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ALTERNATIVE CATHODES FOR MOLTEN CARBONATE FUEL CELLS

by

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Alternative Cathodes for Molten Carbonate Fuel Cells

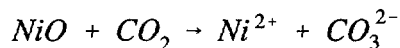
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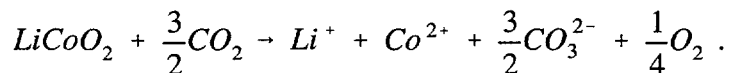
Introduction

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.¹ The rate of transport increases with increasing CO₂ 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 CO₂ partial pressure (about 0.1 atm), transport of nickel to the anode at a higher pressure (e.g., 3 atm) and a high CO₂ 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 (LiCoO₂). The LiCoO₂ cathode has a low resistivity, about 1 Ω-cm, and can be used as a direct substitute for NiO. Analogous to NiO, LiCoO₂ dissolves at high partial pressures of CO₂ according to the reaction²:



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 LiCoO₂ (more than a factor of 10) in the (Li,K)₂CO₃ melt. Once at the anode, the dissolved Co²⁺ 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 (LiFeO₂) and LiCoO₂. Using LiFeO₂-based materials is attractive because the transport of LiFeO₂ is thought to be zero. In contrast to Co²⁺, Fe²⁺ is not reduced at the anode. The LiFeO₂ 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 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 LiCoO_2 – LiFeO_2 binary system was studied to determine solid-solution and two-phase regions. A series of LiCoO_2 – 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 LiCoO_2 – 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 LiCoO_2 and LiFeO_2 are indicated by circles and triangles, respectively. Data from a series of compositions are plotted as the percent LiCoO_2 peak intensity versus LiCoO_2 concentration (see Fig. 2). Here, the percent 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_{LiCoO_2} and I_{LiFeO_2} are the peak intensities from LiCoO_2 ($\langle 003 \rangle$ reflection) and LiFeO_2 ($\langle 200 \rangle$ reflection), respectively. At low (0 to about 6 m/o) LiCoO_2 concentrations, no peaks resulting from excess LiCoO_2 were seen. At high (85 to 100 m/o) LiCoO_2 concentrations, no peaks resulting from excess 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°C as a function of LiCoO_2 – LiFeO_2 composition show the expected trend: resistivity is inversely proportional to cobalt content. The resistivity of 6 m/o LiCoO_2 is $5\ \Omega\text{-cm}$; of 12.5 m/o LiCoO_2 , $3.3\ \Omega\text{-cm}$; and of 87.5 m/o LiCoO_2 , $1.3\ \Omega\text{-cm}$.

Cell Tests

The LiCoO_2 and LiCoO_2 – 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 O_2 – CO_2 gas mixtures to simulate pressurized operation at 3–5 atm.

LiCoO₂ cathode. The potential at $320\ \text{mA/cm}^2$ versus time for an MCFC with a 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.

LiCoO₂–LiFeO₂ cathode. The potential at $160\ \text{mA/cm}^2$ versus time for the MCFC with the 12.5-m/o Co-doped 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_2 -to- CO_2 ratio on the MCFC voltage at 160 mA/cm^2 was measured. In Fig. 6, the effect of CO_2 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 $LiCoO_2$. 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 $LiCoO_2$ 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 $LiCoO_2$ in $LiFeO_2$ show promise for long-lived cathode materials. We have found that small additions of $LiCoO_2$ to $LiFeO_2$ markedly decrease the resistivity of the cathode material. Cells containing the $LiCoO_2$ - $LiFeO_2$ cathodes have stable performance for more than 2100 h of operation and display lower cobalt migration rates than pure $LiCoO_2$. Further tests using the $LiCoO_2$ - $LiFeO_2$ cathodes are planned at higher current density.

