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INTRODUCTION

The effort on near-term development and commercialization of the molten carbonate fuel cell (MCFC) is focused on its operation at ambient pressure. However, the long-term objective is operation at pressures of 5 to 10 times ambient. There are a number of benefits to operating the MCFC under pressure. Some, such as smaller piping and blower size, affect the system cost, and others, such as increased efficiency and higher power density, result from the cell operation itself. A major problem associated with pressurization is the accelerated rate of dissolution of the MCFC's nickel-oxide (NiO) cathode and the subsequent deposition of nickel near the MCFC's nickel anode (1). The dissolution of NiO in the MCFC electrolyte proceeds according to the following reaction, which is driven to the left with increasing CO_2 pressure: $NiO + CO_2 \rightarrow Ni^{2+} + CO_3^{2-}$. The Ni^{2+} in the electrolyte is reduced to nickel metal when it encounters the reducing conditions of the anode environment. The loss of nickel oxide from the cathode becomes critical if a short circuit results or if compaction of the cathode occurs. A solution to this problem is the development of alternative cathode materials.

The selection of an alternative to the NiO cathode is based on a number of criteria. These include 1) chemical stability in the cathode environment, 2) low solubility in the electrolyte, 3) high electronic conductivity, 4) an absence of precipitation mechanisms in the anode environment (as either the metal or an oxide), and 5) overpotential for oxygen reduction (from in-cell tests). Studies at Argonne National Laboratory have focused on the development of various ceramic oxides identified as having chemical stability in the cathode environment. Three of the more promising candidates are $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$. This paper presents the results of studies of these materials with respect to the criteria listed above.

STABILITY

A properly designed stability test for an MCFC cathode reproduces the conditions of the cathode environment. These conditions include temperature, cathode gas, and electrolyte composition. Thus, the tests were conducted on candidate materials held at a temperature of 650°C in a 100 kPa (1 atm) cathode gas consisting of 14% O_2-28% CO_2-balance N_2. The candidate materials were wetted with the electrolyte, 70 mol% Li_2CO_3-30 mol% K_2CO_3, and, to ensure adequate gas access, the amount of electrolyte was controlled so that the materials were not flooded.

Various oxides of iron, manganese, and cobalt were tested under the above conditions. Because the phase rule indicates that each cation has only one stable compound, the test results were expected to be independent of the precursor oxide. Thus, Fe_2O_3, FeO, and Fe_2O_3 all produced $LiFeO_2$; MnO and Mn_2O_3 produced Li_2MnO_3; and CoO and Co_3O_4 produced $LiCoO_2$. These tests show that, under cathode conditions, the stable products are $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$.

SOLUBILITY

The solubilities of $LiFeO_2$, Li_2MnO_3, and NiO in Li_2CO_3-K_2CO_3 melts sparged with cathode gas were determined by Kaun *et al.* (2, 3). Their studies (see Fig. 1) showed that, at 650°C, iron and manganese had lower solubilities than nickel. Therefore, both the $LiFeO_2$ and Li_2MnO_3 cathode materials showed promise because they met two of the necessary criteria (chemical stability and low solubility).

The solubility of $LiCoO_2$ was measured under similar gas and electrolyte conditions at 650°C. Chemical analyses of electrolyte samples, taken periodically for times up to 300 h, showed about 0.5 wppm cobalt, a value also measured for a blank electrolyte sample containing no $LiCoO_2$. Low cobalt solubility was also reported by Plomp *et al.* (4), who state that $LiCoO_2$ has a dissolution rate which is almost an order of magnitude lower than that of NiO at ambient pressure. The data from these solubility studies suggests that $LiCoO_2$ warrants further study as a cathode.

MIGRATION

As indicated above, one of the selection criteria is that a potential cathode material should not form either a metal precipitate or an oxide precipitate at the anode (reducing) side of an operating cell. The candidate materials $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$ were assessed for their tendency to migrate toward the anode during cell operation (see "Cell Testing" section for a description of cell construction). Cells with $LiFeO_2$ and Li_2MnO_3 cathodes were operated only under open-circuit conditions, because the cathodes were not optimized for conductivity or electrode structure. The cells were operated for 2000 h and were quenched when the test was terminated so that any soluble cathode cations would remain in the electrolyte. The quenched electrolyte was analyzed by scanning electron microscopy/energy dispersive x-ray spectrometry (SEM/EDX) and by wet-chemical methods. Table 1 summarizes the results of the wet-chemical assays of electrolytes from the cells containing $LiFeO_2$ and Li_2MnO_3 cathodes and from a cell having a NiO cathode that was operated in a similar manner. The data showed that the concentrations of Fe and Mn from the cells with $LiFeO_2$ and Li_2MnO_3 cathodes were within the background scatter of the other cells. No evidence was found of either Fe- or Mn-containing deposits in the SEM/EDX measurements. These results, when taken with the above stability tests, showed that both $LiFeO_2$ and Li_2MnO_3 met three of the five criteria for an alternative cathode (chemical stability, low solubility, and a lack of migration).

Two $LiCoO_2$ cathodes were also tested in cells. These cells were operated under load; one for about 600 h, and the other for about 800 h. The components from the 600-h cell were examined by optical microscopy and SEM/EDX. The examinations revealed a small number of metallic deposits in the electrolyte tile near the anode and large crystalline deposits in the openings of the perforated sheet that serves as the cathode current collector. The SEM/EDX results showed that both deposits contained cobalt. The location of the deposits may be a reflection of the operating conditions, which varied from open circuit to a current density of 160 mA/cm^2. The components from the 800-h cell are still under examination. However, preliminary SEM/EDX results showed a significant concentration of cobalt at the cathode/electrolyte-tile interface that extended about 200 µm into the 1.3-mm-thick tile. The cobalt concentration decreased through the next 300 µm until a background value was reached. Because the cobalt concentration has not, as yet, been quantitatively determined, it is not certain if its transport represents a life-limiting situation. Researchers at the Netherlands Energy Research Foundation (5) reported finding cobalt in the nickel anode. If the cobalt deposition rate is low, and if all cobalt deposits are located in the anode, then $LiCoO_2$ would still be a promising cathode.

