Electrode materials for intermediate temperature proton-conducting fuel cells

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Abstract

Some electrode materials for intermediate temperature proton-conducting fuel cells are analysed from the perspective of surface reaction and ionic conductivity type. The performance of H_2/O_2 fuel cells using these materials as electrodes with $LiNaSO_4$–Al_2O_3 as the electrolyte indicates that Ni–Al alloy, Ni–Al_2O_3 catalyst and Ni–YSZ cermet are potential candidates for anode materials and that $LiNiO_2$, $LiCoO_2$, Ag–SnO_2 and $La_{0.8}Sr_{0.2}MnO_3$ are good candidates for cathode materials. Among the tested electrode materials, for the same electrolyte, the $LiNiO_2$/Ni–Al_2O_3 electrode pair gives the best cell performance.

1. Introduction

Intermediate temperature fuel cells are currently attracting interest [1–5]. For high temperature oxygen-ion-conducting fuel cells using YSZ as electrolytes it was demonstrated that $La_{0.8}Sr_{0.2}MnO_3$ and Ni–YSZ are ideal cathode and anode materials, respectively. However, reports involving electrode materials for intermediate temperature proton-conducting fuel cells are scarce. According to current investigation, only few materials exhibit high proton conductivity at intermediate temperatures [3, 4]. The proton conduction of $LiNaSO_4$ was demonstrated in a hydrogen concentration cell to be the same, as described elsewhere, for NaCl–Al_2O_3 composite [6]. In this work, the selection of electrode materials for intermediate temperature fuel cells are discussed, the effects of conductivity types on the electrode processes for proton-conducting fuel cells are analysed and, the performance of cells incorporating different electrode materials and using $LiNaSO_4$–Al_2O_3 as the electrolyte are presented.

2. Experimental details

The electrolyte $LiNaSO_4$–Al_2O_3 was prepared as follows. Analytically pure $Li_2SO_4.H_2O$ and Na_2SO_4 with a 1:1 molar ratio was mixed and ground in an agate mortar for 30 min. The mixture was calcined at 700 °C for 12 h, quenched to room temperature and ground to powders again. X-ray diffraction test indicates that the obtained powders are composed of pure $LiNaSO_4$ [7]. A calculated amount of α-Al_2O_3 was then added to the as-prepared $LiNaSO_4$ powders. The mixed powders were ground, pressed as pellets and calcined at 700–800 °C for a furhter 12 h.

The electrode materials were prepared by various methods, such as solid state reaction for preparation of the YSZ in Ni–YSZ and sol–gel processes for Ni–Al_2O_3, Ag–SnO_2, $LiNiO_2$, $LiCoO_2$, $LiMn_2O_4$, $La_{0.8}Sr_{0.2}MnO_3$ [8–10].

The fuel cells were constructed by pressing the electrode and electrolyte powders, sandwiched layer by layer. In general about 10 wt % of carbon powder was added to the electrode materials to ensure porosity to facilitate the diffusion of gases into the three-phase boundary (TPB). The cell configuration was

$$O_2 \,|\, \text{cathode} \,|\, LiNaSO_4\text{–}Al_2O_3 \,|\, \text{anode} \,|\, H_2 \qquad (1)$$
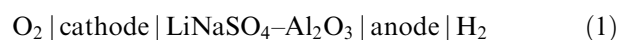
where the H_2 and O_2 were commercially pure.

The set-up for measurements was a single cell as described in [5]. The electrolyte layers were 13 mm in diameter and 1.2 mm in thickness. About 0.6 cm^2 of the cell area was exposed to the gases. The I/V curves of the cells were obtained through TakedaRiken TR6840 digital multimeters (Japan) under various loads at different operating temperatures.

