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Molten Carbonate Fuel Cell Research

CONTRACT INFORMATION

Contract Number	49943
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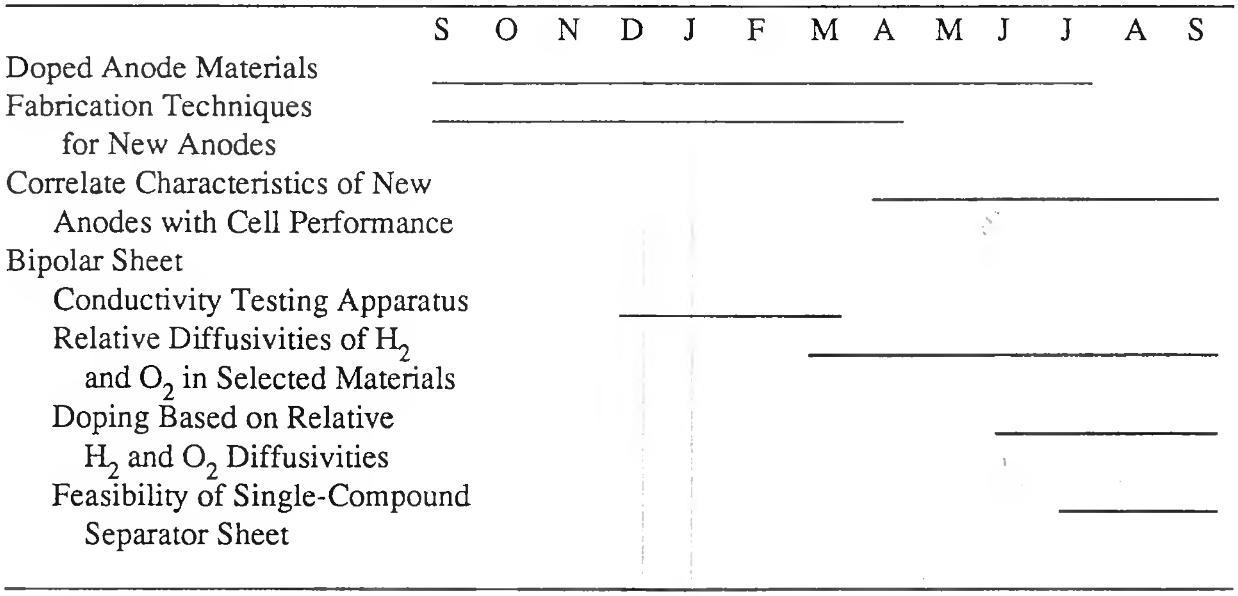
Period of Performance	October 1, 1982, to Open

Schedule and Milestones

FY90 Program Schedule



OBJECTIVE

The emphasis of this project is to develop new electronically conductive ceramic materials that are chemically and polymorphically stable in molten carbonate fuel cell (MCFC) environments and to test these materials as MCFC components (i.e., electrodes and separator sheets). The progression from stable material to actual component requires that significant effort be directed to developing the processes necessary for the fabrication of these materials into either porous electrodes or thin, dense separator sheets. Cell tests and performance data are the bases for component improvement and for insight into the fundamental cell phenomena.

