Improvement of molten-carbonate fuel cell (MCFC) lifetime

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Abstract

At the Netherlands Energy Research Foundation, ECN, two approaches to the molten-carbonate fuel cell (MCFC) cathode lifetime problem have been investigated. In the first approach, efforts have been made to reduce the dissolution rate of the state-of-the-art NiO material by means of electrolyte additives. Thus far, it has been possible to obtain a reduction of *c.* 50% using alkaline-earth oxides or carbonates. The second approach is the development of alternative materials with good performance and very low dissolution rate, suitable to replace NiO. In this respect $LiCoO_2$ is a promising candidate. In addition to a good in-cell behaviour, this material has a dissolution rate which is almost an order of magnitude lower than that of NiO, and its solubility shows favourable gas pressure dependences. In order to explain the significant differences in NiO, $LiCoO_2$ and $LiFeO_2$ performance, porous electrode modelling has been started. Preliminary results indicate that intrinsic materials properties, i.e., catalytic activity and electrical conductivity, play a crucial role in the observed polarization behaviour.

Introduction

In MCFC technology the dissolution of the state-of-the-art lithiated NiO cathode material is one of the major lifetime-limiting factors [1]. The NiO material dissolves in the molten-carbonate electrolyte and is subsequently transported, reduced and precipitated in the electrolyte matrix [2]. The dissolution-precipitation mechanism has been identified as:

$$NiO + CO_2 \rightleftharpoons Ni^{2+} + CO_3^{2-} \tag{1}$$

$$Ni^{2+} + CO_3^{2-} + H_2 \rightleftharpoons Ni + CO_2 + H_2O \tag{2}$$

Figure 1 shows an electron microscopy (SEM-EDAX) image of a post-test 3 cm^2 cell package, from which the location and amount of precipitated Ni can be analysed. The reductions of weight and thickness of NiO cathodes as a function of operation time are about 3% per 1000 h. The processes indicated limit the period of satisfactory cathode performance to *c.* 25 000 h at atmospheric operation pressure. According to a linear relation between dissolution rate and carbon dioxide partial pressure, a NiO cathode in a (external reforming) MCFC system operating at 7 bar (7 10^5 Pa) will therefore only have a lifetime of approximately 3500 h.

The reduction of the nickel solubility through increasing the basicity of the electrolyte is an approach to the cathode lifetime problem. Another strategy is the development of cathodes made from alternative materials suitable to replace NiO.
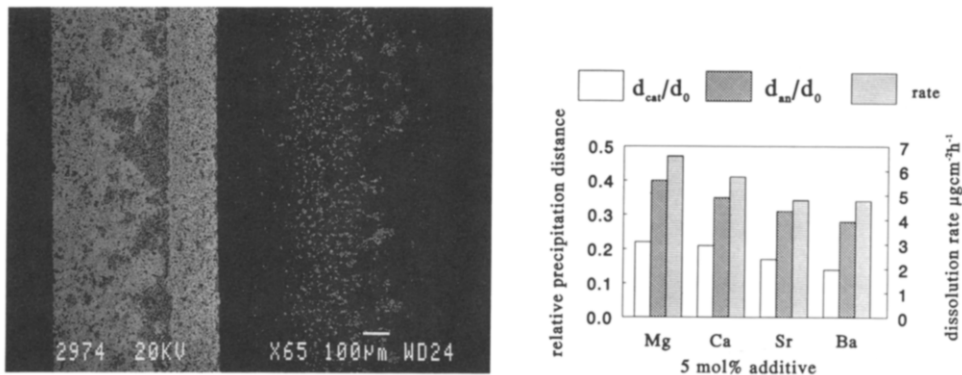
Fig. 1. SEM-EDAX image of a post-test lab-cell package, showing the nickel oxide precipitation. From left to right: anode, bubble-barrier, and matrix with nickel precipitates.

Fig. 2. Influence of the addition of 5 mol% alkaline-earth ion on the nickel dissolution rate and precipitation band, as determined from 1000 h lab-cell tests. The precipitation boundary distance nearest to the cathode (d_{cat}) and nearest to the anode (d_{an}) are normalized to the matrix thickness (d_o).

