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**FUEL CELLS: APPLIED RESEARCH
FUEL CELL MATERIALS AND ELECTROCATALYSIS**

**ANNUAL REPORT
JANUARY 1 - DECEMBER 31, 1977**

December 1978

**ENERGY STORAGE AND CONVERSION DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT**

**BROOKHAVEN NATIONAL LABORATORY
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S. SRINIVASAN, H.S. ISAACS, W.E. O'GRADY, P.G. RUSSELL, H. OLENDER,
C.R. DAVIDSON, L.J. OLMER, AND A.C.C. TSEUNG

December 1978

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SUMMARY

1. Electrocatalysis of Fuel Cell Reactions

One of the main reasons for the loss in performance with time in fuel cells is due to the sintering of the catalyst particles. The fast cycling method was used for the periodic regeneration of unsupported Teflon bonded platinum black electrodes. Experiments were conducted in 85% phosphoric acid at 150°C. The time variation of current density for oxygen reduction at a potential of 0.6 volts vs. the reversible hydrogen electrode was recorded. The surface areas were measured in situ at desired time intervals by the hydrogen adsorption technique. After 1000 hours, there was a decrease in current density and electrochemically active surface areas by about 40%. By cycling the potential of the electrode between 0 and 1.3 volts at the optimum sweep rate of 100 volts/sec, the initial activity and surface area could be restored. The rate of decay of current density with the rejuvenated electrode followed the same pattern as the fresh electrode. On the basis of the results obtained, the mechanism of regeneration by the fast cycling method appears to be by a charge injection on the agglomerated particles, which causes an electrostatic repulsion and hence a dispersion of the particles.

Two classes of mixed oxides were investigated as oxygen electrodes in potassium hydroxide. The first class consisted of some rare earth perovskites ($\text{Ba}_2\text{MnReO}_6$, $\text{Ba}_2\text{CoReO}_6$, Ba_2MnWO_6 , Ba_2CoWO_6 , and Sr_2NiWO_6). These compounds were synthesized by solid state reactions at elevated temperatures. Teflon bonded electrodes were prepared and examined for oxygen reduction in a floating mode. The polarization characteristics indicated evidence for the reduction of the oxides in the potential region for oxygen reduction. The second class of oxides investigated were nickel-iron spinels, $\text{Ni}_{1+x}\text{Fe}_{2-x}\text{O}_6$, with $-0.8 \leq x \leq 0.4$. X-ray powder patterns of the powders prepared by the freeze-drying method and subsequent heating to allow crystallization revealed the spinel structure. Magnetic and oxygen reduction electrode kinetic measurements on the nickel-iron spinels indicated a correlation between electrocatalytic activity and saturation magnetization--the lowest electrocatalytic activity is exhibited by the stoichiometric spinel which has the highest saturation magnetization.

2. Solid Electrolyte Fuel Cells

Alternating and direct current methods were used to investigate over-voltage characteristics of the oxygen reduction reactions on platinum paste electrodes in yttria stabilized zirconia. A three-electrode technique was used. Platinum electrodes of ball type with a single contact with the electrolyte showed the same polarization characteristics as the paste electrodes. The decrease of current with time is due to the sintering of the platinum catalyst particles. Impedance measurements at the electrode-electrolyte interface were analyzed in terms of an analogue of two resistances in series, one of which was paralleled by a capacitor. With the vapor deposited electrolyte, the calculated series resistance was considerably higher than that accounted for by the resistivity of the electrolyte and its thickness. The time constant of the interfacial impedance is independent of potential, unlike that observed for aqueous electrochemical systems. The rate-controlling step involves a concentration gradient of adsorbed oxygen molecules, atoms or ions in the electrode or on the electrolyte. An alternate explanation is that the reaction rate is determined by hole conduction in the electrolyte.

Efforts were made to investigate new types of materials to be used in the fabrication of interconnectors for solid electrolyte fuel cells. One of the important requirements of interconnection materials is that their thermal expansion coefficients must be nearly the same as that of the electrolyte-yttria stabilized zirconia so as to prevent stresses. In addition, such materials must have other requisite properties--high electronic conductivity; chemical and physical compatibility with other cell components; and resistance to degradation in oxidizing (air) or reducing (fuel) environments. The approach used was to examine plastic materials, which could also prevent build-up of stresses. The materials investigated were doped iron and titanium oxides (Fe_2O_3) in soda lime and silica glasses. The resistivities, densities, and the stabilities of these materials in contact with fuel, air, and zirconia were determined. The other variable included sintering temperature. The present work demonstrates that the doped titania-glass composites appear to have the desired properties for fabrication of interconnectors in solid electrolyte fuel cells.

Controlled addition of Nb_2O_5 to TiO_2 increases the electronic conductivity of the material. The glass matrix was found to make only a small contribution to the measured resistance. Further investigations to determine possible recrystallization due to annealing or mass transport in electric fields, compatibility with anode and cathode materials, and methods of fabrication of composite in a pore-free thin layer are essential before using these materials as interconnectors in solid electrolyte fuel cells.

