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FUEL CELLS: APPLIED RESEARCH FUEL CELL MATERIALS AND ELECTROCATALYSIS

ANNUAL REPORT
January 1976 - December 1976

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SEPTEMBER 1977

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ANNUAL REPORT
January 1976 - December 1976

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SEPTEMBER 1977

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SUMMARY

1. Electrocatalysis of Fuel Cell Reactions

The most likely candidates for reversible oxygen electrodes, which are essential for the development of highly efficient regenerative fuel cells and secondary metal-air batteries, are mixed oxides. The mixed oxides NiCo_2O_4 and $\text{RuO}_2/\text{TiO}_2$, with a spinel structure and prepared by the thermal decomposition method on a metallic substrate, exhibit high electrocatalytic activities for oxygen evolution but not for oxygen reduction. The results also indicated the instability of the oxides in the region of potential for oxygen reduction.

The electrocatalytic activity for oxygen reduction on platinum is significantly dependent on the electrolyte. At 80°C , the order of electrocatalytic activity is $\text{KOH} > \text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{KHCO}_3/\text{K}_2\text{CO}_3$. The influence of the electrolyte may be due to anion adsorption on the electrode surface, e.g., adsorption of HSO_4^- or SO_4^{2-} on Pt is appreciable but that of OH^- is low. Of the anions Cl^- , H_2PO_4^- , and I^- , only I^- showed a pronounced effect, i.e., increase of overpotential on Pt.

A buffered $\text{KHCO}_3/\text{K}_2\text{CO}_3$ solution may find application as a CO_2 rejecting electrolyte for methanol-air fuel cells. The oxygen reduction reaction was investigated on several electrode materials in this electrolyte at 80°C . The following order of electrocatalytic activity was found $\text{Pt} > \text{Ni} > \text{Ag} > \text{Au} > \text{Ir}$.

2. Investigations on Some Problems in "First Generation" Phosphoric Acid Fuel Cells

One of the main reasons for the loss in performance with time in "First Generation" Phosphoric Acid Fuel Cells is due to the sintering of catalyst particles. Two electrochemical methods for the periodic regeneration of the surface were investigated. In one, the potential of the electrode is stepped up to a value at which a uniform oxide layer is formed and the potential is then lowered to reduce the oxide. In the second, the potential of the electrode was cycled between 0 and 1.3 volts versus the reversible hydrogen electrode potential. The first method was unsuccessful while using the second one, there was a 30% increase in surface area.

Studies of the temperature dependence of the electrode kinetic parameters for oxygen reduction on platinum in 85% H_3PO_4 showed that there is a progressive improvement in performance with increase of temperature from 25 to 150°C. However, there was a decrease in electrocatalytic activity when the temperature was raised from 150 to 200°C. This may be attributed to the conversion of orthophosphoric acid to pyrophosphoric acid at 200°C. These results suggest that the optimum operating temperature in phosphoric acid fuel cells, from an electrochemical standpoint, is 150°C.

3. Research on "Third Generation" Solid Electrolyte Fuel Cells

Contributions to the overpotentials in solid electrolyte fuel cells have not been clearly delineated in previous publica-

tions. It has generally been assumed that the ohmic overpotentials contribute predominantly to the total overpotential. A transient method was developed to identify the overpotential losses in the interfacial (gas-electrolyte-electrode) regions and in the electrolyte. In this method, the AC voltage response of an electrode, a cell or the interconnecting material interface, can be determined when a rectangular current wave is passed through the cell. The current wave is superimposed on the DC current from a potentiostat. The voltage response is compared to an equivalent network of capacitors and resistors. Tests were conducted on a solid electrolyte (zirconia-yttria) fuel cell with platinum electrodes. The variation of currents, capacitance and resistance of the cell as a function of potential were determined. The results indicate the type of information obtainable from such an equivalent circuit analysis. The preliminary studies show the usefulness of the technique in: (1) characterizing the overpotential losses in solid electrolyte fuel cells; (2) monitoring change in such parameters during long-term operations; and "(3) leading" to modifications in cells with the aim of improving cell performance.

One of the biggest problems in the development of solid electrolyte fuel cells is in finding suitable interconnector materials which must satisfy stringent requirements: (1) chemical stability in air and fuel gas; (2) resistivity in the working environment, of less than 50 ohm cm; (3) thermal expansion

characteristics compatible with other fuel cell components; (4) non-reactivity toward other components; (5) fabricability as a gas-impervious layer 40 mμ in thickness; (6) no phase changes with temperature changes; and (7) no significant mass transfer effects under chemical gradients. A number of mixed oxide systems, being investigated at Westinghouse Research Corporation, satisfy these requirements. A different approach is to use materials which are plastic and have a low modulus of elasticity at the operating temperature. Such materials should reduce cracks developing in multi-cells. Chromium oxide and titanium-doped Fe_2O_3 glasses were prepared and sintered for five hours at over 1000°C . Room temperature resistivities were made on such glasses with different compositions. The values are low enough to indicate suitability, from this point of view, as interconnector materials in solid electrolyte fuel cells at temperatures of over 1000°C . However, all the other criteria, outlined above, should be satisfied. Experiments to determine these properties on the conducting glasses are in progress.

