

## NiO CATHODE DISSOLUTION IN THE MCFC: A REVIEW

J.R. Selman, M.S. Yazici and Y. Izaki\*  
Department of Chemical Engineering  
I.I.T., Chicago, IL

\* Central Research Institute of Electric Power Industry  
Yokosuka, Japan

### ABSTRACT

The slow dissolution of the NiO cathode and precipitation of nickel particles in the electrolyte tile, leading eventually to short circuit, are key phenomena limiting the long-term performance of the MCFC. Although much work has been devoted to analysis of the nickel dissolution/shorting phenomenon, there are still many aspects which are not sufficiently understood to allow a confident prediction of lifetime. In particular, the driving force for displacement of the nickel precipitate particles and the mechanism by which they interact, leading to short circuit, are far from clear. The experimental data available thus far are critically reviewed and information necessary for a more complete quantitative understanding is identified.

### 1. INTRODUCTION.

The molten carbonate fuel cell (MCFC) is an energy producing electrochemical system which is expected to become commercial in the near future[1]. However, it remains a challenge to achieve the aimed-for lifetime of 40,000 h, especially in pressurized operation with fuel gas generated by coal gasification. Among the most important causes of limited lifetime is the dissolution of the cathode. In MCFC stacks operated thus far, the cathode material is lithiated nickel oxide. This material has good catalytic properties and a more than adequate electrical conductivity. However its solubility in the commonly used  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  electrolyte, at 650°C, though only tens of ppm, causes problems. Dissolved nickel is transported from the porous cathode into the electrolyte tile. There it is reduced to metallic nickel, presumably by chemical reaction with dissolved hydrogen, and precipitates as particles. Cathode dissolution has serious implications for long-term cell performance. This is not so much due to the loss of active cathode material, as to the accumulation of metallic nickel in the tile. Especially in large cells, this can eventually lead to a high-ohmic short which causes performance decline.

The implications of cathode dissolution for long-term performance of the MCFC have been recognized early, and much work has been done to circumvent or alleviate the problem. Alternative cathode materials have been pursued. However, such materials, which must be less soluble than nickel oxide or less easily reduced upon contact with dissolved fuel gas in the tile, are few in number and may require a remodeled cell design. On the other hand, certain additives which enhance the basicity of the electrolyte have been found to retard cathode dissolution, at least initially. Williams and George [2], reviewing the status of this issue as of 1991, do not consider it an impediment to commercial stack development, but emphasize the need for a better understanding of the phenomenon. The challenge is to quantify the factors which delay or accelerate it. The following is a brief summary of the

most important experimental findings and interpretations, with the purpose to assemble elements for a comprehensive predictive model.

## 2. EXPERIMENTAL OBSERVATIONS

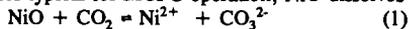
Small metallic nickel inclusions are found in the electrolyte of MCFC cells after thousands of hours. These particles are initially concentrated in a rather narrow zone, but are found later in a gradually widening band (see Section 6). The information available in the literature largely concerns the quantity of nickel deposited in the tile as a function of time. Kishida [10] reviewed MELCO data up to 1990 for hot-pressed and tape-cast matrices (of different thickness) in cells operated up to 10,000 h. He concluded that the nickel precipitation rate is approximately constant, approximately  $4 \mu\text{g}/\text{cm}^2\cdot\text{h}$ . Urushibata [11] arrived at a similar conclusion and value. Other authors [3,4,12], however, conclude that beyond 2000 h the dissolution rate decreases. They correlate their data with the square root of time, as illustrated in Figs. 1 and 2. It is difficult to resolve this discrepancy because of the large scatter in data points, as Fig. 1 illustrates. In addition, long-term data are relatively scarce. In such tests shorting effects may start to occur, caused by accumulation of nickel (see Section 7), which of course affect further precipitation.

## 3. INITIAL INTERPRETATION

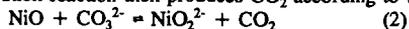
Since the earliest observations it has been assumed that nickel precipitation is caused by reduction of dissolved nickel (e.g.,  $\text{Ni}^{2+}$  ions) reacting with hydrogen counterdiffusing from the anode toward the cathode. This is shown schematically in Fig. 3. If the electrolyte tile is without defect and the reduction of dissolved nickel occurs by means of a fast chemical reaction, the nickel particles should first accumulate in a sharply defined reaction zone. Based on this assumption one can apply known, or estimated, solubilities and diffusivities in molten carbonate to predict the location of the reaction zone. As discussed in the next section, there are important uncertainties in both nickel solubility and diffusivity. The calculations show that with hydrogen-rich fuel gas and standard oxidant, the reaction zone lies closer to the cathode than to the anode, in agreement with experimental observations. However, this "diffusion-reaction" model does not explain the time-dependent behavior of the precipitation.