CONDUCTIVITY

The conductivity of a material is important in determining its usefulness as an MCFC cathode, since the material must be capable of delivering electrons to reaction sites where CO_3^{2-} is formed from O_2 and CO_2. The precise requirement for the conductivity of an alternative cathode material is unknown; however, an initial target was set at 0.1 ohm^{-1}cm^{-1} at 650°C. This is about a factor of 10 lower than that of the NiO cathode. Our calculations (6) using an existing model (7) indicated that a thinner electrode of less conductive materials would give a performance equivalent to the NiO cathode.

Conductivity measurements as a function of temperature were employed to determine the electrical properties of the candidate cathode materials. The measurements were made on sintered disks (about 2.5-cm dia x 0.2-cm thick) of $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$ using the van der Pauw method (8). The conductivity of $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$ in cathode gas (14% O_2-28% CO_2-balance N_2) is shown in Fig. 2 as a function of temperature. The data showed that the conductivity at 650°C (the typical MCFC operating temperature) was about 0.003 $ohm^{-1}cm^{-1}$, 0.0014 $ohm^{-1}cm^{-1}$, and 1 $ohm^{-1}cm^{-1}$ for $LiFeO_2$, Li_2MnO_3, and $LiCoO_2$, respectively. The values for $LiFeO_2$ and Li_2MnO_3 were too low for cathode use. However, their response to temperature is typical of a semiconductor. The electrical conductivity of a semiconductor depends on its charge-carrier concentration and carrier mobility and can be increased by dopants that increase the number and/or mobility of charge carriers.

Doping of $LiFeO_2$. Because the conductivity of $LiFeO_2$ was about a factor of 30 lower than the target value of 0.1 $ohm^{-1}cm^{-1}$, dopants were incorporated to improve its conductivity. The dopants Mn, Co, and Cu were successfully incorporated into the $LiFeO_2$ lattice. Manganese-doped $LiFeO_2$ was studied more extensively than the others. Manganese was added to the $LiFeO_2$ lattice until the incorporation limit was reached. This occurred when the mole ratio of manganese to iron was about 1:7. The result of these additions was that the conductivity at 650°C was increased from 0.003 $ohm^{-1}cm^{-1}$ to about 0.04 $ohm^{-1}cm^{-1}$. The correlation between dopant concentration and conductivity (Fig. 3) and between dopant concentration and lattice parameter (Fig. 4) indicated that the dopant was fully incorporated and homogeneously distributed in the parent material.

Cobalt-doped $LiFeO_2$ was studied at dopant concentrations ranging from 5 to 14 mol%. The conductivity at 650°C as a function of dopant concentration is shown in Fig. 5. The data show good correlation between dopant concentration and conductivity with the maximum conductivity being 0.1 $ohm^{-1}cm^{-1}$ when the mole ratio of cobalt to iron is about 1:8.

Copper-doped $LiFeO_2$ was studied at two concentrations, 10 and 20 mol% Cu. At a dopant concentration of 10 mol% Cu, the conductivity at 650°C was about 0.08 $ohm^{-1}cm^{-1}$. At 20 mol% Cu, the conductivity was similar to that of the material with 10 mol% Cu, but a second phase consisting of CuO was present. This shows that the incorporation limit was exceeded at the higher concentration of CuO.

The conclusions to be reached from the above studies are that the charge-carrier concentration is proportional to the dopant concentration, the conductivity of $LiFeO_2$ can be enhanced with the use of dopants, and the target value of 0.1 ohm^{-1}-cm^{-1} can be achieved with doped $LiFeO_2$. Of the three dopants initially studied, only cobalt and copper were evaluated further.

Doping of Li_2MnO_3. As noted above, the conductivity of undoped Li_2MnO_3 (about 0.0014 $ohm^{-1}cm^{-1}$) is too low for cathode use. As with $LiFeO_2$, doping was employed to increase the conductivity. Six dopants (Mg, Ca, Zn, Al, Nb, and W) were initially selected, but only Mg, Zn, and Nb showed promise. The conductivities at 650°C of Li_2MnO_3 with several concentrations of these three dopants are given in Table 2. The highest concentration shown in Table 2 for each dopant is its limit of incorporation. The conductivity, even though it was increased by a factor of nearly sixty by niobium (0.0014 $ohm^{-1}cm^{-1}$ when undoped *vs* 0.08 $ohm^{-1}cm^{-1}$ for Nb doped), was still below the target value. However, these doping studies demonstrated that the charge-carrier concentration could be increased through incorporation of a dopant in the crystal lattice of the parent material. Despite their low conductivities, both the Nb- and Mg-doped Li_2MnO_3 were evaluated further to determine their conduction mechanisms.

Seebeck Coefficients. The Seebeck coefficient (μV/K) is the potential difference generated by applying a temperature gradient to a conductive material. The sign of the Seebeck coefficient is the same as the sign of the dominant charge carrier. Thus, when the coefficient is negative, electrons are the dominant charge carriers, and, when it is positive, holes are the dominant charge carriers. A measurement of the Seebeck coefficient, therefore, provides information concerning the conduction mechanism of the material. A p-type conductor, where hole conduction dominates, is desired for a cathode material.

