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ALTERNATIVE CATHODES FOR MOLTEN CARBONATE FUEL CELLS

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## Alternative Cathodes for Molten Carbonate Fuel Cells

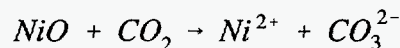
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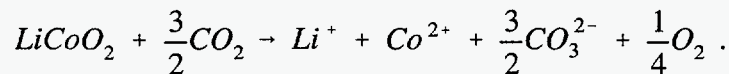
### Introduction

Argonne National Laboratory (ANL) is developing advanced cathodes for pressurized operation of the molten carbonate fuel cell (MCFC). The present cathode, lithiated nickel oxide, tends to transport to the anode of the MCFC, where it is deposited as metallic nickel.<sup>1</sup> The rate of transport increases with increasing CO<sub>2</sub> pressure. This increase is due to an increased solubility of nickel oxide (NiO) in the molten carbonate electrolyte via the reaction:



Although a life of 40,000 hours is projected for MCFCs operated at 1 atm and a low CO<sub>2</sub> partial pressure (about 0.1 atm), transport of nickel to the anode at a higher pressure (e.g., 3 atm) and a high CO<sub>2</sub> partial pressure (e.g., about 0.3 atm) may be excessive. This transport is expected to lead eventually to poor MCFC performance and/or short circuiting.

An alternative cathode is lithium cobaltate (LiCoO<sub>2</sub>). The LiCoO<sub>2</sub> cathode has a low resistivity, about 1 Ω-cm, and can be used as a direct substitute for NiO. Analogous to NiO, LiCoO<sub>2</sub> dissolves at high partial pressures of CO<sub>2</sub> according to the reaction<sup>2</sup>:



The transport rate for cobalt-containing species to the anode is expected to be lower than that of NiO. The lower transport rate is due to the lower solubility of LiCoO<sub>2</sub> (more than a factor of 10) in the (Li,K)<sub>2</sub>CO<sub>3</sub> melt. Once at the anode, the dissolved Co<sup>2+</sup> species are reduced to metallic cobalt and may lead to poor MCFC performance and short circuiting.

The advanced cathodes currently being developed at ANL are based on solid solutions of lithium ferrate (LiFeO<sub>2</sub>) and LiCoO<sub>2</sub>. Using LiFeO<sub>2</sub>-based materials is attractive because the transport of LiFeO<sub>2</sub> is thought to be zero. In contrast to Co<sup>2+</sup>, Fe<sup>2+</sup> is not reduced at the anode. The LiFeO<sub>2</sub> cathode, because of its high resistivity (about 300 Ω-cm), cannot be employed as a direct substitute for the lithiated NiO cathode. Solid solution formation is expected to lower the resistivity

of  $\text{LiFeO}_2$  to an acceptable level (about  $1 \Omega\text{-cm}$ ). Transport of cobalt-containing species to the anode is also expected to decrease because of lower cobalt activity in the cathode.

### Phase Diagram Studies

The  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  binary system was studied to determine solid-solution and two-phase regions. A series of  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  compositions was prepared and characterized by X-ray diffraction (XRD) and scanning electron microscopy. The resistivity of selected compositions was also measured.

X-ray diffraction data from compositions along the  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  join show that there are two regions of homogeneity. Typical X-ray diffraction results are given in Fig. 1. Here, peaks of interest from  $\text{LiCoO}_2$  and  $\text{LiFeO}_2$  are indicated by circles and triangles, respectively. Data from a series of compositions are plotted as the percent  $\text{LiCoO}_2$  peak intensity versus  $\text{LiCoO}_2$  concentration (see Fig. 2). Here, the percent  $\text{LiCoO}_2$  peak intensity is defined as

$$\% \text{LiCoO}_2 \text{ peak intensity} = \frac{I_{\text{LiCoO}_2}}{I_{\text{LiCoO}_2} + I_{\text{LiFeO}_2}} \times 100\%,$$

