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Evaluation of TiO_2-glass composites as interconnector material for solid oxide electrolyte fuel cells[*]

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Electronically conducting interconnector materials are required to connect consecutive anodes and cathodes in high-temperature solid oxide fuel cells. Nb-doped TiO_2–glass composites, prepared by cold pressing and sintering in air above 1200° C, possess adequate conductivity and resistance to oxidizing and reducing atmospheres, as well as compatibility with Y_2O_3-doped ZrO_2. They thus show promise as interconnector materials.

1. Introduction

Solid oxide electrolyte fuel cell stacks, operating at 900–1000° C, require an electronically conducting interconnection between the consecutive anodes and cathodes [1]. The interconnection materials must be both chemically and physically compatible with the other cell components and resist degradation by the oxidizing air or reducing fuel environments. In recent designs, fuel cell components have been deposited on to a porous, stabilized zirconia supporting tube. Most interconnection materials that have been considered are oxides or mixed oxides [2]. The difficulties encountered with these oxides results from cracking due to porosity or differences in thermal expansion coefficients from the stabilized zirconia. However, they do meet the other requirements for the interconnections [3].

An alternative material for interconnections is a plastic which prevents the build-up of stresses. Glasses have attractive physical properties, but their electrical resistances are high and they are usually ionic conductors. Composite materials in which the resistance could be decreased using a highly conducting oxide may be of value. The oxide phase could give the required electrical properties, and the glass could act as a plastic matrix to give the necessary mechanical properties. A wide range of combinations is available, and many oxides and glasses are possible candidates. The optimum physical and chemical properties may also be obtained by changing the ratio of glass to oxide.

Enamels and glazes have been used for coating both metals and ceramics. According to a recent article, a conducting coating can be produced on steel using doped Fe_2O_3 in soda-lime glass [4, 5]. In another study, it was found that glasses could be made electronically conducting by addition of titania [6]. Doped titania has been considered for interconnection material because of its high conductivity at elevated temperatures. These studies suggest that a glass–titania composite could give the required properties for the interconnection material. Doped titania may be more suitable than the iron oxide–glass composites for this purpose because of the likely possibility of reduction of Fe_2O_3 by the fuel in a solid electrolyte fuel cell.

2. Results and discussion

Studies were conducted on Analar grade TiO_2, soda-lime glass and SiO_2 composites. Cold-pressed powdered compacts (8000 psi) were sintered over a temperature range and their densities measured;

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Table 1. Densification of TiO_2–soda-lime glass composites

	Densification† *obtained at various sintering temperatures (%)* ‡						
Glass (wt%)	1000° C	1100° C	1200° C	1250° C	1300° C	1350° C	1400°C
0.0	93.0	93.9	93.0	92.0	92.0	92.3	92.3
5.18	91.2	91.2	90.5	89.8	88.1	86.1	84.9
10.0	86.1	84.6	75.6	80.1	80.4	81.6	82.1
15.2	82.0	78.6	76.3	77.0	77.6	78.1	76.0
20.9	79.2	75.9	71.4	71.9	74.3	72.7	70.0

† Densities calculated for oxide and glass densities of 4.26 and 2.47 g cm^{-3} respectively.

‡ Measurements are made on samples after sintering at each temperature, starting at 1000° C.

these were compared with the calculated values based on the glass and oxide constituents. These calculations assumed no significant density changes due to dissolution or interaction between the glass and the oxide. Tables 1 and 2 show the results for soda-lime and SiO_2 composites respectively. Pure TiO_2 is included for comparison. It is seen that the relative density compared to the calculated value is greater than 90% for TiO_2 up to 1500° C. Above this temperature, the density decreased. The decrease in density with temperature is unusual and was observed with all composites tested. The cause of the decrease in density was not clear, but could be the result of degassing of the TiO_2. The samples which showed the least variations in density with sintering temperatures contained 15 wt% soda-lime and 10 wt% SiO_2. The greatest variation with temperature was shown by the 20% SiO_2 samples where the density decreased rapidly when the sintering temperature increased from 1500 to 1700° C. This decrease in density did not occur with SiO_2 contents of 10% or less. Hence, by sintering at 1400° C, the relative densification increased with SiO_2, but at 1700° C the opposite trend was observed.