Seebeck-coefficient measurements were made on $LiFeO_2$ doped with Co^{2+} and Cu^{2+}, on Li_2MnO_3 doped with Nb^{5+} and Mg^{2+}, and on undoped $LiCoO_2$. The measurements were made over a range of temperatures and employed a cover gas of 14% O_2-28% CO_2-balance N_2. Figure 6 shows the results of these measurements for the temperature range of 600 to 800°C. The Seebeck coefficients for the Nb- and Mg-doped Li_2MnO_3 were negative, indicating that both are n-type semiconductors, where electrons are the dominant charge carriers. These data suggested that Nb^{5+} substituted on Mn^{4+} sites and that Mg^{2+} substituted on Li^+ sites. In both cases, the conduction mechanism was electron hopping between the parent cation Mn^{4+} and Mn^{3+}. The Seebeck results combined with the conductivity results suggested that Nb- and Mg-doped Li_2MnO_3 were not good candidates for the MCFC cathode, because p-type conduction is desired.

The Seebeck coefficient for the Co-doped $LiFeO_2$ was positive and nearly constant throughout the temperature range studied. The positive coefficient indicated that the material was a p-type conductor; the small slope indicated little or no concentration of electrons as charge carriers. The Cu-doped $LiFeO_2$ changed from a p-type to an n-type conductor at about 675°C, a temperature within the typical operating temperature range of an MCFC. Therefore, of the doped materials assessed, only the Co-doped $LiFeO_2$ material appeared to be a good candidate for testing as a cathode.

The Seebeck data for undoped $LiCoO_2$ showed that this material was also a p-type conductor (its coefficients were positive). The good conductivity and the positive Seebeck coefficient of undoped $LiCoO_2$ suggested that the material was nonstoichiometric with respect to lithium and/or oxygen. Excess lithium (substituted on a cobalt site) or interstitial oxygen would give the observed characteristics. This material continues to be a good candidate for an alternative cathode.

CELL TESTING

Both full and half cells were used to test the cathodes. The 25-cm^2 full cells contained the candidate cathode, a nickel-chrome anode, and an electrolyte tile containing 50 vol% electrolyte (70 mol% Li_2CO_3-30 mol% K_2CO_3) and 50 vol% $LiAlO_2$. The cathode-gas composition was generally varied to determine the effects of O_2 and CO_2 pressures on cathode performance. The anode gas was 80 mol% H_2-20 mol% CO_2. The 2.5-cm^2 half cells contained the candidate cathode, again with a range of cathode gases, a gold reference electrode bathed in the same cathode gas, and a Type 316 stainless-steel counter electrode employing carbon dioxide gas as the reductant ($CO_2 + 2e^- \rightarrow CO + O^{2-}$). The cells were typically operated at 650°C.

Half-Cell Tests of Co-doped $LiFeO_2$. The effect of cathode-gas composition on the performance of a Co-doped $LiFeO_2$ cathode was measured over a range of oxygen partial pressures (5 to 70 kPa) at a fixed carbon dioxide partial pressure (30 kPa). The results are shown in Fig. 7. The data at 160 mA/cm^2 show a dramatic increase in performance (decrease in overpotential) with increasing O_2 partial pressure (i.e., about 300 mV on increasing the O_2 partial pressure from 5 to 70 kPa). The best performance was still about 75 mV poorer than that of NiO; however, under operation at ten times ambient pressure, the O_2 partial pressure is expected to be higher than 70 kPa. The performance of the cathode was also examined over a range of carbon dioxide partial pressures (5 to 60 kPa) at a fixed oxygen partial pressure (15 kPa). The results are shown in Fig. 8. The data at 160 mA/cm^2 showed an unexpected trend; the best performance occurred at the lowest partial pressure of CO_2.

Both the O_2 and CO_2 partial pressures affected the performance of the Co-doped $LiFeO_2$ cathode, and the greatest changes were seen at current densities greater than 100 mA/cm^2. Based on these results, an alternative cathode-gas mixture was formulated to take advantage of the gas-composition effects and attain the best cathode performance. The mixture consisted of 20% O_2, 5% CO_2, balance N_2. This cathode gas yielded good cathode performance; the test results are shown in Fig. 9. The performance of a NiO cathode operated in a half cell is shown for comparison. The data show that the alternative cathode gas results in a performance similar to that of a cathode gas having an O_2 partial pressure of 70 kPa.

Full-cell Tests of Co-doped $LiFeO_2$. Cobalt-doped $LiFeO_2$ cathodes were operated in full cells to determine if the altered cathode gas, which gave improved performance in the half-cell test, would have similar benefits in full cells. The polarization curves for a cell operated at ambient pressure with a Co-doped $LiFeO_2$ cathode and tested with the standard cathode gas (14% O_2-28% CO_2-balance N_2) and with an altered cathode gas (80% O_2-20% CO_2) are shown in Fig. 10. The data show that at a current density of 120 mA/cm^2 the voltage of the $LiFeO_2$ cathode under altered gas conditions is 300 mV higher than under standard gas conditions.

Full-cell Tests of $LiCoO_2$. Lithium-cobaltate cathodes were tested in full cells under conditions similar to those used with the Co-doped $LiFeO_2$ cathodes. The polarization curves for a cell operated at ambient pressure and tested with the standard cathode gas and with an altered cathode gas (64% O_2-36% CO_2) are shown in Fig. 11. The data indicated an increase in performance when the O_2 partial pressure was increased from 14 kPa to 64 kPa. With altered cathode-gas conditions, the performance was equivalent to that of NiO with the standard cathode gas.

CONCLUSIONS

Both $LiFeO_2$ and Li_2MnO_3 were stable in the cathode environment, had low solubility, and were non-precipitating in the anode environment. Dopants were employed to enhance the electronic conductivity of both materials. Cobalt-doped $LiFeO_2$ was a factor of 30 more conductive than the undoped $LiFeO_2$; Nb-doped Li_2MnO_3 was a factor of 60 more conductive than its undoped form. However, only the Co-doped $LiFeO_2$ exhibited the desired p-type conduction. Half- and full-cell tests with Co-doped $LiFeO_2$ as the cathode material showed that its performance strongly depended on the oxygen partial pressure. Under simulated high-pressure conditions, where the O_2 partial pressure was 70 kPa, the performance was good.