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FUEL CELLS: APPLIED RESEARCH
FUEL CELL MATERIALS AND ELECTROCATALYSIS

1. Electrocatalysis of Fuel Cell Reactions

1.1 Mixed Oxides as Oxygen Electrodes (G. Singh, M. H. Miles, C. R. Davidson)

The oxygen electrode reactions are of special importance in fuel cells, water electrolyzers and some battery systems (e.g., zinc-air, aluminum-air, and iron-air) because activation overpotential at this electrode is the main cause of efficiency losses in these devices. Oxygen evolution always takes place on oxide-covered metallic surfaces, while the oxygen reduction reaction may occur on bare metallic surfaces, oxides or mixed oxides. The most likely candidates for reversible oxygen electrodes are oxides, mixed oxides, or compound oxides. Mixed oxides, including spinels, appear to be better catalysts for several reactions than simple oxides. One particular feature of mixed oxides is their increased stability over simple oxides. In spinels, the mixed valencies of the cations help in the reversible adsorption of oxygen by providing donor-acceptor sites for chemisorption.

With a view to understanding and developing reversible oxygen electrodes, the electrocatalytic activities of a simple oxide (NiO_x) and of the mixed oxides NiCo_2O_4 and $\text{RuO}_2/\text{TiO}_2$ were studied. The oxygen evolution reaction was studied on all the oxides and oxygen reduction on the mixed oxides. The electrolyte was 30% KOH and the operating temperature 80°C . The NiO_x and NiCo_2O_4 electrodes were prepared by thermal decomposition of their

salts (nitrates) on a metallic substrate. The $\text{RuO}_2/\text{TiO}_2$ electrode was similar to those used in the chlor-alkali cells. The Tafel lines for oxygen evolution and reduction are shown in Figures 1 and 2, respectively. The electrode kinetic parameters, obtained from these plots, are presented in Table 1. The true surface areas of the electrodes were calculated from double layer capacitors at the electrode-solution interfaces, as obtained from the slopes of the plots of double layer charging currents as a function of sweep rate. The oxide electrodes, prepared by the thermal decomposition method, are highly active as electrocatalysts for oxygen evolution but not so for oxygen reduction. There is evidence that nickel cobalt oxide and $\text{RuO}_2/\text{TiO}_2$ are reduced in the region of potential for oxygen reduction. From the values of Tafel slopes and exchange current densities for the oxygen evolution and reduction reactions on the spinels, NiCo_2O_4 and $\text{RuO}_2/\text{TiO}_2$, it is clear that reversibility of the electrode reaction was not attained in these systems. Details of experimental techniques, analysis of results and of mechanistic conclusions in this investigation are found in a recent publication(1).

Work was commenced on the preparation of Teflon-bonded oxide electrodes by the freeze-drying method, used by Tseung and coworkers(2,3). Electrodes, prepared by this method, have a high roughness factor (ratio of real to apparent surface area) and are mechanically stable. The initial studies were carried out with nickel cobalt oxide and these electrodes were tested for oxygen evolution. There was good agreement of the results obtained in

this work with those of Tseung and coworkers. It is proposed to extend this study to other spinels as well as perovskites. There is some evidence to indicate that a correlation exists between electrocatalytic activities of electrode reactions and magnetic properties. This aspect will be investigated in detail in our future studies. Magnetic measurements may serve as a guide for electrocatalyst selection on a rational basis.

1.2 Electrolyte Effects on the Oxygen Reduction Reaction (H. Olender, M. H. Miles, E. A. Klaus)

The difficulties, associated with the reduction of oxygen, arise because the double bond in the oxygen molecule is not easily broken and that a stable species H_2O_2 or " HO_2 is formed" either as an intermediate or in a parallel reaction(4). The kinetics of electrode reactions are significantly dependent on the electrode material and quite often on the electrolyte as well. To date, there had been no extensive systematic investigation on the effect of the electrolyte on the oxygen reduction reaction, which is the main purpose of the study reported in this section(5). The electrolytes, chosen for this study, are listed in Table 2. It is worthwhile noting the reasons for the selection of these electrolytes. Phosphoric acid (85%) is the electrolyte used in the most advanced fuel cell system, being developed by United Technologies Corporation. The alkaline fuel cell with 30% KOH as the electrolyte, also shows promise for terrestrial application. It has been shown previously(6) that the performance of hydrogen-air fuel cells in trifluoromethane sulfonic acid (TFMSA)

monohydrate, $\text{CF}_3\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, is superior to that in 85% phosphoric acid. The buffered electrolyte ($\text{K}_2\text{CO}_3/\text{KHCO}_3$) may prove to be useful for the development of direct methanol-air fuel cells. Sulfuric acid and HClO_4 appear to be the best acid electrolytes for fuel cells operating at temperatures below 100°C .