3. Results and discussion

3.1. *Selection of anode materials*

For the anode material of a proton-conducting fuel cell high electronic conductivity and good catalytic activity to the following electrode reaction are necessary:

$$H_2 - 2e^- \rightarrow 2\,H^+ \tag{2}$$

Generally, precious metals (e.g., Pt or Pd) are good choices from this point of view but their application is limited due to their cost. The alternative choices are certain transition metal elements, such as Co and Ni, although Co is relatively expensive. Therefore, nickel is usually selected as the main component of the anode materials of fuel cells. As a metal, nickel powders, particularly those with small particle sizes, are easy to sinter at high temperature. Two methods are available to prevent the coarsening of nickel particles: the addition of a second support phase, as in the case of Ni–YSZ cermet for high temperature ceramic fuel cells [11], and the formation of alloys, such as Ni–Cr or Ni–Al, as have been applied in molten carbonate fuel cells (MCFC) [12]. In our experiments, Ni–Al alloy was used as the anode. When used with LiNaSO$_4$–Al$_2$O$_3$ as the electrolyte, LiCoO$_2$ was used as the cathode. The performance of such a cell shown in Figure 1 indicates that Ni–Al alloy is a candidate for anode materials for intermediate temperature fuel cells. Ni–YSZ, which has been used in high-temperature ceramic fuel cells, was also used as anode material for our intermediate temperature proton-conducting fuel cells as shown in Figure 2. Eguchi et al. [13] reported that, below 950 °C, Ni–Al$_2$O$_3$ catalysts absorb much more hydrogen than Ni–YSZ, which would be beneficial to the catalytic activity of Reaction 2. In an oxygen–ion conducting fuel cell using YSZ as the electrolyte, the oxygen–ion conductivity of YSZ in the Ni–YSZ cermet allows the electrode processes to occur over the entire anode surface [14]. If Ni–YSZ is used as the anode in a fuel cell using a proton conducting electrolyte, the beneficial effects that the oxygen–ion conductivity of YSZ has on the anode reaction process in an oxygen–ion conductor fuel cell [12], may not be occurred. Therefore, from this point of view, there may be no difference between using YSZ or Al$_2$O$_3$ as the second phase for a proton conductor fuel cell, as shown in Figure 3(a) in which the black profile represents YSZ or Al$_2$O$_3$ support. The
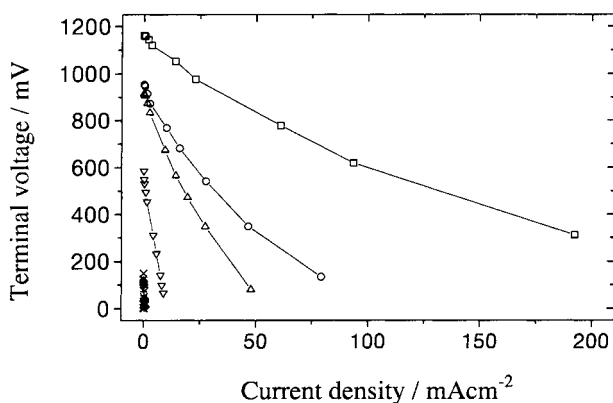

Fig. 2. Performance of cell La$_{0.8}$Sr$_{0.2}$MnO$_3$/LiNaSO$_4$–Al$_2$O$_3$/Ni–YSZ in H$_2$/O$_2$. Key: ($\Diamond$) 600, ($\triangledown$) 650, ($\triangle$) 700 and ($\bigcirc$) 750 °C.

anode reaction (Reaction 2) is expected to occur only at the three-phase (electrode, electrolyte and gas) boundary (TPB) sites. By analogy, a cermet anode composed of nickel and a support with high proton conductivity may benefit the anode reaction processes in fuel cells using proton conductors as electrolytes, because Reaction 2 can occur at both the TPB sites and the boundary sites between nickel and the support particles (Figure 3(b)). It is supposed that both YSZ and Al$_2$O$_3$ do not exhibit proton conduction. As shown in Figure 3(a), Reaction 2 can occur at the TPB sites. Under these circumstances, the main difference of this anode material may be attributed to its catalytic activity to Reaction 2. Referring to the experimental results of [13], Ni–Al$_2$O$_3$ was selected as the anode. The chemical and thermal compatibility between the electrolyte (LiNaSO$_4$–Al$_2$O$_3$) and the anode (Ni–Al$_2$O$_3$) was also considered in the

