2[Ru_{1.67}Pb_{0.33}]O_{6.5}$ was in the O_2 generation mode (Figure 9). This can be explained by pointing out that the inhibition of the anodic dissolution, i.e., the slowing down the progressive changes in the surface composition of the material that would occur during the dissolution. This in turn gives better performance in the O_2 generation mode.

The pre-cast ionomer layer was not expected to have a significant effect on the oxygen reduction, and this turned out to be the case (Figure 8). With the hydrogel coating, however, the ionomer can come into more intimate contact with the catalyst in the porous layer and possibly improve the performance through an increase in the oxygen concentration associated with the polymer fluorocarbon backbone. With both ionomers there was an improvement in the oxygen generation performance (Figure 9). This was not expected, but can be explained by pointing out that the inhibition of the anodic dissolution would slow down the progres-

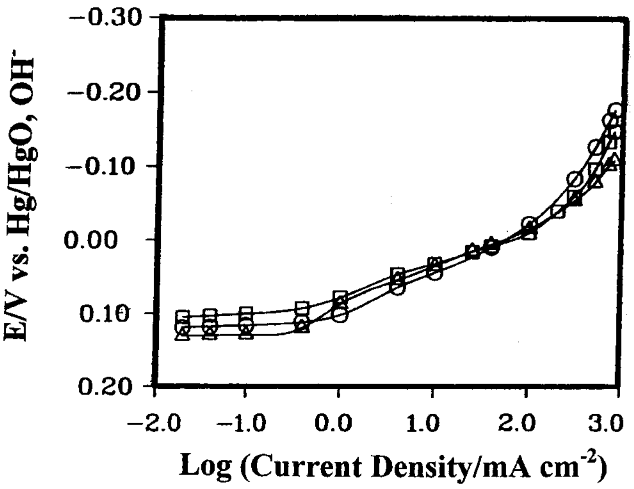

Fig. 8. Polarization curves for O_2 reduction with porous O_2-fed (1 atm) ruthenium pyrochlore $Pb_2[Ru_{1.67}Pb_{0.33}]O_{6.5}$ electrodes in 5.5 M KOH at 25 °C. The electrode contained 15.8 mg cm^{-2} ruthenium pyrochlore, 14.6 mg cm^{-2} air-oxidized Shawinigan black, and 12.2 mg cm^{-2} Teflon T30-B, and was heat treated at 280 °C for 2 h in flowing helium. The preparation of the hydrogel coating for curve 2 is described in the text. The RAI membrane was pressed onto the solution side of the electrode. (○) RAI (4035); (□) No membrane; (△) Hydrogel (DMDAAC + Nafion).

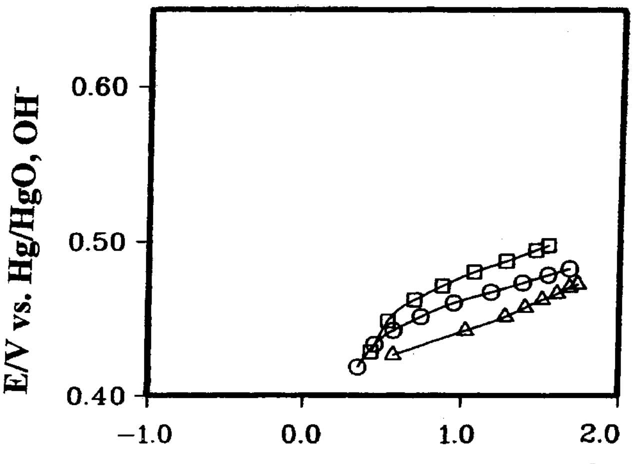

Fig. 9. Polarization curves for O_2 generation with the porous $Pb_2[Ru_{1.67}Pb_{0.33}]O_{6.5}$ electrodes with an O_2-fed (1 atm) ruthenium pyrochlore electrodes containing ionically conductive polymer membranes in 5.5 M KOH at 25 °C. Other experimental conditions are the same as in Figure 8. (○) Hydrogel (DMDAAC + Nafion); (□) No membrane; (△) RAI (4035).

sive changes in the surface composition of the material that would occur during the dissolution.