BACKGROUND INFORMATION

Previous work at Argonne National Laboratory (ANL) on identifying anode- and cathode-stable materials[1] demonstrated the merit of the philosophy and the approach taken. Briefly, the approach focused on the fact that the cell environment governs the stable materials and their properties. Thus, temperature, oxygen partial pressure, and alkali metal activity determine not only the compound formed but also its stoichiometry. This is particularly evident for a number of compounds that have the same nominal composition (e.g., $LiFeO_2$, Li_3NbO_4, Li_3TaO_4, etc.) in both the anode and cathode environments, but have significantly different stoichiometries. This difference in stoichiometry results in different conductivities; for example, the conductivity of undoped, cathode-prepared $LiFeO_2$ is 0.003 $ohm^{-1}cm^{-1}$, while that of undoped, anode-prepared $LiFeO_2$ is about 3.0 $ohm^{-1}cm^{-1}$. The probability that conductivity can be enhanced by doping the stable compounds is high because the parent material was chosen to contain a cation capable of existing in more than one valence state. This was demonstrated in doping experiments on $LiFeO_2$ and Li_2MnO_3, where the conductivity was increased from 0.003 $ohm^{-1}cm^{-1}$ for undoped $LiFeO_2$ to 0.3 $ohm^{-1}cm^{-1}$ for the Co-doped compound and from 0.0014 $ohm^{-1}cm^{-1}$ for undoped Li_2MnO_3 to 0.04 $ohm^{-1}cm^{-1}$ for the Mg-doped compound. However, stable conductive compounds are only the first step in producing the desired cell component.

For the progression from conductive material to electrode, state-of-the-art NiO structures served as the initial guide for the cathode. Initial quantitative microstructural requirements were defined by use of a code from Physical Sciences, Inc. (PSI).[2] These analyses suggested that for cathode materials with the developed conductivities (0.03-0.3 $ohm^{-1}cm^{-1}$) porous, thin electrodes (0.2 cm thick) having agglomerates <10 microns in diameter and consisting of submicron particles were desirable. This objective was accomplished through the development of a novel process for making small polycrystalline ceramic fibers.[3]

Cell testing with both full cells (25 cm^2) and diagnostic half-cells is the basis for enhancing the understanding of cathode performance. The effect of varying microstructures and material resistivities on relative performance provides insight into cathode mechanisms. Results for a number of doped $LiFeO_2$ cathodes suggested that active surface area was an important parameter in overall performance.[1] The active surface area can be affected by both cell design and modifications and electrode surface area. The first significant improvement in performance was the result of a cell design change.

PROJECT DESCRIPTION

The overall project consists of three general areas that define the steps necessary in component development. The first area concerns the component material and the material properties. The emphasis of this portion of the project is on assessing in-cell behavior of the experimentally determined anode- and cathode-stable oxides, which includes migration and inferred solubility, and on evaluation/development of component conductivity. The second area encompasses the structure requirements of specific components and the fabrication procedures needed to meet the requirements. The final area centers around the in-cell evaluation of the component; for electrodes, this includes performance as well as catalytic/kinetic behavior. The components under development in this project include ceramic anode and cathode electrodes, as well as a ceramic separator, with each in a different state of progress.

The development of conductive ceramics as fuel cell components is aided by an understanding of the conduction mechanisms of the stable ceramics. Because environment produces changes in phase and stoichiometry, it is necessary to control the conditions under which a material is made and studied. This is best demonstrated by comparing the product of Fe_2O_3 reacted with electrolyte in a dry, reducing environment to that in humidified anode gas. In the absence of water vapor and CO_2, metallic iron is formed; in the humidified anode gas, $LiFeO_2$ is formed. With a variety of specialized equipment (designed and fabricated in-house), the materials can be synthesized, sintered, and studied in the necessary environments. Thus, Seebeck measurements, differential thermal analysis, thermogravimetry, and conductivity measurements are done under varying gas compositions, and, in the case of the last two measurements, under a range of pressures also. The data from studies such as these provide the evidence for deducing the conduction mechanisms. Based on the knowledge gained from the study of undoped $LiFeO_2$, $LiFeO_2$ was successfully doped with manganese, copper, and cobalt, and its conductivity was developed to a level thought to be adequate for practical cathode use. Similarly, it was demonstrated that Li_2MnO_3 could be doped with magnesium.

The approach followed in the development of conductive cathode materials is applicable to both anode materials and protective coatings and forms the basis for the current study of anodes and separators. Current work on electrode materials focuses on determining the effect of gas composition and doping on the electronic behavior of iron- and manganese-based anode materials.