where  $I_{\text{LiCoO}_2}$  and  $I_{\text{LiFeO}_2}$  are the peak intensities from  $\text{LiCoO}_2$  ( $\langle 003 \rangle$  reflection) and  $\text{LiFeO}_2$  ( $\langle 200 \rangle$  reflection), respectively. At low (0 to about 6 m/o)  $\text{LiCoO}_2$  concentrations, no peaks resulting from excess  $\text{LiCoO}_2$  were seen. At high (85 to 100 m/o)  $\text{LiCoO}_2$  concentrations, no peaks resulting from excess  $\text{LiFeO}_2$  were seen. Diffraction peaks due to free end-member oxides were clearly seen at the intermediate compositions.

Plots of resistivity in air at  $650^\circ\text{C}$  as a function of  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  composition show the expected trend: resistivity is inversely proportional to cobalt content. The resistivity of 6 m/o  $\text{LiCoO}_2$  is  $5 \Omega\text{-cm}$ ; of 12.5 m/o  $\text{LiCoO}_2$ ,  $3.3 \Omega\text{-cm}$ ; and of 87.5 m/o  $\text{LiCoO}_2$ ,  $1.3 \Omega\text{-cm}$ .

### Cell Tests

The  $\text{LiCoO}_2$  and  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  cathodes were tested in  $5 \times 5\text{-cm}$  cells using pressed  $(\text{Li,K})_2\text{CO}_3$  electrolyte tiles. The MCFCs were operated with  $\text{O}_2$ - $\text{CO}_2$  gas mixtures to simulate pressurized operation at 3-5 atm.

*LiCoO<sub>2</sub> cathode.* The potential at  $320 \text{ mA/cm}^2$  versus time for an MCFC with a  $\text{LiCoO}_2$  cathode is given in Fig. 3. Here, the average decline in cell voltage was approximately  $300 \mu\text{V/h}$ . Post-test analysis of the cell showed that cobalt-containing species were present in the electrolyte tile. An example micrograph is given in Fig. 4; the cobalt-containing species appear as bright spots in the figure. These species are present from the cathode/tile interface to the anode/tile interface.

*LiCoO<sub>2</sub>-LiFeO<sub>2</sub> cathode.* The potential at  $160 \text{ mA/cm}^2$  versus time for the MCFC with the 12.5-m/o Co-doped  $\text{LiFeO}_2$  cathode is given in Fig. 5. After the break-in period, the average decline in cell voltage was  $7 \mu\text{V/h}$ . Another cell test is planned at  $320 \text{ mA/cm}^2$ .

At various times during cell operation, the effect of O<sub>2</sub>-to-CO<sub>2</sub> ratio on the MCFC voltage at 160 mA/cm<sup>2</sup> was measured. In Fig. 6, the effect of CO<sub>2</sub> mole fraction in the cathode gas on the area specific resistance (ASR) of the MCFC is plotted for four different times during the test. The ASR curves exhibit a minimum early in the test, increases, then flattens out with time. Thus, the minimum is a transitory phenomenon that does not impact the long-term performance of the cathode.

Since the cathode composition is just outside the region of homogeneity, some cobalt migration is expected. It is much less than that observed with pure LiCoO<sub>2</sub>. Post-test analysis of this cell after more than 2100 h of operation showed that the cobalt migration had decreased dramatically. Cobalt-containing species were detected at the cathode/tile interface; these crystals were smaller and more widely spaced than those found in the LiCoO<sub>2</sub> cathode. From energy dispersive analysis of X-rays, the cobalt content of these species starts at about 3 at.% and decreases markedly (to less than 0.3 at.%) as distance from the cathode increases. Interestingly, chromium- and iron-containing species, possibly from corrosion of the steel housing, are the major transition-metal-containing materials in the electrolyte tile. The chromium and iron species tend to occur together and form semicontinuous bands in the tile. An example band is shown as a back-scatter electron image in Fig. 7.