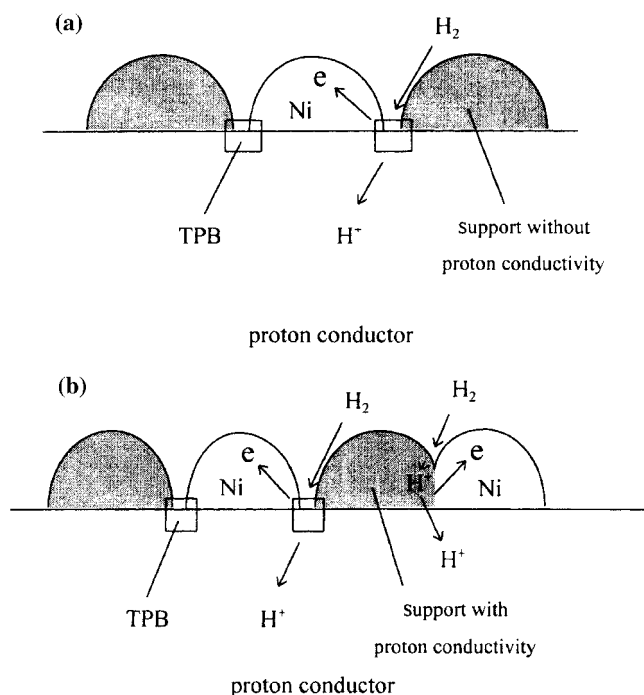
Fig. 3. Schematic diagram of the anode surface (a) without and (b) with a proton-conducting support for a proton-conducting fuel cell.

Fig. 1. Performance of cell LiCoO$_2$/LiNaSO$_4$–Al$_2$O$_3$/Ni–Al in H$_2$/O$_2$. Key: ($\times$) 450, ($+$) 500, ($\Diamond$) 550, ($\triangledown$) 600, ($\triangle$) 650, ($\bigcirc$) 700 and ($\square$) 730 °C.

selection of Al_2O_3 as the support for the composite anode because of the same component Al_2O_3 [9]. Figure 4 shows the measured I/V curves of a H_2/O_2 fuel cell using $Ni-Al_2O_3$ as the anode material. The performance is better than that of the cell using the Ni–YSZ as anode mateial (Figure 2). This can be seen in the output current density at the same temperature even though the same cathode and electrolyte materials were used in the experiments. This may have been mainly a result of the difference in the catalytic activity of anodes as previously described. In brief, Ni–Al alloy, $Ni-Al_2O_3$ and Ni–YSZ can be good candidates for anode materials of intermediate temperature proton-conducting fuel cells. Fuel cells using $Ni-Al_2O_3$ as the anode exhibit superior performance than those using Ni–YSZ.

3.2. Selection of cathode materials

Candidate cathode materials for proton-conducting fuel cells must exhibit high electronic and proton or oxygen–ion conductivity and, good catalytic activity for the following electrode reaction:

$$2H^+ + \tfrac{1}{2}O_2 + 2e^- \rightarrow H_2O \qquad (3)$$
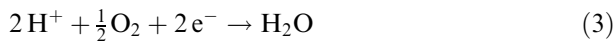
As shown in Figure 5, Reaction 3 occurs not only at the three-phase boundary (TPB), but over the entire surface when an O^{2-}/e^- mixed conductor (Figure 5(a)) or a H^+/e^- mixed conductor (Figure 5(b)) is used as the cathode. When a H^+/e^- mixed conductor is utilized, the cathode reactions could be,

