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Short communication

Effect of Dy on the corrosion of NiO/Ni in molten (0.62Li,0.38K)₂CO₃

Z.P. Liu, P.Y. Guo, C.L. Zeng*

State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, 62 Wencui Road, Shenyang 110016, China

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Abstract

The dissolution of NiO cathodes and the balance between the corrosion and contact ohmic resistance of current collector materials in molten carbonates are great obstacles to the commercialization of molten carbonate fuel cells (MCFC). Rare-earth element dysprosium was proposed to modify the NiO cathodes and to alloy nickel to explore its possible applications in MCFC. The measured solubility of NiO impregnated with 0.5-3 wt.% Dy in $(0.62Li, 0.38K)_2CO_3$ at $650 \,^\circ$ C in $60\% CO_2-40\% O_2$ indicated that Dy addition increased noticeably the stability of NiO, while 1 wt.% Dy content produced better effectiveness. An investigation of the passive behavior of nickel and of Ni–Dy alloys containing 1–10 wt.% Dy in molten (Li,K)₂CO₃ with dynamic polarization measurements as well as X-ray diffraction and X-ray photoelectron spectroscopy indicated that the addition of Dy to nickel decreased its passive anodic current, and thus improved its corrosion resistance. The lithiation of NiO in the melt was a very significant reaction that could be promoted by the Dy additives to a certain extent, and increased the electrical conductivity of NiO. © 2007 Elsevier B.V. All rights reserved.

Keywords: Molten carbonate fuel cell; Dy; Ni-Dy alloys; NiO solubility; Electrochemical polarization

1. Introduction

Molten carbonate fuel cell (MCFC) is a power-generation device that transforms chemical energy into electricity directly through an electrochemical reaction between hydrogen and oxygen, and therefore is expected to be a highly efficient and environmentally clean mean of power generation with respect to the conventional electrical production systems. Unfortunately, the state-of-the-art cells and cell stacks cannot reach the commercial goal of at least a 40,000 h lifetime [1]. Major problems of materials are related to the dissolution of the cathode in the carbonate melt and corrosion of the metal separator plate and the current collectors.

NiO is commonly used as the cathode material for MCFC because of its high catalytic activity for oxygen reduction reaction and high electrical conductivity. However, it is known that NiO dissolves slowly into molten carbonates by an acidic dissolution mechanism, and metallic nickel precipitates in the matrix, eventually giving rise to the short-circuiting of the cell [2]. The dissolution of the NiO cathodes led to explore novel materials

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with comprehensive performances such as appropriate electrical conductivity, catalytic activity for the oxygen reduction reaction and sufficiently high chemical stability in the melt [3–6]. Three different methods have been attempted to solve this problem. One is to modify the composition of the electrolyte to decrease the dissolution of NiO. More basic molten Li/Na carbonates instead of Li/K carbonates or the addition of alkaline earth salts based on Mg or Sr have been found to decrease the NiO dissolution in the melt [7,8]. Matsuzawa et al. [9] examined the effects of rare-earth additives (Y2O3, CeO2, Gd2O3, La2O3) on the solubility of NiO in eutectic (Li,Na)₂CO₃ mixtures. The solubilities of NiO with the Y2O3, CeO2 or Gd2O3 additives in the melt were approximately 25, 10, and 35% less than without any additive, but these were greater than that with the La additive. A second approach is to find a completely new material. For example, LiCoO₂ and LiFeO₂, which have higher chemical stability in the melt, but lower electrical conductivity than the lithiated NiO, have been developed [10]. Because the cathode lithiated NiO has high electrical conductivity and catalytic activity for the oxygen reduction reaction, the easiest method is expected to modify the existing NiO to increase its chemical stability in the melt. In this way, many studies have been carried out, including oxides-doped and coated NiO [5,11-16]. Daza et al. [5] modified nickel oxide cathodes by impregnation with cerium and found

^{*} Corresponding author. Tel.: +86 24 23904553; fax: +86 24 23893624. *E-mail address:* clzeng@imr.ac.cn (C.L. Zeng).

that cerium additives could retard the corrosion process of the NiO cathode and favor the lithiation process. Huang et al. [13] confirmed that the solubility of NiO was decreased greatly by the addition of 0.3-1.0 wt.% RE oxides (CeO₂, La₂O₃, Pr₂O₃ or Nd₂O₃). LiFeO₂ [15], LiCoO₂ [16] and La_{0.8}Sr_{0.2}CoO₃ [17] coatings have also been proposed to inhibit the dissolution of NiO. These modifications have proved effective in decreasing the dissolution of NiO.