Acknowledgments

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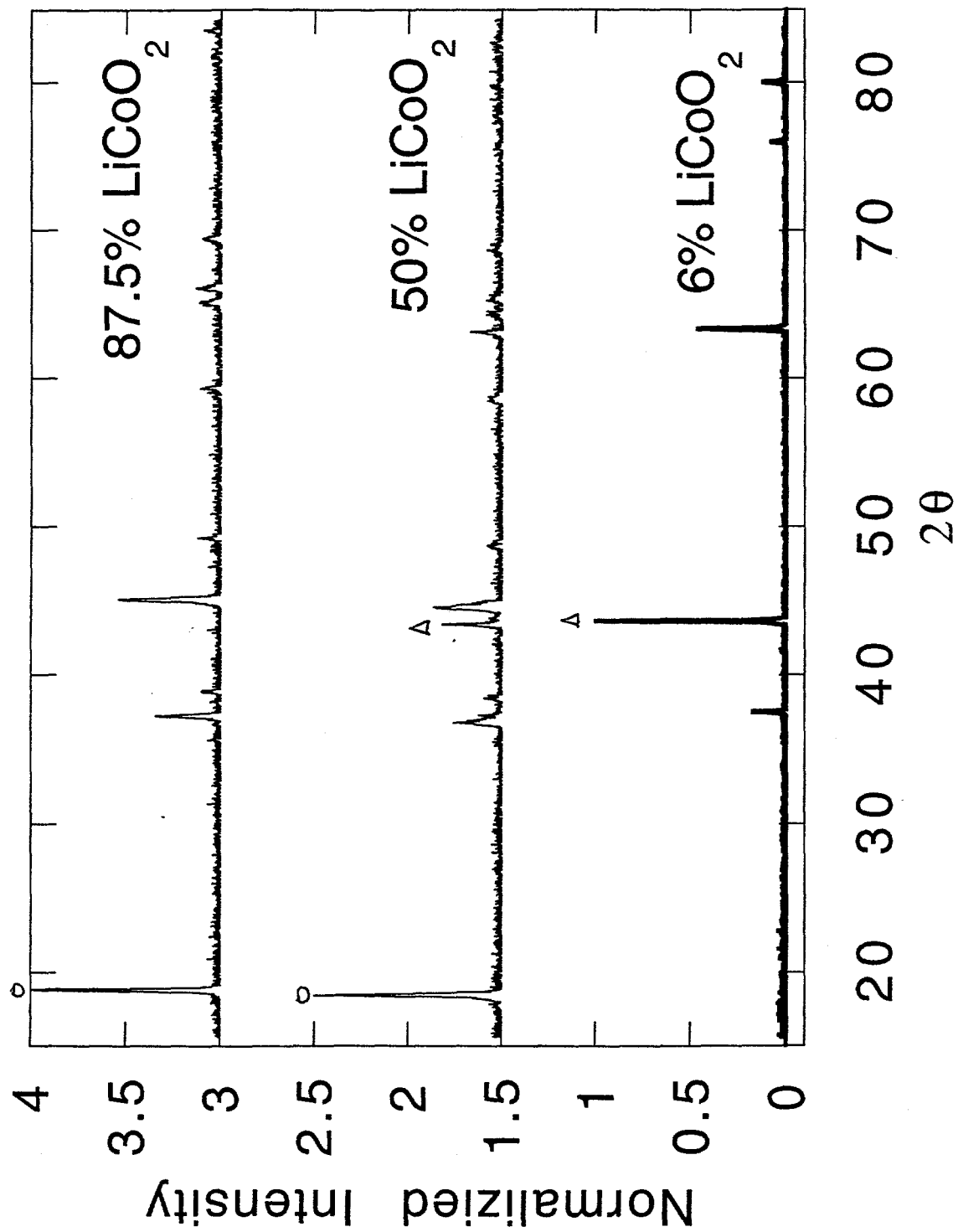


Fig. 1. X-ray diffraction patterns from LiCoO_2 - LiFeO_2 mixtures. Peaks of interest from LiCoO_2 and LiFeO_2 are indicated by circles and triangles, respectively.