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FUEL CELLS: APPLIED RESEARCH
FUEL CELL MATERIALS AND ELECTROCATALYSIS

1. Electrocatalysis of Fuel Cell Reactions ###

1.1 Inhibition of Sintering of Fuel Cell Catalyst Particles -
Electrochemical Methods for Surface Regeneration (H. Olender,
H.S. Isaacs, A.C.C. Tseung and W.E. O'Grady)

A major factor in the deterioration of the performance of fuel cells with time, particularly in the first 1000 hours, arises from the loss of surface area of the catalyst particles(1). This deterioration arises primarily from recrystallization or sintering of the catalyst particles and the rate is governed by the smaller catalyst particles, 2-10 nm, for practical fuel cell electrodes. Efforts to inhibit this deterioration by alloying and substrate modification have not been altogether successful because the alloys are not sufficiently catalytically active or the new substrates are not sufficiently stable(2).

Investigations on the use of fast electrochemical potential cycling methods for regeneration of active surface areas of fuel cell type electrodes were continued. The cycling was carried out on the electrodes in situ. Also, the long-term performance of these electrodes was followed in order to compare the performance of the periodically regenerated electrodes with their initial performances. This performance testing also allows us to determine the rate of decay after the regeneration treatment.

The electrodes, used in this study, were unsupported Teflon-bonded Pt-black electrodes (11.6 mg Pt/cm^2), prepared by the method of Vogel and Lundquist(3). All the data were obtained in 85% phosphoric acid at 150°C and the potential was measured with respect to a dynamic hydrogen electrode. Electrodes were utilized in three different configurations: a gas-fed floating electrode, which was for only monitoring the performance; a second electrode was used as a flooded electrode, only for determining the change in surface area with time; the third electrode was operated in the gas-fed mode with O_2 for performance characterization and with N_2 for surface area determination. These electrodes were not pre-aged but were placed directly in the 85% phosphoric acid and brought up to 150°C in the furnace. The initial aging was done in the operating cell.

The surface areas were determined in situ in 85% phosphoric acid at 150°C by the hydrogen adsorption technique. Prior to this time, the electrochemical surface areas were determined by transferring the electrodes from phosphoric acid into 0.1 N H₂SO₄ in which solution the hydrogen adsorption experiments were conducted on the electrodes in a flooded mode. Flooding of course wets the entire electrode and tends to destroy the capability to operate the electrode in the gas-fed mode. Such types of experiments, in which the performance characteristics and the surface areas of fuel cell electrodes are monitored on the same electrodes, have not been reported previously.

The electrode in the gas-fed mode performed very well for a period of 2100 hours. Figure 1 shows the performance behavior of the gas-fed electrode up to 1400 hours. Within a short time, the current passes through a maximum. This type of behavior is characteristic of the conditioning of a new hydrophobic electrode and is due to changes in the wetting characteristics of the electrode. After reaching the maximum, the performance decays rapidly, ~ 5 mA/day, and then after 200 hours, this rate of decay changes to ~ 1 mA/day and remains constant for 940 hours. After the first 1140 hours, there was a decrease of 40% of the initial performance, based on the current, as well as an approximately equivalent loss of surface area. The change in surface area can be seen very clearly from the cyclic voltammograms shown in Figures 2 and 3 which were used to determine the surface area changes.

After the performance of the electrode decreased to 40% of its initial value, it was cycled between 0 and 1.3 V at several different sweep rates and the surface area was determined following each treatment and these results are summarized in Table 1. The accumulated effect of the cycling treatment shown in Figure 4, where the total number of cycles is plotted against increased charge or surface area, reveals that the area reaches a plateau. The data in this Figure are on accumulated cycles at different sweep rates and the rate at which the plateau is reached may depend on the sweep rate. The sweep rate effects are under further investigation at this time.

Figure 1. Change of performance with time in 85% H_3PO_4 at 150°C. Teflon bonded electrode, 11.6 mg Pt/cm².

Figure 2. Cyclic voltammogram of a teflon bonded PtBlack electrode in 85% H_3PO_4 at 150°C after 40 hours at +0.6V/DHE.

Figure 3. Cyclic voltammogram of a teflon bonded PtBlack electrode in 85% H_3PO_4 at 150°C after 1140 hours at +0.6V/DHE.

Figure 4. Dependence of the anodic charge on the number of cycles at a teflon bonded PtBlack electrode in 85% H_3PO_4 at 150°C.

Table 1
Dependence of Surface Area on Sweep Rate

Fast Cycling Time 0-1.3 V/DHE min	Sweep Rate V/sec	H ₂ Oxidation Charge 0-0.5 V/DHE Coulombs	Surface Area Increase Factor
0		0.11	1.0
60	10	0.13	1.182
60	50	0.148	1.346
20	100	0.154	1.40
15	100	0.155	1.41
15	100	0.155	1.41
15	100	0.155	1.41
15	100	0.155	1.41
10	100	0.155	1.41

Table 1 shows that the surface area increases with all of the fast cycling treatments; however, there is a very definite dependence on the sweep rate. A sweep rate of 100 V/sec appears to produce the largest increases. Overall, 95% of the original performance and surface area are regenerated by the fast cycling process. The rate of decay of the regenerated surface appears to be following the same pattern as the initial electrode surface, as can be seen in Figure 1.