The emphasis in electrode structure development is to devise a fabrication scheme that is applicable to most fuel cell electrode materials, with only minor modification to accommodate surface area effects, and that is scaleable. Using a fabrication process based on small-diameter polycrystalline ceramic fibers, porous ceramic bodies were produced from a variety of oxide-based materials (e.g., $LiFeO_2$, Li_2MnO_3, Mn_3O_4, MgO, $LiAlO_2$). In general, the materials and structures produced were those that are stable in an oxidizing (cathode) environment. Adaptation of cathode fabrication techniques to anode materials was demonstrated for $LiFeO_2$ as an anode electrode. The major concern in the cathode/anode adaptation has to do with binder burn-off procedures. A method that proved to be effective involved flash firing and sintering the fibers, which were made from anode-produced material, in air and then holding the tape-cast electrode in anode gas for 100 h at the temperature needed to assure sintering and stoichiometric equilibration. In principle, this method should be effective for any material that has nominally the same composition in both the fuel and oxidant environments. The practical aspect of this procedure remains to be demonstrated for other doped and undoped anode materials and is an area of continuing study.

Cell testing with full cells (25 cm^2) and diagnostic half-cells is the basis not only for evaluating ANL alternative materials, but also for enhancing the understanding of electrode mechanisms. Material resistivity and surface area are being studied. Previously, four types of $LiFeO_2$ cathodes were studied, namely, Mn-, Cu-, Co-doped, and high surface-area undoped $LiFeO_2$. The 650 °C bulk resistivity of these materials ranges from 300 ohm-cm (undoped) to 3 ohm-cm (Co-doped).[1] Previous and current cell data suggest that with the current cathodes the effects of low active surface area predominate over material resistivity effects. Cell design changes and increased electrode surface area resulted in a significant improvement in cell performance; however, the best cell performance was still a factor of about 1.5 poorer than that of NiO (based on current density). Recent emphasis is on methods/modifications to produce higher surface area cathodes.

RESULTS AND ACCOMPLISHMENTS

The electronic conductivity of undoped and niobium-doped $LiFeO_2$ and undoped MnO was measured under anode inlet gas humidified with room temperature water. (MnO and $LiFeO_2$ were previously determined to be stable in the anode environment.) The resistivity data for anode-prepared undoped and Nb-doped $LiFeO_2$ are shown in Fig. 1 for the temperature range 140-650 °C. These data show a significant difference in resistivity between the two undoped $LiFeO_2$ specimens. While the reason for the difference has not been quantitatively defined, a qualitative assessment is possible. In our early studies, it was determined that $LiFeO_2$ reduced to iron metal when heated to 800-900 °C in a dry reducing environment (i.e., 6% H_2 balance He or Ar). In environments containing H_2, CO_2, and water vapor, however, the oxygen partial pressure is high enough (about 10^{-23} atm) to keep Fe in an oxidized state. The material in curve A was synthesized at 700 °C in an environment that represents an extreme in fuel inlet conditions (i.e., 35% H_2, 51% CO, 9.5% CO_2, 3% H_2O, balance N_2). In this case, the pO_2 is about 0.9×10^{-23} atm. The material in curve B was prepared at 700 °C under fuel inlet conditions of 80% H_2, 20% CO_2, humidified with 60 °C water. The pO_2 is about a factor of 5 higher than in the previous case. Thus, the starting materials would be expected to have different Fe^{2+}/Fe^{3+} ratios. In the resistivity measurements, the relevant gas for each sample was humidified to 3%. As a result, the pO_2 was similar in both resistivity-test cover gases. The low-temperature measurements, <400 °C, would tend to reflect the stoichiometry of synthesis conditions [pO_2 (A) about 1/5 pO_2 (B)], whereas at temperatures higher than 400 °C, the material in curve B would equilibrate at an increased rate to the lower pO_2 level. Thus, the resistivity values at higher temperatures should be similar. It would be expected that if longer equilibration were used, the 650 °C values would be equivalent in curves A and B. These data highlight the necessity of being cognizant of fuel cell environments throughout synthesis and processing.

