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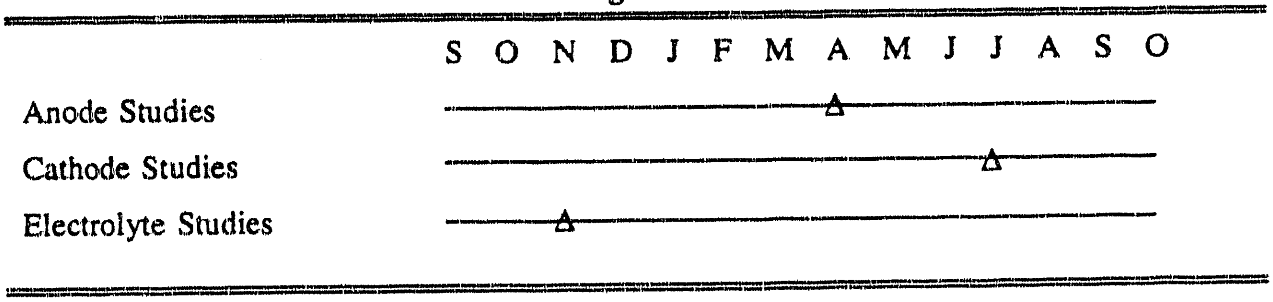
ANL'S RESEARCH AND DEVELOPMENT OF ALTERNATIVE COMPONENTS FOR MCFC'S

CONTRACT INFORMATION

Contract Number:	49943
Contractor:	Argonne National Laboratory 9700 S. Cass Avenue Argonne, IL 60439
Contractor Project Manager:	K. M. Myles
Principal Investigator:	G. H. Kucera
Co-Investigators:	A. P. Brown, M. Roche, D. Chu, E. Indacochea
METC Project Manager:	W. J. Huber/W. C. Smith
Period of Performance:	October 1, 1982 to Open

Schedule and Milestones

FY92 Program Schedule



OBJECTIVES

Molten carbonate fuel cell (MCFC) systems are currently limited by several technical problems. The objectives of this project are to focus on these problems and develop materials and cell components that will ameliorate or eliminate them. Specifically, new ceramic materials are being investigated for dimensionally stable electrode materials with improved chemical and electrochemical properties over the present NiO cathode and Ni/Cr and Ni/Al anodes. Also, alternative electrolyte formulations to the present Li_2CO_3-K_2CO_3 are being studied to reduce nickel

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MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED oxide solubility, minimize differential electrolyte migration, and reduce component corrosion.

BACKGROUND INFORMATION

Many of the technical problems associated with the development of advanced fuel cells are materials related. In previous work (1) at Argonne National Laboratory (ANL), various ceramic materials were identified as being stable in the anode environment, the cathode environment, or both environments of the MCFC. To enable the use of these stable materials in anodes or cathodes, dopants were selected to improve their electronic conductivity. In addition, techniques were developed to form fibrous agglomerates of the materials, which could then be tape cast into electrode bodies with the desired, bimodal pore distribution (1).

From the materials identified as stable in the cathode environment, $LiFeO_2$ was selected as a promising candidate for the cathode material. Cathodes were prepared from undoped $LiFeO_2$ and from $LiFeO_2$ doped with Cu, Mn, or Co. These cathodes were tested in a 25-cm^2 full cell and a 2.5-cm^2 cathode half cell. In initial full-cell tests of up to 1000 h, these cathodes demonstrated excellent stability, and no evidence could be found for any deleterious dissolution/reprecipitation reactions. However, the performance of these cathodes was relatively poor compared to that of a state-of-the-art (SOA) NiO cathode (1).

To help understand the reasons for the poor performance, extensive half-cell tests were carried out using Co-doped $LiFeO_2$ cathodes. Experimental variables included BET surface areas up to about 10 m^2/g, temperatures between 600 and 700°C, oxygen partial pressures between 0.05 and 0.7 atm, and carbon dioxide partial pressures between 0.05 and 0.6 atm (2). These tests showed that the performance of the Co-doped $LiFeO_2$ cathodes could be significantly improved by increasing the surface area, increasing the temperature, increasing the oxygen partial pressure, or decreasing the carbon dioxide partial pressure (2). With a surface area of about 2 m^2/g, a temperature of 675°C, and an oxidant composition of 95% air/ 5% CO_2, the performance of the Co-doped $LiFeO_2$ cathode was very close to that of an SOA NiO cathode under standard operating conditions. It was also determined that there are two competitive reaction mechanisms for the MCFC cathode reaction on the Co-doped $LiFeO_2$ electrode. The changes in operating conditions noted above that improve the cathode performance do so by promoting the faster, catalytic reaction mechanism.