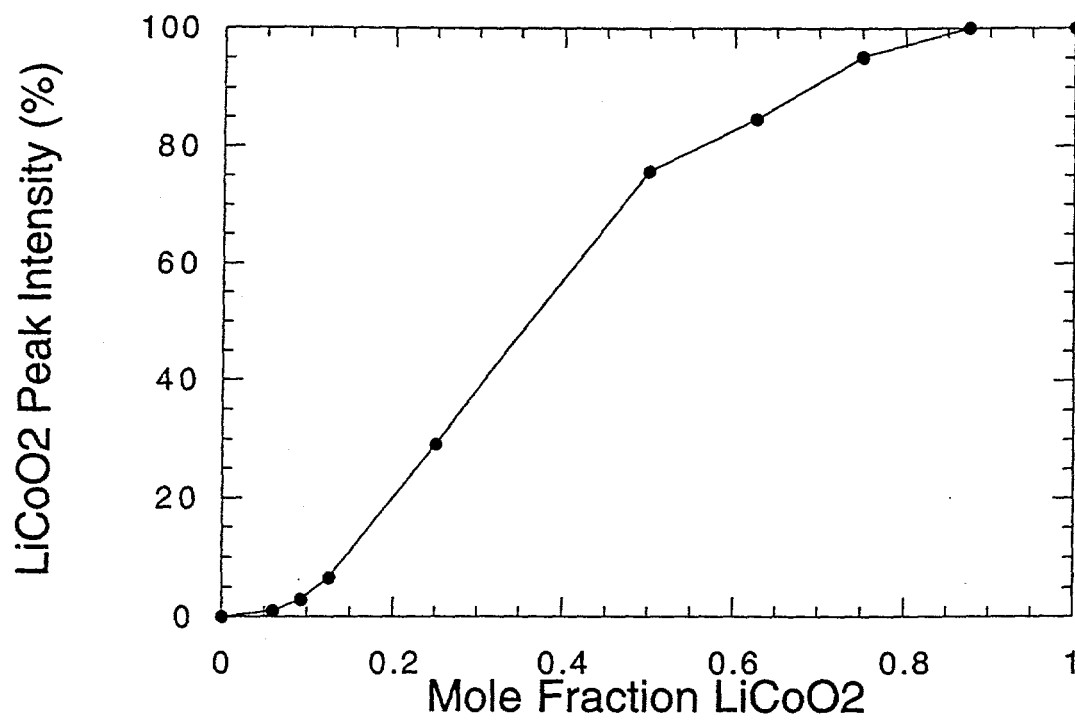


Fig. 2. Plot of LiCoO₂ peak intensity vs. mole fraction LiCoO₂.