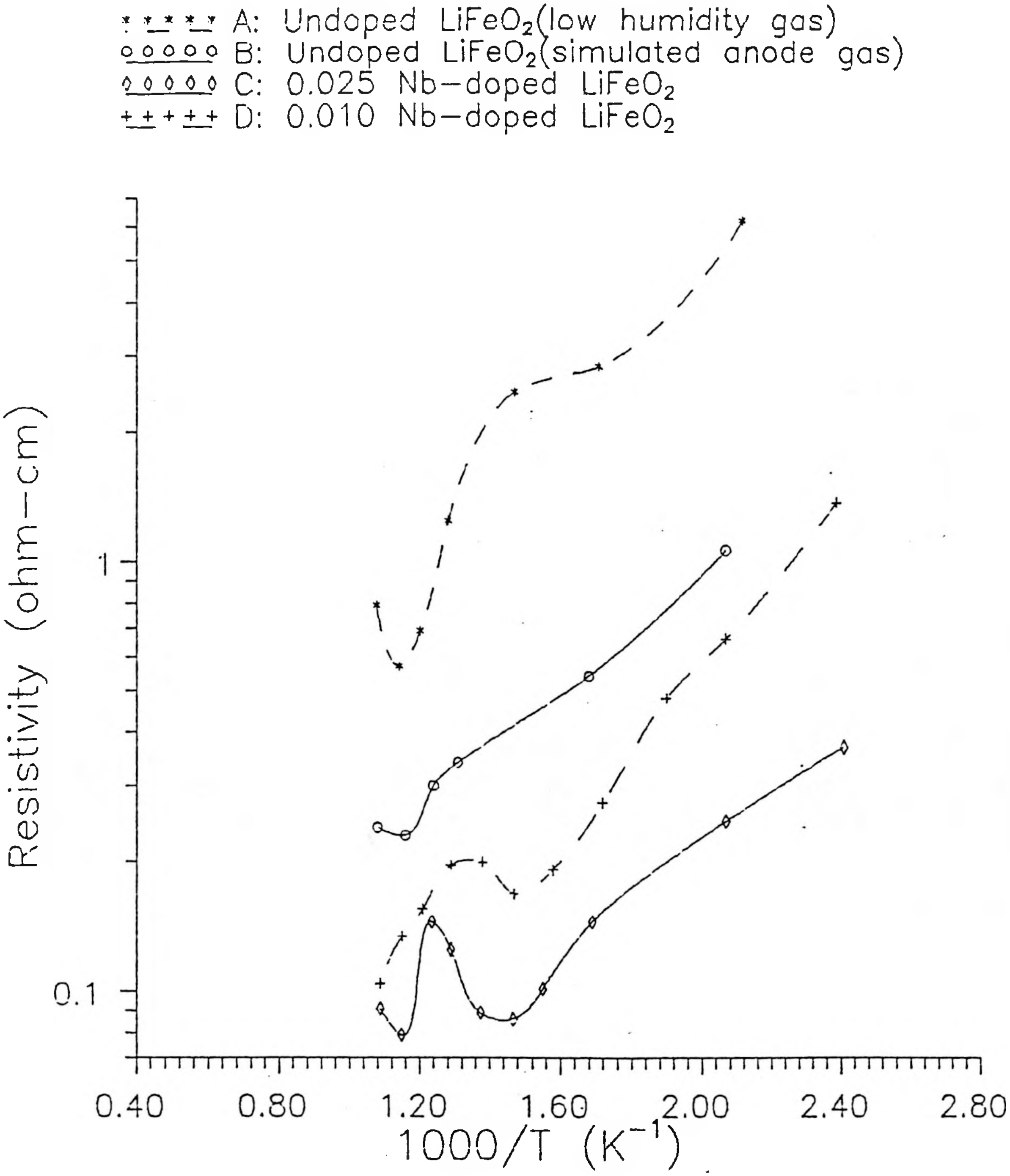


Fig. 1. Resistivity of Anode-Prepared Undoped and Niobium-Doped $LiFeO_2$

The effect of niobium-doping on anode-prepared $LiFeO_2$ is shown in curves C and D of Fig. 1. The synthesis gas composition was the same as that used to prepare the material in curve B. The data show that niobium doping results in an increase in conductivity in $LiFeO_2$. The data show little difference, however, between the 0.025 and the 0.10 Nb-doped material. While a greater difference would be expected normally, the nature of the anode-prepared material probably precludes this. It was reported previously[1] that undoped, anode-prepared $LiFeO_2$ contains about 35 mol% Fe^{2+} ($Fe^{3+}/Fe^{2+} \sim 1.8$). In the simplest case,the maximum conductivity, via electron hopping from Fe^{2+} to Fe^{3+}, would occur when the Fe^{3+}/Fe^{2+} ratio = 1. For 0.025 Nb-doped material, assuming complete incorporation, the Fe^{3+}/Fe^{2+} ratio is about 1.4 and ~0.6 for 0.10 Nb-doped material. Thus, it is likely that at the higher dopant level a barrier to electron hopping comes from excess Fe^{2+} and Nb sites. From this simple model, it appears that slightly less than 0.06 Nb-doping would give maximum conductivity.

The resistivity of anode-prepared MnO was measured over the temperature range 525 to 650 °C in anode gas humidified with room temperature water vapor. The 650 °C bulk resistivity was 23 ohm-cm, about two orders of magnitude larger than that of $LiFeO_2$. Stoichiometric MnO is green in color while the anode-prepared material is black, suggesting *in situ* lithium doping analogous to the case of NiO. Crevecoeur and DeWit[4] in their study of Li-doped MnO, prepared in both CO/CO_2 and H_2/N_2 mixtures, report a resistivity of ~20 ohm-cm at 650 °C when the lithium concentration was about 0.1 at%. The effect of other dopants on the resistivity of MnO will be studied.

Our emphasis in structure development was to devise a fabrication scheme for producing anode electrodes from iron- and manganese-based compounds. Techniques to produce an anode electrode from $LiFeO_2$ were discussed previously.