Table 2. Densification of TiO_2–SiO_2 composites

	Densification† *at various sintering temperatures (%)* ‡		
SiO_2 (wt%)	1500° C	1600° C	1700° C
0.0	90.1	85.8	84.7
4.96	73.0	77.0	75.4
10.2	72.9	72.5	72.0
15.2	81.0	68.9	67.6
20.5	88.3	70.0	61.8

† Densities calculated for oxide and glass densities of 4.26 and 2.18 g cm^{-3} respectively.

‡ Measurements are made on samples after sintering at each temperature, starting at 1500° C.

In order to increase its conductivity, TiO_2 was doped with Nb_2O_5. The addition was found to influence the densification. When Nb_2O_5 was simply mixed with the TiO_2 and soda-lime glass before sintering, a lower apparent density was observed, as seen from Table 3. This effect was reduced by pre-reacting Nb_2O_5 with TiO_2 at 1700° C prior to preparation of the glass composite. With this preparation the apparent densities were still less than those observed without Nb_2O_5. With SiO_2 the pre-reaction of Nb_2O_5 with TiO_2 did not improve the densification and gave still lower densities.

The variation in the structure of the composites was examined microscopically. The TiO_2 particles in the soda-lime glass matrix increased in size with time and temperature, but little change was observed after sintering the SiO_2 components. Fig. 1 shows the grain size of the TiO_2 in a SiO_2 matrix after sintering at 1500° C. The light-coloured TiO_2 grains were approximately the same size as the starting material. With the soda-lime glass, grain growth of the TiO_2 was observed after sintering at 1200° C, as shown in Fig. 2. Figs. 2a and b show the influence of the sintering temperature which increases the grain size for a fixed period of sintering. The grains continued to grow on holding the composites at 1400° C, as shown in Fig. 2c after 168 hours.

Crystal growth is a function of the solubility of the titanium oxide in the glass and the properties of

Table 3. Effect of composition and pretreatment of the oxide component on densification

Sample	*Density*	*Theoretical density*	*Densification (%)*
Composites containing 5 wt% soda-lime glass, sintered at 1200° C			
TiO_2 + 5.08 wt% glass	3.70	4.11	90.1
(TiO_2 + 2.60 mol% Nb_2O_5, sintered 1700° C) + 4.84 wt% glass	3.54	4.22	83.9
(TiO_2 + 2.65 mol% Nb_2O_5) + 5.25 wt% glass	3.38	4.20	80.5
Composites containing 15 wt% soda-lime glass, sintered at 1200° C			
TiO_2 + 15.2 wt% glass	2.98	3.84	77.6
(TiO_2 + 2.60 mol% Nb_2O_5, sintered 1700° C) + 15.1 wt% glass	3.24	3.92	82.7
(TiO_2 + 2.65 mol% Nb_2O_5) + 14.9 wt% glass	2.89	3.93	73.6
Composites containing 20 wt% silicon dioxide, sintered at 1500° C			
TiO_2 + 20.5 wt% SiO_2	3.13	3.56	87.9
(TiO_2 + 2.60 mol% Nb_2O_5, sintered 1700° C) + 20.1 wt% SiO_2	2.48	3.64	68.1
(TiO_2 + 2.65 mol% Nb_2O_5) + 20.0 wt% SiO_2	2.89	3.64	79.4

the glass. The phase diagram of Na_2O–SiO_2–TiO_2 [7] indicates that a liquid phase is present below 1200° C and thus during the initial sintering smaller particles could dissolve. In addition, extensive solid solubility to the extent of 40% is expected at temperatures up to 1300° C; this would assist grain growth by Oswald ripening. In contrast, no solubility of TiO_2 in SiO_2 was expected [7] and there is little grain growth, as can be seen from Fig. 1.