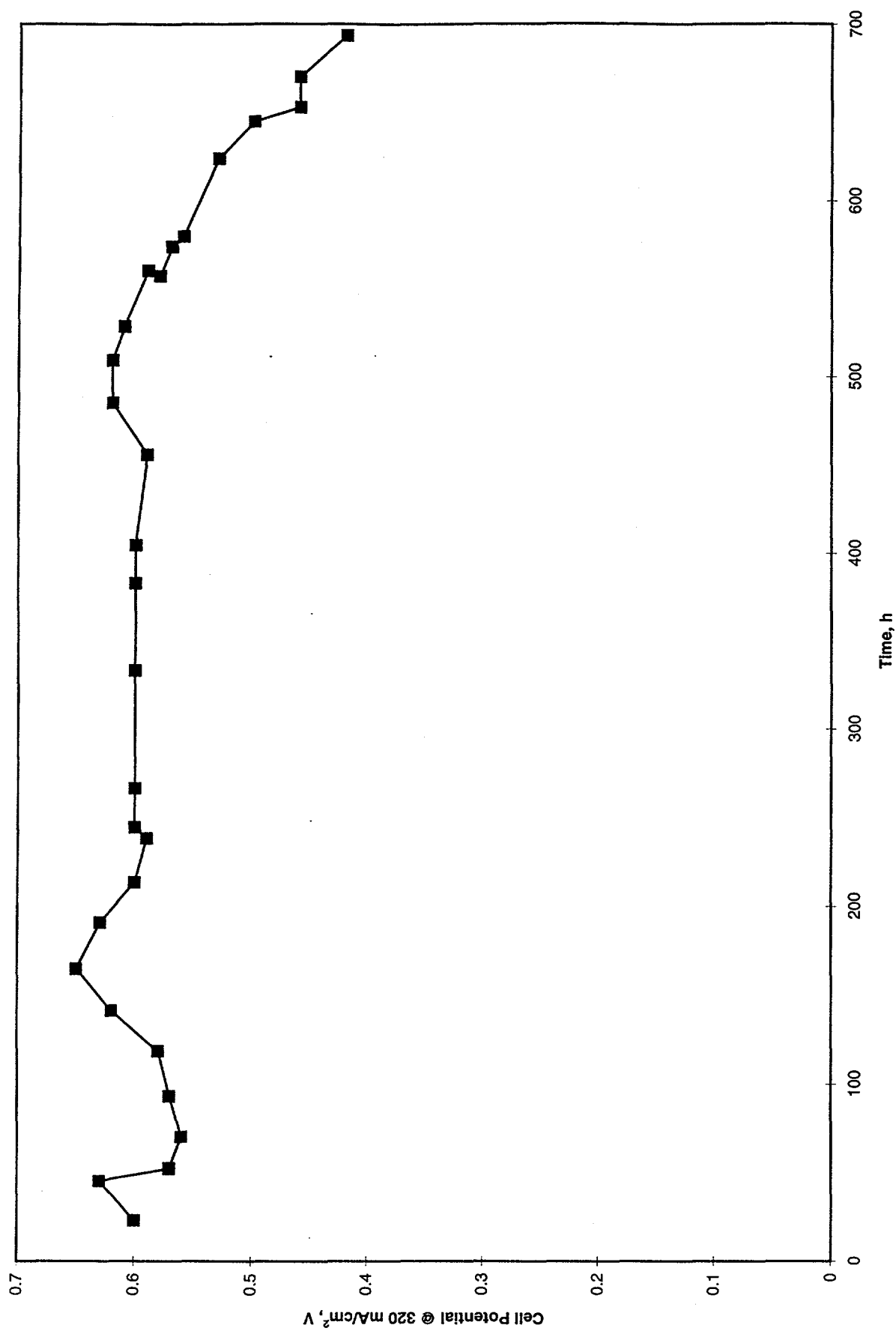


Fig. 3. Cell potential vs. time for an MCFC containing a LiCoO_2 cathode operated at 320 mA/cm^2 under simulated pressurized conditions.