Electrode kinetic parameters for oxygen reduction on platinum in these electrolytes at 80°C were obtained from potentiostatic measurements of current density-voltage relationships and are presented in Table 2. In addition to potentiostatic measurements, slow potential sweeps ($0.1\text{--}0.5\text{ mV sec}^{-1}$) were often used. Generally, the results using the two techniques, were in good agreement. Before each experiment, reduction currents of the order of $1\text{--}10\text{ ma cm}^{-2}$ were applied for 5-10 minutes to remove reducible oxides from the electrode surface as well as to help build up a steady state concentration of the peroxide intermediate. The experiments in the acid electrolytes were conducted in a two or three compartment glass cell. For the experiments in alkaline electrolytes, Teflon cells were used. Dynamic hydrogen or calomel reference electrodes were used. The potentials of each of these electrodes versus the reversible hydrogen electrodes, in each of the electrolytes, were measured from which the potential of the reversible oxygen electrode was deduced. It was then possible to calculate the electrode kinetic parameters presented in Table 2. All solutions were prepared with reagent grade chemicals and distilled deionized water. Typical Tafel lines for oxygen reduction on Pt in these electrolytes are found in Figures 3 and 4.

Investigations were also made of the effect of concentration of the electrolytes TFMSA, H_2SO_4 , and KOH-on the electrode kinetic parameters for oxygen reduction on Pt at 80°C . The results are summarized in Table 3.

The prerequisites for a good electrocatalyst are high exchange current densities (i_0) and low Tafel slopes (b). The latter corresponds to high values of the transfer coefficients (α). In cases where the Tafel slopes are different, it is quite often necessary to ascertain the order of electrocatalytic activity by comparing the overpotentials at a desired current density (say, the operating current density in a fuel cell). This is clearly evident when one examines the Tafel lines for oxygen reduction on Pt in TFMSA and KOH. At low current densities, the overpotentials are lower in TFMSA but at higher current densities, the opposite behavior is true. Thus, for purposes of comparison of the results from a practical point of view, the potentials of the Pt electrode versus the reversible hydrogen electrode at a current density of 10^{-4} amp cm^{-2} (this is roughly equivalent to a current density of 100 ma cm^{-2} at a porous electrode) are given in the last column of Table 2. The present results suggest the order of electrocatalytic activity on Pt in these electrolytes as $\text{KOH} > \text{CF}_3\text{SO}_3\text{H} \cdot \text{H}_2\text{O} > \text{H}_2\text{SO}_4 > \text{H}_3\text{PO}_4 > \text{KHCO}_3/\text{K}_2\text{CO}_3$. Most investigators suggest that anion adsorption is responsible for oxygen reduction overpotential being greater in acid electrolytes than in alkaline ones(4). Since the reversible potential, E_R , for the oxygen electrode reaction shifts in the negative direction as the pH increases, it is likely

that oxygen reduction occurs in alkaline solution at potentials negative to the potential of zero charge where anion adsorption is largely absent. For example, E_R vs SCE is 0.985V in 1.0M H_2SO_4 , but shifts to 0.115V in 1.0M KOH. Thus, oxygen reduction in H_2SO_4 is possibly retarded by specific adsorption of HSO_4^- and of SO_4^{2-} on the electrode surface, whereas in KOH, any adsorption of OH^- is small. The present results with $CF_3SO_3H \cdot H_2O$ offer some explanation for this electrolyte being better than H_3PO_4 for fuel cell applications. The limiting current is smallest in KOH which is due to the low solubility of oxygen in 30% KOH. However, this will not cause serious limitations when porous gas diffusion electrodes are used, as in fuel cells.

Concentration variation studies (Table 3) show the expected behavior in KOH, i.e., improvement in performance with increase in concentration. With sulfuric acid, there is a considerably better performance at higher concentration, which is predominantly due to a significant increase in Tafel slope on lowering the acid concentration. An unusual behavior is observed in TFMSA. The monohydrate shows the highest activity. It is then followed by the lowest concentration (0.1M). With increase of acid concentration, there is a decrease of electrocatalytic activity of Pt for the oxygen reduction reaction. Measurements of coverage of the electrode with oxygen should help in the explanation of the anomalous behavior.

1.3 Anion Effects on the Oxygen Reduction Reaction (M. H. Miles, E. A. Klaus)

According to the preceding section, it appears that the electrocatalytic activity for the oxygen reduction reaction on platinum is dependent on the electrolyte. It has been suggested that this effect may be correlated with anion adsorption on the electrode surface. The main aim of the present study was to elucidate the effects of adsorbable anions (chloride, iodide or phosphate) on the electrocatalysis of the oxygen reduction on platinum or silver in 1.0M H_2SO_4 or 1M KOH at 80°C. Measurements were made of the steady state current densities for oxygen reduction as a function of potential using potentiostatic techniques without and with addition of small amounts of desired anions.

A typical plot of overpotential versus current density showing the effect of chloride ion on the oxygen reduction reaction on Ag in 1M H_2SO_4 is found in Figure 5. The influence of the anions Cl^- and H_2PO_4^- on the electrode kinetic parameters for oxygen reduction on Pt and Ag are tabulated in Table 4. The phosphate ion hardly changes the electrode kinetic parameters. Attempts to study the effect of I^- ion failed due to the oxidation of this ion by sulfuric acid in the potential region of interest. A summary of the study of anion effects on oxygen reduction in 1M KOH is presented in Table 5. A negligible effect of chloride ion was observed. However, this was not the case when the I^- ion was added to the electrolyte, with Pt as the test electrode. A significant increase of overpotential was observed.