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \qquad (4)$$

$$2H^+ + O^{2-} \rightarrow H_2O \qquad (5)$$

Reaction 4 occurs at the cathode surface, but Reaction 5 occurs at the TPB when an O^{2-}/e^- mixed conductor is used, as shown in Figure 5(a). In this case, the yielded water has to flow out from the three-phase boundary, which is not as easy as in the case where a H^+/e^- mixed
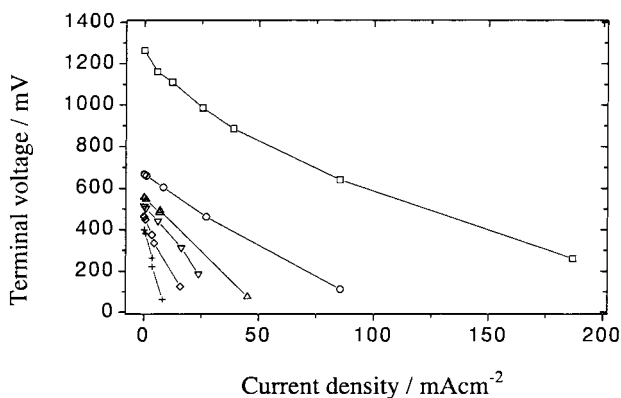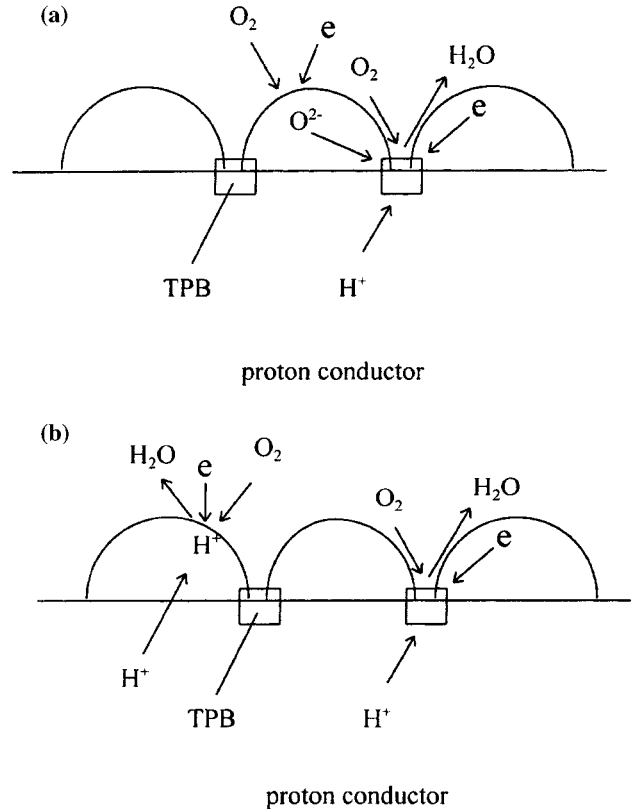

Fig. 5. Schematic diagram of the cathode surface (a) with an O^{2-}/e^- and (b) with a H^+/e^- mixed conductor as cathode for a proton-conducting fuel cell.

conductor is used. The produced water can only diffuse from the TPB sites when an O^{2-}/e^- mixed conductor is used as the cathode in a proton-conducting fuel cell (Figure 5(a)). However, the water can diffuse over the whole cathode surface, including the TPB sites, when a H^+/e^- mixed conductor is used, as shown in Figure 5(b). From this point of view, theoretically, a proton-conducting fuel cell using a H^+/e^- mixed conductor as the cathode (Figure 5(b)) would exhibit faster electrode processes and, therefore, superior cell performance than the case where an O^{2-}/e^- mixed conductor is used (Figure 5(a)).

In general, three types of cathode material can be considered for proton-conducting fuel cells: the simple electronic conductors, O^{2-}/e^- mixed conductors and H^+/e^- mixed conductors. In the electronic conductor category, silver is usually chosen because of its good catalytic activity to Reaction 4. However, similarly to the case of using pure nickel as the anode, pure silver particles tend to sinter or agglomerate, resulting in the loss of specific surface area, which directly affects their catalytic activity. Therefore, a support is needed to prevent the coarsening of the silver particles.

The particle size of SnO_2 is around 10 nm at 750 °C when prepared by a sol–gel process. Moreover, it can absorb different species of oxygen and oxygen-ions at the surface, which might be beneficial to the electrode reactions at the cathode [15]. Therefore, a $Ag-SnO_2$ composite was tested as the cathode. The cell perfor-

Fig. 4. Performance of cell $La_{0.8}Sr_{0.2}MnO_3/LiNaSO_4-Al_2O_3/Ni-Al_2O_3$ in H_2/O_2. Key: (+) 500, (◇) 550, (▽) 600, (△) 650, (○) 700 and (□) 730 °C.

mance is shown in Figure 6. The Ag–SnO$_2$ cathode exhibits relatively good properties above 700 °C, which may have resulted from the catalytic activity related to silver at that temperature.