Two mechanisms have been proposed for the sintering process taking place on fuel cell electrodes. These are: the migration and coalescence of the catalyst particles; and the dissolution-precipitation mechanisms. In the case of Pt-black electrodes, the dissolution-precipitation mechanism is favored. However, this mechanism cannot explain the observations made in the present study: namely, that only the original surface area may be regained by cycling; on the contrary, increases over this value can in principle be attained by involving the dissolution-precipitation mechanism. On the basis of these results the following scheme is proposed for the regeneration by the fast cycling method: (i) charge injection on agglomerated particles during fast cycling; (ii) repulsion of charged particles; (iii) dispersion of charged particles; (iv) return to initial surface area.

✓ 1.2 Oxides as Oxygen Electrodes (C.R. Davidson)

The most likely candidates for reversible oxygen electrodes, essential for regenerative fuel cells and secondary metal-air batteries are the electronically conducting oxides. Mixed oxides with a spinel or perovskite structure appear to have higher stability and catalytic activity than simple oxides. The oxides NiO_x , $\text{RuO}_2/\text{TiO}_2$ and NiCo_2O_4 (prepared by the thermal decomposition method) were investigated at BNL, during the previous reporting period, as oxygen electrocatalysts in alkaline medium (KOH). Though the catalytic activities (particularly with NiCo_2O_4 and $\text{RuO}_2/\text{TiO}_2$) were high both for oxygen evolution and reduction, these studies indicated that the reduction of the oxides occurred in the desired region of potential for oxygen reduction.

Two classes of mixed oxides were investigated as oxygen electrodes in the reporting period. The first were rare earth perovskites with good catalytic properties for some heterogeneous reactions. The mixed oxides ($\text{Ba}_2\text{MnReO}_6$, $\text{Ba}_2\text{CoReO}_6$, Ba_2MnWO_6 , Ba_2CoWO_6 , and Sr_2NiWO_6) were prepared by solid state reactions at elevated temperatures*. After grinding the oxides into powder, Teflon bonded electrodes were prepared. The catalyst loading was maintained at approximately 10 mg cm^{-2} . The electrodes were examined for oxygen reduction activity in a floating mode in 0.1-1.0 N KOH, generally at 80°C . The studies on BaMnReO_6 were conducted in the temperature range from 22 to 130°C . Current-potential measurements were made using the linear sweep technique ($0.1\text{-}1.0 \text{ mV sec}^{-1}$) in the cathodic direction, starting at the rest potential and ending at 100 mV vs the potential of the Dynamic Hydrogen Electrode (DHE). The rest potentials (800-900 mV/DHE) were significantly lower than the reversible potential for oxygen reduction. Further, with all these oxides, the polarization behavior indicated evidence of reduction of the oxides in the potential region for oxygen reduction.

*These samples were furnished by Dr. C. P. Khattak, of the Physics Dept. at BNL, who was examining these oxides as potential candidates for MHD electrodes.

The mixed oxide $\text{Ba}_2\text{MnReO}_6$ was examined in somewhat greater detail. The crystal structure of $\text{Ba}_2\text{MnReO}_6$ has been derived from neutron diffraction and magnetic measurements(4). It has a perovskite structure with Ba in twelve fold coordination and both Mn and Re in six fold coordination with oxygen. Alternate (111) planes are occupied by Mn and Re. The oxide is ferrimagnetic with a Curie temperature of 105°C . Typical potential-current density (based on geometric area) relations for the oxygen evolution and reduction reactions on this perovskite are shown in Figure 5. As an oxygen evolution electrocatalyst, the catalytic activity is nearly the same as on nickel. From Figure 5, one may also note the instability of the oxide in the oxygen reduction potential region.

The second class of compounds investigated were nickel-iron spinels. The main aim of this study was to determine if there is any correlation between electrocatalytic activities and magnetic properties. The nickel-iron spinels ($\text{Ni}_{1+x}\text{Fe}_{2-x}\text{O}_4$) with $-0.8 \leq x \leq 0.4$ were prepared by the freeze drying method. The oxide powders thus prepared had an amorphous structure giving no X-ray pattern and possessing no ferrimagnetism. The oxide samples were heated in air at 850°C for 40 minutes to allow crystallization. X-ray powder patterns, obtained using MoK_α radiation, revealed the spinel structure. The saturation magnetizations of these samples were determined using a vibrating sample magnetometer. The oxides were then used for the fabrication of Teflon bonded electrodes. The electrochemical activity of the nickel-iron spinels for oxygen reduction were determined in 30% KOH at room temperature using a slow sweep technique. The electrode kinetic parameters for oxygen reduction on $\text{Ni}_{1+x}\text{Fe}_{2-x}\text{O}_4$ are presented in Table 2. In each case, the oxide reduction current in an argon atmosphere is at least one order of magnitude below the oxygen reduction current. After the first two cathodic scans, the oxygen reduction performance on each electrode was not reproducible. Oxide reduction causes a significant change in the oxygen reduction characteristics. This change is irreversible - the subsequent anodic polarization did not restore the initial performance.