1.4 Selection and Evaluation of Electrocatalysts for Oxygen Reduction in $\text{KHCO}_3/\text{K}_2\text{CO}_3$ Buffered Electrolytes

(M. H. Miles, E. A. Klaus)

As seen from Table 2, potassium hydroxide should be the favored electrolyte for fuel cells because in this medium the oxygen overpotential is the least, when compared with other electrolytes. Further, in an alkaline medium it is easier to find cell component materials (e.g., electrode materials, current collectors, gaskets, seals, cell container materials, etc.) than in acid electrolytes. There is, however, the problem of CO_2 contamination of the electrolyte in fuel cells when using air as the oxidant and hydrogen, produced by steam reforming or coal gasification, as the fuel. Another approach to finding CO_2 rejecting electrolytes, as alternatives to acid electrolytes, is to use buffered carbonate electrolytes. With such electrolytes, one may even envisage the possibility of developing direct methanol-air fuel cells. According to Table 2, the performance of the platinum electrode in the $\text{KHCO}_2/\text{K}_2\text{CO}_3$ electrolyte was not satisfactory. Thus, it was decided to examine other materials (Au, Ag, Ir, Ni, and WC) for their electrocatalytic activities of this reaction.

In Figure 6 are presented the overvoltage versus current density relations for oxygen reduction on these electrode materials, as well as on Pt, in $0.5\text{M KHCO}_3/0.5\text{M K}_2\text{CO}_3$ at 80°C . Platinum was found to be the best catalyst. At current densities below 10^{-5} amp cm^{-2} , where well-defined Tafel regions exist, the order of electrocatalytic activity is $\text{Pt} > \text{Au} > \text{Ag} > \text{Ir} > \text{Ni} \gg \text{WC}$. No clearly defined Tafel region was observed on WC. At higher current

densities ($i_0 > 10^{-4}$ amp cm^{-2}), the order of electrocatalytic activity changed to Pt > Ni > Ag > Au > Ir. A low Tafel slope on Ni is the reason for its improved performance at higher current densities. The electrode kinetic parameters, deduced from the Tafel plots (Figure 6) are presented in Table 6. The unusually low Tafel slope for oxygen reduction on Ni accounts for its very low exchange current density.

2. Investigations on Some Problems in "First Generation" Phosphoric Acid Fuel Cells

2.1 Inhibition of Sintering of Fuel Cell Catalyst Particles -- Electrochemical Methods for Surface Regeneration (H. Olender, A. C. C. Tseung)

One of the main reasons for deterioration in the performance of fuel cells with time, particularly during the first thousand hours, is caused by the loss of surface area of catalyst particles, due to the recrystallization or sintering phenomenon(7). The rate of sintering is governed by the smaller catalyst particles, which in practical fuel cell electrodes is in the range of 20-100 $\text{\AA}$. Attempts have been made to inhibit sintering of catalyst particles by alloying or by altering the substrates for deposition of the catalyst(8,9). The methods have not been too successful because (i) the catalytic activity of the alloys is lower than that of Pt and (ii) of the instability of some of the substrate materials. In the present work, two electrochemical approaches were selected for the periodic regeneration of the catalytically active surface. In one, the potential of the electrode is stepped up to a value at which a uniform oxide layer is formed and then the potential is lowered to reduce the oxide. In the second, the potential of the

electrode is cycled at a fast rate between 0 and 1.3 volts versus the reversible hydrogen electrode. During this procedure, it is expected that platinum dissolves and reprecipitates on the surface as fine particles. For a quantitative evaluation of the method, it was decided to measure the charge required for the adsorption or desorption of a monolayer of hydrogen on the electrode surface using potentiodynamic techniques. Assuming one hydrogen atom is adsorbed on each of the Pt atoms on the surface and that the area required per platinum atom is $8.9 \text{ \AA}^2$ on a polycrystalline platinum surface, the charge required for monolayer adsorption or desorption of hydrogen is $210 \text{ } \mu\text{C cm}^{-2}$. The ratio of the charge required on a high surface area electrode to that on the polycrystalline Pt surface (same geometric surface areas in both cases) gives the roughness factor of the former electrode.

Studies on the adsorption and desorption of hydrogen and of oxygen on platinum have been extensively made, using cyclic voltammetric techniques, with sulfuric acid as the electrolyte. The adsorption and desorption characteristics are quite sensitive to impurities. In the initial experiments of the present work, sulfuric acid was used as the electrolyte. Phosphoric acid was the electrolyte in this study after establishing the experimental procedures. Smooth platinum (platinum foil) and platinum black electrodes were used. The platinum black electrodes were Teflon bonded and supported on a platinum screen. Phosphorous acid is an impurity in the analytic reagent 85% H_3PO_4 . It was oxidized to phosphoric acid by addition of small amounts of H_2O_2 and heating

to 100°C. The excess of H_2O_2 was removed by increasing the temperature to 160°C. Prior to the experiments, the acids were purified by pre-electrolysis.

