TECHNOLOGICAL STATUS OF NICKEL OXIDE CATHODES IN MOLTEN CARBONATE FUEL CELLS — A REVIEW*

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Summary

The technological status of NiO cathodes in molten carbonate fuel cells is examined in terms of four properties: electrode conductivity, electrode kinetics, electrode structure, and electrode material stability. Several problems must be solved before the cathode can meet the requirements for commercial applications of fuel cells. The major problem is the instability of NiO over long-term operations; other concerns are the compaction of the cathode structure during cell operation and the lack of definite information on the electrode kinetics. This paper critically examines efforts by industry (especially in the U.S.) and other investigators in addressing those problems.

Introduction

Molten carbonate fuel cells (MCFCs) are presently under development for electric utility power generation [1]. The attractive feature of MCFCs is their expected clean and efficient generation of electricity from hydrocarbon fuels including coal. The state-of-the-art MCFC consists of a porous nickel (containing dispersed chromium to provide strength and sintering resistance) anode (fuel electrode), a porous, lithium-doped, nickel oxide cathode (oxidant electrode), and a lithium aluminate matrix filled with lithium and potassium carbonates (62 - 70 mol% Li_2CO_3) as the electrolyte. The cell is operated at a temperature of about 925 K and at a pressure of 1 to 10 atm; the fuel gas is a humidified mixture of H_2 and CO, and the oxidant is a mixture of O_2 and CO_2 which may contain water vapor. The overall reactions at the fuel cell anode and cathode are as follows:

Anode

$$H_2 + CO_3^{2-} = H_2O + CO_2 + 2e^- \tag{1}$$

$$CO + CO_3^{2-} = 2CO_2 + 2e^- \tag{2}$$

Cathode

$$1/2O_2 + CO_2 + 2e^- = CO_3^{2-} \tag{3}$$

In cell construction, the anode, electrolyte, and cathode are thin, flat plates (typical thickness of the components: anode 0.8 - 1.5 mm, electrolyte 0.5 - 1.8 mm, and cathode 0.4 - 1.5 mm). However, the anode is sometimes ribbed to provide passages for fuel gas. Practical electrical power generation is achieved by stacking a series of repeating cell components to build voltage. In a stack of cells, cell separator plates, current collectors, and cell-to-cell seals are required. Figure 1 shows the essential components in a cell stack. As shown in the Figure, a corrugated or perforated plate provides oxidant gas passages, cathode support, and current collection. A bilayer nickel/ stainless steel separator plate also serves as a current collector and provides the anode–cathode electrical interconnection. Figure 2 shows micrographs of a typical cathode, electrolyte support, and anode. (In this Figure, the cathode contains electrolyte, but the $LiAlO_2$ and anode are "dry".)

In coal-based applications with an optimized bottoming cycle, a fuel cell stack must meet the following criteria (besides cost) for performance and lifetime: (i) a performance equivalent to approximately 640 mV at a current density of approximately 400 mA cm^{-2}, and (ii) a lifetime of 40 000 h (4.5 years). A major determinant for satisfying these criteria is the stability and behavior of various cell components under operating conditions. In this respect, the stability and behavior of the NiO cathode play a vital role. This paper examines and summarizes the status of NiO as the MCFC cathode in terms of four properties: electrode conductivity, electrode kinetics, electrode structure, and electrode material stability. Emphasis will be given to the current problems with the NiO cathode and to the efforts pursued by various companies and workers in addressing those problems.
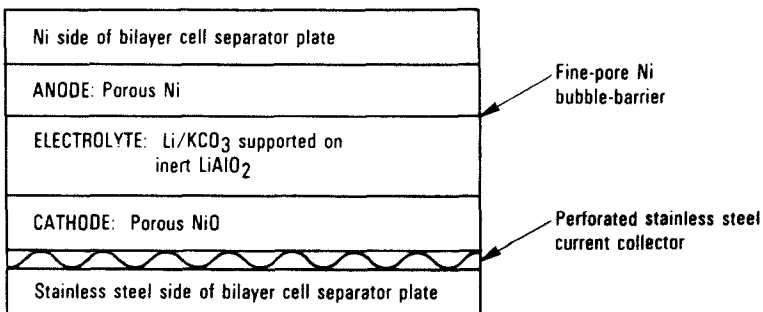
Ni side of bilayer cell separator plate	
ANODE: Porous Ni	Fine-pore Ni bubble-barrier
ELECTROLYTE: Li/KCO₃ supported on inert LiAlO₂	
CATHODE: Porous NiO	Perforated stainless steel current collector
Stainless steel side of bilayer cell separator plate	

Fig. 1. Essential components of molten carbonate fuel cell stacks [1].