### **Conclusions**

Solid solutions of LiCoO<sub>2</sub> in LiFeO<sub>2</sub> show promise for long-lived cathode materials. We have found that small additions of LiCoO<sub>2</sub> to LiFeO<sub>2</sub> markedly decrease the resistivity of the cathode material. Cells containing the LiCoO<sub>2</sub>-LiFeO<sub>2</sub> cathodes have stable performance for more than 2100 h of operation and display lower cobalt migration rates than pure LiCoO<sub>2</sub>. Further tests using the LiCoO<sub>2</sub>-LiFeO<sub>2</sub> cathodes are planned at higher current density.

### **Acknowledgments**

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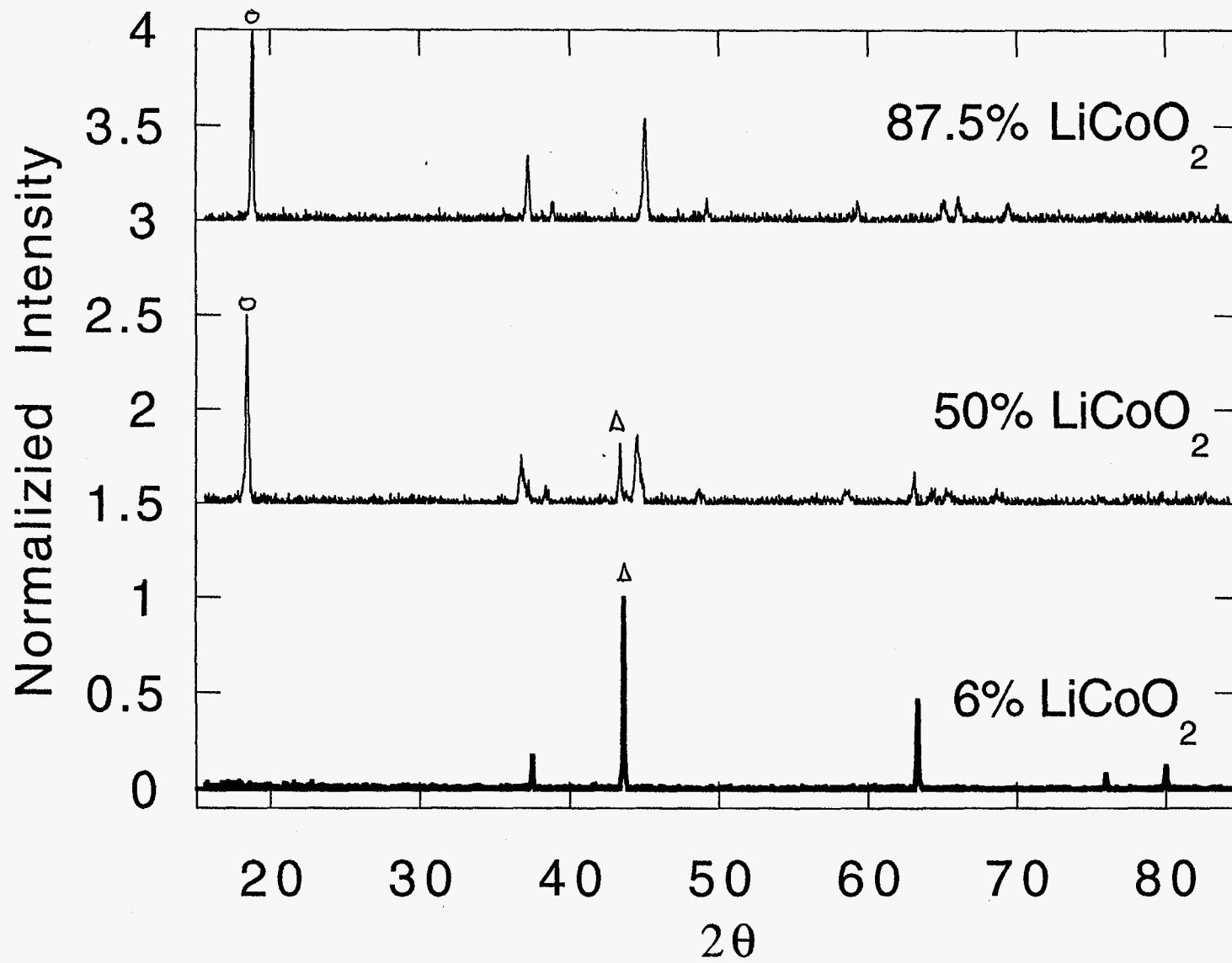