Preliminary experiments were conducted in both 5N H_2SO_4 and 85% H_3PO_4 to determine optimum values of sweep rates and the desired potential range for measurements of hydrogen coverage. There were marked differences, in this series of experiments, when H_3PO_4 was used as the electrolyte. It was soon realized that the problem was caused by impurities. One probable source of impurities is from pyrex glass, which are leached out at elevated temperatures. This was overcome using a quartz cell. The first method proposed for regeneration of surface, i.e., by stepping up potential to 1.3 volts and lowering it to 0.5 volts to reduce the oxide, was not successful. However, the second method, i.e., fast cycling ($10 \text{ volts sec}^{-1}$) over the range from 0 to 1.3 volts/RHE, had a beneficial effect. These results are shown in Table 7. Before the fast cycling, charge for hydrogen adsorption was 0.13 coulombs, while after the potential cycling, the comparable charge was 0.18 coulombs. Thus, this procedure accounts for an increase in surface area by 30%. The future plans are to carry out the studies under more realistic conditions as in fuel cells. Oxygen reduction will be carried out at a fixed potential using high surface area electrodes. The current will be recorded as a function of time. The electrodes will be periodically activated using the fast cycling technique and the increase in the currents noted as a function of time. Attempts will also

be made to further quantify the results by measurements of the surface areas before and after activation treatment.

2.2 Temperature Effects on the Oxygen Reduction Reaction at Platinum in Phosphoric Acid Electrolyte (H. Olender)

From the point of view of minimizing the problem of CO poisoning of the fuel electrodes, it is necessary to operate at high temperatures; but to inhibit the sintering phenomenon of catalyst particles, lower operating temperatures are preferable. It is interesting to examine the performance of the oxygen reduction reaction on Pt in 85% phosphoric acid as a function of temperature(10,11), covering the temperature range of operation of "First Generation" phosphoric acid fuel cells. Since this information was not found in the published literature, a systematic study of the oxygen reduction reaction on Pt in 85% phosphoric acid electrolyte was carried out over the temperature range from 25 to 200°C. Current density-potential relations were obtained using the steady state potentiostatic method. For purposes of comparison, in some cases, the slow potential sweep method (sweep rate 0.1 mV sec⁻¹) was used. A dynamic hydrogen electrode (DHE) was used as the reference electrode. The potential of this electrode was determined with respect to the reversible hydrogen electrode, in the same solution, as a function of temperature and the results are graphically presented in Figure 7. The reversible potential for the oxygen electrode reaction was calculated as a function of the temperature using the equation:

$$E_T^O = E_{25}^O - 8.456 \times 10^{-4} (T-298) \quad (1)$$

Tafel lines for oxygen reduction on Pt in 85% H_3PO_4 are shown as a function of temperature in Figure 8. The electrode kinetic parameters, deduced from these plots, are presented in Table 8. With increasing temperature, both electrode kinetic parameters (b and i_0) become more favorable. The exchange current density increases by four orders of magnitude when the temperature is raised from 25 to 150°C. There appears to be no advantage in increasing the operating temperature from 150 to 200°C. Orthophosphoric acid converts to pyrophosphoric acid in appreciable quantities at 200°C. The solution turned opaque and solidified when cooled. The limiting current density increased by a decade over the temperature range investigated.

3. Research on "Third Generation" Solid Oxide Electrolyte Fuel Cells

3.1 Characterization of Overpotentials in Solid Electrolyte Fuel Cells (H. S. Isaacs, L. J. Olmer)

The present versions of high temperature solid electrolyte fuel cells employ zirconia, doped with yttria, as electrolyte. A battery of cells is arranged along a porous tube, through which the fuel passes. The external surface of the tube is exposed to air and oxidation of the fuel occurs electrolytically with the generation of power(12). The voltage losses in fuel cells have been analyzed in terms of series resistance losses within the electrolyte, the electrodes and the interconnections between the electrodes. Other losses are due to polarization in the electrochemical interfacial processes. The electrochemical reaction mechanisms are not well understood and it is not, at present, feasible to separate polarization effects at

the electrode-gas-electrolyte interfacial regions from those within the electrolyte due to concentration of the migrating oxygen defects or other solid state processes.

In order to improve the performance of solid electrolyte fuel cells, the polarization losses should be clearly defined so as to indicate where improvements could be made, for example, by changing the composition of the electrode materials or by altering the composition of the electrolyte. At present, it is usually considered that the resistance of the electrolyte is the major factor leading to power losses but this has not been clearly demonstrated. The electrolytic processes(13) or impurity segregation at grain boundaries(14) may also contribute to the resistance of the cell. The solid electrolyte, employed in the fuel cell stack, is deposited by an electrochemical vapor deposition technique and offers the advantage that thin layers of the oxide can be produced. The method of production is significantly different from oxides prepared by conventional ceramic techniques, and any differences in electrochemical performance, due to method of preparation of the oxides, should be determined.

The difficulty of defining the rate-limiting processes taking place within the electrochemical cell, leading to voltage losses, has necessitated the study of the electrochemistry of these cells. The techniques, which have clarified the behavior of the aqueous electrochemical systems, are used. Methods for studying the electrolyte directly will also be incorporated, in view of

the contribution it has been shown to add to the polarization characteristics(14). The measurements will be made on oxides prepared via the normal methods and then compared with oxides prepared by electrochemical vapor deposition.