<table>
<tr><td>2 μm</td><td>2 μm</td><td>2 μm</td></tr>
<tr><td>CATHODE</td><td>ELECTROLYTE SUPPORT</td><td>ANODE</td></tr>
<tr><td>Lithiated Nickel Oxide
(wetted with carbonate salt)</td><td>LiAlO₂</td><td>Nickel-Chromium</td></tr>
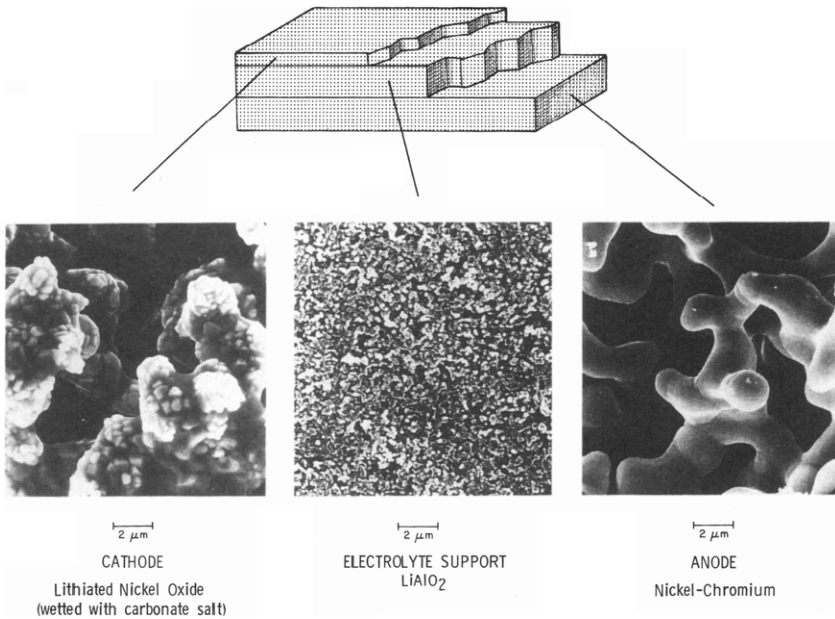</table>

Fig. 2. Micrographs of molten carbonate fuel cell electrodes and electrolyte support.

Electrode conductivity

NiO is a p-type semiconductor [2 - 5]; thus, when it is used as the cathode material in the fuel cell, its conductivity is enhanced by doping with lithium provided by Li_2CO_3 in the molten electrolyte. The incorporation of lithium into NiO is accompanied by the creation of an electron hole (Ni^{2+} is replaced by Ni^{3+}) [2 - 5]:

$$x/2Li_2O + (1 - x)NiO + x/2O_2 = Li_x^{+}Ni_{1-x}^{2+}Ni_x^{3+}O \qquad (4)$$
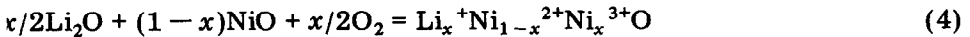
Consequently, the electronic conductivity of NiO increases significantly, due to the exchange of electron holes between nickel ions of 2+ and 3+ valence states. For example, the conductivity of NiO at 700 °C increases from about 0.03 ohm^{-1} cm^{-1} to about 47 ohm^{-1} cm^{-1} after NiO is doped with 3.4 at.% lithium [6]. In the fuel cell cathode environment, the equilibrium lithium dopant content in NiO is about 2 at.% [7]. This dopant level yields more than adequate electronic conductivity for NiO for its use as an MCFC cathode material.

From eqn. (4), it can be seen that the equilibrium lithium content, and thus the conductivity of the Li-doped NiO cathode, depends on the partial pressure of oxygen. However, the change in the oxygen partial pressure during cell operation is not enough to cause sufficient change in the conductivity to influence significantly the performance of the NiO cathode.

Since the conductivity of Li-doped NiO results from the presence of Ni^{2+} and Ni^{3+} in the NiO lattice, the introduction of a foreign trivalent species would be expected to decrease the material conductivity (due to formation of Li^+-trivalent ion pairs, with a corresponding decrease in the formation of Ni^{3+} ion). In an MCFC, the NiO cathode is in intimate contact with a stainless steel current collector that oxidizes to form a scale; this scale contains predominantly Fe_2O_3, $LiFeO_2$, and Li–Cr–O and K–Cr–O compounds. The Fe^{3+} and Cr^{3+} ions may be introduced in the carbonate electrolyte from the dissolution of those corrosion products. The incorporation of either Fe^{3+} or Cr^{3+} into the NiO structure, from either the current collector or its dissolved corrosion products, might have significant impact on cell performance in long-term operation via their effects on the cathode conductivity.

General Electric (GE) [8, 9] examined NiO cathodes in cells operated from 50 to 10 080 h. Four regions of the NiO cathode were analyzed for Fe and Cr content:
  —Region 1: in direct contact with the stainless steel current collector
  —Region 2: adjacent to Region 1, in contact with the open gas passage
  —Region 3: located within the body of the cathode
  —Region 4: in contact with the electrolyte structure
The GE results showed that samples of Region 1 contain iron within the NiO lattice. No iron was found in Regions 2, 3, and 4, and no chromium was observed in any sample. For samples of Region 1, iron has been found to penetrate only superficially into the NiO grain, diffusing to a depth of about 10 nm after 10 080 h of testing. Therefore, even though Fe^{3+} and Cr^{3+} incorporation into a Li-doped NiO cathode could dramatically reduce cell performance by decreasing cathode conductivity, such a mechanism apparently plays an insignificant role. Neither impurity readily enters the Li-doped NiO cathode structure under fuel cell operating conditions.

Consequently, there are no concerns or problems with the MCFC NiO cathode in terms of conductivity.

Electrode kinetics

The kinetics of the oxygen reduction at the NiO cathode plays an important role in cell performance via its influence on polarization losses at the cathode. Knowledge of the cathode kinetics is useful to predict and optimize performance.

The oxygen electrode has been studied in molten carbonates. It has been established that the rest potential on gold electrodes corresponds to the Nernst potential for the four-electron reduction of an oxygen molecule, along with two CO_2 molecules, to give carbonate ions [10]. However, the mechanism of the reaction is still controversial.

Nearly all investigations of the oxygen reduction kinetics were carried out on gold electrodes. Many such early measurements were made using partly immersed electrodes, where the meniscus probably sustained a very

high current density. Thus, they have to be interpreted with caution [11]. The most quoted investigations of the oxygen kinetics in molten carbonates are those of Appleby and Nicholson [12 - 15]. They proposed two mechanisms for oxygen reduction. The key concept in their work is the importance of peroxide (O_2^{2-}) and superoxide (O_2^-) in oxygen reduction.