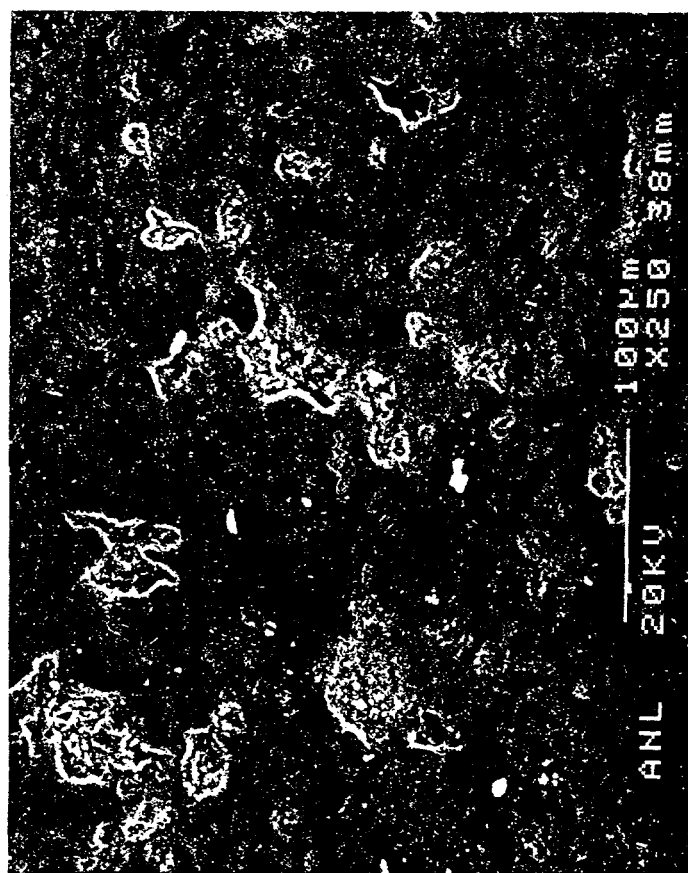


Fig. 4. Back-scatter electron image showing cobalt-containing species (white objects) in the electrolyte tile (LiCoO₂ cathode).