Figure 5. Steady state polarization for $\text{Ba}_2\text{MnReO}_6$ in 1 N KOH at 87°C .

Figure 6. Exchange current density and saturation magnetization of $\text{Ni}_{1+x}\text{Fe}_{2-x}\text{O}_4$.

Table 2
Kinetic Parameters for O₂ Reduction on
Ni_{1+x}Fe_{2-x}O₄ in 30 w/o KOH at 22°C.

x in Ni _{1+x} Fe _{2-x} O ₄	b(V)	i ₀ (A cm ⁻²)
-0.8	0.146	5.8 x 10 ⁻¹¹
-0.4	0.130	2.6 x 10 ⁻¹¹
0.0	0.132	1.6 x 10 ⁻¹¹
0.4	0.164	2.9 x 10 ⁻¹¹

The results of the magnetic and electrochemical measurements indicate a correlation between electrocatalytic activity and saturation magnetism (Figure 6). The lowest activity is exhibited by the stoichiometric spinel, which has the highest saturation magnetization. These results are consistent with the corresponding ones on Ni_{1+x}Mn_{2-x}O₄(5).

The theory of magnetic influences on catalytic activities revolves around the conservation of spin momentum in chemical and presumably electrochemical reactions. The electronic configuration of oxygen is such that there is one σ bond and one π bond between the oxygen atoms with an additional two unpaired electrons in a π^* (antibonding) orbital. It has been proposed that good oxygen electrocatalysts will promote back-bonding with the π^* oxygen orbitals on adsorption. This can occur only if the spin moments of the electrocatalysts are free enough to orient in a favorable manner. The correlation, reported here, seems to be supportive of this premise. The higher the saturation magnetization of the electrocatalyst, the stronger the internal interactions of the magnetic movements. Back-bonding to the oxygen π^* orbitals with spin conservation may be hindered on such a material, resulting in a lower activity (i.e., lower i₀) as observed.

2. Solid Electrolyte Fuel Cells ^{###}

2.1 Analysis of Overpotentials in Solid Electrolyte Fuel Cells (H.S. Isaacs and L.J. Olmer)

The efficiency of a fuel cell system depends on voltage losses resulting from component resistances and interfacial overpotentials within cells. These losses have been measured and are presented in Table 3 from the work of Rohr(6). The overvoltages at the anode and cathode interfaces account for about 40% of the voltage losses. The electrolyte, which in this case was 0.4 mm thick, accounted for 25%. The electrolyte thickness is about 20 times greater than that being used in solid oxide fuel cells now being developed(7). The use of the thinner electrolyte, which should greatly decrease the electrolyte losses, will further emphasize losses at the electrode-electrolyte interfaces.

Table 3
Solid Oxide Fuel Cells Voltage Losses
(Rohr - Brown Boveri and Cie)

Polarization Anode + Cathode	39%
Electrolyte Resistance	26%
Cathode Resistance	16%
Interconnection Resistance	10%
Open Circuit Deviation from Theoretical	6%
Anode Resistance	<u>3%</u>
	100%

Several possible rate-controlling steps have been suggested for the reduction of oxygen at fuel cell cathodes (8-10) on solid electrolytes. They include diffusion of oxygen through the pores in the electrode(11,12) or in the electrolyte(11), diffusion of oxygen in the electrode(13), and migration of electronic defects in the electrolyte(8,14). Many of these steps, suggested as rate controlling, are based on different experimental

approaches, cell designs, variations in electrode preparations, and methods of measurement, but there have been few definitive results. There is, at present, no accepted model for the electrode reaction, which can be used to optimize the performance of fuel cell electrodes.

The overvoltage characteristics of the oxygen electrode reactions were measured on a range of cells, with electrolytes prepared by different methods. All potentials were measured against a reference electrode. The cells were prepared from sections of electrolytes, usually with four electrodes. Two sets of electrodes were painted adjacent to each other across the electrolyte thickness. When one of the four electrodes was tested, the adjacent electrode acted as an auxiliary or counter electrode to carry the current and one of the second set of electrodes was used as a potential reference. Figure 7 shows a schematic of the cell. The results for a platinum-paste electrode in air at 1000°C are shown in Figure 8. Curve A was obtained on first heating the cell to 1000°C . The anodic and cathodic portions of the curve are symmetrical. The currents decreased with time as shown by the subsequent measurements, curves B and C. The cathodic currents decreased more rapidly than the anodic currents, which showed relatively small changes. At -600 mV , the cathodic current decreased by an order of magnitude as the polarization increased with prolonged aging. The effect of time on the current has been shown to be caused by sintering of the platinum particles. Figure 9 shows the variation of the cathodic reduction current for an electrode held at -50 mV . The current decreased continuously and after a few hundred hours reached one tenth of its original value. The electrodes were made by repeated coatings with the platinum paste. The sintering of the platinum particles for a single coating (see insets in Figure 9) shows the platinum morphology and coarsening after the indicated periods of time.