[1] The current effort centered on MnO. In the previous section, we discussed a scheme involving flash firing and sintering of anode fibers in air and the successful conversion of the electrode back to anode equilibrium conditions. It was stated that the procedure would be effective for any material having the same nominal composition in both oxidizing and reducing environments. In considering a fabrication scheme for MnO, it was apparent that another form of oxide would exist in air. This problem was dealt with in the following manner. Fibers were made from Mn_3O_4 and were flash fired and sintered in air. They were then converted to MnO in the anode environment. This was accomplished without destruction of the fibrous nature of the material; this demonstrated the feasibility of using an air burn-off/anode-conversion scheme in producing a manganese-based electrode.

Air-sintered Mn_3O_4 fibers were next tape-cast into a thin tape. Binder burn-off and sintering were again done in air, and the structure was exposed to anode conditions to convert the material to the anode-stable MnO. This procedure resulted in an MnO anode that had sufficient strength to be easily handled. At this point, however, the MnO was not yet lithiated, and the structure was the typical green of stoichiometric MnO. The issue under study at this time concerns the sequence of lithiation; namely, must lithium be incorporated during fabrication or can incorporation be done as a final step, or perhaps even *in situ*?

Half-cells and 25 cm^2 full cells are being operated to evaluate iron- and manganese-based cathodes. The focus of this study to date has been on assessing the performance and reaction kinetics of doped $LiFeO_2$. In our earlier studies, the cell data from full cells suggested that performance is dominated by low active surface area. Several electrodes were also run in a diagnostic cathode half-cell. The polarization data from these tests give linear Tafel plots; Figure 2 shows Tafel plots as a function of oxygen partial pressure for an undoped $LiFeO_2$ half-cell cathode. Curves that are linear in the Tafel region (i.e., at high overpotential) indicate that the rate-limiting step is electron transfer. In comparison, NiO cathodes produce nonlinear Tafel plots because the reaction rates are diffusion controlled. Thus, increasing the active surface area should make the $LiFeO_2$ cathodes perform kinetically more like NiO and also improve the in-cell performance of the cathodes.