Several potential anode materials were identified, including MnO doped with Nb or Mg, undoped $LiFeO_2$, and $LiFeO_2$ doped with Mn, Co, or Ni (2). Electrode fabrication techniques for these materials were developed that ensure that the chemical state of the electrode material is known and reproducible when the electrodes are introduced into the anode environment of the MCFC (2).

In a separate effort at ANL (3-6), the Conformal Ionic Solution Theory (3) and the Coordination Cluster Theory (4) were used to predict the solubility of NiO (actually $NiCO_3$) in binary alkali metal carbonate melts. Good agreement was found between the measured and predicted NiO solubility in Li_2CO_3/K_2CO_3 melts (5,6). Both theories lead expressions that relate the activity coefficient of NiO in the binary solvent to the activity coefficients of the alkali carbonate salts and the solubilities of NiO in the individual components of the binary mixture (5); the higher the activity coefficient of NiO, the lower will be its solubility in the carbonate melt.

PROJECT DESCRIPTION

This project consists of work in several areas of MCFC component development:

alternative anode and cathode materials are being developed and evaluated in full and half cells, ways to improve the performance of NiO cathodes are being investigated, and alternative electrolytes that possess a low NiO solubility are being studied.

Ceramic anodes are being developed as alternatives to the current Ni/Cr and Ni/Al anodes. These ceramic anodes are expected to minimize creep and provide better tolerance to sulfur-poisoned fuel gases. These anodes will also have specially tailored pore structures and pore size distributions because they will be fabricated with the ANL fibrous agglomerate technology (7). Full-cell tests are being carried out with anodes made from Mg-doped MnO, undoped $LiFeO_2$, and $LiFeO_2$ doped with Co, Mn, Nb, and Ni. An anode half-cell test stand is also being designed and fabricated. This apparatus will allow the performance of the various anodes to be studied in more detail, including mechanistic studies related to sulfur poisoning. Additional potential anode materials are being developed by careful selection of the parent oxide and electronic conductivity enhancement through doping.

Half-cell tests are being carried out with $LiFeO_2$ cathodes doped with Cu, Mn, and Ni and Li_2MnO_3 cathodes doped with Mg. The performance of these cathodes is being studied over the same ranges of temperature, oxygen partial pressure, and carbon dioxide partial pressure as were used earlier with a Co-doped $LiFeO_2$ cathode (2). These cathodes are being developed as alternatives to the current *in-situ*-oxidized NiO cathode because they chemically stable in the MCFC cathode environment and will not undergo the same life-limiting dissolution/reprecipitation as the NiO.

Another approach to solving the dissolution/reprecipitation problem with the NiO cathodes is to use an alternative electrolyte with a low NiO solubility. With the likelihood of developing an alternative electrolyte appearing more probable, other concerns with the current NiO cathodes become increasingly dominant. For example, the cathode can also suffer from creep, and the polarization losses associated with the cathode are significantly greater than those of the anode. To address these problems, the ANL fibrous agglomerate technology for electrode fabrication (7) is being applied to the development of lithium-doped NiO cathodes that are oxidized *ex situ*. These cathodes are expected to attain improved performance over the SOA NiO cathodes which are oxidized *in situ*. Stability tests are being carried out to determine the maximum amount of lithium that might be incorporated into NiO to provide optimal electrical conductivity for the cathode. In addition, half-cell tests are being used to assess the performance of the new lithium-doped NiO cathodes as a function of electrode thickness.

To help develop an alternative carbonate electrolyte in which NiO has a low solubility, two molten salt theories, the Conformal Ionic Solution Theory and the Coordination Cluster Theory (5,6), are being used to predict salt compositions with a high $NiCO_3$ activity coefficient. Then, NiO solubilities are being measured in these new electrolytes under an MCFC oxidant environment. For use in a fuel cell, any new electrolyte must meet requirements other than low NiO solubility. Thus, liquidus temperature, corrosion properties, cathode polarization, differential ion migration, and wetting properties also need to be considered. The initial selection of promising alternative electrolytes will be made based on measurements of liquidus temperature and NiO solubility.

RESULTS AND ACCOMPLISHMENTS

Anode Development

Various doped and undoped $LiFeO_2$ anodes and one Mg-doped MnO anode have been tested in a 25-cm^2 full cell against an *in situ* oxidized NiO cathode (fabricated by Gould Inc.). The $LiFeO_2$ dopants were Mn, Co, and Ni, and the tests were carried out using an oxidant of 14% O_2/28% CO_2/bal. N_2, a fuel of 80% H_2/20% CO_2, an electrolyte of 70% Li_2CO_3/30% K_2CO_3, and a temperature of 650°C. None of these anodes performed as well as an SOA Ni/Cr anode (also fabricated by Gould Inc.). Additionally, none of these alternative anodes would support current densities greater than about 80 mA/cm^2. Open-circuit potentials were close to that obtained with the Ni/Cr anode, as were the area specific resistances (ASR) for the cells, except for the cell with the Mn-doped $LiFeO_2$ anode where the ASR was about 1.6 Ω cm^2 (with the Ni/Cr anode, the cell ASR was about 0.44 Ω cm^2) . The cell behavior observed was generally similar to that observed by the Institute of Gas Technology (IGT) (8) although the IGT $LiFeO_2$ anodes would not run for long periods at current densities above about 40 mA/cm^2.