The $LiCoO_2$ material had low solubility and was a good electronic conductor in the undoped form. In addition, it exhibited p-type conduction, and, when used as a cathode material, gave good cell performance. It precipitated as cobalt metal under the reducing conditions present in the anode. However, neither the rate of deposition nor the conditions influencing the deposition and location of deposits are known at present.

Further study of the Co-doped $LiFeO_2$ cathode under pressurized conditions is needed to determine if the performance projections are realistic. Further study of the $LiCoO_2$ cathode is also needed to determine if its dissolution and deposition in the anode are life limiting.

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Table 1. Electrolyte Analysis for Cathode Cations
(2000 h Test)

	Cations (wppm)		
	Fe	Mn	Ni
Unused Electrolyte	23	4	<3
Electrolyte from Li_2MnO_3 Cathode Cell	64	19	30
Electrolyte from $LiFeO_2$ Cathode Cell	59	5	10
Electrolyte from NiO Cathode Cell	60	1	162

Anode Gas: 64 mol% H_2-16 mol% CO_2-20 mol% H_2O.
Cathode Gas: 27 mol% O_2-53 mol % CO_2-20 mol % H_2O.

Table 2. Conductivity of Doped Li_2MnO_3 at 650°C

Dopant	Mole Fraction Dopant/Mn	$\sigma(\text{ohm}^{-1}\text{cm}^{-1})$
Mg	0.01	0.0067
	0.025	0.014
	0.05	0.05
Zn	0.013	0.0068
	0.025	0.01
	0.05	0.012
	0.08	0.04
Nb	0.013	0.0047
	0.025	0.0075
	0.05	0.01
	0.075	0.08

Figure 1. Solubilities of Nickel Oxide and Alternative Cathode Materials as a Function of Temperature

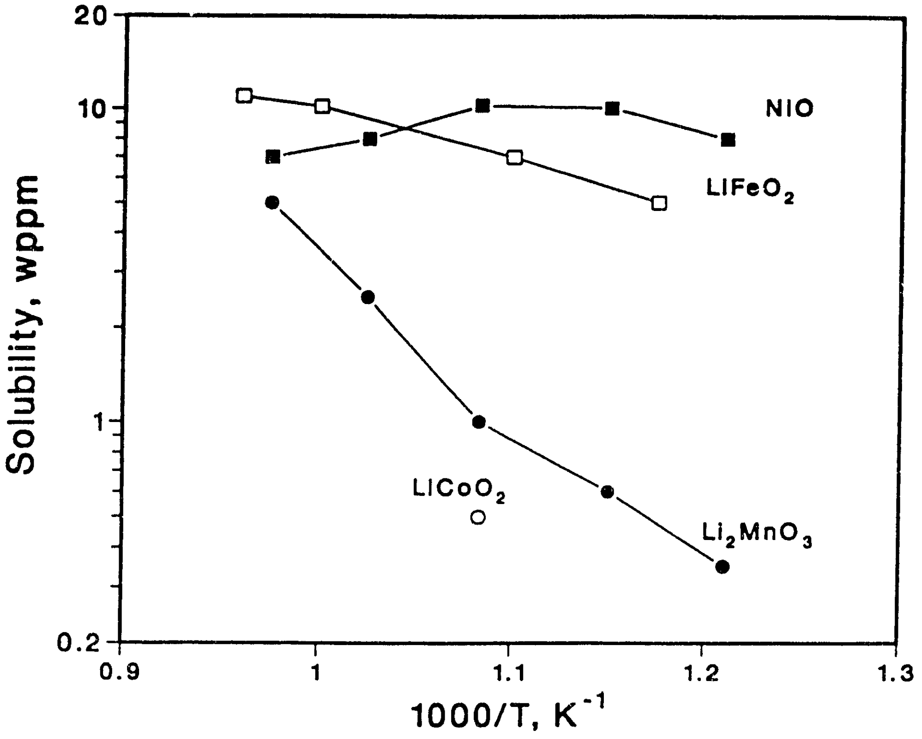


Figure 2. Conductivities of Alternative Cathode Materials (undoped) as a Function of Temperature