Supportive evidence that the active surface area is an important parameter comes from cell tests with $LiCoO_2$ cathodes. $LiCoO_2$ has a resistivity similar to that of Co-doped $LiFeO_2$. It was found that preparing $LiCoO_2$ with very small particle size was relatively simple, and that these small particles gave high surface-area cathodes. These cathodes performed comparably to state-of-the-art NiO except for a slightly higher area-specific resistance, but of course, cobalt metal deposited in the electrolyte.

The focus of our work to improve cell performance is, therefore, on methods to increase cathode surface area. Several methods are currently being explored.

One method for developing increased surface area results from our MnO anode work. In an effort to evaluate the effect of reducing an Mn_3O_4 structure to MnO, a portion of an air-prepared electrode was broken in half, and one piece was exposed to anode gas conditions for 100 h. These two specimens were examined by Hg porosimetry. Figure 3 shows the effect of this treatment on surface area. These data show a significant increase in surface area in the small pore range (0.01 to 0.07 microns). It is likely that the increase is the result of the phase and the accompanying density change that occur when Mn_3O_4 (4.9 g/cm^3) is reduced to MnO (5.4 g/cm^3). This change of ~10% could cause micro-cracking of the individual particles that make up the fibers/structure. A variation of this procedure is being applied to an $LiFeO_2$ structure in an effort to increase surface area. In this case, the change will not be as great because the compound remains the same, but the lattice volume undergoes a 3% change in going from anode-prepared $LiFeO_2$ (4.200 Å) to air-prepared $LiFeO_2$ (4.158 Å). The procedure being examined is to take a cathode-prepared $LiFeO_2$ structure, expose it to anode gas, and then re-equilibrate the structure in air. Thus, the lattice constant would change from 4.158 Å to 4.200 Å to 4.158 Å. This procedure may induce a sufficient surface-area enhancement, and its merit is still under assessment.

Another approach to increasing cathode surface area results from application of the PSI code/model, which indicates that the active surface area for a typical cathode microstructure is a strong function of agglomerate diameter. With large agglomerates, the rate-limiting step is the diffusion of the reactants through the electrolyte that floods the agglomerate. The core of large agglomerates may be essentially inactive. Our experience with producing fibers suggests that uniform, small-diameter agglomerates can be produced by controlling the rate at which the slurry is injected into the air stream. A screw-driven pump has been built, and its effectiveness in producing uniform, small-diameter fibers has been verified by scanning electron microscopy.