Peroxide mechanisms

$$O_2 + 2CO_3^{2-} = 2O_2^{2-} + 2CO_2 \tag{5}$$

$$O_2^{2-} + e^- = O^{2-} + [O^-] \tag{6}$$

$$[O^-] + CO_2 + e^- = CO_3^{2-} \tag{7}$$

$$O^{2-} + CO_2 = CO_3^{2-} \tag{8}$$

The exchange current density is given by

$$i_o = i_o^o P_{O_2}^{(2-\alpha)/4} P_{CO_2}^{-(1+\alpha)/2} \qquad \alpha = 0.5 \tag{9}$$

(at 650 °C and in $Li_2CO_3-K_2CO_3$, $i_o^o = 0.012$ mA cm^{-2})

Superoxide mechanism

$$3O_2 + 2CO_3^{2-} = 4O_2^- + 2CO_2 \tag{10}$$

$$O_2^- + e^- = O_2^{2-} \tag{11}$$

followed by the reactions for O_2^{2-} shown above.
The exchange current density is given by

$$i_o = i_o^o P_{O_2}^{(3-\alpha)/4} P_{CO_2}^{-(1+\alpha)/2} \qquad \alpha = 0.5 \tag{12}$$

(at 650 °C and in $Li_2CO_3-K_2CO_3$, $i_o^o = 0.003$ mA cm^{-2}).
The peroxide mechanism is favored in pure Li_2CO_3 and in melts with a predominance of Li$^+$ ions.

The study of White and coworkers [16 - 18] on the electrochemistry of oxygen and carbon dioxide at gold electrodes in $Li_2CO_3-Na_2CO_3-K_2CO_3$ eutectic (43.5–31.5–25 mol%) supported the conclusions of Appleby and Nicholson. Peroxide and oxide ions have been found to be present simultaneously in this melt. The cathodic reduction of peroxide at gold electrodes, $O_2^{2-} + 2e^- = 2O^{2-}$ is shown to be diffusion-controlled. On the other hand, limiting currents obtained by Vogel, Smith and Bregoli [19] with rotating gold wire electrodes indicate that oxygen dissolves in $Li_2CO_3-K_2CO_3$ melt (62–38 mol%) predominantly as superoxide. The dissolved oxygen is reduced completely on gold in a single wave.

Physical Sciences Inc. (PSI) proposed a mechanism involving superoxide species to describe the kinetics of oxygen reduction on NiO [20]. A

mechanism proposed by Dunks and Stelman [21] involves a hypothetical percarbonate species, CO_4^{2-}, to account for their results in gas-sparged Na_2CO_3 at 900 °C. Lu and Selman [22] observed the acceleration of the kinetics of oxygen reduction by oxide addition. This observation is explained by a rapid interaction of added O^{2-} with O_2, generating excess peroxide and superoxide ions. Recent kinetic measurements of oxygen reduction by Uchida *et al.* [23 - 25] indicate that the exchange current density is at least two orders of magnitude larger than the values reported by Appleby and Nicholson.

Thus far, the kinetics of oxygen reduction at nickel oxide electrodes in the carbonate electrolyte has not been determined. Efforts to prepare smooth electrodes of NiO for kinetic studies have proved unsuccessful in many cases owing to rapid disintegration of initially smooth electrodes in molten carbonates. Therefore, little definite information about oxygen reduction on NiO is available.

Although it has now been recognized that O_2^{2-} and O_2^{-} are the electroactive species in the oxygen reduction [11], there are differences in opinions concerning kinetics between gold and NiO electrodes. For example, a recent study of oxygen reduction on porous NiO electrodes by Winnick and Ross [26] shows that the results are not consistent with the reaction mechanisms proposed by Appleby and Nicholson for gold electrodes. Because of the effects of diffusion within the porous electrode, Winnick and Ross could not draw conclusions on the mechanism; however, the reaction orders are very different from the values reported by Appleby and Nicholson. A discussion of possible catalytic effects of NiO must be largely speculative at this point. Several studies [27 - 29] reported in the literature tend to support the view that the electrode material can influence the oxygen reduction kinetics, but no quantitative interpretation can be made. On the other hand, the data obtained by Uchida *et al.* [23 - 25] show that Au, Pt, NiO, and other conductive oxide electrodes (IrO_2 and Sb-doped SnO_2) have the same order of exchange current density values. Scott *et al.* [30] found that porous NiO and perovskite electrodes have equivalent kinetic performance.

As discussed earlier, melt composition is a major factor influencing the kinetics of the oxygen reduction since the concentration of various oxide species (O_2^{-}, O_2^{2-}, O^{2-}) depends on the melt composition and the gas environment. There is also a strong influence of cation composition on the oxygen reduction kinetics. This can be seen from Fig. 3, which shows cyclic voltammograms for the oxygen reduction obtained in various carbonate melts. Knowledge of reaction kinetics as a function of electrolyte composition is presently lacking.