Figure 1 shows the full-cell polarization curves for the various alternative anodes and the Gould Ni/Cr anode. As can be seen in this figure, the polarization curves for the MnO and $LiFeO_2$ anodes do not extend beyond about 80 mA/cm^2. At higher current densities, the cell voltages did not stabilize but continued to slowly decrease until a pre-defined cutoff of 0.6 V was reached. Most of the cells would recover at least partially if left on open circuit for several hours, although the extent of recovery was usually depended on how long the cell had been on test. As can be seen in Figure 1, the Co-doped $LiFeO_2$ anode performed better than any of the other alternatives, while the Mg-doped MnO anode performed the worst. (These performance comparisons should not be taken as absolute because these tests were part of a preliminary investigation, and several important parameters, such as the anode thickness and the anode pore-size distribution, were not strictly controlled.)

Post-test analysis of these cells showed that all of the anodes suffered from at least some chemical instability. With the Mg-doped MnO anode, a broad band of Li_2MnO_3 particles was found in the electrolyte adjacent to the cathode. Smaller quantities of $LiFeO_2$ were found next to the cathode in all of the $LiFeO_2$ anode cells. The Co-doped $LiFeO_2$ anode reacted to produce a CoFe alloy both in the anode and in the electrolyte adjacent to the anode; similar behavior was found with the Ni-doped $LiFeO_2$ anode, except that the alloy was NiFe.

Cathode Development

Previously, the half-cell performance of Co-doped $LiFeO_2$ cathodes was reported as a function of temperature, oxygen partial pressure (pO_2), and carbon dioxide partial pressure (pCO_2)(2). To determine any possible effects on performance of the chemical nature of the $LiFeO_2$ dopant or the electronic conductivity of the $LiFeO_2$ cathodes, a series of $LiFeO_2$ cathodes with dopants of Ni, Mn, and Cu was fabricated and tested in half cells. Both the BET surface areas and the pore-size distributions of these cathodes were made to match as closely as possible those of the Co-doped $LiFeO_2$ cathode. The electronic conductivities for the various doped lithium iron oxides are compared in Table 1. As can be seen in this table, the conductivities vary by about a factor of 37.

With an oxidant of 15% O_2/30% CO_2/55% N_2 and an operating temperature of 650°C, the performance of these doped $LiFeO_2$ cathodes was very similar, as shown in the plots of iR-free overpotential versus current density in Figure 2. The polarization curves for both the Co- and Ni-doped $LiFeO_2$ cathodes are approximately "S" shaped, while the polarization curves for the other two cathodes show only a single arc. The effect of increasing the pO_2 is shown in Figure 3. All the cathodes improve in performance with increasing

pO_2, and the Co-doped $LiFeO_2$ cathode improves the most. Increasing the temperature has a similar effect to increasing the pO_2. Figure 4 shows a similar comparison for a decrease in the pCO_2. In this case both the Co- and Ni-doped $LiFeO_2$ cathodes improve in performance with decreasing pCO_2 at all current densities, while the other two cathodes show an improvement in performance at low current densities but a decrease in performance at high current densities.

An Mg-doped Li_2MnO_3 cathode of similar BET surface area and pore-size distribution to the doped $LiFeO_2$ cathodes was also tested in the half cell. This cathode performed similarly to the Mn-doped $LiFeO_2$ cathode, both in the magnitude of the overpotentials and in the effect of temperature, pO_2, and pCO_2 on the overpotentials.

The relative performances of the various cathodes do not appear to follow the order of the cathode material conductivities. Nevertheless, the greater performance improvements seen with the Co-doped $LiFeO_2$ cathode could be the result of the higher conductivity of that material being borderline to that required for good cathode performance. Alternatively, the performance differences between the cathodes may be due to the relative catalytic activities of the various dopants or to the type of charge carriers in the various lithium iron oxides. The general conclusion from these studies is that under normal MCFC conditions, the performance of the $LiFeO_2$ and Li_2MnO_3 cathodes is independent of the cathode conductivity. This indicates that all of the electrode reaction will be localized very strongly at the current collector/electrode interface. For improved cathode performance under standard MCFC operating conditions, it will be necessary to either increase the stable, active surface area of the cathode; improve the catalytic activity of the cathode material; or expand the reaction zone into the cathode by increasing the cathode electronic conductivity (probably by at least one order of magnitude over that of the Co-doped $LiFeO_2$).