In the high temperature cell, the current passes from the fuel electrode (a cermet structure of nickel and yttria-doped zirconia) through the zirconia-yttria electrolyte to the air electrode (tin-doped indium oxide) and then through an interconnecting material with high electron conductivity, which connects the air electrode to the next fuel electrode. The interconnecting material is thus exposed to a wide range of oxygen activity. This range of activity can produce a range of electrical conductivities in the interconnecting material and thus contact resistances between the electrodes could develop. Techniques should be available to measure the electrical properties of the interconnecting material interfaces in a battery of fuel cells during operation.

The electronic equipment, for the study of the properties of the electrode/electrolyte and other interfacial regions, was built at BNL and has been tested with a solid electrolyte cell. The concept was first used by W. T. Denholm(15). In principle, the AC voltage response of an electrode, a cell or the interconnecting material interface can be determined when a rectangular current wave is passed through the cell(16). The current wave is superimposed on the DC current from a potentiostat. This is accomplished by reducing the time constant of the potentiostat, so that it is

insensitive to the alternating potential induced by the current wave but still controls the DC level. The potentiostat controls the potential across one or more components in a cell or battery of cells. The DC potential and current are measured and the AC components can be analyzed using different methods. The most rapid method is to compare the voltage response to a analogue network of capacitors and resistors or, in other words, to balance the response as in a bridge. Another method is to record and mathematically analyze the voltage-time relationship.

The advantages of this technique include the following: (i) simplicity of operation; (ii) the rectangular wave covers a wide range of frequencies; (iii) any series resistance in the system can be measured directly; (iv) the DC potential can be controlled and the direct current measured; and (v) any component of the cell can be separated from the others and measured without having to subtract their unwanted contributions. In essence, it is analogous to a three-or-four-point system for measuring resistance, as opposed to a two-point system.

In order to test the electrochemical equipment, a simple cell was constructed without any reference electrode. A 1.2 cm diameter zirconia-yttria tube, closed at one end, was coated with a thin layer of platinum at the closed end of the tube, both on the inside and outside. The coatings, 4 cm in length, were applied with a single platinum organic compound layer and fired in air. Platinum leads were connected to both layers. The cell was tested with an 8% hydrogen gas passing through the tube, while its outer

surface was in contact with air.

The test conducted on the cell showed that the equipment operated well with the solid electrolyte cell. As the initial measurements were conducted to test the equipment and not the behavior of the system, the results obtained were not representative of the expected behavior of the fuel cells. The results shown in Figure 9 are, therefore, only indicative of the type of information that will be obtained. In Figure 9, the variations of current and parallel capacitance and resistance of the cell are shown as a function of potential. These preliminary results show that the rate of potential change, after holding at each potential for one minute, was too rapid for steady state conditions to be attained. This is seen from the hysteresis, which demonstrates decreased polarization or increased currents on increasing the potential, as compared with the results obtained while decreasing the potential. A similar behavior is reflected in the measured capacitance and resistance. Other indications, from these results are marked capacitance and resistance minimum at 1.4 volts and the different types of relationships between the current and resistance at the low and high potentials.

Interpretations of the results are premature as it is not possible with the simple cell arrangement to separate the extent to which the fuel or air electrode dominate the observed behavior. This will be determined in future measurements having an unpolarized electrode acting as a reference. The preliminary work shows the

usefulness of the technique for obtaining impedance and polarization characteristics of high temperature fuel cells and for monitoring changes in these parameters during long-term operation. Such measurements should lead to modifications in cells with the aim of improving cell performance.

3.2. Selection and Evaluation of Interconnector Materials (P. G. Russell, A. C. C. Tseung)

The main problem, in the multi-cell development of solid oxide electrolyte fuel cells, has been the cracking observed in fuel cell stacks caused by the difference in the coefficient of thermal expansion of the chromium sesquioxide interconnector material and the stabilized zirconia support tube and electrolyte(17). Recently, a mechanically stronger nickel-zirconia cermet structure was prepared by carrying out the reduction of the nickel oxide component at 1350°C , i.e., closer to the sintering temperature(18). Even with the development of this stronger anode bond to the other cell components, especially to the interconnection layer and porous support tube, alternate oxide systems will have to be evaluated for possible use as an interconnector material in an operational fuel cell.

Any interconnector material, that gives an adequate performance at the proposed operating stack temperature of 1000°C , must meet the following criteria(17): (i) chemical stability in air and fuel gas; (ii) resistivity in the working environment of less than 50 ohm-cm; (iii) thermal expansion characteristics compatible with other fuel cell components; (iv) non-reactivity toward other

components; (v) fabricability as a gas-impervious layer, 40 μm or less in thickness; (vi) no phase changes with temperature changes and/or after extended periods of time; (vii) no significant mass transfer effects under the chemical gradient which, for example, may lead to the formation of voids or high resistance contacts. Furthermore, there will be additional thermal stresses due to the inevitable temperature differences in the system. A number of mixed oxide systems, which are being considered, may satisfy these requirements. A different approach, to satisfy these requirements is to use a connector material which is plastic and has a low modulus of elasticity at the temperature of operation. In this case, even if there were differences in the coefficient of thermal expansion between the connector and the solid oxide electrolyte and/or differences in temperature between different parts of the cell, thermal stresses will be much lower and, hence, the chances of cracking will be greatly reduced. Work at The City University (19) has shown that Fe_2O_3 doped with TiO_2 and mixed with soda-lime glass forms a conducting and impervious coating on mild steel. The advantages of the approach are: (i) the coefficient of thermal expansion of this material can be adjusted within wide limits; (ii) there is a wider choice of semiconducting oxides since considerations of the coefficient of thermal expansion are relaxed; (iii) the composite coating has a very low modulus of elasticity at 700-1200°C, thus, greatly reducing thermal stresses in the cell; (iv) it is far easier to achieve gas tightness, since these materials are similar to enamels and glazes used in the ceramic industry.