Fig. 1. X-ray diffraction patterns from  $\text{LiCoO}_2$ - $\text{LiFeO}_2$  mixtures. Peaks of interest from  $\text{LiCoO}_2$  and  $\text{LiFeO}_2$  are indicated by circles and triangles, respectively.

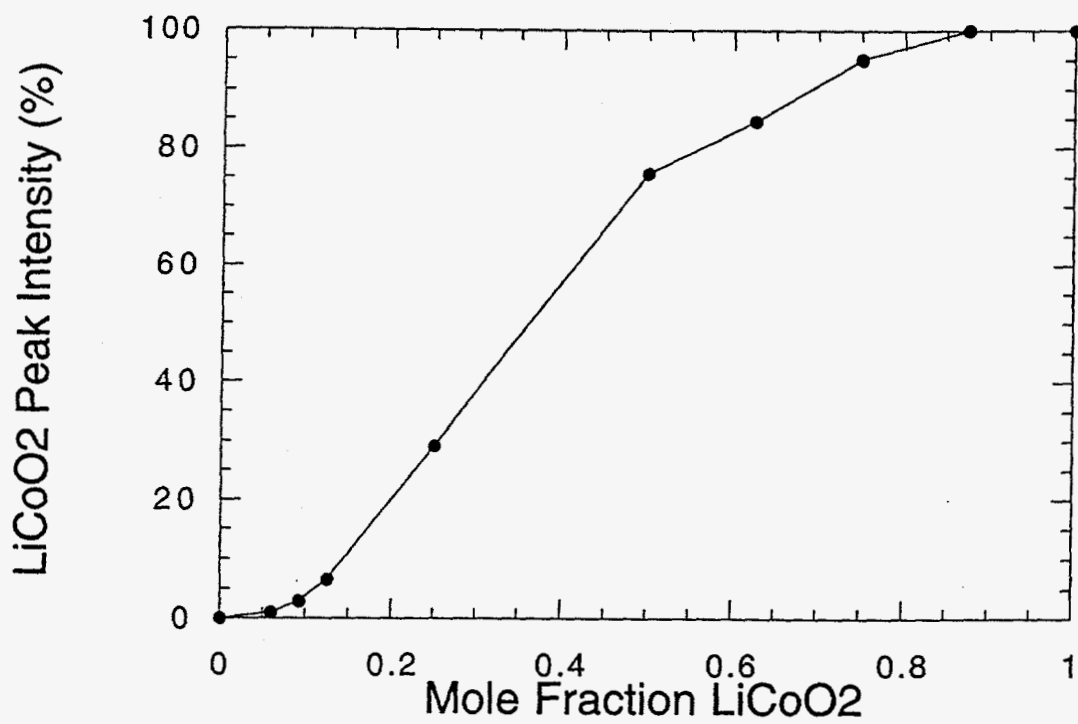
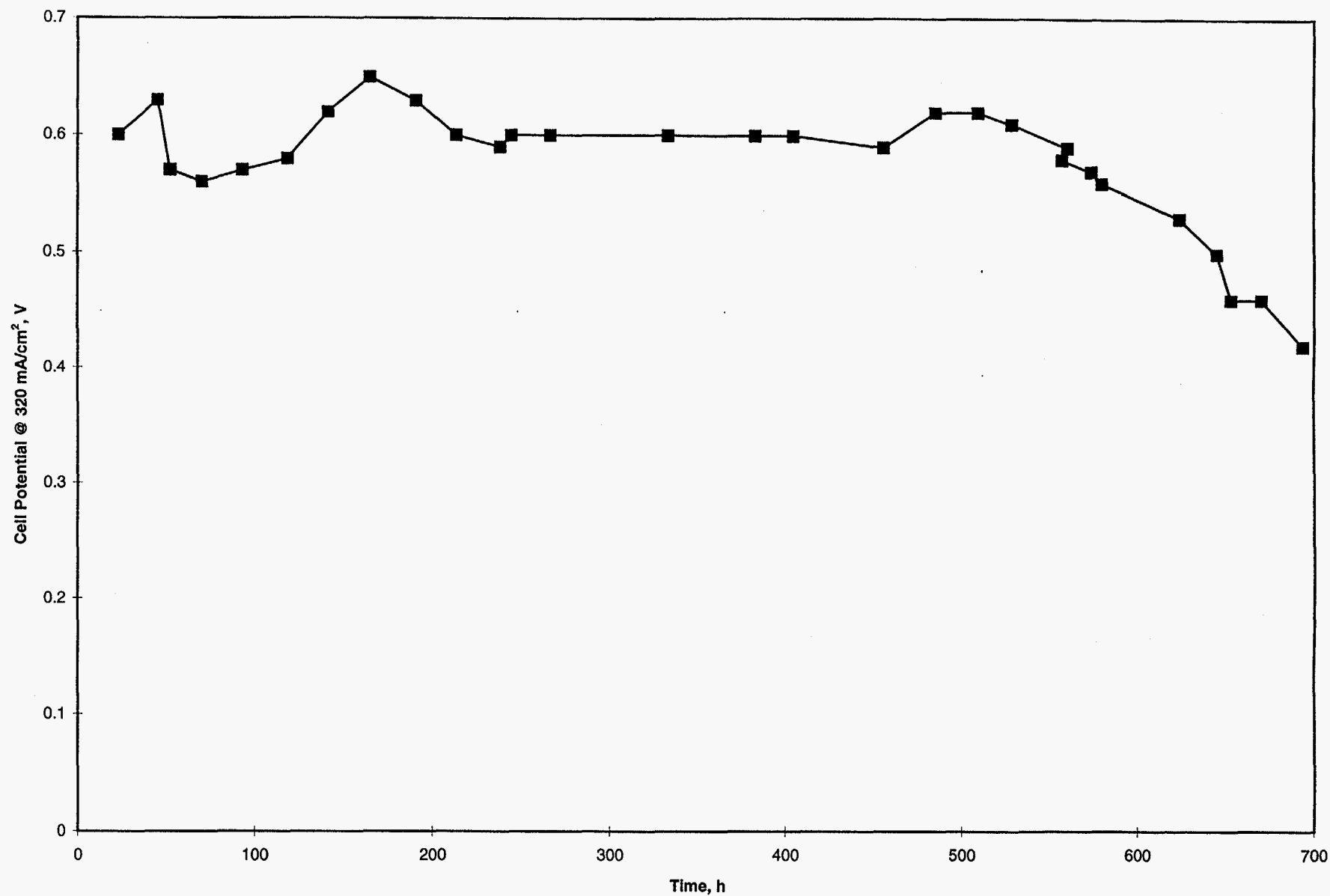
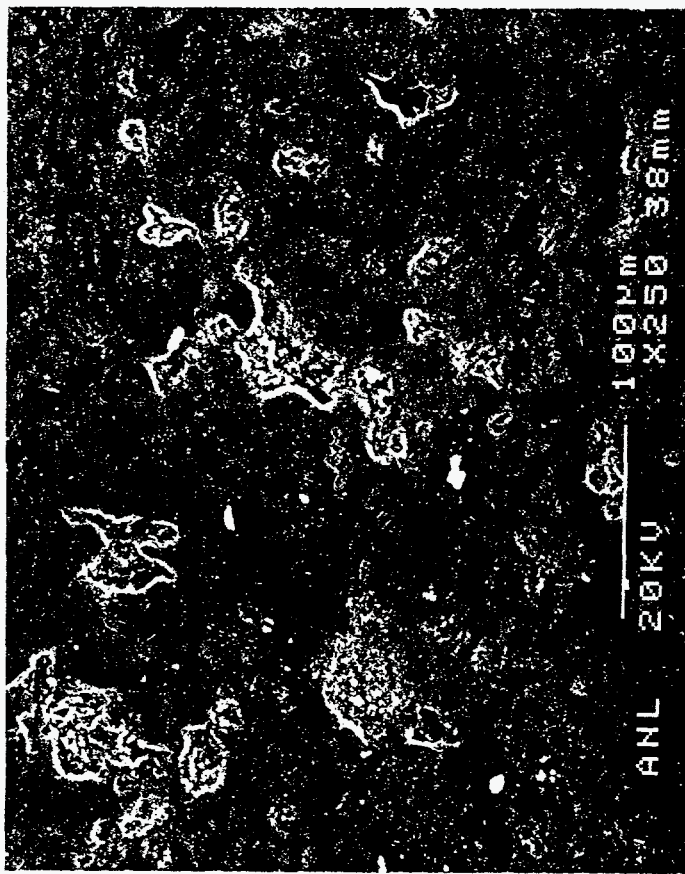