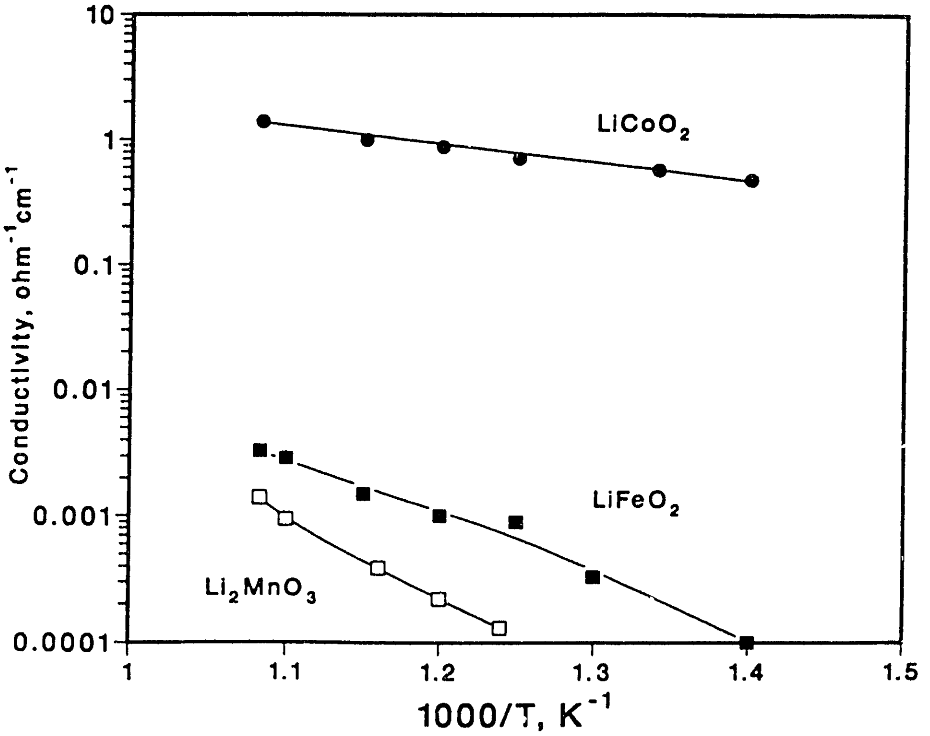


Figure 3. Conductivity of Mn-doped $LiFeO_2$ as a Function of Dopant Concentration

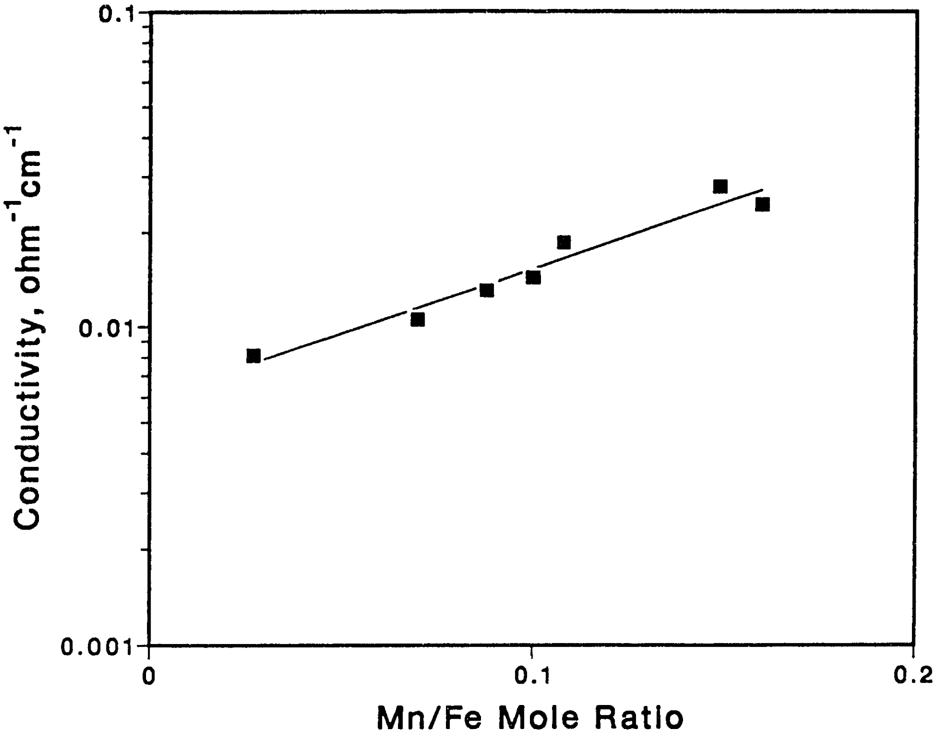


Figure 4. Lattice Parameter Change of Mn-doped $LiFeO_2$ as a Function of Dopant Concentration

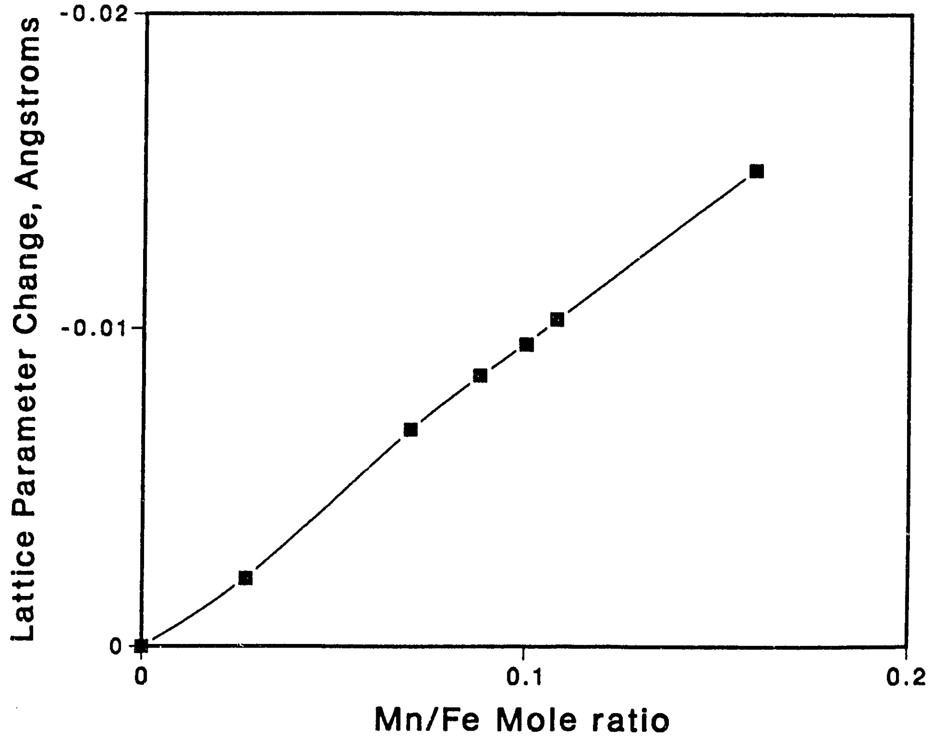


Figure 5. Conductivity of Co-doped $LiFeO_2$ as a Function of Dopant Concentration