The second category of cathode materials are O^{2-}/e$^-$ mixed conductors, for example, perovskite-type oxide La$_{0.8}$Sr$_{0.2}$MnO$_3$. The performances of cells using La$_{0.8}$Sr$_{0.2}$MnO$_3$ as cathode shown in Figures 2 and 4 are acceptable.

The third category of cathode materials for proton-conducting fuel cells are H$^+$/e$^-$ mixed conductors. These are theoretically superior to the ionic-conducting type and the electrode process is shown in Figure 5(b). It has been reported that protons can insert into layered transition metal oxides [16, 17]. It is assumed that if there is a potential difference between the two sides and that the interactions between protons and transition oxides are not very strong, the inserted protons in the oxides may become mobile resulting in protonic conduction. These oxides may not be chemically stable in hydrogen, but they would be stable as cathodes in a mainly oxygen-containing environment. Protons from the electrolyte are assumed to insert into the oxides and transport to the other side where they can react with O$_2$ or O^{2-} according to Reactions 3 or 5, respectively, as shown in Figure 5(b). The cell is expected to exhibit the best performance when a H$^+$/e$^-$ mixed conductor is used as the cathode because the entire surface can be used for cathode reactions and it is also easy for the diffusion of water. The cell performance using LiCoO$_2$ as the cathode, as shown in Figure 1, is reasonable. Figure 7 shows performance of a H$_2$/O$_2$ fuel cell using LiNiO$_2$ as cathode material. Among the tested cells, that using LiNiO$_2$ as the cathode and Ni–Al$_2$O$_3$ as the anode exhibited the best performance. In our experiments, LiNiO$_2$ was found to be a better cathode than LiCoO$_2$, which is partially due to the difference in electronic conductivity [10]. The electronic conductivity of Li$_{0.86}$NiO$_2$ is generally an order of magnitude higher than that of LiCoO$_2$ above 350 °C [10]. The cell performance using LiMn$_2$O$_4$ as the cathode is shown in Figure 8. Compared to the results in Figure 1 for a cell with the same electrolyte and counter anode material, the cell

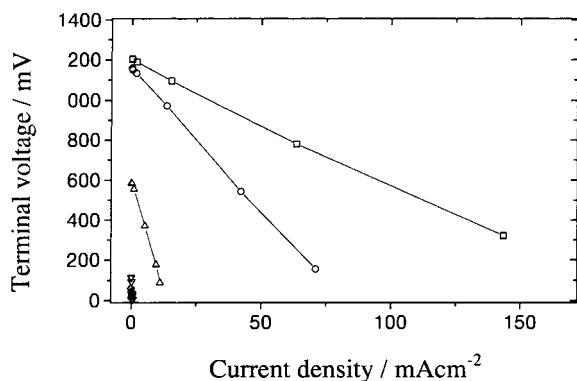*Fig. 7.* Performance of cell LiNiO$_2$/LiNaSO$_4$–Al$_2$O$_3$/Ni–Al$_2$O$_3$ in H$_2$/O$_2$. Key: (×) 450, (+) 500, (◇) 550, (▽) 600, (△) 650, (○) 700 and (□) 730 °C.

performance using LiMn$_2$O$_4$ is inferior. This is because of the three layered transition metal oxides LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$, LiMn$_2$O$_4$ exhibits the lowest electronic conductivity [8]. However, LiNiO$_2$ exhibits the highest electronic conductivity, which might relate to the good cell performance when used as cathode. Therefore, of the layered transition metal oxides, LiNiO$_2$ and LiCoO$_2$ are good candidates for cathode materials for intermediate temperature proton-conducting fuel cells. In summary, LiNiO$_2$, LiCoO$_2$, Ag–SnO$_2$, La$_{0.8}$Sr$_{0.2}$MnO$_3$ are potential materials for cathodes for proton-conducting fuel cells.