Chromium sesquioxide and titanium-doped Fe_2O_3 have been used in the preparation of composite materials. Initial studies indicate that a sample Fe_2O_3 , properly doped with titanium has a low resistivity making it suitable for use as the oxide component in a semiconducting oxide-glass composite material. Room temperature resistivity measurements were made on a series of Ti-doped Fe_2O_3 pellets, pressed at room temperature and 12,000 psi, and sintered for five hours at 100°C and 1200°C . The resistivity, ρ , of pure Fe_2O_3 is quite high ($\rho \sim 10^7$ ohm-cm) but drops by five orders of magnitude to a minimum value when approximately 1 atom % of Ti is present ($\rho \sim 75$ ohm-cm for a sintering temperature of 1200°C). In addition, different composites were made from unsintered 1 atom % Ti-doped Fe_2O_3 and soda-lime glass. The minimum value of resistivity ($\rho \sim 120$ ohm-cm) was obtained with a 5 wt % glass component. These values are higher than the true values, because of the presence of a large contact resistance. In further measurements, fired-on gold coatings will be used to minimize the effect of contact resistance. A substantial decrease in resistivity can be obtained by sintering the samples for longer periods of time. These initial findings indicate that Ti-doped Fe_2O_3 -glass composites may meet some of the essential criteria for interconnector materials (since the resistivity will be less at the operating temperature of 1000°C); the other properties, stated above, should also be satisfied.

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Table 1. Kinetic Parameters for the Oxygen Evolution
and Reduction Reactions in 30 wt % KOH at 80°C

Electrode	Tafel Slope (v)	α^a	i_o (A/cm ²) ^b x10 ⁹	$\Delta E^\ddagger^c$ Kcal/mol
Evolution				
NiCo ₂ O ₄	0.042	1.67	29.9	9.2
RuO ₂ /TiO ₂	0.045	1.56	194.5	9.2
NiO _x	0.047	1.49	71.0	8.2
Reduction				
Pt	0.033	2.1	8.7x10 ⁻⁴	
NiCo ₂ O ₄	0.060	1.2	6.8x10 ⁻¹	
RuO ₂ /TiO ₂	0.070	1.0	1.0	

^aTransfer coefficient

^bExchange current densities, i_o , are given in terms of geometric areas. The roughness factors of various electrodes are, Pt = 2, NiCo₂O₄ = 400 and RuO₂/TiO₂ = 700

^cArrhenius activation energy

Table 2. Dependence of Electrode Kinetic Parameters
for Oxygen Reduction at Pt on Electrolyte at 80°C

Electrolyte	Conc. % or M	Tafel Slope b, volts	Exchange c.d.-2 i_{O_2} , A cm ⁻²	Transfer Coefficient α	Potential vs RHE at 10 ⁻⁴ A cm ⁻² , volts
H ₃ PO ₄	85%	0.070	2x10 ⁻¹⁰	1.0	0.780
H ₂ SO ₄	2.5M	0.080	3x10 ⁻⁹	0.87	0.820
HClO ₄	1M	0.080	2x10 ⁻¹⁰	0.87	0.735
CF ₃ SO ₃ H·H ₂ O	100%	0.100	7x10 ⁻⁸	0.7	0.850
KHCO ₃ /K ₂ CO ₃	0.5M/0.5M	0.082	4.9x10 ⁻¹¹	0.85	0.660
KOH	30%	0.060	3x10 ⁻⁹	1.17	0.890

Table 3. Dependence of Electrode Kinetic Parameters for Oxygen Reduction at Pt on Electrolyte Concentration at 80°C

Electrolyte	Conc. % or M	Tafel Slope b, volts	Exchange c.d. i_o , A cm ⁻²	Transfer Coefficient α	Potential vs RHE at 10 ⁻⁴ A cm ⁻² , volts
CF ₃ SO ₃ H	0.1M	0.140	1.5x10 ⁻⁸	0.5	0.650
CF ₃ SO ₃ H	1.0M	0.095	1.0x10 ⁻¹¹	0.74	0.280
CF ₃ SO ₃ H	5.0M	0.095	3.0x10 ⁻¹²	0.74	0.060
CF ₃ SO ₃ H·H ₂ O	100%	0.100	7.0x10 ⁻⁸	0.7	0.850
H ₂ SO ₄	1.0M	0.120	2.5x10 ⁻¹²	0.57	0.255
H ₂ SO ₄	2.5M	0.080	3.0x10 ⁻⁹	0.87	0.820
KOH	1.0M	0.058	2.0x10 ⁻¹⁰	1.2	0.880
KOH	30%	0.060	3.0x10 ⁻⁹	1.17	0.890
KHCO ₃ /K ₂ CO ₃	0.5M/0.5M	0.082	4.9x10 ⁻¹¹	0.85	0.660