## 4. SOLUBILITY OF NiO

Because it is considered a primary controlling parameter, the solubility of NiO in carbonate melts of various compositions and temperatures has been determined, for a range of gas compositions [2,13]. The generally accepted conclusion from this work is that under  $\text{CO}_2$  partial pressures typical for MCFC operation, NiO dissolves according to the equilibrium:



The saturation solubility of NiO thus depends on the acid-base properties of the molten carbonate or carbonate mixture since the first step in this mechanism presumably produces  $\text{Ni}^{2+}$  and  $\text{O}^{2-}$  ions. This acid mechanism applies in low- $\text{O}^{2-}$  activity ("acid") melts, while in "basic" (high- $\text{O}^{2-}$  activity) melts the initial step may be association of NiO and  $\text{O}^{2-}$ . The overall "basic" dissolution reaction then produces  $\text{CO}_2$  according to the equilibrium:



Therefore, the saturation solubility of nickel oxide shows a minimum, whose location depends on the composition and temperature of the carbonate mixture, as illustrated in Fig. 4. Recent data of Ota et al. [13] indicate a minimum solubility in Li-K carbonate eutectic at  $650^\circ\text{C}$  of

approximately 1 molar ppm, at a partial pressure of 0.01 atm CO<sub>2</sub>; both the minimum solubility and the associated CO<sub>2</sub> partial pressure increase with temperature. Fig.4 also shows that an increased Li<sup>+</sup>/K<sup>+</sup> ratio lowers NiO solubility under CO<sub>2</sub> partial pressures typical for normal MCFC operation. As Fig. 2 illustrates, small additions of alkaline-earth carbonates have a significant effect on NiO solubility, presumably due to the enhanced basicity of the melt. Direct addition of alkaline-earth metal oxides to the cathode appears to decrease the NiO solubility even further, but the effect may be temporary.

##### 5. SPECIATION AND TRANSPORT OF DISSOLVED NICKEL

To understand the accumulation of nickel in the tile, it has generally been assumed that the transported species is Ni<sup>2+</sup>, based on the thermodynamic equilibrium discussed in the previous section. However, there is actually reason to doubt that the species is as simple as that. If the concentration of dissolved nickel at the boundary between cathode and electrolyte tile is assumed to equal the saturation solubility of nickel, the resulting flux into the electrolyte to the initial precipitation zone would be several times higher than that measured experimentally. The calculated flux, however, is based on scarce experimental data for the diffusivity of dissolved Ni<sup>2+</sup>, which may be too high. The occurrence of Ni complexes cannot be excluded, or at the very least Ni<sup>2+</sup> may be more strongly coordinated with the large CO<sub>3</sub><sup>2-</sup> ions than with alkali ions. Molecular dynamic calculations have shown that this is likely to occur and that it can cause a significantly lower mobility of dissolved nickel [14]. Thus the actual flux may be smaller than calculated. In any case, in modeling of cathode dissolution, the diffusivity of dissolved nickel should not be treated simply as an a priori fixed parameter.

A different way to account for the lower-than-expected nickel flux is to assume a kinetic rate limitation of the NiO dissolution in the cathode, so that the nickel concentration in the cathode is not equal to the saturation concentration. This assumption was adopted in a systematic study by Shores, et al.[8]. They applied a simple transport model combining diffusion and convection (due to the net flux of carbonate ions) with slow dissolution kinetics, characterized by a forward rate constant. The convective velocity and the rate constant were treated as adjustable parameters. There is some justification for assuming a kinetic limitation of NiO dissolution, as suggested by dissolution transients in bulk carbonate melt (Fig.5). This modeling approach yields a convective velocity of plausible magnitude and a fairly consistent set of kinetic parameters. It also predicts fairly well how NiO dissolution depends on applied current, as shown in Fig.6. However, the reality of a kinetic limitation is not established without a doubt.

A different but more probable cause for depressed NiO solubility in the cathode is the high degree of basicity expected in the pores of the cathode under load, due to the slow recombination kinetics of O<sup>-</sup> ions and CO<sub>2</sub> [15].