Measurements, conducted on a simple electrode consisting of a platinum ball pressed against the electrolyte(15), exhibited the same characteristics as the aged platinum-paste electrode. Porous particulate and single contact electrodes, similar to the platinum ball, were prepared with doped lanthanum chromite. The porous electrodes showed a behavior similar to curve B in Figure 7, i.e., a tendency for greater cathodic polarization,

Figure 7. Schematic of cell construction.

Figure 8. Influence of aging of a platinum paste electrode on the variations of current with potential for a slip cast zirconia yttria electrolyte at 1000°C. Curve A was obtained on first heating and curves B and C were taken following subsequent aging.

Figure 9. Effect of aging after recoating a platinum paste electrode on the cathodic current at 50mV vs. air electrode. The break in the curve occurred during a period on open circuit. The scanning electron micrograph insets were taken after indicated times and showed sintering of the platinum.

Figure 10. Potential variations of the anodic (i_a) and cathodic (i_c) currents, the equivalent parallel resistance (R_p), capacitance (C_p), series resistance (R) of the electrode and the differential polarization resistance ($R_{DC} = dE/di$). Measurements were performed on an electrochemically vapour deposited zirconia-yttria anode layer with platinum paste electrode at 1000°C in air.

while the ball-type oxide electrode results exhibited marked differences in anodic currents as observed with aged platinum electrodes. These characteristics were also observed with gold electrodes.

Measurements were also made with a series of electrolytes and platinum paste electrodes. Figure 10 shows the polarization for an electrochemically vapor deposited zirconia electrolyte. The overvoltage behavior with aged electrodes was similar to that in Figure 8, indicating that the electrolyte did not have any major influence on the results. Differences caused by electrolytes have been observed in other tests and are still being investigated. A major inconsistency was the high apparent series resistance observed with the vapor deposited electrolyte, which was significantly greater than that calculated simply from the electrolyte resistivity (10 ohm-cm at 1000°C) and the thickness of the EVD electrolyte.

The polarization behavior of the electrodes suggests that activation, concentration and resistance polarization are present. The unaged platinum electrode (curve A, Fig. 8) is dominated by resistance polarization because the symmetrical shapes of the anodic and cathodic curves are consistent with the results that would be obtained if a single resistance (~ 2.5 ohm) was being measured. With aging, the interfacial contribution potentials increase and the polarization curves become more and more asymmetrical. The cathodic behavior at the negative potentials is characteristic of concentration polarization where diffusion or mass transfer of a reacting species limits the reaction rate. At positive potentials, the current increases rapidly with potential but the observed current is limited by the resistance polarization. On compensating for this resistance, the current increases approximately logarithmically with potential as would be expected for activation polarization where the electrode/electrolyte interface controls the reaction rate.

Impedance measurements of the electrode/electrolyte interfaces on EVD electrolytes(16) were analyzed in terms of an analogue of two resistances in series, one of which (R_p) was paralleled by a capacitor (C_p)(17), as shown in Figure 10. In general, the parallel resistance decreased and the capacitance increased with potential. The dc resistance, obtained by differentiating the polarization curve, and the parallel resistance show

the same potential trends, indicating that the same factors controlled their behavior. The time constant of the interface, however, was almost independent of potential.

The observation that the time constant of the interface is independent of potential is unexpected when compared with aqueous electrochemical systems, where the time constant varies with potential. The simplest interfacial impedance for an electrode in an aqueous electrolyte consists of a capacitance resulting from the electrical double layer and shows only small changes with potential. The resistance is associated with the electrochemical reactions that take place at the electrode and for an activation controlled reaction is a pure resistance. This resistance is equivalent to the slope of the polarization curve, i.e., dE/di . The variation of the time constant (i.e., the product of the parallel capacitance and resistance) with potential is caused by the parallel resistance because the double layer capacitance remains approximately constant. When the reactions are concentration dependent, a capacitance is also associated with the reactions. This pseudocapacitance and the inverse resistance are related (the Warburg impedance) and both show a maximum at the reversible potential with increasing values as the measuring frequency is decreased.

The solid-solid interface characteristics may differ from aqueous electrolytes, because of the role of electronic (hole) conduction in the electrolyte. This leakage electronic current prevents the build-up of high potential gradients at the interface. Therefore, activation polarization or a high field conduction mechanism cannot be invoked. The anodic and cathodic interfacial polarization probably results from concentration effects. The rate controlling step involves a concentration gradient of adsorbed oxygen molecules, atoms or ions on the electrode or electrolyte surfaces or hole conduction in the electrolyte.