The stability of NiO doped with various concentrations of lithium was determined by exposing these oxides to a 70% Li_2CO_3/30% K_2CO_2 melt at 650°C in air or in MCFC oxidant for 500 h. In air, the stable lithium-doped NiO appeared to be about 30 mol% lithium (the maximum solubility of lithium ions in NiO). In the MCFC cathode environment, however, the lithium-doped NiO appeared to stabilize at about 5 mol% lithium. As a result, fiber-based cathodes were fabricated from 5 mol% lithium-doped NiO at various thicknesses (0.04 cm to 0.02 cm) and tested in half cells using *in situ* sintering. (Cathodes thinner than 0.02 cm have not yet been fabricated with a reproducible pore-size distribution similar to the thicker cathodes.)

Figure 5 shows the cathode overpotentials measured at 160 mA/cm^2 after about 150 h of testing for three thicknesses of the 5% lithium-doped NiO cathodes and an SOA *in situ* oxidized NiO cathode (fabricated by Gould Inc.). As can be seen in this figure, the new cathodes perform significantly better than the Gould cathode, and the performance improves with decreasing cathode thickness, such that the overpotential at 160 mA/cm^2 for the 0.02 cm cathode is about 43 mV better than that for the Gould cathode; less than half this improvement can be accounted for by reductions in cathode ASR. The performance of a 5% Li-doped NiO cathode (0.033 cm thick) at 200 mA/cm^2 as a function of time up to about 500 h is shown in Figure 6. As can be seen, the performance after about 150-200 h is almost constant, although some minor oscillatory changes do occur.

Electrolyte Development

The use of fundamental molten salt theories to predict NiO solubilities in binary alkali metal carbonate melts (3-5) was expanded to include ternary systems. Calculations indicated that ternary melts containing a binary alkali metal carbonate plus an alkaline earth carbonate would have a low NiO solubility. In particular, for a Li/K or Li/Na carbonate base with an alkaline earth carbonate, the NiO solubility would be in the order:

$$MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$$

Because $MgCO_3$ readily dissociates into MgO and CO_2 at the operating temperature of the MCFC, this compound was not considered for use in an alternative electrolyte. Thus, initial NiO solubility measurements were made with the addition of $CaCO_3$ to the binary alkali metal carbonates. Experimentally, an excess of NiO was added to a molten carbonate mixture at 650^{0}C which was stirred by sparging in a particular cover gas, either dry CO_2, or 14% O_2/28% CO_2/Bal. N_2 humidified at room temperature. The amount of dissolved NiO was followed as a function of time by sampling the melt and then analyzing those samples for nickel by atomic adsorption spectroscopy. Figure 7 shows the nickel concentration versus time plots for three melts: 70% Li_2CO_3/30% K_2CO_3, 54% Li_2CO_3/25% K_2CO_3/21% $CaCO_3$, and 55% Li_2CO_3/15% Na_2CO_3/30% $CaCO_3$; the temperature was 650°C and the cover gas was dry CO_2. The curves indicate that about 150-200 h is required for the nickel concentrations to reach their maximum values, and that the $CaCO_3$ addition is very effective in lowering the NiO solubility. A summary of the NiO solubilities in the melts currently studied is given in Table 2. Also shown in this table are the approximate liquidus temperatures of the various melts. The Li/Na/Ca melt has the lowest NiO solubility, about 1 wt ppm. However, this melt has a liquidus temperature of about 610°C, making it unsuitable for use in an MCFC.

FUTURE WORK

The anode half cell will be used to obtain a more detailed understanding of the behavior of the various anode electrode materials being tested. Development of additional, alternative anode materials will continue, with emphasis being placed on the selection of materials that should show more tolerance to sulfur-poisoned fuels than the current nickel-based anodes.

Because of the significant performance improvements seen with the Co-doped $LiFeO_2$ cathodes when the oxygen partial pressure is increased, it is planned to study these cathodes in a half cell at overall pressures up to 10 atm. The possible influence of the semiconductor carrier type on the performance of $LiFeO_2$ cathode will also be investigated.

Design parameters associated with the Li-doped NiO cathodes will be varied, and their effects on performance will be studied. These parameters include BET surface area, particle size, agglomerate size, pore structure, and pore-size distribution.

Many parts of the MCFC are affected by the properties of the electrolyte. Development of an alternative electrolyte with low NiO solubility will continue by measuring ionic transference numbers and calculating relative ion migration rates. Other factors that will be considered in optimizing an alternative electrolyte composition include liquidus temperature, wetting characteristics, ionic conductivity, corrosion properties, and electrode performance.

ACKNOWLEDGEMENT

We would like to thank M. Blander for many useful discussions concerning his molten salt theories and solubility predictions. This work was performed under the auspices of the United States Department of Energy, under Contract number W-31-109-Eng-38.