##### 6. PRECIPITATION, PARTICLE MOVEMENT AND SHORTING

There are ample reasons to assume that the nickel particles precipitated by reduction of dissolved nickel are unstable, and that some of them grow at the expense of others (Ostwald ripening). The overall growth of nickel particles, of course, must correspond to the flux of nickel into the tile, but the latter must also drive the spreading of the precipitation zone. This phenomenon, qualitatively similar to that of periodic precipitation (Liesegang rings), presents

one of the most difficult to analyze aspects of NiO dissolution and precipitation/shorting. A key question concerns the role played by the net flux of  $\text{CO}_3^{2-}$  ions in the convection of particles.

The number density and distribution of particles is important intermediate information in trying to establish a correlation between the nickel content of the electrolyte and the occurrence of shorting. Kunz and Pandolfo [16] have indicated a way to establish such a correlation, however, without considering specific features of the particle distribution. important to predict. For improved prediction, a more accurate representation of convection would be desirable, and particle distribution must be accounted for. Systematic data (Fig.7) are now becoming available which should help to verify such a correlation.

#### ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Morgantown Energy Technology Center, under contract DE-AC21-86MC 23263.

#### REFERENCES

- [1] J.R. Selman, "Research, Development and Demonstration of Molten Carbonate Fuel Cell Systems", in "Fuel Cell Systems"(L.J. Blomen and K. Mugerwa, Ed.), Plenum, London(1993)
- [2] M.C. Williams and T.J. George, "Cathode Corrosion in Molten Carbonate Fuel Cells", Proc.26th Intersoc.Energ Conv. Eng. Conf.(1991)
- [3] H. Kasai and A. Suzuki, Proc. 3rd Int. Symp. Carbonate Fuel Cell Technology, PV 93-3, The Electrochemical Soc. Inc., Pennington, NJ, p.240 (1993)
- [4] K. Yamashita and K. Murata (Toshiba Corp., Kawasaki, Japan), Priv. Comm.(1990)
- [5] K.N. Lee and D.A. Shores, J.Electrochem.Soc. **137**, 859 (1990)
- [6] Y. Qu, G. Zhao and D.A. Shores, "The Dissolution of NiO in Molten Carbonate Mixtures", in Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, PV90-16, The Electrochemical Society Inc., Pennington, NJ, p.338 (1990)
- [7] E.T. Ong, "MCFC Endurance Issues", in Proc.Intern.Fuel Cell Conf. Makuhari (Japan), p.219 (1992)
- [8] D.A. Shores, J.R. Selman, S. Israni and E.T. Ong, in Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, PV90-16, The Electrochemical Society Inc., Pennington, NJ, p.290 (1990)
- [9] Y. Mugikura, Y. Izaki, T. Watanabe, E. Kouda, H. Kinoshita, T. Abe, "Development Status of MCFC at CRJEPI", in Fuel Cell Seminar Abstracts (1992)p.109
- [10] K. Kishida, Ber. Bunsen Ges. Phys. Chem. **94**, 941 (1990)
- [11] H. Urushibata, "Life Issues of MCFC" in Proc.Intern. Fuel Cell Conf., Makuhari (Japan), p.1223 (1992)
- [12] J.B.J. Veldhuis, S.B. van der Molen, and R.C. Makkus, Ber. Bunsen Ges. Phys.Chem. **94**, 947 (1990)
- [13] K. Ota, S. Mitsuhashi, K. Kato, and N. Kamiya, in Proc. 2nd Symp. Molten Carbonate Fuel Cell Technology, PV 90-16, The Electrochemical Society Inc., Pennington NJ, p.318 (1990)
- [14] J. Tissen and G. Janssen (ECN, The Netherlands), Private Communication (June 1992)
- [15] S.H. Lu and J.R. Selman, J.Electrochem.Soc. **137** (1990) 1125.
- [16] H.R. Kunz and J.W. Pandolfo, J.Electrochem.Soc. **139**, 1549 (1992)