Because of the lack of information on oxygen reduction kinetics on NiO, modeling of the NiO cathode must either use the gold electrode kinetics or else postulate a reaction mechanism [31 - 34]. For example, Kunz and coworkers [34] used the mechanism involving superoxide proposed for gold electrodes in their modeling; on the other hand, the peroxide mechanism appears to give a better fit of cathodic data for the model proposed
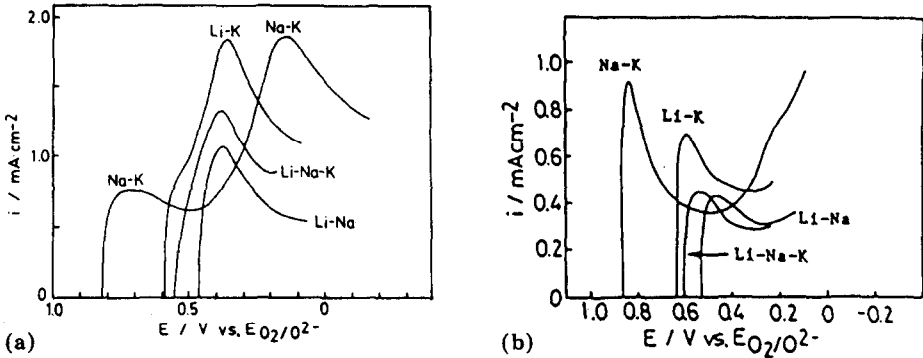
Fig. 3. Comparison of cyclic voltammograms obtained for oxygen reduction at gold electrodes in various carbonate melts [23]. (Reprinted from I. Uchida and T. Nishina, *Tech. Rep. Tohoku Univ.*, *50* (1985) 51, by kind permission of the publisher.) (a) P_{O_2} = 0.9 atm, P_{CO_2} = 0.1 atm, sweep rate = 1 V s^{-1}, T = 750 °C; (b) P_{O_2} = 0.33 atm, P_{CO_2} = 0.67 atm, sweep rate = 1 V s^{-1}, T = 750 °C.

by Yuh and Selman [32]. This discrepancy indicates that the reaction kinetics of NiO electrodes must be investigated to optimize and predict cell performance.

Electrode structure

The electrode structure was recognized early as one of the principal factors determining cell performance; porosity, pore size distribution, and mean pore size all play an important role. In addition to dealing with these three factors, the NiO cathode structure should also be dimensionally stable. Any compaction of the cathode structure not only decreases the active surface area but also may cause loss of contact and high resistances between components. Compaction may also cause significant tolerance requirements for stack hardware design.

The NiO cathode is presently fabricated from a porous, metallic nickel plaque which is oxidized and lithiated *in situ*. The porosity of the plaque before oxidation is about 70 - 80%. The nickel plaque has a mean pore size of 6 - 10 μm [7]. The NiO cathode appears to consist of agglomerates of nickel oxide particles, with the electrolyte filling the space between individual particles (micropores). The agglomerates are separated by gas-filled spaces (macropores) which correspond to the pores of the original metal plaque. Since lithiated NiO is completely wetted with the carbonate electrolyte, the agglomerates are covered by a thin film of electrolyte [7]. Gases diffuse through the film to react at the electrode (agglomerates). Therefore, it is important to avoid flooding the entire electrode. The MCFC NiO cathode has been found to be sensitive to carbonate electrolyte flooding and to the degree of filling. The porous NiO cathode now operates best within a window of 15 - 30% filling of total pore volume [35].

The cathode thickness is important in the cathode polarization. Ohmic losses in both the liquid (electrolyte) and solid (electrode) phases increase as the cathode thickness increases. Diffusional losses in the gas phase also increase with cathode thickness. On the other hand, activation and liquid phase diffusion losses decrease as the cathode thickness increases. The optimum cathode thickness is attained when the total losses are at a minimum. United Technologies Corporation (now International Fuel Cells (IFC)) found that NiO cathodes performed optimally at a thickness of 0.8 mm (32 mils) [36] (Fig. 4). It should be noted that the cathode thickness also affects the cathode dissolution and the cathode compaction. Therefore, the cathode thickness used in a fuel cell may be different from the optimum thickness.

Recently, with the advent of dimensionally stable anodes, the compaction of the NiO cathode has been observed. For example, the average compaction of NiO cathodes tested in one IFC stack was found to be approximately 0.09 mm (3.5 mils) per cell (cell thickness of about 2.54 mm or 100 mils) [37]. This degree of compaction is believed to be unacceptable for stacks used in commercial applications.

Several approaches have been investigated by IFC to accommodate the dimensional change of the cathode. Attempts to resist compaction by increasing the cathode's strength have not been successful. Cell tests with an alloyed nickel-based cathode showed little reduction in cathode compaction [38]. A cell with a nickel-fiber-reinforced, sintered-nickel-powder cathode structure was also tested by IFC [38]. Although no compaction of the cathode was observed, the cell displayed a limiting current due to unacceptable cathode polarization. The presence of nickel fibers probably changed the cathode microstructure, thus affecting the electrode performance.

Cells are being tested at IFC using thinner cathodes in order to evaluate the effect of cathode thickness on cathode compaction [39]. If compaction is linear, decrease in thickness will reduce the overall compaction. As mentioned earlier, this approach may have some implications on the electrolyte
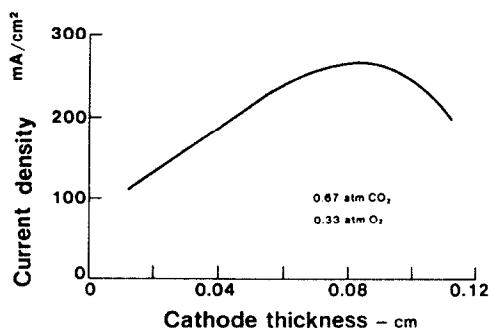

Fig. 4. Current density of an NiO cathode at a 60 mV overpotential as a function of cathode thickness [36]. (Reprinted from L. J. Bregoli and H. R. Kunz, *J. Electrochem. Soc.*, *129* (1982) 2711, by kind permission of the publisher, The Electrochemical Society, Inc.)

content and the performance of the cathode. The start-up procedure has also been modified to allow the cathode to oxidize more slowly, thereby hoping to improve its resistance to compaction. Thus far, the results obtained are far from conclusive, as can be seen from some IFC data shown in Table 1.