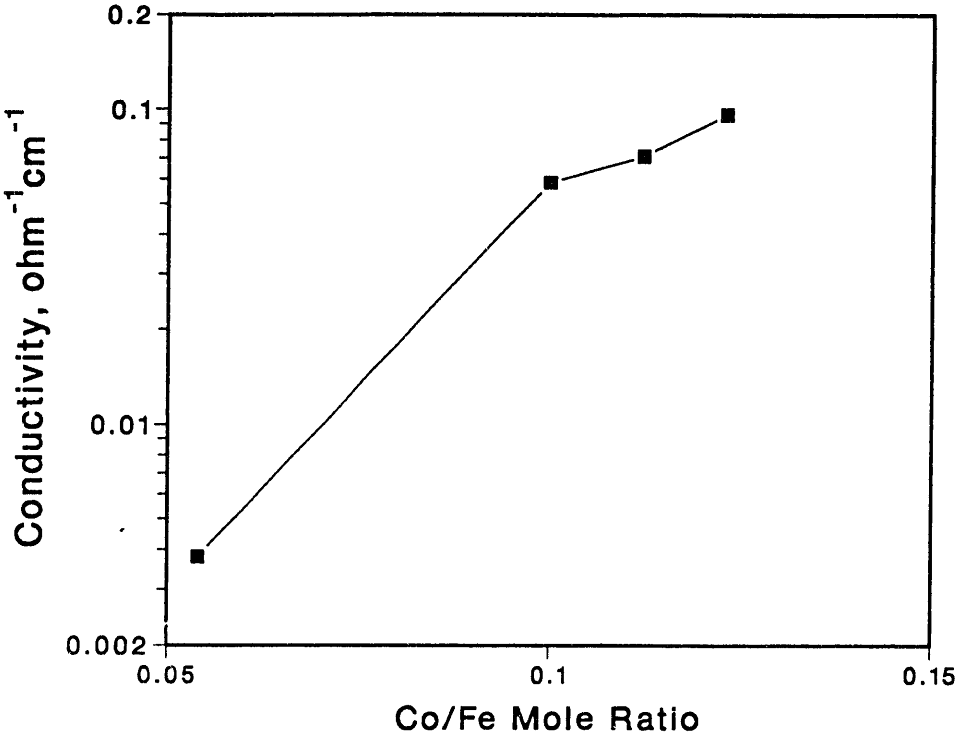


Figure 6. Seebeck Coefficients of Doped $LiFeO_2$ and Li_2MnO_3 and Undoped $LiCoO_2$

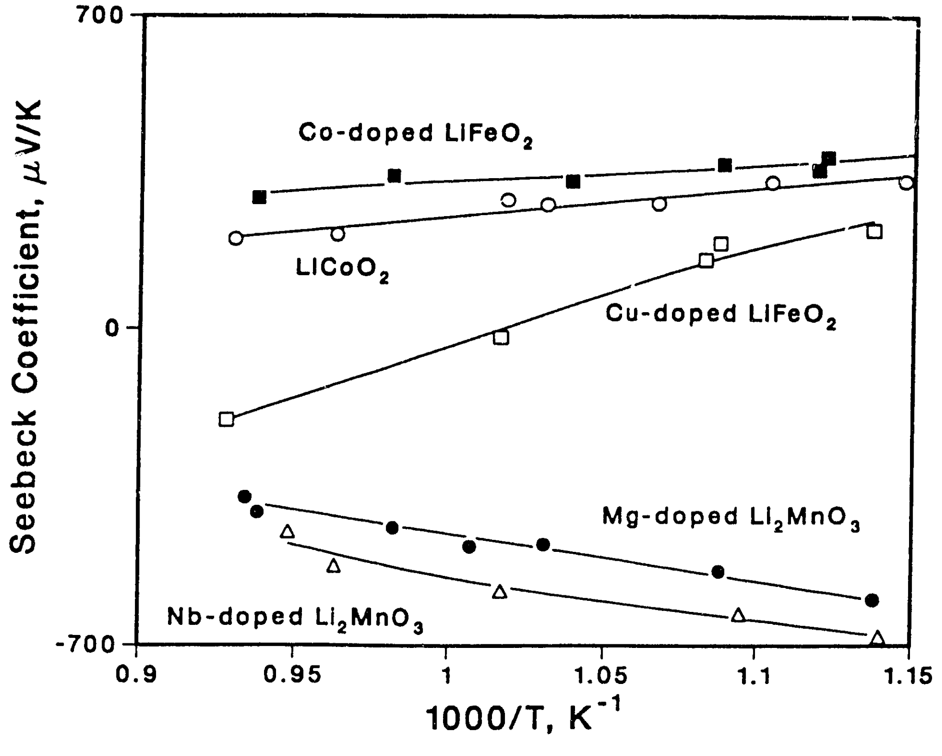


Figure 7. Polarization Curves for Co-doped $LiFeO_2$ at 650°C as a Function of O_2 Partial Pressure (CO_2 = 30% and $O_2 + N_2$ = 70%)