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Table 1. Comparison of the Electrical Conductivities at 650°C for Doped Lithium Iron Oxides

Material	Electrical Conductivity, $\Omega^{-1}cm^{-1}$
Ni-doped $LiFeO_2$	0.0087
Mn-doped $LiFeO_2$	0.033
Cu-doped $LiFeO_2$	0.083
Co-doped $LiFeO_2$	0.33

Table 2. NiO Solubilities in Various $CaCO_3$-Containing Melts at 650°C in Dry CO_2

Melt	Approximate Liquidus Temperature, °C	NiO Solubility, wt ppm
70% Li_2CO_3/30% K_2CO_3	532	9.40
58% Li_2CO_3/17.3% K_2CO_3/24.7% $CaCO_3$	575	3.90
49.8% Li_2CO_3/21.5% K_2CO_3/28.7% $CaCO_3$	556	3.25
54% Li_2CO_3/25% K_2CO_3/21% $CaCO_3$	535	3.00
55% Li_2CO_3/15% Na_2CO_3/30% $CaCO_3$	610	1.00

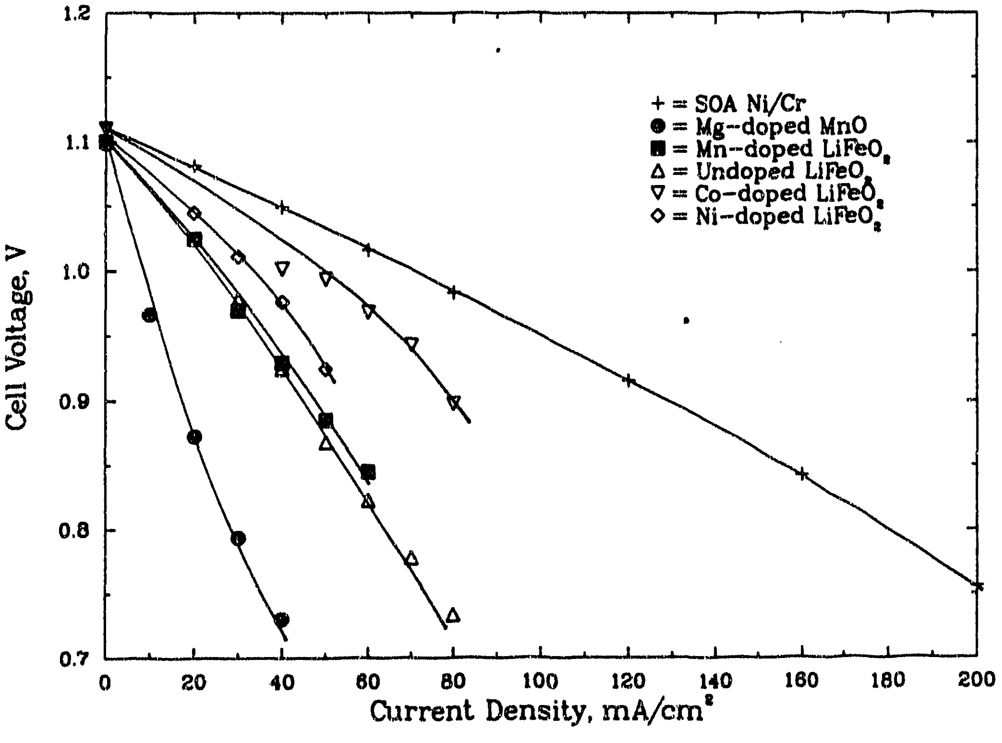

Figure 1. Cell Voltage versus Current Density for Various Anode Materials in Full-Cell Tests.