It appears that other uncontrolled factors play a part in the observed compaction. It may be possible that, in each of the above cells, the structure of the cathode was different and uncontrolled because there might be differences in the start-up procedure. Thus, different degrees of compaction were observed.

When the cathode structure and the compaction mechanism are understood and can be controlled, the cathode compaction problem probably can be solved. As discussed earlier, the NiO cathode consists of agglomerates of NiO particles with electrolyte-filled micropores and gas-filled macropores. One can see that the distribution and size of micropores and macropores are important in the cathode strength, and thus its compaction resistance. In general, the cathode microstructure in a fuel cell is determined by two factors: the original microstructure of the nickel plaque and the degree of crystallite fragmentation. These two factors can be controlled for tailoring an optimum structure. In the present fabrication process of NiO cathodes, the structure of Ni plaques (not the macropores) changes dramatically when oxidized and lithiated *in situ*. Therefore, it is somewhat difficult to tailor or control the cathode structure, which may be necessary to control compaction. It has been shown by Argonne National Laboratory (ANL) [40, 41] that the structure of a preoxidized metal plaque is markedly different from that of *in situ* oxidized material. Work at GE [8, 42] indicates that *ex situ* fabricated cathodes have desirable microstructure characteristics and possess a significantly improved strength which is the result of improved particle bonding. However, the structure of *ex situ* fabricated cathodes tends to transform to that of *in situ* fabricated cathodes with time in the fuel cell.

If all cell components (especially the electrolyte, cathode, and anode) are hard and noncompliant, a poor fit of components may result; this poor

TABLE 1

Cathode compaction observed from IFC cells

Cathode thickness (IFC cell no.)	Start-up procedure	Cell operating time (h)	Cathode compaction (mil)	Ref.
thin (596)	normal	680	8	38
thin (597)	modified	530	4	38
thin (600)	modified	480	8	38
standard (579)	normal	1050	2	38
standard (581)	modified	1000	8	38
standard (592)	modified	990	8	38
standard (605)	modified	430	3.5	39

fit may cause assembly problems, high contact resistance, and poor cell performance. Correcting this situation would require close manufacturing tolerances, and thereby increase manufacturing and assembly costs. A small amount of compliant capability for at least some components may be necessary.

Electrode material stability

The instability of NiO during cell operation is now considered one of the major technical difficulties facing MCFC development. Nickel oxide has a small degree of solubility in the carbonate electrolyte in the fuel cell cathode environment (about 10 - 15 ppm) [43 - 46]. However, the dissolved nickel ions diffuse, under a concentration gradient, from the cathode toward the anode. At some location between the two electrodes and under the influence of reducing conditions caused by the anode gas, the dissolved nickel precipitates as nickel metal. The precipitation of nickel creates a sink for the nickel ions, which facilitates further NiO dissolution. Thus, the dissolution of NiO can be a major life-limiting factor for the MCFC. Figure 5 is a photomicrograph of an electrolyte structure after cell operation [41]. The bright-colored flecks have been identified as nickel metal. Figure 6 shows electron microprobe traces of nickel concentration across the electrolyte structure thickness [8]. As can be seen from this Figure, the precipitation of nickel metal increases with test time. The 1000 h test shows some precipitation, while the 10 000 h test shows a high level of precipitation.
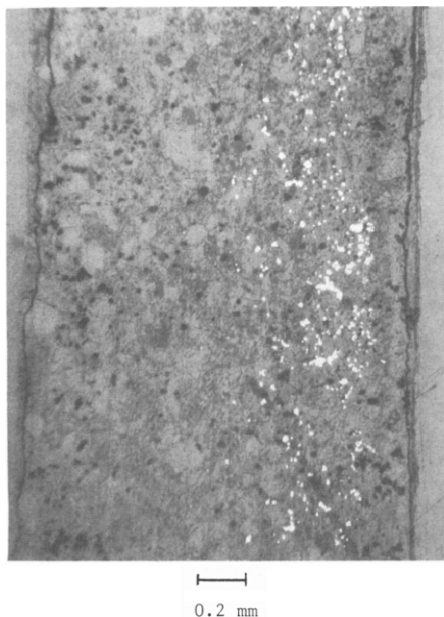

0.2 mm

Fig. 5. Micrograph of nickel deposit in the electrolyte structure. (Cathode interface is at right.)
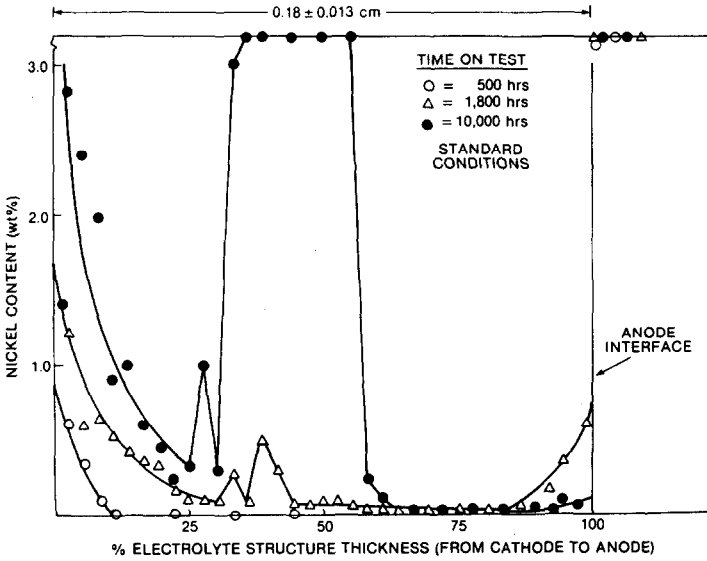
Fig. 6. Electron microprobe traces of nickel across thickness of electrolyte structures from cells operated (at 1 atm) with NiO cathodes [8]. (Inlet oxidant: 30% CO_2/air, inlet fuel: 8%CO–20%CO_2–32%H_2–40%H_2O.)