A possible model depends on the migration of holes in the electrolyte. There will be no significant oxygen flux to areas in direct contact between the electrode and electrolyte, except for the case where there is a high diffusion rates of oxygen in the electrode material. This interfacial area then acts as an oxygen blocking electrode. Changes in potential (E) and corresponding changes in oxygen activity (P_{O_2}) in the electrolyte results

from changes in the concentration of electronic holes (h^+). This may be shown from the equation:

where V_0^{++} is an oxygen lattice vacancy and O_0 is an oxygen ion at an oxygen site. The activities of V_0^{++} and O_0 in doped zirconia remain essentially constant at their standard states, hence substitution into the Nernst equation:

$$E = \frac{RT}{4F} \ln (P_{O_2}/P_{O_2}^0) \quad (2)$$

yields:

$$E = \frac{RT}{F} \ln(h^+/h_0^+) \quad (3)$$

where h_0^+ is the hole concentration when $E = 0$ and $P_{O_2} = P_{O_2}^0$ i.e. the reference gas pressure. This equation gives the variation of hole concentration with applied potential where areas of the electrolyte are blocked by the electrode. The hole concentration, where the electrolyte is in contact with the gas, will be (h_0^+) and migration of holes could take place in the electrolyte or on the electrolyte surface, which would effectively increase the active area of the electrode. Increases in the active area lead to increases in the current and capacitance and corresponding decreases in the resistance. If the reaction rate per true active surface area remains constant, the time constant for the measured impedance will be independent of potential or active surface area.

These measurements indicate that the morphology of the oxygen electrodes will be of major importance. The regions of electrolyte, adjacent to the conducting electrode, is probably small. An optimum design of the electrode deposits, which do not show significant oxygen diffusion rates, will consist of fine grains with many contacts but each particle will not require a large interfacial contact area with the electrolyte. The latter is similar to the Hebb-Wagner model for electronic defect migration under activity rather than potential gradients(18).

2.2 Selection and Evaluation of Interconnector Materials (P.G. Russell, H.S. Isaacs, and A.C.C. Tseung)

Fuel cell stacks require an electronically conducting interconnection between the consecutive anodes and cathodes(19). The interconnection material 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 are deposited on a porous stabilized zirconia supporting tube. Most interconnection materials, which have been considered are oxides or mixed oxides(20). The difficulties, encountered with these oxides, resulted from cracking due to porosity or differences in thermal expansion between the interconnection and zirconia. Stresses in the cells, which develop due to expansion mismatch, led to cracking of fuel cell stacks. These stresses could be reduced by using oxides, now being developed, that have the same thermal expansion coefficients as stabilized zirconia and meet the other requirements for the interconnections(21).

An alternative possible interconnection is a plastic material, which could prevent the buildup of stresses. Glasses have attractive physical properties, but their electrical resistances are high, and they are usually ionic conductors. The use of duplex materials, where the resistance could be decreased using a highly conducting oxide, was considered. 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 possible combinations are available and many oxides and glasses are possible candidates. The optimum properties could also be obtained by changing the ratios of glass to oxide.

Plastic enamels and glazes have been used for coating both metals and ceramics. Recent work with doped Fe_2O_3 in soda-lime glass has shown that a conducting coating on steel could be produced(22). Other work has shown that addition of titania to glass gives rise to electronic conduction(23). Doped titania has been considered as a possible interconnection material, as its conductivity is high at elevated temperatures. These factors suggest that a glass-titania composite could give the required properties for the interconnection material.

Measurements to determine the characteristics of glass-oxide systems were carried out on Ti-doped Fe_2O_3 and three glasses. As previous work was available and resistance measurements could be conducted at room temperature, the iron oxide system was chosen for the initial screening studies. The Fe_2O_3 would, however, not be expected to be stable in the reducing atmosphere of the fuel compartment of the fuel cell.

The influence of glass composition on the resistances of oxide/glass composites was studied using titanium-doped iron oxide and three glasses. A series of titanium doped Fe_2O_3 samples were prepared. Depending on sintering temperature, a minimum in resistivity was observed between 0.7 and 1.5% TiO_2 . Other investigators(22,24) found that composites with glass had a minimum in resistance when the Fe_2O_3 contained 1% TiO_2 .

Room temperature resistivity measurements were made on two series of Ti doped Fe_2O_3 glass composite samples sintered at 1000°C and 1200°C . In the series containing soda-lime glass, the logarithm of the resistivity increases approximately linearly with glass additions, while in the series containing borosilicate glass the resistivity remains approximately constant as the glass content is increased to 16.7 w/o. In each case, the minimum value of the resistivity occurs close to the maximum relative density. A maximum densification of $\sim 88\%$ was obtained with a sample containing 2.14 w/o * soda-lime glass sintered at 1200°C (Table 4). The actual densification is somewhat greater because the pore volume is included in the measurement of sample volume. A densification of over 95% has been reported previously with a Ti doped Fe_2O_3 sample containing 20 w/o soda-lime glass sintered at 1250°C (22). In this study, the samples containing 15.4 and 20.6 w/o soda-lime glass were too distorted to make accurate density and resistivity measurements after sintering at 1200°C . The value for the resistivity of each composite, obtained after sintering at 1000°C , decreased by a factor of ~ 100 after sintering at 1200°C . In a 25 w/o sample containing silica glass (densification $\sim 78\%$), the resistivity is still relatively low (~ 100 ohm-cm).