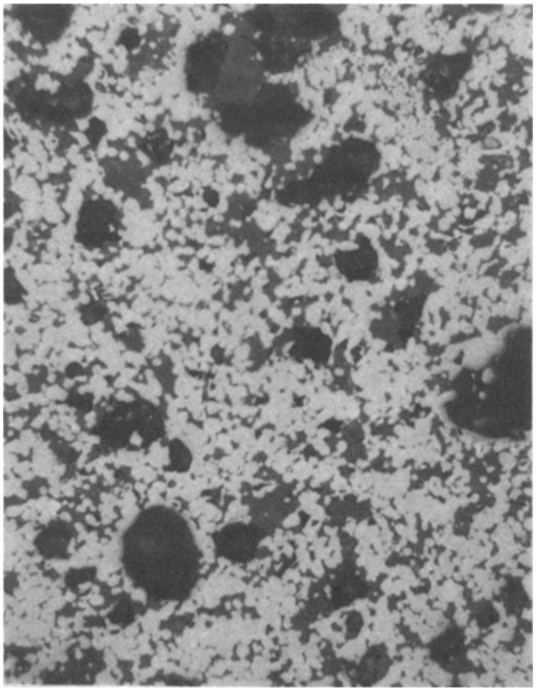

Fig. 1. Photomicrograph of TiO_2, 20 wt% SiO_2 composite sintered at 1500° C for 24 h.

It is essential that during fuel cell operation there should be no interaction between cell components. The solid oxide electrolyte (yttrium-stabilized zirconia, YSZ) and the Nb-doped TiO_2 in the interconnection material should be compatible in both air and a reducing environment at the operating temperature of 1000° C. Polished surfaces of the YSZ and TiO_2 sample discs were therefore placed in contact at various temperatures in both air and a reducing environment of H_2 plus argon. Visual examination of the surfaces indicated no interaction at 1200° C in both environments (Table 4). However, at 1400° C some diffusion of titanium into the YSZ surface did take place in air, while in the reducing environment extensive damage occurred to both samples, creating a liquid phase. As no interaction was observed at 1200° C between the electrolyte and TiO_2, these components would be expected to be compatible at 1000° C for extended periods of time.

The voltage loss in fuel cells will depend on the resistance of the interconnection material. The resistance of doped TiO_2 and composites was measured as a function of temperature with additions of 20 wt% SiO_2 and with soda-lime