4. Conclusion

From theoretical analysis, and according to tentative experimental results, among the tested electrodes pairs, the LiNiO$_2$/Ni–Al$_2$O$_3$ pair was found to be the best. Other factors such as the microstructure, porosity, pore size, interface integration between electrode and electrolyte materials have not been seriously considered, and require further investigation. Based on theoretical analyses, the materials with good catalytic activity, ideally with high proton conductivity for the anode and with

Fig. 6. Performance of cell Ag–SnO$_2$/LiNaSO$_4$–Al$_2$O$_3$/Ni–Al in H$_2$/O$_2$. Key: (+) 500, (◇) 550, (△) 600, (▽) 650, (○) 700 and (□) 730 °C.
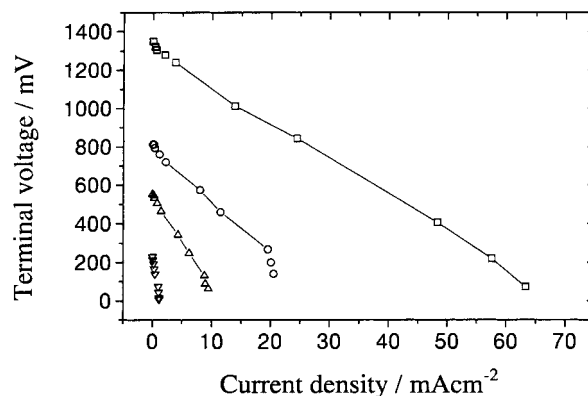
Fig. 8. Performance of cell LiMn$_2$O$_4$/LiNaSO$_4$–Al$_2$O$_3$/Ni–Al in H$_2$/O$_2$. Key: (▽) 600, (△) 650, (○) 700 and (□) 750 °C.

O^{2-}/e^- or H^+/e^- mixed conductivity for the cathode, are good candidates for proton-conducting fuel cells. The experimental results for fuel cell performance indicate that this analysis is valid although the assumed proton conductivity of layered transition metal oxides at evaluated temperatures still needs to be demonstrated. Unfortunately, the long-term performance of the cells was not satisfactory, effective operation being limited to several hours only.

Acknowledgements

References

1. R.L. Cook, J.J. Osborne, J.H. White, R.C. MacDuff and A.F. Sammells, *J. Electrochem. Soc.* **139** (1992) L19.
2. J.B. Goodenough, J.E. Ruiz-Diaz and Y.S. Zhen, *Solid State Ionics* **44** (1990) 21.
3. B.-E. Mellander and B. Zhu, *Solid State Ionics* **61** (1993) 105.
4. B. Zhu and B.-E. Mellander, *J. Power Sources* **52** (1994) 289.
5. B.C.H. Steele, *Mater. Sci. Eng., B* **13** (1992) 25.
6. S.W. Tao and G.Y. Meng, *J. Mater. Sci. Lett.* **18** (1999) 81.
7. S.W. Tao, B. Zhu, D.K. Peng and G.Y. Meng, *Mater. Res. Bull.*, in press.
8. S.W. Tao, Thesis, University of Science and Technology of China (1998).
9. S.W. Tao, Z.L. Zhan, D.K. Peng and G.Y. Meng, *J. Mater. Sci. Lett.*, **18** (1999) 707.
10. S.W. Tao, Q.Y. Wu, Z.L. Zhan and G.Y. Meng, *Solid State Ionics* **124** (1999) 53.
11. H. Itoh, T. Yamamoto, M. Mori, T. Horita, N. Sakai, H. Yokokawa and M. Dokiya, *J. Electrochem. Soc.* **144** (1997) 641.
12. J.R. Selman and Y.P. Lin, *Electrochim. Acta* **38** (1993) 2063.
13. K. Eguchi, Y. Kunisa, M. Kayano and K. Sekizawa, *Denki Kagaku* **64** (1996) 596.
14. H. Miyamoto, M. Sumi, in S.C. Singhal and H. Iwahara (Eds.), Proceeding of the Third International Symposium on Solid Oxide Fuel Cells, Electrochemical Society Pennington, NJ (1993), p. 504.
15. X.Q. Liu, S.W. Tao and Y.S. Shen, *Chin. J. Appl. Chem.* **13** (1996) 65.
16. R.A. Huggins, H. Drinz, M. Wohlfahrt-Mehrens, L. Jorissen and W. Witschel, *Solid State Ionics* **70/71** (1994) 417.
17. B. Ammundsen, P.B. Aitchison, G.R. Burns, D.J. Jones and J. Roziere, *Solid State Ionics* **97** (1997) 269.