3.5. *Self-supported pyrochlores*

Under conditions of high temperature and O_2 pressure, such as would be used in high-performance alkaline fuel cells, it may be necessary to completely avoid the use of carbon matrices. This is because the use of carbon as support material in the O_2 cathodes presents problems with respect to its oxidation, which may result in structural failures. Consequently, it is important to find some other compounds that can act as a catalyst as well as a support. Ruthenium pyrochlores offer a good possibility for this purpose [15]. These oxides have very high area and metallic conductivity. Gas-fed electrode measurements for oxygen reduction and generation on the pyrochlore $Pb_2Ru_2O_{6.5}$ in self-supported form (i.e., without high-area carbon in the active layer) were taken and these are shown in Figures 10 and 11. It was found that the catalyst is very active both for O_2 reduction and generation. The activity, however, for O_2 reduction diminishes with time in short term tests. This is due to the problems in optimizing the electrode structure due to less porous nature of the material. Within the statistical accuracy of the measurement, the oxygen reduction current was first order with respect to the O_2 partial pressure over the range 1 to 10 mA cm^{-2}. Deviations from linearity of the polarization curves in the low-current density range are associated with the surface redox couples on the pyrochlore and the rate-determining peroxide decomposition within the porous electrode. Deviations in the high-current density range are most likely due to ohmic and/or mass-transport limitations. Yeager and coworkers [16] have also observed that the structure and performance of the self-supported electrode can be greatly improved with the use of a poreformer such as ammonium carbonate. This is because the use of poreformers provides better pore due to decomposition products formed during the heat-treatment of the electrode.

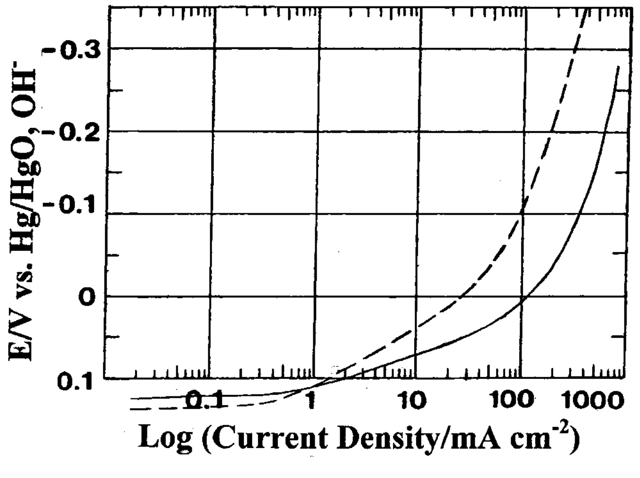

Fig. 10. Polarization curves for O_2 reduction with the self-supported $Pb_2Ru_2O_{6.5}$ porous O_2-fed (1 atm) electrodes in 5.5 M KOH at 25 °C. The electrode contained 54.2 mg cm^{-2} pyrochlore, 4.1 mg cm^{-2} Teflon T30-B, and was heat treated at 280 °C for 2 h in flowing helium. (Solid line: First oxygen reduction run; Dashed line: Sixth oxygen reduction run).

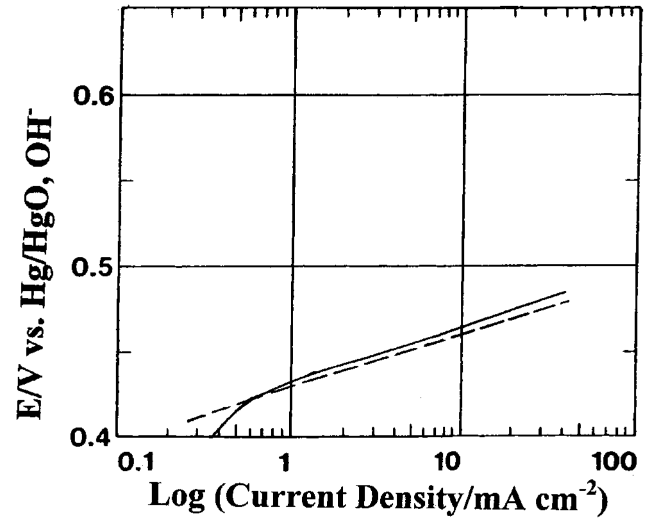

Fig. 11. Polarization curves for O_2 generation with the self-supported $Pb_2Ru_2O_{6.5}$ porous electrodes with an O_2-fed (1 atm) electrode in 5.5 M KOH at 25 °C. The electrode preparation was the same as described in Figure 10. (Dashed line: First oxygen generation run; Solid line: Second oxygen generation run).

4. Conclusions

The performance of porous gas-fed electrodes shows that these ruthenium-based pyrochlores are quite effective catalysts for the oxygen reduction and generation reactions. However, they suffer with stability problems in the anodic mode. There are several factors responsible for the stability problems of these pyrochlores. Such factors include the crystallinity and the presence of impurity phases such as RuO_2 and PbO. One can determine the importance of the crystallinity as long as one realizes that the crystallinity of a given sample can not be improved without decreasing the BET area. However, use of anion-conducting polymers both as membrane overlayers and as an integral component of the gas-diffusion electrode promises to alleviate this problem. Further improvements are also needed in gas-diffusion electrode fabrication techniques in order to achieve higher performance and stability.

Acknowledgements

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