*percent by weight

Table 4
Densification of $\text{Fe}_2\text{O}_3 + 0.70 \text{ a/o Ti}$ - Soda Lime Glass Composites
Sintered at 1200°C

Weight Percent Glass	Theoretical ^a Density	Experimental Density	Percent Densification
0.0	5.24	4.09	78.0
2.14	5.12	4.49	88.0
3.06	5.08	4.33	85.0
4.08	5.01	4.00	80.0
6.23	4.90	3.79	77.0
7.35	4.84	3.70	76.0
8.16	4.80	3.53	75.0
9.47	4.74	3.52	74.0
10.1	4.71	3.39	72.0

^a The densities were calculated based on d_{oxide} and d_{glass} of 5.24 and 2.47 g cm^{-3} respectively. The small amount of TiO_2 added to the Fe_2O_3 and compound formation are neglected in these calculations.

Similar studies were conducted with TiO_2 and additions of soda-lime glass and SiO_2 . Components were sintered over a temperature range and their measured densities were compared with the calculated densities 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 5 and 6 shows the results for soda-lime and SiO_2 composites respectively. The pure TiO_2 is included for comparison. It is seen that the relative density compared to the calculated values is greater than 90% for the TiO_2 up to 1500°C . Above this temperature the density decreased. The decrease in density with temperature is unusual and was observed with many composites tested. The cause of the decrease in density was not clear, but could be the result of degassing or reaction with TiO_2 . The samples, which showed the least variations in density with sintering temperatures, contained 15 w/o soda-lime and 10 w/o SiO_2 . The greatest variation with temperature was shown by the 20% SiO_2 samples, where the density decreased rapidly on sintering from 1500 to 1700°C (see Table 6). This decrease

in density did not occur with 10% or lower SiO₂ contents. Hence, by sintering at 1500°C, the relative densification increased with SiO₂, but at 1700°C the opposite trend was observed.

Table 5
Densification of TiO₂ - Soda Lime Glass Composites

Weight Percent Glass	Percent Densification ^a Obtained at Various Sintering Temperatures ^b in °C						
	1000	1100	1200	1250	1300	1350	1400
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

^a Densities calculated based on oxide and glass densities of 4.26 and 2.47 g-cm⁻³ respectively.

^b Measurements are made on samples after sintering at each temperature starting at 1000°C.

Table 6
Densification of TiO₂ - SiO₂ Composites

Weight Percent SiO ₂	Percent Densification ^a at Various Sintering Temperatures ^b in °C		
	1500	1600	1700
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

^a Densities calculated based on oxide and glass densities of 4.26 and 2.18 g-cm⁻³ respectively.

^b Measurements are made on samples after sintering at each temperature starting at 1500°C.

In order to increase the conductivity of TiO_2 , it was doped with Nb_2O_5 . These additions were 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 (Table 7). This effect was reduced by predissolving the Nb_2O_5 in TiO_2 at 1700°C , prior to preparation of the glass composite. With this preparation, the apparent densities were still less than that observed without Nb_2O_5 . With SiO_2 , the predissolution did not improve the densification and resulted in still lower densities.

The variations in the structure of the composites were determined from photomicrographs. 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. Figure 11 shows the grain size of the TiO_2 in a SiO_2 matrix after sintering at 1500°C . The grains were approximately the same size as the starting material. With the soda-lime glass, grain growth was observed after 1200°C sintering. This can be seen by comparing Figure 11 with Figure 12 as well as by observing the influence of temperature (Figures 12 and 13). The grains continued to grow on heating the composites at 1400°C for 168 h (Figure 14).

The crystal growth is a function of the solubility of the titanium in the glass and the properties of the glass. The phase diagram of $\text{Na}_2\text{O-SiO}_2\text{-TiO}_2$ (24) indicates that a liquid phase will be present below 1200°C during the initial sintering, which would dissolve the smaller particles. In addition, extensive solid solubility will be expected up to at least 40% TiO_2 up to 1300°C , and this will assist grain growth by Oswald ripening. In contrast, no solubility of TiO_2 in SiO_2 is shown (24), and therefore, there is little grain growth. The lack of grain growth can be seen from Figure 11.

During fuel cell operation, there should be no interaction between cell components. The solid oxide electrolyte (YSZ) and the Nb doped TiO_2 oxide 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 and

Figure 11. Photomicrograph of TiO_2 , 20 w/o SiO_2 composite sintered at 1500°C for 24h.

Figure 12. Photomicrograph of TiO_2 , 5 w/o soda lime glass sintered at 1200°C for 24h.

Figure 13. Photomicrograph of TiO_2 5 w/o soda lime glass sintered at 1400°C for 24h.

Figure 14. Photomicrograph of TiO_2 5 w/o soda lime glass sintered at 1400°C for 168h.