Fig. 2. Plot of LiCoO<sub>2</sub> peak intensity vs. mole fraction LiCoO<sub>2</sub>.



**Fig. 3.** Cell potential vs. time for an MCFC containing a  $\text{LiCoO}_2$  cathode operated at  $320 \text{ mA/cm}^2$  under simulated pressurized conditions.



**Fig. 4.** Back-scatter electron image showing cobalt-containing species (white objects) in the electrolyte tile (LiCoO<sub>2</sub> cathode).



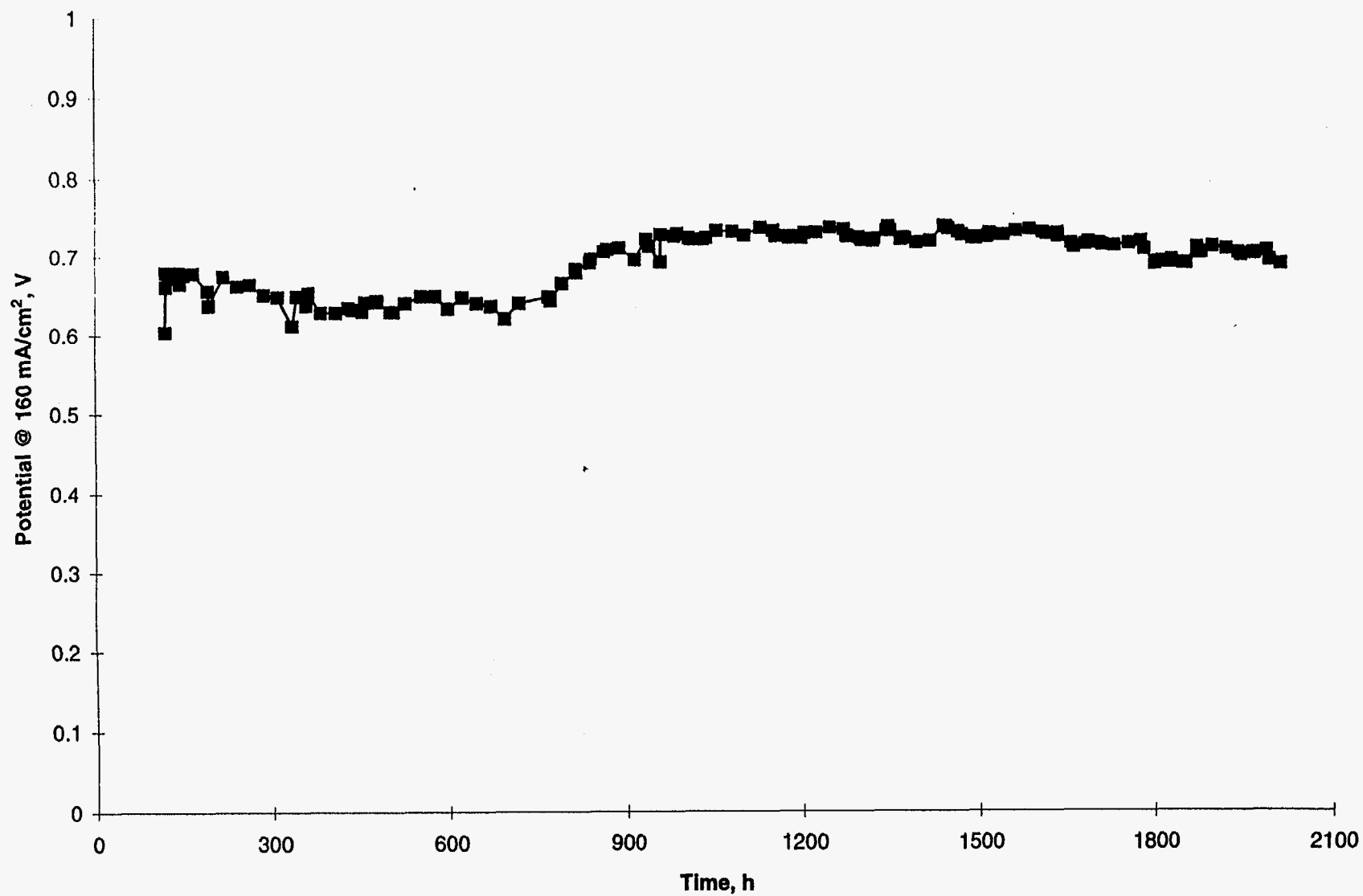


Fig. 5. Cell potential vs. time for an MCFC containing a  $\text{LiCoO}_2\text{-LiFeO}_2$  cathode operated at  $160 \text{ mA/cm}^2$  under simulated pressurized conditions.