The phenomenon of nickel dissolution, transport, and precipitation is quite complex. An accurate description of the phenomenon would involve the kinetics of the dissolution in the cathode (where potential and partial pressure of CO_2 vary), the kinetics of metal nuclei formation and growth, and the complex transport of the ionic nickel, as well as the transport of gases across the matrix and their reactions. However, to predict the approximate lifetime of NiO cathodes, one can use a simplistic model. The model assumes NiO dissolution equilibrium at the cathode/matrix interface, neglects the effect of electric field, and assumes Ni metal precipitation at a certain distance. The rate of NiO transport, J_{Ni}, is given as:

$$J_{Ni} = \gamma D \, d[Ni]/dx \tag{13}$$

where γ is a factor that is dependent on the tortuosity and the volume fraction (V_{melt}/V_{matrix}) of the matrix, D is the diffusion coefficient of Ni ion, and x is the distance away from the cathode. Using the above equation, Pierce et al. [41] show that the rate of NiO transport is about 9×10^{-10} g Ni per cm^2 s. At this rate, the fraction that dissolved after 10 000 h would be about 0.35 for a cathode that was originally 0.5 mm thick and 65% porous.

Most testing to date has shown that the common failure mode is cell shorting due to nickel metal precipitation. However, the maximum loss of NiO a cathode can tolerate and remain functional is not known. IFC tested a used cathode (in a half-cell test), which showed 2 - 4% NiO loss after being operated for 1964 h at 5 atm total pressure with 0.74 atm CO_2 [47]. The half-cell test results by IFC indicated that the performance of the cathode was not affected by the amount of nickel lost. New cathodes of the same

type tested previously yielded nearly identical performance characteristics. According to a paper published by Vogel *et al.* [48], a reasonable guess of the tolerable cathode weight loss limit would be around 20%. Thus, a useful life of the order of 2000 h is predicted for a 0.76 mm (30 mil) cathode if run at 10 atm pressure, where the typical CO_2 pressure is 1.5 atm with a cell containing a matrix 0.38 mm (15 mil) thick and 42% porous. Recently, Energy Research Corporation (ERC) data show that an NiO cathode is able to withstand 30% weight loss without performance loss (at 1 atm operation) [49]. However, there are no experimental data to define the tolerable cathode weight loss limit.

The most important factor which determines the rate of NiO dissolution and transport (and, thus, the cathode lifetime) is the magnitude of the NiO solubility under fuel cell operating conditions. Therefore, knowledge of NiO solubility under various conditions is essential for evaluating NiO cathode endurance. The equilibrium solubility of NiO has been determined in several studies. Data on the solubility as a function of several factors such as temperature, gas atmosphere (composition and pressure), and carbonate composition have been reported [43 - 46]. There is considerable disagreement among the data. The main reason for this disagreement is probably the technical difficulties in determining the low solubility of NiO in carbonate melts. Special care must be taken to ensure equilibrium among the gas phase, the molten carbonate, and the solid NiO during measurements. The sampling method has the potential problem of trapping NiO particulates, and it is difficult to determine the low concentration of nickel in the sample accurately by chemical and other analytical techniques. The impurities in the carbonate must be taken into account. A GE report [8] indicates that nickel impurity in Li_2CO_3–K_2CO_3 is as high as 25 ppm; that value is higher than the solubility of NiO in Li_2CO_3–K_2CO_3 at 650 °C. Also, the trend of the NiO solubility as a function of several factors is not well understood. For example, in a study by Kaun [44], the solubility of NiO was found to increase with increasing temperature in Li_2CO_3–K_2CO_3 (62–38 mol%), but the trend reversed in 38/62 Li/K carbonate (Fig. 7). No explanation could be given because the dissolution mechanism has not been clearly identified. Thus, one can see that further study is desirable on the solubility of NiO and the dissolution mechanism. The elucidation of the dissolution mechanism will help not only in explaining several phenomena (*e.g.*, effects of temperature, pressure, and additives on solubility of NiO) observed in MCFCs, but also in more accurately predicting the endurance of the NiO cathode.

Since one way to prolong the life of the NiO cathode is to lower its solubility, knowledge of the chemistry of dissolution is important. The chemistry of the dissolution of transition metal oxides (such as NiO) in oxyanion melts (such as molten carbonate) is believed to be a function of the basicity of the melt. The theory of the acid/base behavior of molten salts is analogous to the Brönsted theory for aqueous solutions. In molten salts, the oxide ion defines the basicity of the system in the same way that the hydrogen ion defines the acidity of an aqueous system [50 - 52]. Thus,
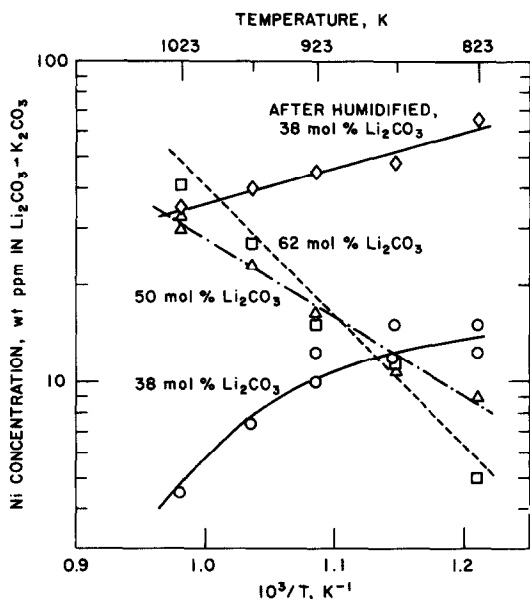
Fig. 7. Solubility of NiO as a function of temperature in a 33% O_2–67% CO_2 atmosphere (1 atm total) [44]. (Reprinted from T. D. Kaun, in M. Blander (ed.), *Proc. Fourth Int. Symp. on Molten Salts*, The Electrochemical Society, Inc., Pennington, NJ, 1984, p. 489, by kind permission of the publisher, The Electrochemical Society, Inc. This figure was originally presented at the Spring 1983 Meeting of The Electrochemical Society, Inc. held in San Francisco, California.)