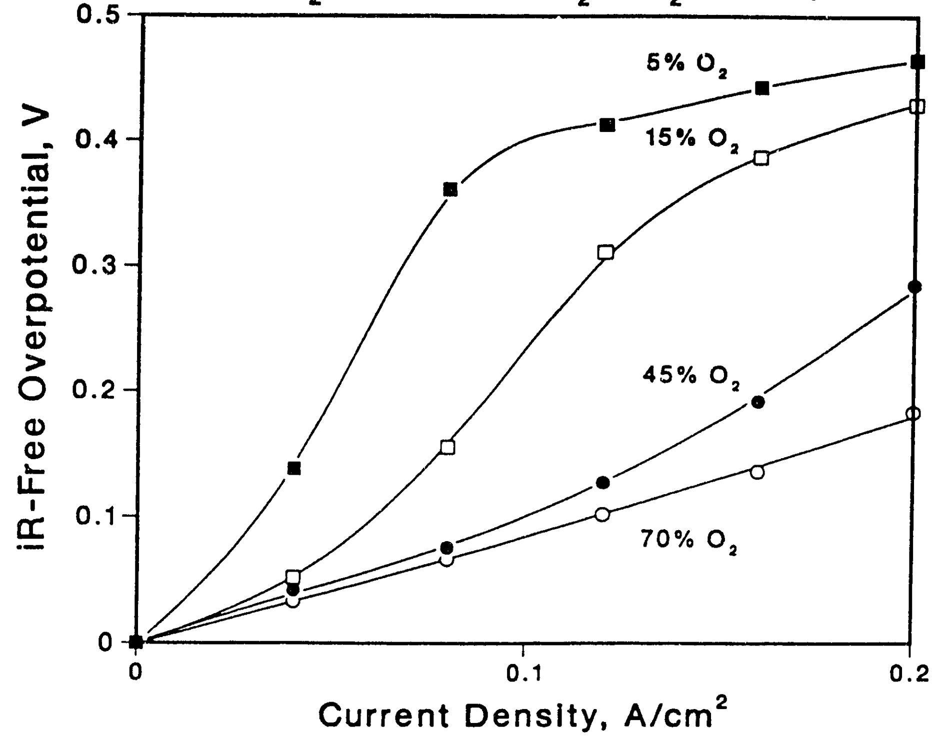


Figure 8. Polarization Curves for Co-doped $LiFeO_2$ at 650°C as a Function of CO_2 Partial Pressure (O_2 = 15% and $CO_2 + N_2$ = 85%)

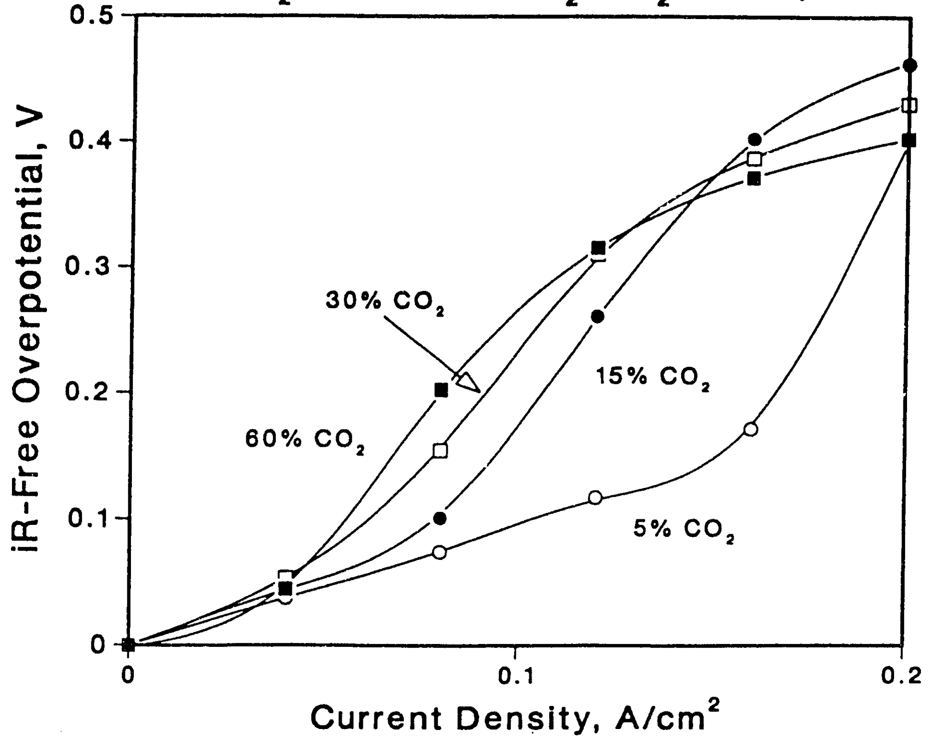


Figure 9. Performance of Co-Doped $LiFeO_2$ Cathode in 20% O_2-5% CO_2-Bal. N_2 and NiO Cathode in 14% O_2-28% CO_2-Bal. N_2