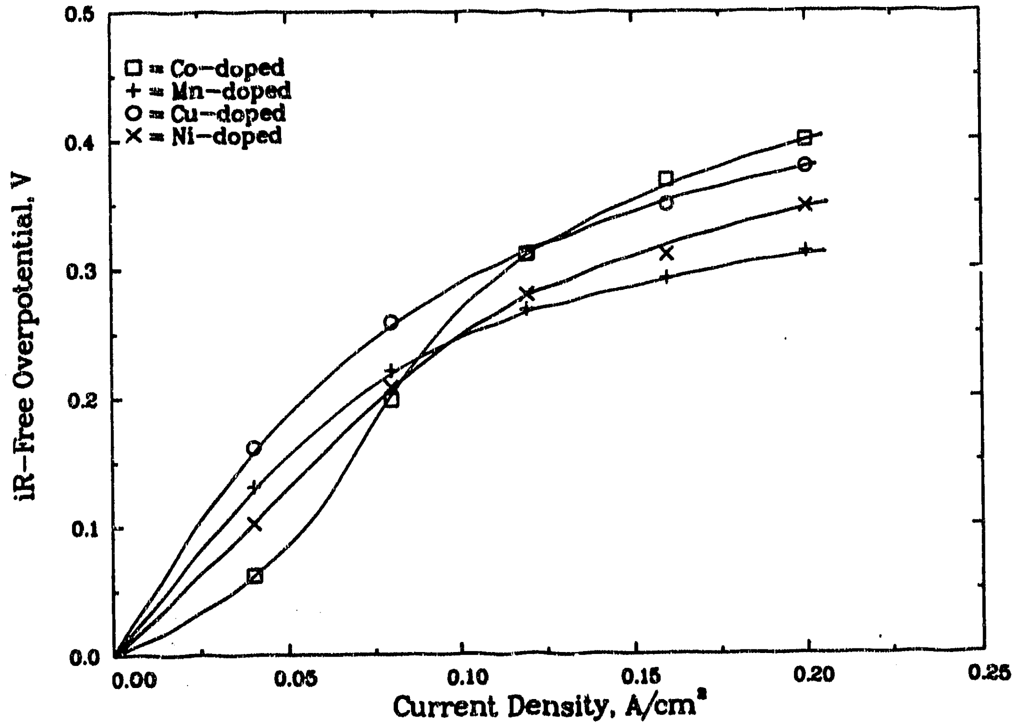

Figure 2. Plot of iR-Free Overpotential versus Current Density for Doped $LiFeO_2$ Cathodes in Half Cell Tests. Oxidant = 15% O_2, 30% CO_2, bal. N_2; temperature = 650^0C.

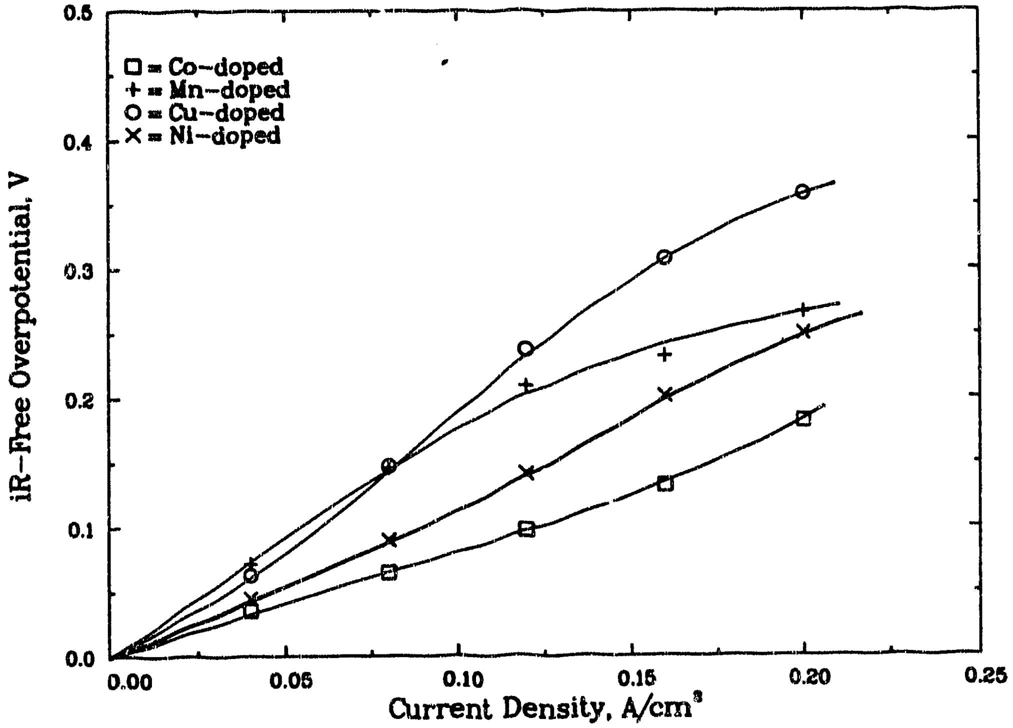

Figure 3. Plot of iR-Free Overpotential versus Current Density for Doped $LiFeO_2$ Cathodes in Half Cell Tests. Oxidant = 70% O_2, 30% CO_2; temperature = 650^0C.