NiO dissolution and electrolyte additives

At ECN, a model describing dissolution, transport and precipitation of nickel in the electrolyte matrix has been developed and experimentally verified [3]. From this, a time-averaged value of 4 μg cm^{-2} h^{-1} for the dissolution rate of NiO could be established. It became clear that the cathode dissolves preferentially at the cathode matrix interface, apparently leaving the microstructure of the remaining material unchanged. Furthermore, a correlation between dissolution rate and precipitation distance appears. A higher dissolution rate is accompanied by a larger precipitation distance and a wider precipitation band.

The solubility of NiO, which was identified as a crucial factor in the dissolution rate, can be reduced through increasing the basicity of the electrolyte. This can be done by addition of small amounts of alkaline earth ions. Figure 2 shows the influence of such additions on the dissolution rate and the precipitation band of NiO, as determined from post-test analyses of 3 cm^2 cell packages after 1000 h operation time. Reductions of the NiO dissolution rate up to $c.$ 50% can be obtained [4].

Development of alternative cathodes for MCFC

Another strategy to overcome the cathode lifetime problem is the development of cathodes made from alternative materials suitable to replace NiO. These materials should have good in-cell performance, preferably on the same level as that of NiO, and a very low dissolution rate. In this respect, the thermodynamically-stable ceramic oxides $LiFeO_2$ and $LiCoO_2$ have been investigated. $LiFeO_2$ does not precipitate in the electrolyte matrix and has therefore a dissolution rate equal to zero. However, according to lab-cell tests $LiFeO_2$ cathodes have a rather low performance, whereas $LiCoO_2$ performs very well [5]. With an optimized porous microstructure [6], $LiCoO_2$ cathodes perform on NiO level as can be seen in Fig. 3.
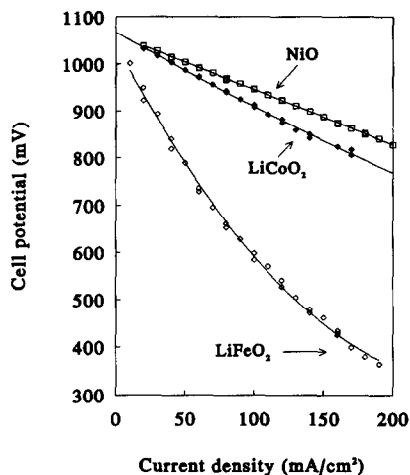
Fig. 3. Cell voltage (mV) as a function of current density (mA cm^{-2}) for 3 cm^2 lab-cells at 650 °C, equipped with: standard NiO cathode, LiCoO$_2$ cathode, or LiFeO$_2$ cathode.

From post-test analyses after 1000, 1500 and 3500 h of testing at 160 mA cm^{-2}, the dissolution rate of LiCoO$_2$ was found to be less than 0.5 μg cm^{-2} h^{-1}, which is almost an order of magnitude lower than the corresponding number for NiO. Small amounts of cobalt were found in the bubble-barrier area of the cell packages.

The dissolution mechanism of LiCoO$_2$ was studied in pot cells, using square wave voltammetry (SWV) to determine the concentration of cobalt ions dissolved in the carbonate [7]. The application of SWV enables high sensitivity and a low dependence on the (planar gold) electrode geometry. Since the electrode area is not exactly known, a calibration of peak current against the concentration of cobalt as determined by ICP-AES (inductive coupled plasma-atomic emission spectroscopy) is necessary for each experimental run. SWV facilitates continuous monitoring of cobalt ion concentration under various gas environments and at various temperatures. From the dependences of the cobalt solubility on pCO$_2$ and pO$_2$ the following dissolution mechanism can be postulated:

$$LiCoO_2 + \tfrac{1}{2}CO_2 \rightleftharpoons Co(II)O + \tfrac{1}{4}O_2 + \tfrac{1}{2}Li_2CO_3 \tag{3}$$

Comparison of the dependences of the solubility on the partial gas pressures of carbon dioxide ($p(CO_2)$) and oxygen ($p(O_2)$) with those of NiO (see eqn. 1) shows a favourable mechanism.

Across a cathode there will be a simultaneous decrease in pCO$_2$ and pO$_2$ in large MCFC's. For LiCoO$_2$ this will result in a more uniform precipitation band, reducing the probability of short circuiting. Moreover, the solubility of LiCoO$_2$ shows a $p^{1/4}$ dependence on operating pressures (p) instead of a linear dependence. This, of course, is a great advantage for application in pressurized systems. Estimated lifetimes for LiCoO$_2$ cathodes are 150 000 and 90 000 h at 1 and 7 bar (1 and 7 10^5 Pa), respectively. Table 1 gives a review of the dissolution rates and pressure dependences for NiO and LiCoO$_2$ cathode materials.