for a solvent such as Li_2CO_3–K_2CO_3 under a partial pressure of CO_2, the basicity of the molten salt is given by the equilibrium

$$CO_3^{2-} = O^{2-} + CO_2 \tag{14}$$

The basicity of the melt may be altered by varying the partial pressure of CO_2 and by varying the mole fractions of the components.

NiO is an amphoteric oxide and can dissolve as a base or as an acid [53, 54]. In a relatively acidic melt, NiO dissolves by dissociation

$$NiO = Ni^{2+} + O^{2-} \tag{15}$$

In a basic melt, NiO reacts with oxide ions to produce one of two forms of nickelate ions

$$NiO + O^{2-} = NiO_2^{2-} \tag{16}$$

or

$$2NiO + O^{2-} + 1/2O_2 = 2NiO_2^{-} \tag{17}$$

In the MCFC cathode environment, the melt is relatively acidic and the acidic dissolution is important. It should be noted that MCFC NiO cathodes which are lithiated can dissolve as Ni^{3+} as well as Ni^{2+}. However, the dissolution of nickel in the 3+ valence state is relatively small at the fuel cell cathode conditions.

For the acidic dissolution of NiO in molten carbonates, the solubility of the oxide decreases with increasing oxide activity of the melt (increasing basicity). Therefore, making the MCFC cathode environment more basic is a means to lower the solubility of NiO and prolong the life of the NiO cathode. Basicity of the molten carbonate can be altered by (i) a change in the gas phase in equilibrium with the melt (*e.g.*, lowering the partial pressure of CO_2 increases basicity), and (ii) a change in the carbonate melt composition (*e.g.*, increasing the lithium content in $Li_2CO_3-K_2CO_3$ or adding basic oxides increases basicity).

Both IFC (*e.g.*, see ref. 38) and ERC (*e.g.*, see ref. 55) are addressing the NiO dissolution problem. Their approaches are quite similar and are based on the principle of increasing the electrolyte basicity as described above. IFC uses an electrolyte with high lithium content and low partial pressure of CO_2 to prolong the life of NiO. IFC also attempts to vary the cathode thickness to control the NiO dissolution rate. The following semi-empirical equation [47, 48] has been used by IFC to describe the NiO dissolution rate

$$\frac{m}{A} = nK\frac{\theta^{1.5}P_c t}{\delta} \tag{18}$$

where m/A is the amount of Ni lost from the cathode per unit cross-sectional area, n is the distance from the cathode where nickel is assumed to precipitate, θ is V_{melt}/V_{matrix}, P_c is the partial pressure of CO_2, t is the time, and δ is the matrix thickness. Data on the mass of nickel found deposited in the matrix of a number of IFC cells [48] appeared to show a linear relationship with the factor $(\theta^{1.5}P_c t)/\delta$, although there is a large amount of data scattering (Fig. 8). The above relationship has been used to make an estimate of the length of time that NiO will serve as a viable cathode under various conditions. However, for the above equation to be used to predict the rate of NiO dissolution, two assumptions have to be made. The first assumption is that nickel is deposited in a narrow band of defined n value (however, in fuel cells, the location of the nickel band in the matrix depends on the operating conditions). The second assumption is that nickel precipitation on the anode is negligible.

IFC (*e.g.*, see ref. 37) conducts a test program to define the operating limits that are suitable for extending the life of NiO cathodes to an acceptable level. At present, IFC is using a reaction-controlled model to predict time to short (the time when NiO dissolution and deposition cause a 10 mV decay in open circuit voltage to occur). It appears that by reducing the partial pressure of CO_2 and using an electrolyte with high lithium content, IFC is able to extend the life of NiO cathodes [37, 38]. However, as will be discussed later, it is not clear whether under those conditions, the NiO cathode will meet the lifetime requirement of 40 000 h.

ERC takes an approach somewhat similar to that of IFC to address the NiO cathode endurance problem. ERC attempts to extend the life of NiO by using low partial pressure of CO_2 and at the same time modifying the
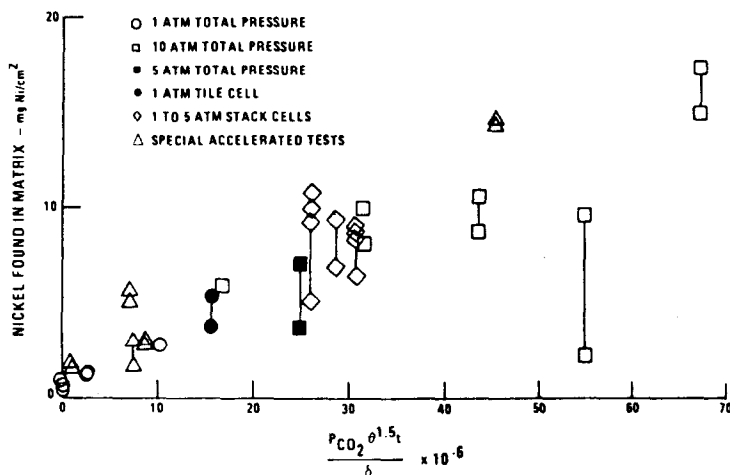
Fig. 8. Mass of nickel found in electrolyte structure as a function of the factor $(P_{CO_2}\theta^{1.5}t)/\delta$ from IFC cells [48]. (Reprinted from W. M. Vogel, L. J. Bregoli, H. R. Kunz and S. W. Smith, in J. R. Selman and T. D. Claar (eds.), *Proc. Symp. on Molten Carbonate Fuel Cell Technology*, The Electrochemical Society, Inc., Pennington, NJ, 1984, p. 443, by kind permission of the publisher, The Electrochemical Society, Inc. This figure was originally presented at the Spring 1982 Meeting of The Electrochemical Society, Inc. held in Toronto, Canada.)