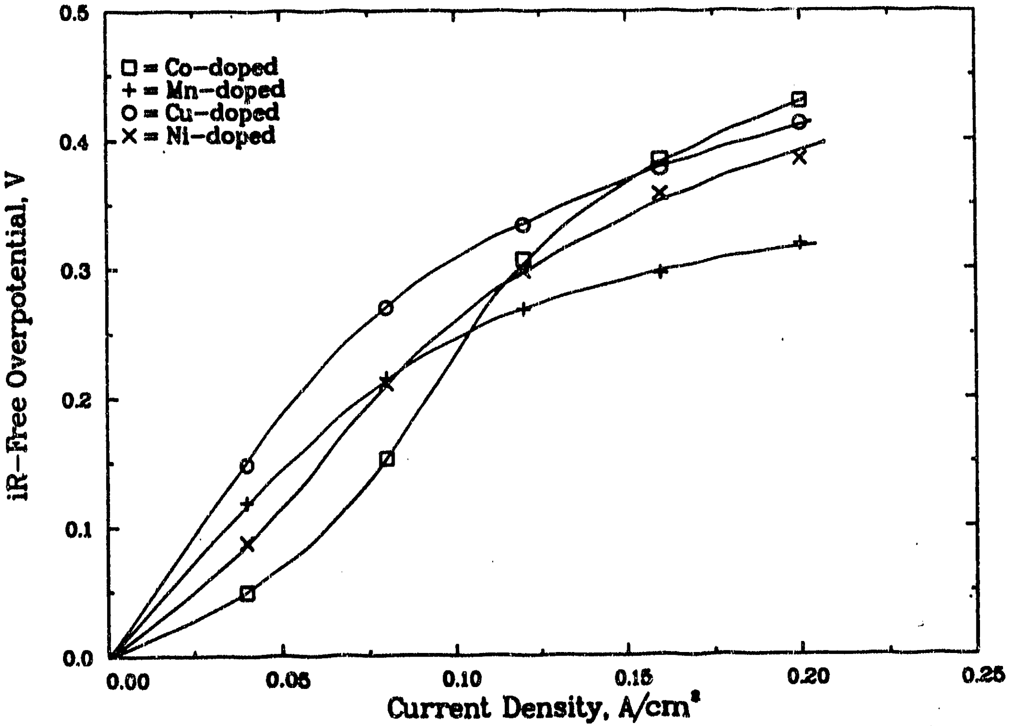

Figure 4. Plot of iR-Free Overpotential versus Current Density for Doped $LiFeO_2$ Cathodes in Half Cell Tests. Oxidant = 15% O_2, 5% CO_2, bal. N_2; temperature = 650^0C.

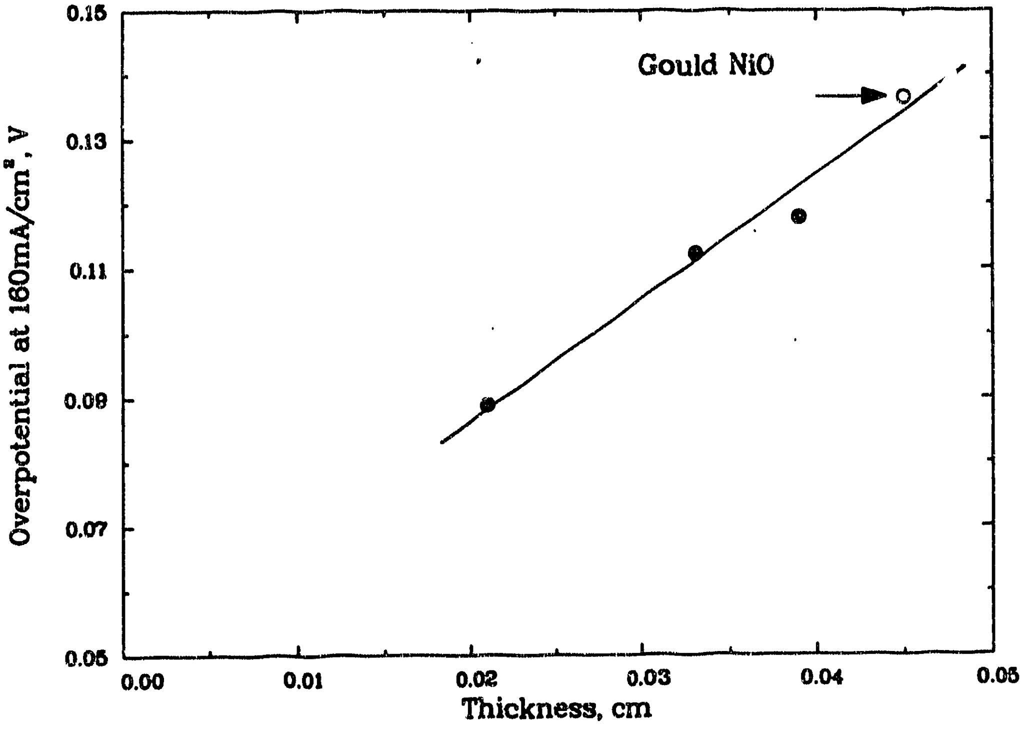

Figure 5. Plot of Electrode Potential Measured at 160 mA/cm² versus Electrode Thickness for 5% Li-Doped NiO Cathodes in the Half Cell.