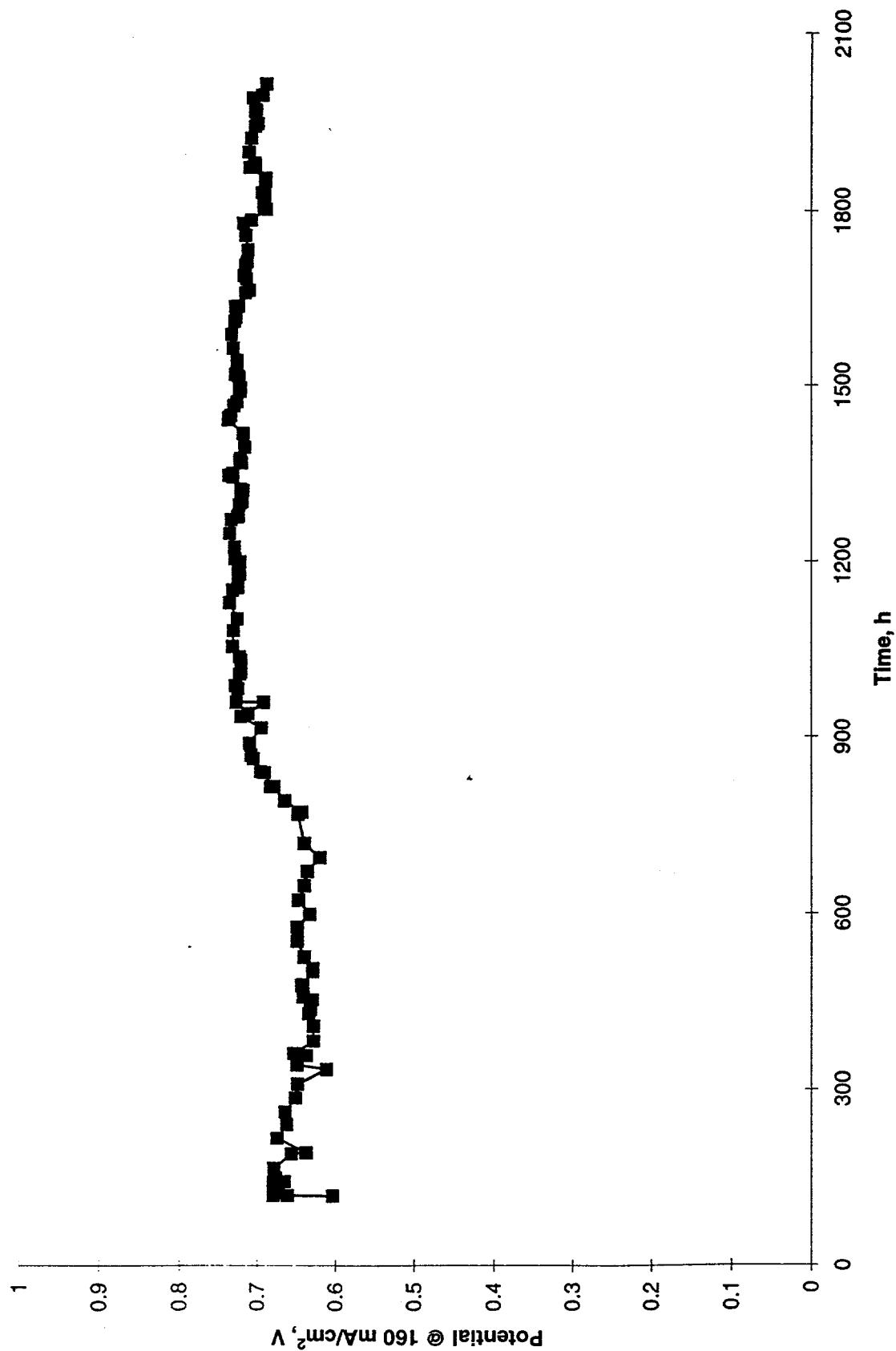


Fig. 5. Cell potential vs. time for an MCFC containing a $\text{LiCoO}_2\text{-LiFeO}_2$ cathode operated at 160 mA/cm^2 under simulated pressurized conditions.