Table 7

Effect of Composition and Pretreatment of the
Oxide Component on the Densification

Sample	Density	Theoretical Density	Percent Densification
A. Composites Containing 5 w/o Soda-Lime Glass Sintered at 1200°C			
I TiO ₂ + 5.08 w/o glass	3.70	4.11	90.1
II (TiO ₂ + 2.60 m/o Nb ₂ O ₅ , sintered 1700°C) + 4.84 w/o glass	3.54	4.21	84.0
III (TiO ₂ + 2.65 m/o Nb ₂ O ₅) + 5.25 w/o glass	3.38	4.20	80.5
B. Composites Containing 15 w/o Soda-Lime Glass Sintered at 1200°C			
I TiO ₂ + 15.2 w/o glass	2.98	3.84	77.6
II (TiO ₂ + 2.60 m/o Nb ₂ O ₅ , sintered 1700°C) + 15.1 w/o glass	3.24	3.92	82.6
III (TiO ₂ + 2.65 m/o Nb ₂ O ₅) + 14.9 w/o glass	2.89	3.93	73.6
C. Composites Containing 20 w/o Silicon Dioxide Sintered at 1500°C			
I TiO ₂ + 20.0 w/o SiO ₂	3.13	3.57	87.7
II (TiO ₂ + 2.60 m/o Nb ₂ O ₅ , sintered 1700°C) + 20.1 w/o SiO ₂	2.48	3.64	68.1
III (TiO ₂ + 2.65 m/o Nb ₂ O ₅) + 20.0 w/o SiO ₂	2.89	3.64	79.4

argon. Visual examination of the surfaces indicated no interaction at 1200°C in either environment (Table 8). However, at 1400°C a solid state interaction occurs at the YSZ surface in air, while in a reducing environment extensive damage occurred to both samples. As no interaction was observed at 1200°C between the electrolyte and TiO₂, these materials would be expected to be compatible at 1000°C, for extended periods of time.

Table 8
Interaction Between ZrO₂^a and TiO₂^b

Temperature (°C)	Environment	Times(Hrs)	Results
1200	air	50	No visible interaction
1400	air	24	Brown stain develops in the center of ZrO ₂ pellet. Metallurgical polishing of surface does not remove stain.
1000	8.5 v/o H ₂ in argon	96	No interaction
1200	8.0 v/o H ₂ + argon	50	No interaction
1400	8.0 v/o H ₂ + argon	50	Face of ZrO ₂ pellet retains polished surface and does not stick to TiO ₂ . Color of surface changes from white to brown. The TiO ₂ sample became brittle and crumbled easily.

^aThese samples contain 12 w/o Y₂O₃ and were sintered at 1700°C for 24 hours.

^bThese samples were sintered at 1700°C for 24 hours.

The voltage loss in fuel cells will depend on the resistance of the interconnection material. The resistance of doped TiO_2 and composites were measured as a function of temperature with soda-lime additions of up to 15 w/o and with additions of 20 w/o SiO_2 . The influence of reducing and oxidizing gaseous environments were also studied.

The variation of resistivity of doped TiO_2 with 2.4% Nb_2O_5 is shown in Figure 15 for measurements in air and 5% hydrogen. In air, the resistance decreases with increased temperature. With hydrogen, the resistance was lower than in air and increased slowly with temperature.

The conduction of doped titania is electronic. At low temperatures, the defect structure of TiO_2 was shown to be due to doubly ionized anion vacancies(25); additions of niobium increased the electronic conduction without affecting the lattice defect structure. At high temperatures, good agreement has been found between theory, based on a conduction model by quasi-free electrons and both triply and quadruply ionized titanium interstitials(26), and experiment. A change in mechanism with temperature is also indicated by the non-linear 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 increases 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(27).

The composites with soda-lime glass showed the same resistance changes with temperature and gas composition (Figures 16 and 17). In air, the resistance again decreased with temperature, while with hydrogen the resistances were low and increased. With 4.8% soda-lime glass, the resistances were about 35% lower than the doped titania. With 15% glass, the resistance in air was significantly higher, but was unchanged in hydrogen. At 1000°C , the resistivities in both environments were in the range of 10 ohm-cm. With higher soda-lime additions, the resistances were much greater at the lower temperatures and decreased more rapidly with temperature in air, whereas the hydrogen exposure gave the same dependence as lower glass compositions.

Figure 15. Variation of resistivity of niobium doped TiO_2 in air and hydrogen.

Figure 16. Variation of resistivity of a composite of TiO_2 , 2.6 w/o Nb_2O_5 with 4.8 w/o soda lime in air and hydrogen.

Figure 17. Variation of resistivity of a composite of TiO_2 , 2.6 w/o Nb_2O_5 with 15 w/o soda lime glass.

The similarities between the resistances 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 would be expected based on other measurements(18) on $\text{Na}_2\text{O-SiO}_2\text{-TiO}_2$ glasses with concentrations of 40 w/o TiO_2 . These glasses had conductivities within an order of magnitude of the values for doped TiO_2 over the range of temperature considered here.

Measurements were also conducted with SiO_2 composites and titania doped with niobium. The additions of SiO_2 markedly increased the resistance of the composites and gave a single activation energy of 14.6 kcal/g mole and resistivity of $30 \Omega\text{-cm}$ at 1000°C . These resistances are too high for this composite to be considered as an interconnection material.

This work has demonstrated that the resistances and chemical compatibility of the TiO_2 soda-lime glass composites have properties required by interconnections for solid oxide electrolyte fuel cells. Further work is still required before these materials could be used as interconnectors. These include the absence of recrystallization at operating temperatures due to annealing or mass transport during electrical current flow, compatibility with anode and cathode materials, and fabrication of the composite in a pore-free thin layer.

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