TABLE 1

Dissolution rates of cathode materials in $\mu g\ cm^{-2}\ h^{-1}$, as obtained from 1000 h lab-cell tests at 650 °C; also indicated are the dependences of NiO and $LiCoO_2$ solubilities on the carbon dioxide, $p(CO_2)$ and oxygen, $p(O_2)$, partial pressures and the total pressure p

Electrolyte	NiO	LiFeO$_2$	LiCoO$_2$
62:38 (Li:K)$_2$CO$_3$	7.1	0.0	0.5
+5 mol% MgO	6.6		
+5 mol% CaCO$_3$	5.8		
+5 mol% SrCO$_3$	4.8		
+5 mol% BaCO$_3$	4.7		
50:50 (Li:K)$_2$CO$_3$	10.3		
70:30 (Li:K)$_2$CO$_3$	4.2		
pressure	$p(CO_2)$		$p(CO_2)^{1/2}$; $p(O_2)^{-1/4}$
dependences	p		$p^{1/4}$

TABLE 2

Exchange current densities as obtained from fitting the film-agglomerate model to experimental polarization curves of cathode materials, using the electrical conductivities indicated

Electrode	Data points	σ_0 S cm^{-1}	d_{eq} μm	R μm	i_0^0 mA cm^{-2}
NiO	22	13	8.0	8.0	0.81
LiCoO$_2$	30	0.45	6.5	6.5	0.53
LiFeO$_2$	23	0.05	5.5	5.5	0.09

Porous electrode modelling

In order to explain the significant differences in the performance of NiO, $LiCoO_2$ and $LiFeO_2$ cathodes, porous electrode modelling activities have recently been started at ECN. The objectives of this work are to evaluate the intrinsic catalytic properties of the cathode materials and to determine the relative influence of intrinsic materials properties and porous microstructure on the in-cell performance.

The film-agglomerate model of Yuh and Selman was modified to include the electrical conductivity of the cathode material [8]. The electrical conductivities (σ_0) of the three materials were evaluated from lab-cell experiments and out-of-cell measurements. Average gas-pore and agglomerate radii were estimated from pore size distributions and SEM images. Using the gas-pore radii d_{eq}, the carbonate fill degree of the cathodes, and an estimated carbonate film thickness of 0.1 μm, agglomerate radii R were calculated and checked with the values obtained from the SEM images. Then, best values for the standard exchange current density i_0^0 were obtained by optimal fit to experimental polarization curves, using the calculated agglomerate radii. The results are shown in Table 2. The i_0^0 values obtained reflect the in-cell performances of the cathode materials, i.e., NiO and $LiCoO_2$ cathodes perform on about the same level, whereas $LiFeO_2$ cathodes have a much lower performance. Since the structural properties of $LiCoO_2$ and $LiFeO_2$ cathodes are nearly the same, it can be concluded that the low performance of the $LiFeO_2$ cathodes is due to intrinsic materials properties,

i.e., the electrical conductivity σ_0 and the catalytic activity for the MCFC cathode reactions ($i_0{}^0$). Also, differences in electrolyte wetting behaviour of the materials cannot be ruled out, because, thusfar, no experimental data exist to verify the assumption of equal carbonate film thickness used in the model.

Conclusion

The above-described results can be summarized as follows: (i) the dissolution rate of NiO cathodes can be reduced by c. 50% using electrolyte additives; (ii) the dissolution rate of $LiCoO_2$ under MCFC cathode conditions is about an order of magnitude lower than that of NiO; (iii) $LiCoO_2$ has a dissolution mechanism with favourable gas pressure dependence as compared to that of NiO; (iv) estimated lifetimes for NiO and $LiCoO_2$ cathodes at 7 bar (7 10^5 Pa) are 3500 and 90 000 h, respectively; (v) the performance of $LiCoO_2$ cathodes in an MCFC is on about the same level as that of NiO; (vi) the low performance of $LiFeO_2$ cathodes is probably due to intrinsic materials properties, (i.e., catalytic activity and electrical conductivity).

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