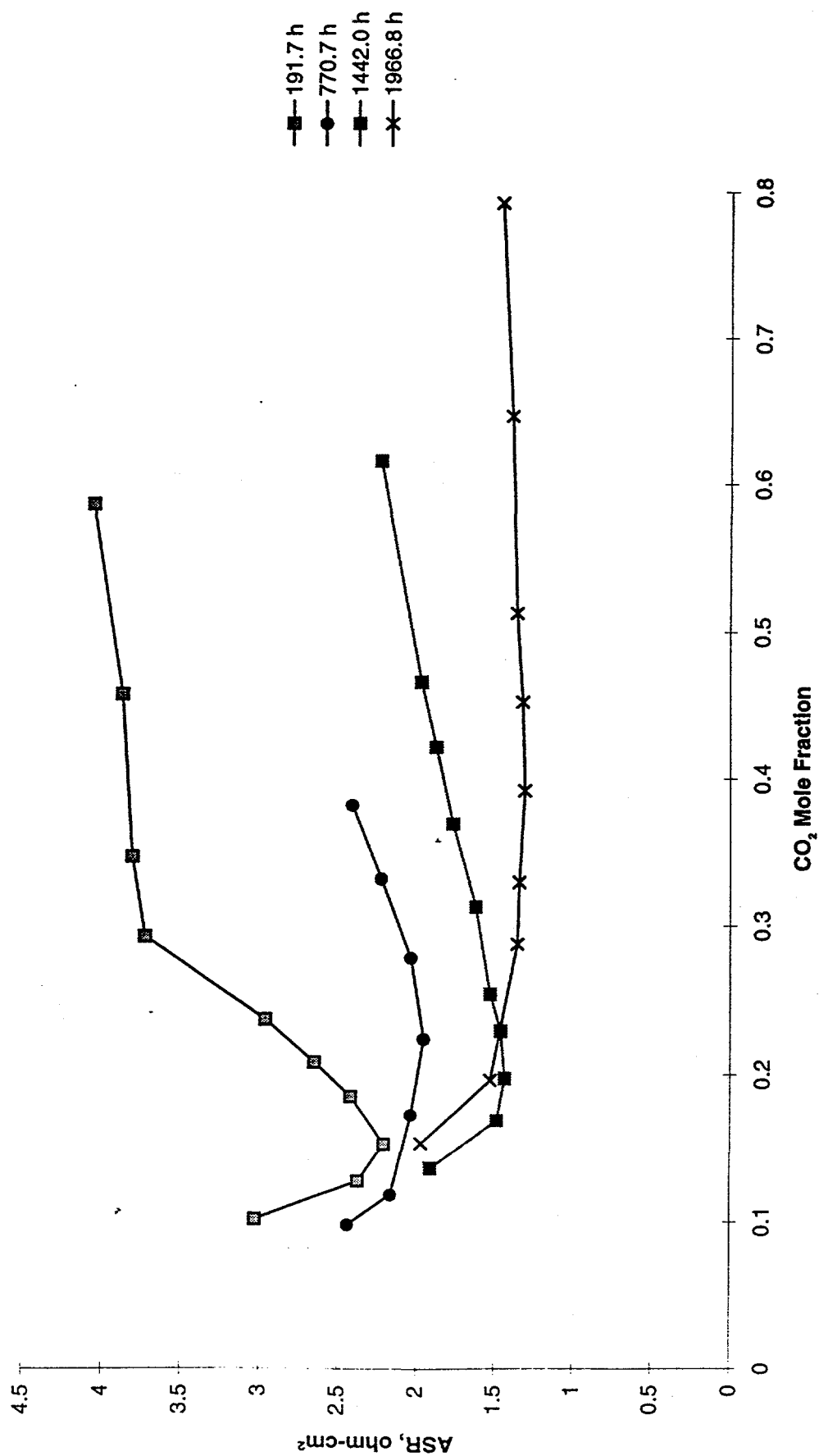


Fig. 6. Changes in cell area-specific resistance vs. CO₂ mole fraction with time.

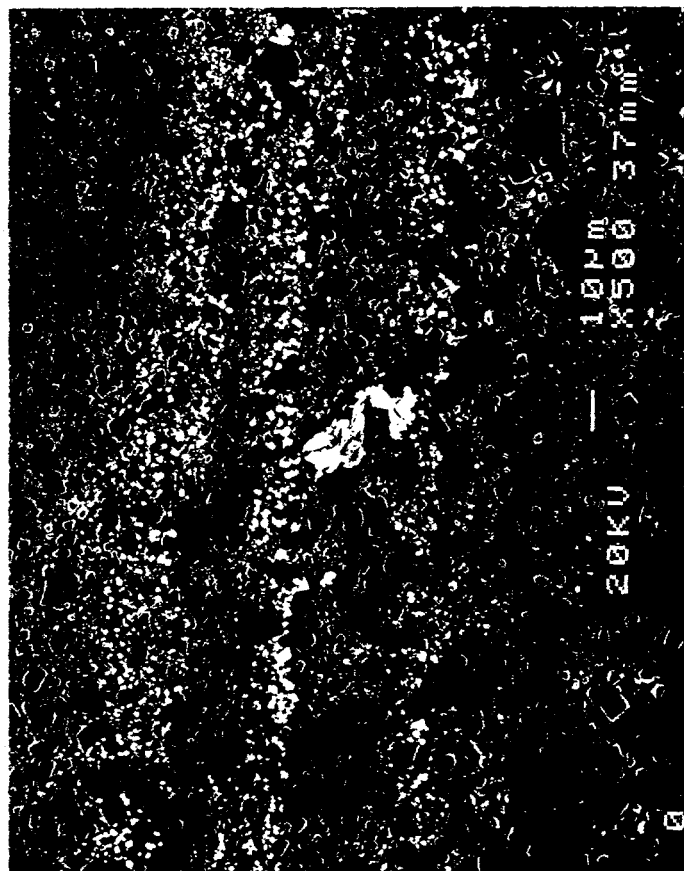


Fig. 7. Back-scatter electron image showing cobalt-containing species (white objects) in the electrolyte tile (LiCoO₂-LiFeO₂ cathode).