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M. T. Lanagan, I. Bloom,* T. D. Kaun,* J. Wolfenstine,[1] and M. Krumpelt*
Energy Technology Division
Chemical Technology Division*
Argonne National Laboratory
Argonne, IL 60439

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LITHIUM-FERRATE-BASED CATHODES FOR MOLTEN CARBONATE FUEL CELLS

M. T. Lanagan, I. Bloom,† T. D. Kaun,† J. Wolfenstine,[1] and M. Krumpelt†

Energy Technology Division, Chemical Technology Division†
Argonne National Laboratory
Argonne, IL 60439–4838

Introduction

Argonne National Laboratory is developing advanced cathodes for pressurized operation of the molten carbonate fuel cell (MCFC) at ~650°C [2–5]. To be economically viable for stationary power generation, molten carbonate fuel cells must have lifetimes of more than 25,000 h while exhibiting superior cell performance [6]. In the present technology, lithiated NiO is used as the cathode. Over the lifetime of the cell, however, Ni^{2+} ions tend to transport to the anode, where they are reduced to metallic Ni [7]. With increased CO_2 partial pressure, the transport of Ni increases because of the increased solubility of NiO in the carbonate electrolyte. Although this process is slow in MCFCs operated at 1 atm and a low CO_2 partial pressure (about 0.1 atm), transport of nickel to the anode may be excessive at a higher pressure (e.g., 3 atm) and a high CO_2 partial pressure (e.g., about 0.3 atm). This transport is expected to lead eventually to poor MCFC performance and/or short circuiting.

Several alternative cathode compositions have been explored to reduce cathode solubility in the molten salt electrolyte [2–5,8]. For example, $LiCoO_2$ has been studied extensively [8,9,10] as a potential cathode material. The $LiCoO_2$ cathode has a low resistivity, about 1 Ω-cm, and can be used as a direct substitute for NiO. However, the high material cost may prevent large-scale implementation.

Argonne is developing advanced cathodes based on lithium ferrate ($LiFeO_2$), which is attractive because of its very low solubility in the molten $(Li,K)_2CO_3$ electrolyte [11]. Because of its high resistivity (about 300 Ω-cm), however, $LiFeO_2$ cannot be used as a direct substitute for NiO. Cation substitution is, therefore, necessary to decrease resistivity.

We determined the effect of cation substitution on the resistivity and deformation of $LiFeO_2$. The substituents were chosen because their respective oxides as well as $LiFeO_2$ crystallize with the rock-salt structure.

Experimental

Materials Synthesis and Characterization. Stoichiometric amounts of Li_2CO_3, Fe_2O_3, CoO, NiO and/or MgO were mixed and heat treated at 825°C for 4 h. The powders were pressed into disks and sintered at 1000°C for 4 h. Upon cooling, the phase distribution of the sintered disks was characterized by X-ray diffraction. The relative densities of the pellets were in the range of 60–90%; $LiCoO_2$ had the highest (93% of theoretical) and pure $LiFeO_2$, the lowest (81%). All materials except $LiCoO_2$ had equiaxed grains (0.96–1.43 μm). $LiCoO_2$ had acicular grain morphology (5 × 1.5 μm).

Resistivity and Deformation Rate Measurements. Resistivity was determined using the four-wire, dc, van der Pauw method at 650°C in air. Parallelepipeds (2 × 2 × 4 mm) were cut from the sintered pellets. The samples were deformed by compression at a constant deformation rate in air at 1000°C.

Cell Tests. Promising materials were tested in a 5 × 5-cm cell with a pressed $(Li,K)_2CO_3$ electrolyte tile. The test cell was operated at 650°C using an O_2-CO_2 gas mixture which simulated pressurized operation at 3–5 atm.

Results and Discussion

Materials. We found that the range of homogeneity for Co-substituted $LiFeO_2$ is limited; several phases are formed during synthesis. All of the diffraction peaks for Mg-substituted $LiFeO_2$ were indexed to a rock-salt structure. Further analysis shows that the lattice parameter increases monotonically with MgO concentration, indicating a complete solid solution (Fig. 1). Fayard found that both CoO and MgO formed complete solid solutions with $LiFeO_2$ [12]. Apparently, Co solubility is affected by differences in synthesis conditions.

Resistivity Measurements. Resistivity results for MgO-substituted $LiFeO_2$ samples show that the minimum resistivity is approximately 100 Ω-cm (at 650°C in air) and appears in the MgO concentration range of 6–12 mol% (Fig. 2). Clearly, the resistivity of Mg-substituted $LiFeO_2$ is too high; lower resistivity values (~1 Ω-cm) are necessary for MCFC cathodes. By using different cation substituents, we lowered the resistivity of a $LiFeO_2$-based material (designated Material 1) to 1.3 Ω-cm at 650°C.

Deformation Rate Studies. Figure 3 shows a log-log plot of the deformation rate *vs* stress at 1000°C for five materials: (a) pure $LiFeO_2$, (b) 12.5 m/o NiO-$LiFeO_2$, (c) 9 m/o MgO-$LiFeO_2$, (d) pure $LiCoO_2$, and (e) 5 m/o Li_2O-NiO. Here, the deformation rate was normalized with respect to grain size and stress to the material density, and it was assumed that the deformation rate is controlled by lattice diffusion. The slope of all curves is close to unity, implying that they all exhibit the same deformation mechanism (e.g., diffusional creep and/or grain boundary sliding). Materials (a) and (d) have higher deformation rates than (e), lithiated NiO; Material (d) has the highest deformation rate. Doping $LiFeO_2$ with NiO or MgO decreases the deformation rate as compared to that of pure $LiFeO_2$. Materials (a), (b), (c), and (d) will compact more than lithiated NiO at 650°C.