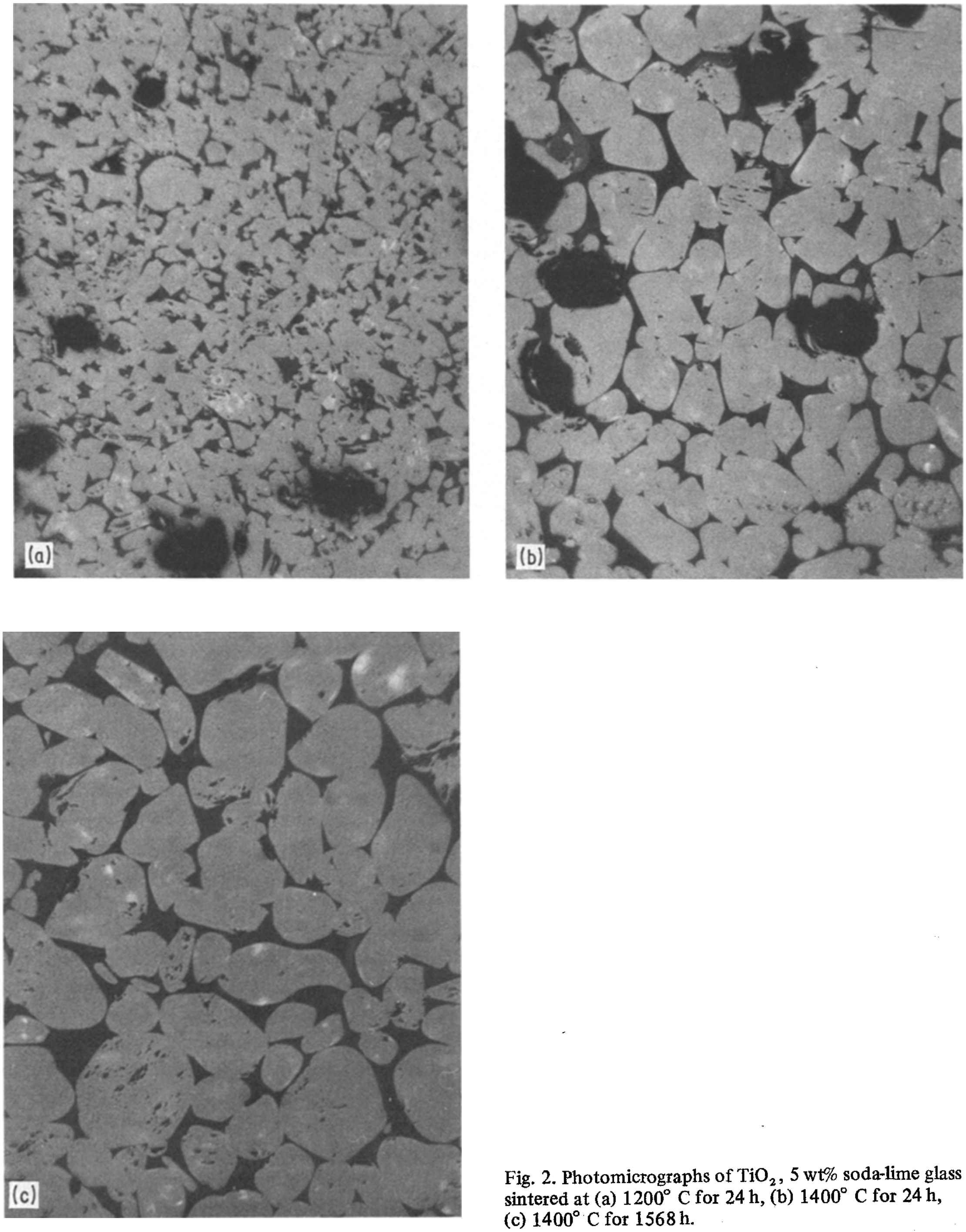

Fig. 2. Photomicrographs of TiO_2, 5 wt% soda-lime glass sintered at (a) 1200° C for 24 h, (b) 1400° C for 24 h, (c) 1400° C for 1568 h.

additions of up to 15 wt%. The influence of reducing and oxidizing gaseous environments was also investigated.

The conduction of doped titania is electronic. At low temperatures the defect structure of TiO_2 has been shown to consist of doubly ionized anion vacancies [8]; the addition of niobium increases the electronic conduction without affecting the lattice defect structure. At high temperature, good agreement has been found between theory and ex-

Table 4. Interaction between ZrO_2[†] and TiO_2[‡]

Temperature (° C)	*Environment*	*Time* (h)	*Results*
1200	Air	50	No visible interaction
1400	Air	24	Brown stain developed in the centre of ZrO_2 pellet. Metallurgical polishing of surface did not remove stain
1000	8.5 vol% H_2 in argon	96	No interaction
1200	8.0 vol% H_2 in argon	50	No interaction
1400	8.0 vol% H_2 in argon	50	Face of ZrO_2 pellet retained polished surface and did not stick to TiO_2. Colour of surface changed from white to brown. The TiO_2 sample became brittle and crumbled easily.

[†] These samples contain 12 wt% Y_2O_3 and were sintered at 1700° C for 24 hours.
[‡] These samples were sintered at 1700° C for 24 hours.

periment; the theory is based on conduction by quasi-free electrons and both triply and quadruply ionized titanium interstitials [9]. A change in mechanism with temperature is also indicated by the nonlinear Arrhenius plots for the conductivity of air-exposed doped TiO_2 below 1000° C. In reducing environments, the conductivity of the doped TiO_2 appears metallic in nature as it decreases with temperature due to scattering effects. The high electronic conductivity results from the presence of hydrogen in the TiO_2 which acts as an electron donor [10]. The variation of resistivity of doped TiO_2 with 2.4% Nb_2O_5 is shown in Fig. 3 for measurements in air and 8.5% hydrogen. In air, the resistance decreased with increased temperature. With hydrogen the resistance was lower than in air and increased slowly with temperature.

The composites with soda-lime glass gave similar resistance variations with temperature and gas composition, as shown in Figs. 4a and b. In air, the resistance decreased with increasing temperature while with hydrogen the resistances were low and increased. With 4.8% soda-lime glass (Fig. 4a), the resistances were about 35% lower than the doped titania (Fig. 3), while with 15 wt% glass (Fig. 4b) the resistance in air was significantly higher but gave the same values in hydrogen. At 1000° C, the resistivities in both environments were close to 10 Ω cm. With higher soda-lime additions, the resistances were much greater at the lower temperatures and decreased more rapidly with temperature in air, whereas hydrogen exposure gave the same dependence as lower glass compositions.