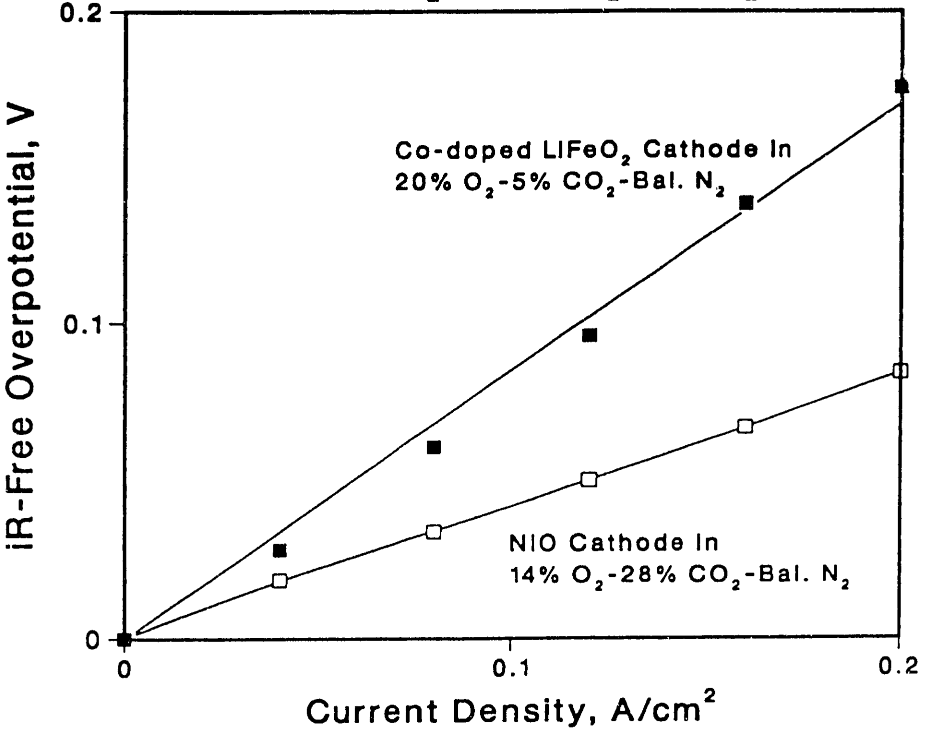


Figure 10. Polarization Curves from an MCFC with a Co-Doped $LiFeO_2$ Cathode in 80% O_2-20% CO_2 and 14% O_2-28% CO_2-58% N_2

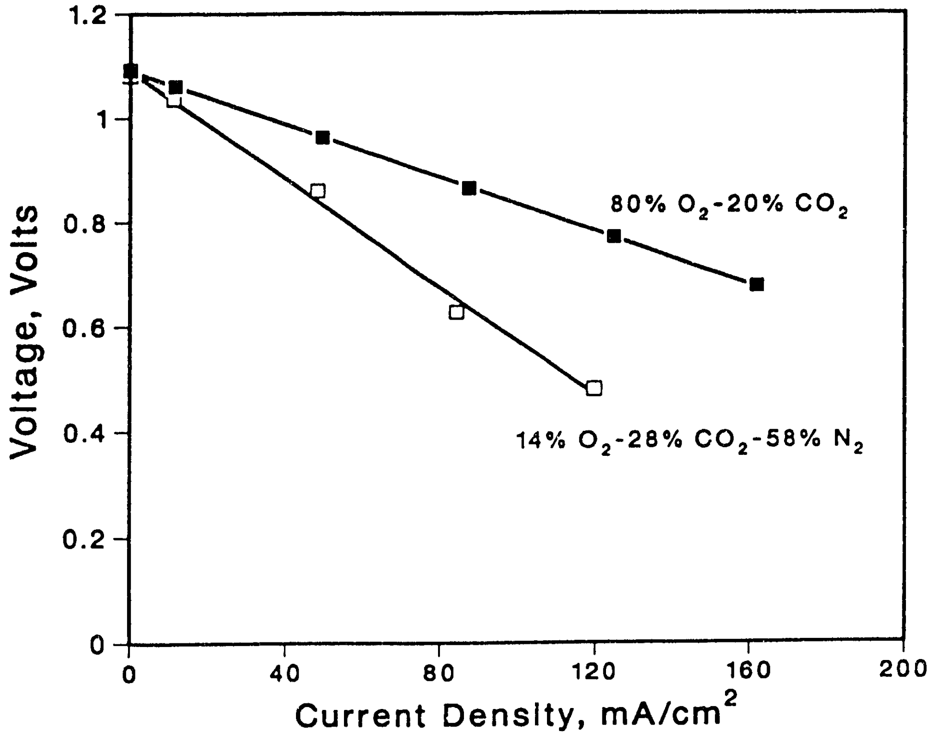
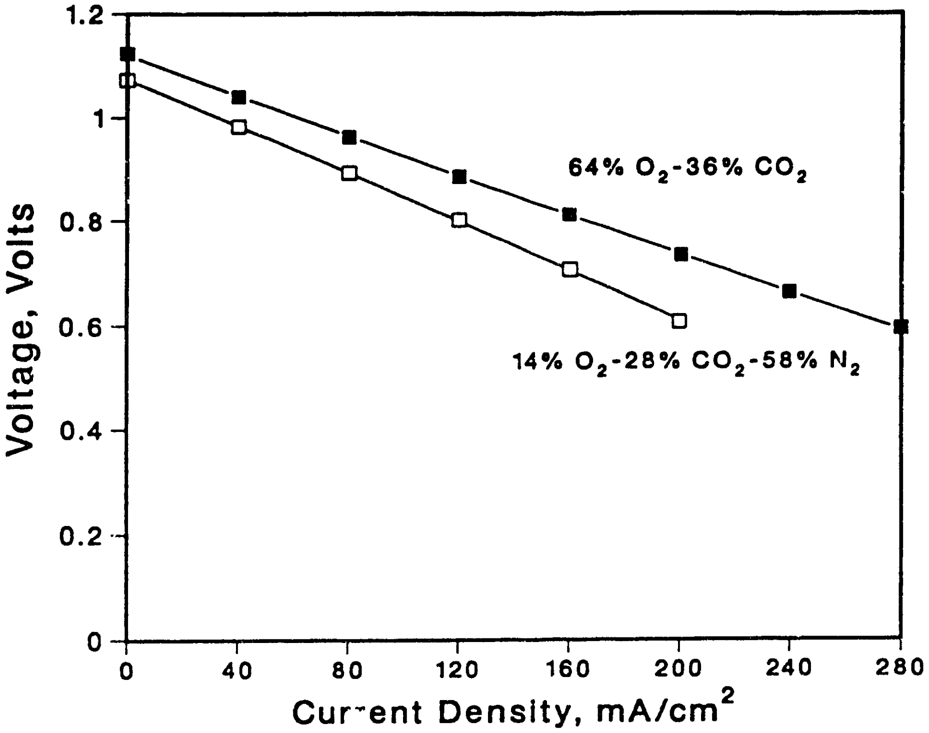


Figure 11. Polarization Curves from an MCFC with a $LiCoO_2$ Cathode in 64% O_2-36% CO_2 and 14% O_2-28% CO_2-58% N_2



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