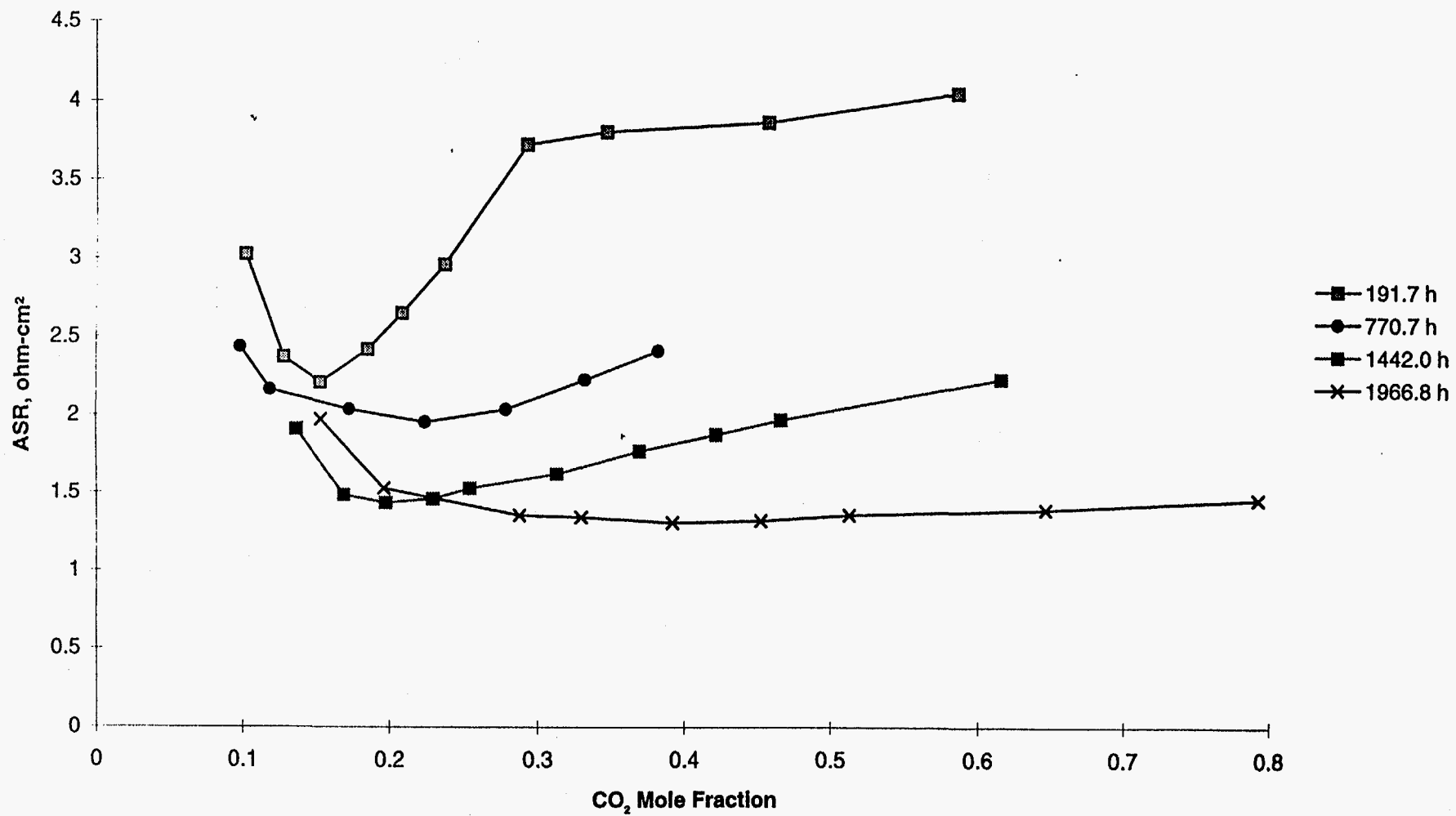


Fig. 6. Changes in cell area-specific resistance vs. CO<sub>2</sub> mole fraction with time.

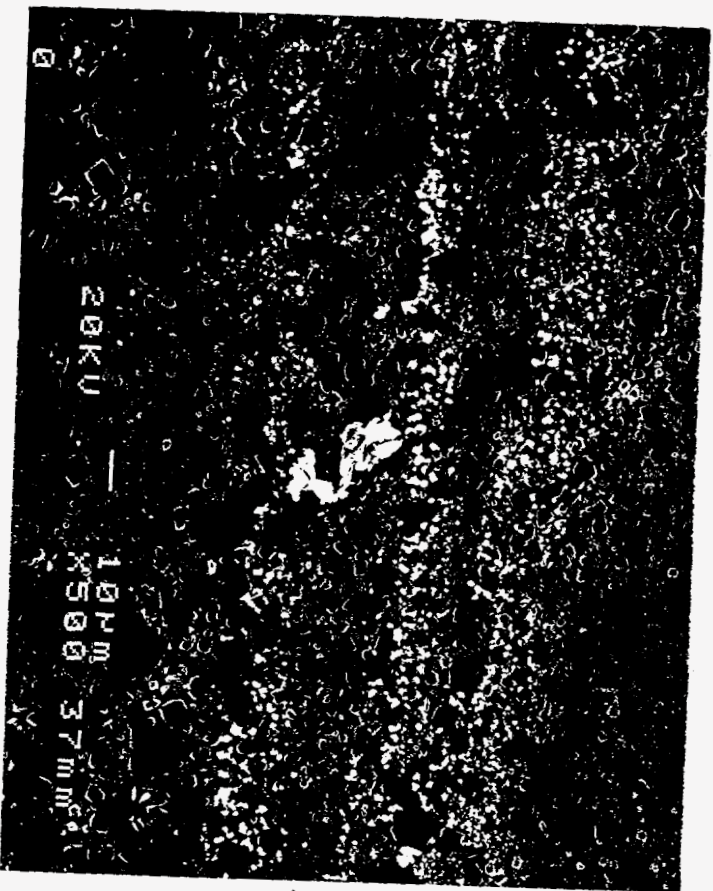


Fig. 7. Back-scatter electron image showing cobalt-containing species (white objects) in the electrolyte tile (LiCoO<sub>2</sub>-LiFeO<sub>2</sub> cathode).