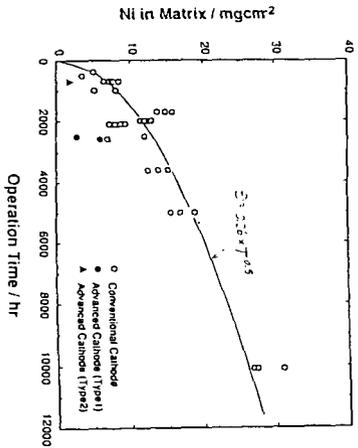


Fig. 1. Nickel in the tiles of 100-cm<sup>2</sup>(single) to 1400-cm<sup>2</sup>(stack)cells, as a function of operating time under average current density 150 mA/cm<sup>2</sup>. Adapted from H. Kasai and A. Suzuki [3]

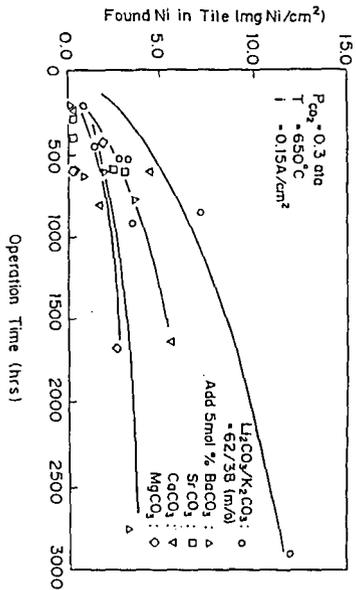


Fig. 2. Nickel found in the electrolyte tiles of terminated cells of Toshiba Corp. [4]

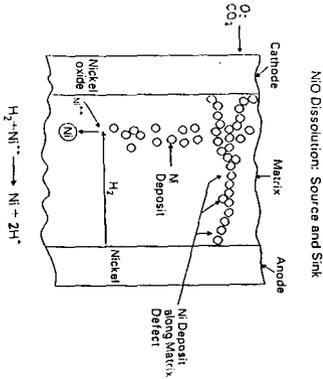


Fig. 3. Schematic representation of a cross-section through a MCFC cell, illustrating nickel oxide dissolution. From Williams and George [2]

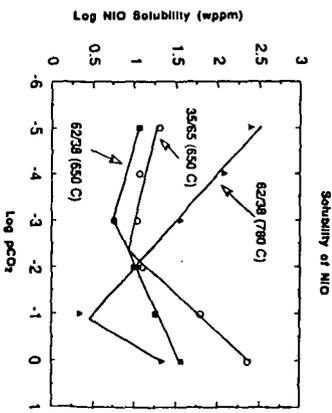


Fig. 4. Solubility of NiO in Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> mixtures, as function of pCO<sub>2</sub>. From Lee and Shores [5]

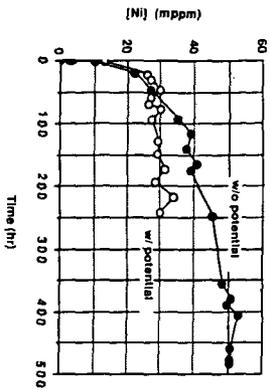


Fig. 5. Dissolution of NiO in bulk  $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$  eutectic as function of time. From Qu, et al. [6]

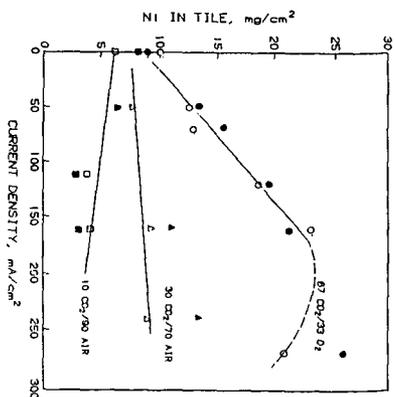


Fig. 6. Model predictions and experimental values of Ni deposited in the tile as function of  $\text{CO}_2$  partial pressure and current density. Adapted from Ong [7], and Shores et al. [8]

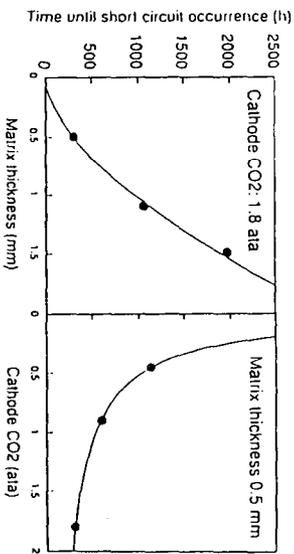


Fig. 7. Effect of matrix thickness and  $\text{CO}_2$  partial pressure on time to start of internal shorting. From Mugikura, et al. [9]