Table 4. Anion Effects on the Kinetic Parameters for the Oxygen Reduction Reaction in 1.0M H₂SO₄ at 80°C

Electrode	Salt or Acid Added, Concentration	Tafel Slope b, volts	Transfer Coefficient α	Exchange c.d. i_o , A cm ⁻²
Pt	--	0.096	0.73	1x10 ⁻¹³
	KCl, 0.05M	0.12	0.59	1x10 ⁻¹²
Pt	--	0.097	0.72	1x10 ⁻¹⁴
	H ₃ PO ₄ , 0.05M	0.11	0.66	7x10 ⁻¹⁴
Ag	--	0.11	0.66	2x10 ⁻¹⁴
	KCl, 0.05M	0.12	0.59	8x10 ⁻¹⁴
Ag	--	0.11	0.65	2x10 ⁻¹³
	H ₃ PO ₄ , 0.05M	0.11	0.63	2x10 ⁻¹³

Table 5. Anion Effects on the Kinetic Parameters for the Oxygen Reduction Reaction in 1.0M KOH at 80°C

Electrode	Salt Added, Concentration	Tafel Slope b, volts	Transfer Coefficient α	Exchange c.d. i_o , A cm ⁻²
Pt	--	0.075	0.94	5x10 ⁻⁹
	KCl, 0.05M	0.074	0.95	4x10 ⁻⁹
Pt	--	0.058	1.2	2x10 ⁻¹⁰
	KI, 0.05M	0.063	1.1	6x10 ⁻¹²
	$i > 2 \times 10^{-5}$ A/cm ²	0.22	0.31	4x10 ⁻⁷
Ag	low i	0.045	1.6	3x10 ⁻¹²
	$i > 6 \times 10^{-6}$ A/cm ²	0.26	0.27	5x10 ⁻⁷
	KI, 0.05M, high i	0.30	0.23	7x10 ⁻⁷

Table 6. Kinetic Parameters for the Oxygen Reduction
Reaction in 0.5M KHCO_3 /0.5M K_2CO_3 at 80°C

Electrode	Tafel Slope b , volts	Transfer Coefficient α	Exchange c.d. i_o , A cm^{-2}
Pt	0.082	0.85	5×10^{-11}
Au	0.069	1.0	3×10^{-12}
Ag (low i)	0.068	1.0	6×10^{-13}
(high i)	0.13	0.55	1×10^{-9}
Ir (low i)	0.091	0.77	6×10^{-12}
(high i)	0.24	0.30	7×10^{-8}
Ni	0.038	1.9	4×10^{-21}

Table 7. Effect of Fast Potential Cycling at 10 v/sec on Electrode Surface Area

Cycle No.	<u>Before</u>		<u>After</u>	
	Coulombs	True Surface Area, cm ²	Coulombs	True Surface Area, cm ²
1	1.5×10^{-1}	830	2.4×10^{-1}	1330
25	1.3×10^{-1}	720	1.87×10^{-1}	980

Table 8. Dependence of Electrode Kinetic Parameters for Oxygen Reduction at Pt in H₃PO₄ on Temperature

Temperature °C	Tafel Slope b, volts	Exchange c.d. i_0 , A cm ⁻²	Transfer Coefficient α	Potential vs RHE at 10^{-4} A cm ⁻² , volts
25	0.090	1×10^{-11}	0.66	--
50	0.085	6×10^{-11}	0.75	0.585
80	0.070	2×10^{-10}	1.0	0.780
120	0.060	1×10^{-9}	1.3	0.880
150	0.055	1×10^{-7}	1.53	0.950
200	0.055	1×10^{-7}	1.71	0.920

Figure 1. Potential-current density relations for oxygen evolution at NiCo_2O_4 , NiO_x , and $\text{RuO}_2/\text{TiO}_2$ in 30 wt % KOH at 80°C.

Figure 2. Potential-current density relations for oxygen reduction at Pt, NiCo_2O_4 , and $\text{RuO}_2/\text{TiO}_2$ in 30 wt % KOH at 80°C.

Figure 3. Potential-current density relations for oxygen reduction at Pt in some electrolytes at 80°C.

Figure 4. Overvoltage-current density relations for oxygen reduction on Pt in 1M KOH, 0.5M KHCO₃/0.5M K₂CO₃ and 1M H₂SO₄ at 80°C.

Figure 5. Effect of addition of KCl on the oxygen reduction reaction on silver in 1.0M H₂SO₄ at 80°C.

Figure 6. Overvoltage-current density relations for the oxygen reduction reaction on various electrodes in 0.5M KHCO₃/0.5M K₂CO₃ solution at 80°C.

Figure 7. Dependence of the potential of the dynamic hydrogen electrode versus the reversible hydrogen electrode in 85% H₃PO₄ on temperature.

Figure 8. Potential-current density relations for oxygen reduction on Pt in 85% H₃PO₄ at different temperatures.

Figure 9. Variation of current, capacitance, and resistance for a Zirconia-Yttria simulated fuel cell.