basicity by other means [55, 56]. ERC runs cell tests to evaluate relevant changes and their effect on NiO solubility; thus the lifetime of the NiO cathode. ERC uses eqn. (18) to establish its endurance goal for the NiO cathode, assuming 30% allowable cathode loss.

ERC has carried out solubility measurements and cell tests under different conditions. It has generated results consistent with the hypothesis that acid–base conditions strongly influence NiO solubility and dissolution rate. Besides using low partial pressure of CO_2, ERC also has attempted to use additives to further promote the basicity of the electrolyte. The compounds MgO and BaO have been added to the NiO cathode [57]. Good correlation between solubility measurements and NiO loss rates was observed for NiO cathodes with MgO added. MgO appears to increase the electrolyte basicity and lower the NiO dissolution rate. Although MgO may have some beneficial effect on extending the life of NiO, the magnitude of the effect may need further evaluation. In those studies, ERC assumes a simple acidic dissolution of NiO; other solubility studies, especially those of Orfield and Shores [58 - 60], indicate a more complicated dissolution mechanism in binary carbonate mixtures. For example, Orfield and Shores [60] found that the acidic solubility of NiO in carbonate mixtures was not a single-valued function of the melt basicity. Also, this function depends on the nature of the components in the mixture.

All results obtained so far show that the endurance of NiO cathodes in MCFCs can be extended by modifying the operating conditions. The major driving force for longer lifetimes with NiO cathodes is reduction in partial

pressure of CO_2. While low partial pressure of CO_2 is beneficial in reducing the rate of nickel dissolution, it also results in performance penalties and may have a significant effect on power plant economics. It appears that CO_2 partial pressure as low as 0.15 - 0.20 atm can be allowable for the present fuel cell system [7]. The decrease in the dissolution rate of NiO with decreasing CO_2 partial pressure emphasizes the importance of the basicity of the electrolyte on NiO dissolution. Although additives such as MgO may promote the basicity, the extent of their effects on the basicity, thus on the NiO endurance, is not clearly known. An understanding of the dissolution mechanism and the relationship between solubility and basicity will help in clarifying the effect of additives on the endurance of NiO cathodes. IFC data indicate that a decrease in cathode thickness extends the time to cell shorting. This finding implies a reaction-controlled dissolution. This may be the case; however, it needs to be confirmed by further evidence and investigations.

One difficult question to answer is whether one can predict a 40 000 h lifetime for NiO. The problem is that the dissolution and precipitation phenomenon of the NiO cathode is quite complex: any prediction model has to include a number of assumptions and thus can give only rough estimates. Better understanding of the dissolution and transport of NiO will assist in the design of a better model and, therefore, a better prediction. It is hoped that understanding of the fundamentals of the NiO dissolution will help to predict NiO cathode life.

It should be emphasized here that the approaches taken by IFC and ERC are not eliminating the NiO dissolution problem, but rather "delaying" the problem. Because the dissolution and precipitation of nickel still exist, the possibility of cell shorting (earlier than expected) can occur if there are defects in the matrix. It is not known how a shorted cell behaves over long periods of time. Also, it is not known how one, or several, cell shorting in a stack affects the system performance and how many shorted cells a stack can tolerate without being terminated. One can envision ways to prevent shorts. In this case, other cathode failure modes should be considered. For example, excess enlargement of pores leads to thinning of the cathode structure and eventually to its collapse or, if dissolution eventually results in cathode thinning, loss of electrical contact between components may occur.

Concluding remarks

From the above discussions, it can be seen that there are still several problems concerning the viability of MCFC NiO cathodes. The instability of NiO during cell operation is now the most important technical difficulty facing MCFC development. Nickel oxide has a low solubility in the fuel cell cathode environment, but the migration and precipitation of the dissolved nickel make the dissolution (and thus the stability of the NiO cathode) the major life-limiting factor for the MCFC. Other problems include the compac-

tion of the cathode structure during cell operation and the lack of information about the kinetics of the oxygen reduction on NiO.

The present industrial efforts to prolong NiO life employ low partial pressure of CO_2 and high-Li_2CO_3 electrolyte. Additives to increase the basicity of the carbonate melt (thus, lower NiO dissolution) are also attempted. Although the lifetime of NiO can be extended under those conditions, it is not clear whether lowering the CO_2 partial pressure or changing other operating conditions will make the NiO cathode endure 40 000 operating hours. The lack of good prediction appears to be due to the poor understanding of the NiO dissolution and transport phenomena in the fuel cell. A thorough investigation in this area is therefore urgently needed. Other efforts on cell endurance related to the stability of NiO are recommended: *e.g.*, studies of cell failure modes, and models to predict NiO dissolution rate and time to cell failure more accurately. To solve the cathode compaction problem, methods to control the cathode structure are desirable. A clear understanding of the cathode microstructure and compaction mechanism would significantly help to control cathode compaction. Determination of the kinetics of the oxygen reduction process on NiO (as a function of gas composition and electrolyte composition), on the other hand, would be beneficial to modeling fuel cells and predicting their performance.

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