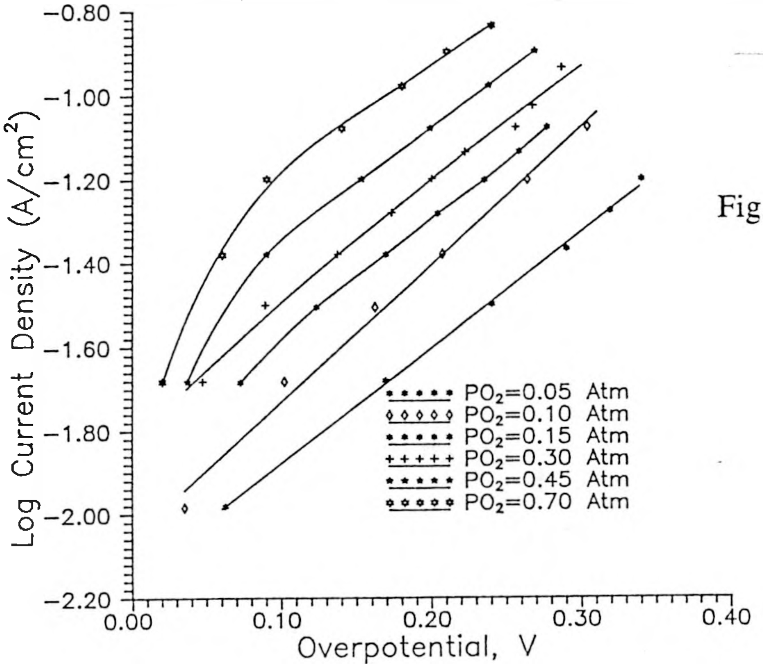
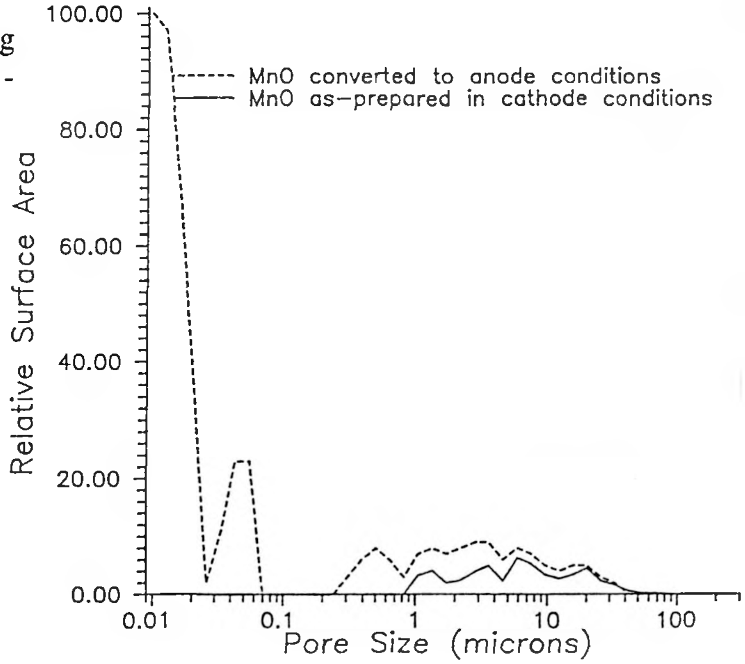


Fig. 2. Tafel Plots as a Function of Oxygen Partial Pressure for an Undoped $LiFeO_2$ Cathode

Fig. 3. Surface Area Enhancement Resulting from Equilibration of Cathode-Prepared MnO to Anode Conditions



In addition to use of smaller diameter fibers to maximize active surface area, another method has focused on minimizing the temperature for fiber sintering as well as that for structure production. Data from half-cells with a cathode consisting of smaller fibers and sintered at lower temperatures showed improved performance suggesting a similar benefit for full cell cathodes.

A final method to maximize surface area involves a technique to produce starting oxides with significantly smaller particle sizes. These powders are being produced by a new modification to the Pechini process. The resulting lithiated oxides have a narrow size distribution in the range of 0.2-0.5 microns and are being used in conjunction with the previously described efforts. Cathodes, thus prepared, are currently under assessment in both full and half-cells.

In addition to the development of electrodes, work has begun on materials and structure for an all-ceramic separator for the MCFC. Equipment to evaluate the relative diffusivity of hydrogen and oxygen and the through-plane conductivity in the presence of fuel and oxidant of the thin ceramic separator is under construction. The initial results will provide the basis for evaluating the need for, and the effect of, dopants.

Technology was transferred to industry in two ways. A report containing complete documentation of materials synthesis and cathode structure fabrication was sent to fuel cell contractors. In addition, the ceramic fiber-making process was transferred to industry as an entity in itself through licensing from DOE.

FUTURE PLANS

The result of material and structure evaluation will continue to be the basis for electrode improvement. Correlations of resistivity and surface area with cell performance will be emphasized for both ceramic anodes and cathodes.

Work will be directed to developing a more corrosion-resistant separator. This includes studying materials stable in both fuel and oxidant, developing adequate conductivity, and assessing the compatibility with adjacent cell components.

Cell testing and development of cells consisting of the materials and structures developed in the preceding studies will form the basis for producing a cell with the new ceramic components that gives the best overall performance.

ACKNOWLEDGEMENT

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