Cell Tests. A fibrous cathode of Material 1 was used in a cell test. The cell potential at 160 mA/cm^2 as a function of time is shown in Fig. 4. After an initial break-in period, a constant potential of 850 mV was observed for 1700 h. Polarization experiments showed a small degradation at 1706 h (see Fig. 5). These results show that $LiFeO_2$-based cathodes have good performance and durability at high CO_2 partial pressures.

Conclusions

Several $LiFeO_2$-based materials with cation substitutions were synthesized and characterized. With the proper choice of substituents, the resistivity of $LiFeO_2$ was lowered to about 1 Ω-cm.

The $LiCoO_2$- and $LiFeO_2$-based cathode materials have deformation rates higher than that of lithiated NiO at 1000°C. They will compact more at 650°C. Doping the alternative cathodes decreases their deformation rates.

The $LiFeO_2$-based cathodes exhibit cell potentials which are stable for long periods of time under simulated pressurized operation. $LiFeO_2$-based materials continue to show promise as cathodes for the MCFC.

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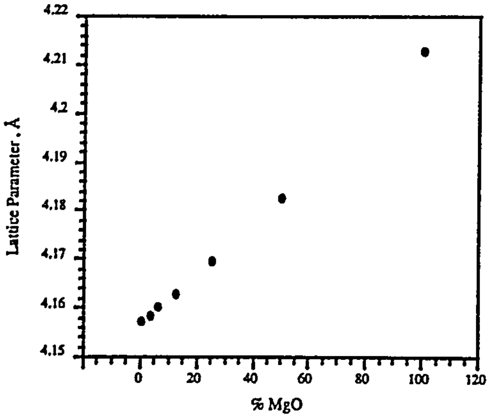

Fig. 1. Effect of MgO concentration on unit cell dimensions.

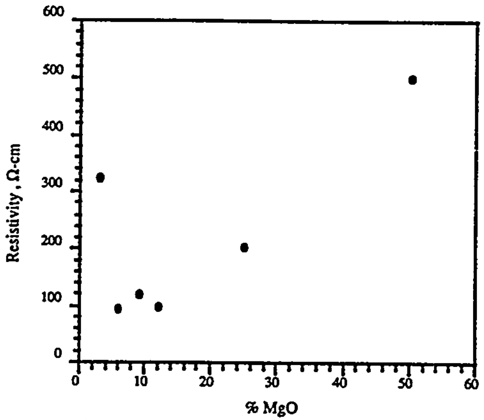

Fig. 2. Effect of MgO concentration on resistivity of $LiFeO_2$ at 650°C in air.

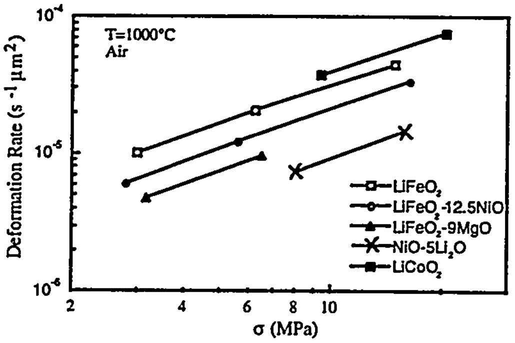

Fig. 3. Grain-size-compensated deformation rate *vs* density-compensated stress.

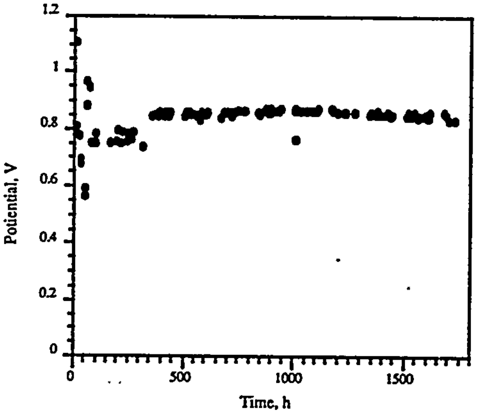

Fig. 4. Cell potential *vs* time of MCFC test cell containing Material 1 cathode.

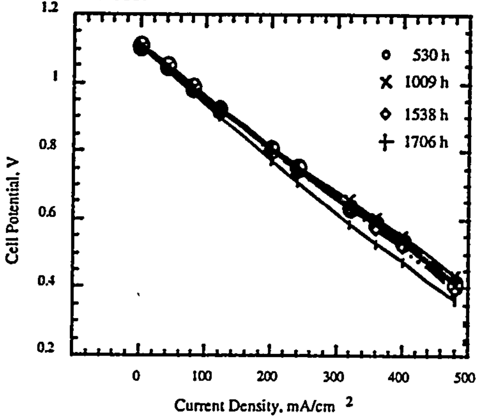

Fig. 5. Changes in polarization curves vs time of MCFC test cell containing Material 1 cathode.