The similarities between the resistance of the doped TiO_2 and the glass composites indicate that the glass matrix only makes a small contribution to the measured resistance. This result is expected based on other measurements [6] using Na_2O–SiO_2–TiO_2 glasses with 40 wt% concentration of TiO_2. These glasses had conductivities within an order of magnitude of that of the doped TiO_2 over the range of temperature considered here. The composites with additions of SiO_2 showed marked increases in the resistance and gave a single activa-

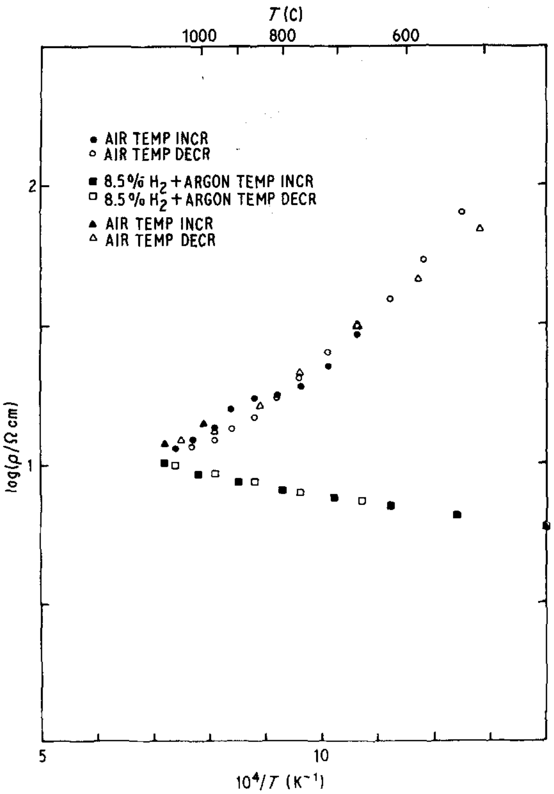

Fig. 3. Variation of resistivity of niobium-doped TiO_2 in air and hydrogen (TiO_2 + 2.42 wt% Nb_2O_5).

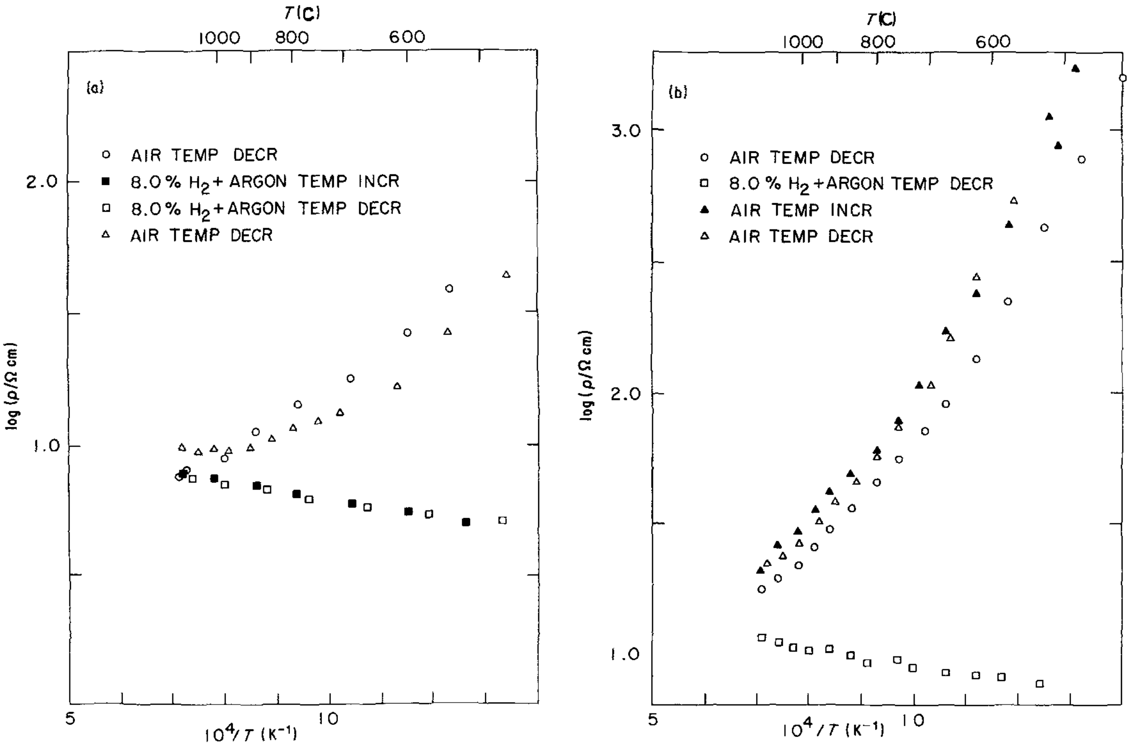

Fig. 4. Variation of resistivity of a composite of TiO_2, 2.6 wt% Nb_2O_5 (sintered at 1700° C) with (a) 4.8 wt% soda-lime in air and hydrogen, (b) 15.1 wt% soda-lime glass.