Corrosion of bipolar current collectors in the presence of molten alkali carbonates in the two quite different environments (reducing fuels at the anode and oxidants at the cathode) presents a challenge to material selection. Corrosion resistance, electrical conductivity and dissolution of the oxides formed should be under consideration in looking for new separator materials or their surface coatings. The presently used bipolar plate is usually made of stainless steels. So far, great attempts have been conducted to improve the corrosion resistance of stainless steel and Ni-based alloys by optimising their composition and developing protective coatings [18–22]. However, the comprehensive performance of the present materials and coatings still cannot reach the goal of commercial application. Oxide scales formed between the cathode and cathode current collector can contribute to increase the cell resistance. A more protective oxide scale usually causes a higher contact resistance. Therefore, it is necessary to balance the corrosion rate and the contact electric resistance. Al₂O₃ or Cr₂O₃-forming alloys or coatings are unsuitable for the production of bipolar current collectors due to the poor electrical conductivity of Al₂O₃ and Cr₂O₃ scales. In order to make full use of the electrically conductive performance of the lithiated NiO, and keep a good match between the cathode NiO and bipolar current collectors, the present authors considered the application of NiO-forming coatings to the current collectors. It is clear in this case that a diffusion barrier may be needed between the coating and the substrate alloy so as to inhibit the counterdiffusion, while the growth of NiO scale should also be controlled effectively. In view of the positive effect of reactive elements on the corrosion resistance of alloys or coatings and on the lithiation process of NiO in molten (Li,K)₂CO₃, one of the present authors proposed to modify NiO/Ni with dysprosium additions [23], aiming at exploring their application potentiality in MCFC. In a study of the corrosion of two-phase Ni-Dy alloys containing 1, 3 and 5 wt.% Dy, respectively, in molten (0.62Li,0.38K)₂CO₃ at 650 °C, it was observed that Dy decreased greatly the weight gain of pure Ni, while it could promote the lithiation reaction of NiO in the melt to some extent [23]. Based on the parabolic law prediction, the scale thickness formed on N-5Dy after corrosion for 40,000 h was estimated to be less than $30 \,\mu m$.

The present paper examines the effect of Dy on the solubility of NiO in molten (0.62Li,0.39K)₂CO₃, and on the electrochemical polarization behavior of nickel.

2. Experimental

2.1. Preparation of Dy-doped NiO powder

The Dy-doped NiO powder was prepared from metallic nickel powder (>99.5%) and Dy_2O_3 powder (>99.9%) by a



Fig. 1. Procedure for preparating Dy₂O₃-dopped NiO particles.

sol-gel method, as shown in Fig. 1. The Dy₂O₃-Ni powder containing 0.5, 1 and 3 wt.% Dy, respectively, was dissolved in HNO₃ solution, followed by the addition of citric acid used as a chelating agent to prevent the segregation of metal components, and the molar ratio of citric acid versus nickel was 1.5:1. The resultant solution was then heated to 90 °C and stirred for 1 h to form a green gel. The gel was kept at 110 °C for 24 h to form a precursor, which was then calcined at 750 °C for 12h in air to obtain Dy-doped NiO powder. The XRD analvsis indicated that the powder was mainly composed of NiO. Traces of Dy_2O_3 were found in the powder containing 3 wt.% Dy, while mixed Ni-Dy oxides were not detected. The powders were compacted into a 20-mm diameter pellet and sintered at 850 °C for 12 h in air. The sintered Dy-doped NiO pellet was reduced to particles of about 1 mm in size. Pure NiO particles were prepared by sintering the Ni powder at 850 °C for 12 h in air, and then the resultant products were reduced to about 1-mm particles.

2.2. Solubility measurements

The solubility measurements were conducted in an eutectic $(0.62\text{Li}, 0.38\text{K})_2\text{CO}_3$ (mole fraction) melt at 650 °C under an atmosphere of 60% CO₂-40% O₂. 80 g of the (Li,K)₂CO₃ mixture were put in an alumina crucible, dried at 350 °C in air for 12 h and then heated to 650 °C. The CO₂-O₂ gas mixture was blown into the melt for 1 h, and then 2 g of the prepared particles were carefully introduced into the melt with an alumina tube. Samples of about 1 g of the eutectic were extracted from the melt after different exposure times using an alumina pipette, and the nickel content was determined by atomic absorption spectrom-



Fig. 2. Microstructure of Ni–1Dy, Ni–3Dy, Ni–5Dy and Ni–10Dy. Bright phase: Ni₁₇Dy₂; grey phase: Ni solid solution.

etry. After 150-h exposure, the oxide particles were separated from the carbonates, cleaned repeatedly in distilled water, dried, and analyzed by XRD.

2.3. Electrochemical polarization

Binary Ni–Dy alloys containing 1, 3, 5, and 10 wt.% Dy, respectively, were employed for electrochemical polarization studies. The alloys were prepared by repeatedly arc-melting mixtures of Ni and Dy under argon. The two-phase alloys were composed of a Ni solid solution and the intermetallic phase Dy₂Ni₁₇, as shown in Fig. 2. Sheet-shaped specimens 1.4 mm thick with a surface area of $3-4.5 \text{ cm}^2$ were cut from the original ingots by an electric spark cutting machine, ground down to 600-grit SiC paper, degreased and dried before use. Dynamic polarization measurements were performed at a scanning rate of 1 mV s^{-1} with a Princeton Applied Research Model 263 potentiostat in molten (0.62Li,0.38K)₂CO₃ at 650 °C under air. A three-electrode system was used for the electrochemical tests. The details for the preparation of working, counter and reference electrodes and for the experimental apparatus have been reported elsewhere [24]. After drying 80 g of the (Li,K)₂CO₃ mixture contained in an alumina crucible at 300 °C for 24 h, the furnace was heated to 650 °C. The anodic polarization test was conducted immediately after immersing the working electrode in molten (Li,K)₂CO₃. The scales formed on the alloy surface were analyzed by XRD and XPS.