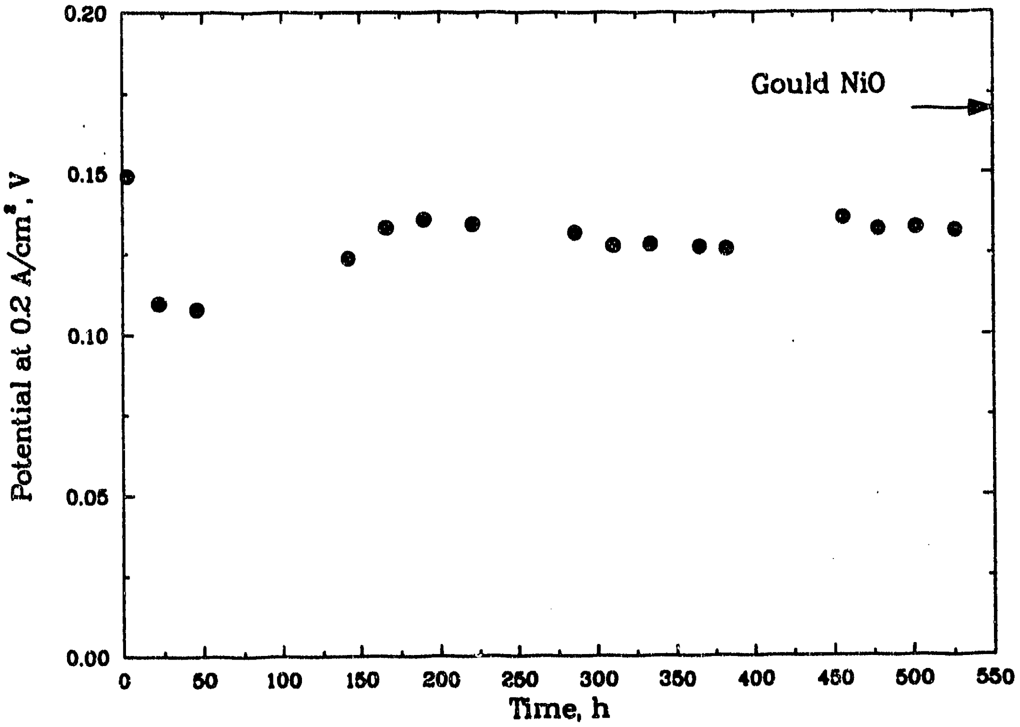

Figure 6. Plot of Electrode Potential Measured at 200 mA/cm^2 versus Time for 0.033-cm Thick, 5% Li-Doped NiO Cathode in the Half Cell.

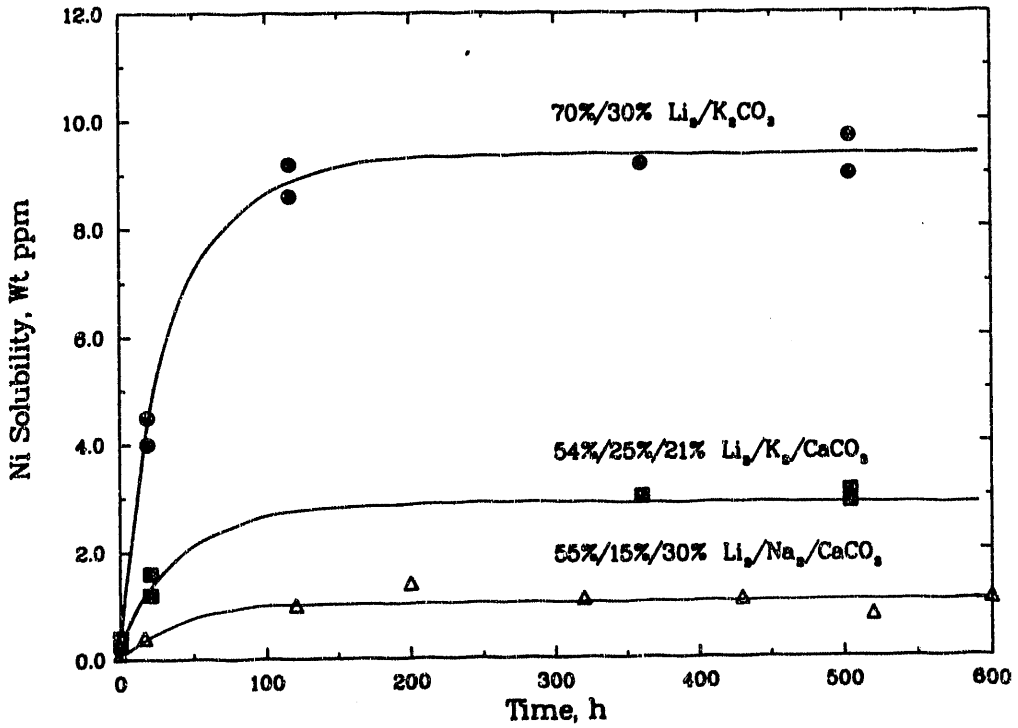

Figure 7. Plot of NiO Solubility Time for Three Carbonate Electrolytes. Cover gas = dry CO$_2$; temperature = 650^{0}C.

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