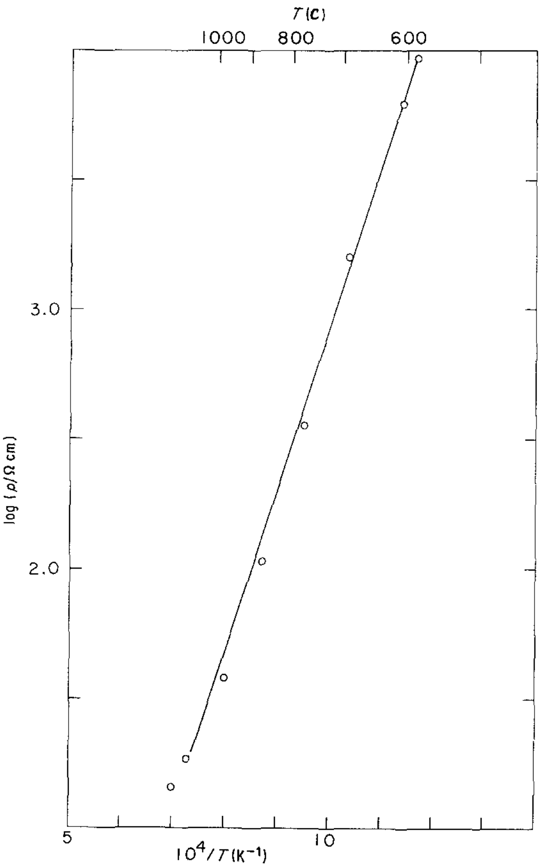

Fig. 5. Temperature dependence of the resistivity of a composite of TiO_2, 2.6 wt% Nb_2O_5 (sintered at 1700° C) with 20.4 wt% SiO_2.

tion energy as shown in Fig. 5. These resistances were too high for this composite to be considered as an interconnection material.

This work has demonstrated that TiO_2–soda-lime glass composites have some properties (resistance, chemical compatibility) required by interconnections for solid oxide electrolyte fuel cells. Further work is still required before these materials could be used as interconnectors. Recrystallization at operating temperatures due to annealing or mass transport under electrical current conditions, compatibility with anode and cathode materials and fabrication of the composite in a pore-free thin layer have still to be investigated.

References

[1] E. F. Sverdrup, C. J. Warde and A. D. Glasser, in 'From Electrocatalysis to Fuel Cells' (edited by G. Sandstede) University of Washington Press, Washington (1972) p. 255.

[2] T. L. Markin, R. J. Bones and R. M. Dell in 'Superionic Conductors' (edited by G. D. Mahan and W. L. Rother) Plenum Press, New York (1967) p. 15.

[3] E. F. Sverdrup *et al.*, 'Project Fuel Cell, Final Report', Research and Development Report No. 57, Office of Coal Research, Washington, DC (1970).

[4] A. S. W. Johnson and A. C. C. Tseung, *J. Appl. Electrochem.* 7 (1977) 445.

[5] D. F. Nuttal, A. C. C. Tseung and M. Phillips, *ibid* 8 (1978) 361.

[6] C. A. Hogarth and M. N. Kahn, *Int. Mater. Sci.* 13 (1978) 402.

[7] E. M. Levin and H. F. McMurdie, 'Phase Diagrams for Ceramists', The American Ceramics Society, Colombus, Ohio (1975).

[8] J. M. Hermann, P. Montgolfier and P. J. Vergnon, *J. Chim. Phys.* 73 (1976) 479.

[9] R. N. Blumenthal, J. Baukas and W. M. Hirthe, *J. Electrochem. Soc.* **114** (1976) 172.

[10] G. J. Hill, *Brit. J. Appl. Phys: J. Phys. D* **1** (1968) 1151.