3. Results and discussion

3.1. Effect of Dy on the solubility of NiO

Fig. 3 shows the solubility of NiO containing 0.5–3 wt.% Dy after 150 h exposure in the melt at 650 °C. The solubility of NiO was 19.4×10^{-6} (mole fraction). The addition of 0.5, 1 and 3% Dy decreased the solubility of NiO to 13.3×10^{-6} , 11.8×10^{-6} and 15.9×10^{-6} (mole fraction), respectively. It is clear that the stability of NiO in molten (Li,K)₂CO₃ is enhanced significantly by the addition of Dy, with a best result for the 1% Dy addition.



Fig. 3. Solubility of NiO as a function of the Dy content for 150-h exposure.



Fig. 4. Polarization curves of pure nickel and of Ni–Dy alloys in molten (0.62Li,0.38K)₂CO₃ at 650 $^\circ\text{C}$ in air. Scanning rate: $1\,\text{mV}\,\text{s}^{-1}.$

The XRD analysis indicated that the powders corroded in the melt for 150 h were still composed of NiO, even though small amounts of Dy_2O_3 were also detected in the samples containing 3% Dy. No new phases were observed.

3.2. Effect of Dy on the anodic polarization and the lithiation of Ni

A previous thermogravimetric study has confirmed the lower corrosion rates of binary Ni-Dy alloys with respect to pure nickel in molten (Li,K)₂CO₃ [23]. In the present study, electrochemical anodic polarization measurements were further performed to examine the effect of Dy on the passive behavior of Ni in molten (0.62Li,0.38K)₂CO₃. Fig. 4 shows the dynamic polarization curves of pure nickel and of binary Ni-Dy alloys. Nickel and Ni-Dy alloys showed similar anodic polarization behavior. The transition potential from cathodic to anodic current was about -740 mV for nickel and ranged from -800 to -900 mV for Ni-Dy alloys. These potentials are close to the standard potential for Ni/NiO determined from the thermodynamic data. Distinctive anodic current peaks (indicated by the arrows) were observed in the potential versus current curves. Moreover, the potentials for the current peaks of pure nickel and of Ni-1Dy, Ni-3Dy and Ni-5Dy were similar, but were more negative than the potential for Ni-10Dy, indicating a slower dissolution kinetics of Ni-10Dy. The fact that Ni-5Dy has an anodic current peak at a more negative potential than Ni-10Dy may be due to the lower fraction of the intermetallic phase Dy₂Ni₁₇ in the alloy. The following reactions are supposed to correspond with the peaks:

$$Ni \rightarrow Ni^{2+} + 2e^{-} \tag{1}$$

$$Ni + CO_3^{2-} \rightarrow NiO + CO_2 + 2e^-$$
(2)

accompanied by

$$Ni^{2+} \rightarrow Ni^{3+} + e^{-} (NiO + Li^{+} \rightarrow Li_x Ni_{1-x}O + e^{-})$$
 (3)

Additionally, the oxidation/dissolution of Dy also occurred during the anodic polarization process. With the formation of a



Fig. 5. XRD patterns for the scales formed on pure and on Ni–Dy alloys after 70-h exposure in $(0.62Li, 0.38K)_2CO_3$ at 650 °C.

passive oxide scale, the current density decreased to minimal values, and then increased with the polarization potential. The anodic current minimum for nickel electrode was lower than that for Ni-Dy alloy electrodes, suggesting a higher conductivity of the oxide layer formed on Ni-Dy alloys than that formed on nickel. In addition, the passive current density for the nickel electrode was close to that for Ni-3Dy, but larger than that for Ni-1Dy, Ni-5Dy and Ni-10Dy alloys. The passive current density of Ni-Dy alloys decreased with increasing the Dy content, except for Ni-1Dy. Ni-10Dy showed the minimal passive current, related to the formation of Dy oxides. The different passive behavior of Ni-1Dy was due to the fact that 1 wt.% Dy content showed a more obvious effect on the lithiation process of NiO [23]. The further increase in the polarization potential gave rise to a rapid increase in the polarization current, which was ascribed to the decomposition reaction of the carbonates $(CO_3^{2-} \rightarrow CO_2 + 1/2O_2 + 2e^{-})$. The different polarization behavior between nickel and Ni-Dy alloys may be related to the formation of Dy oxides and the effect of Dy on the growth mechanism of NiO and lithiation process. In order to understand the effect of Dy on the growth of NiO, XRD was used to analyze the scales on pure nickel and Ni-Dy alloys, respectively, as shown in Fig. 5. The results indicated that the formation of NiO was inhibited significantly by the Dy additions, especially for the alloys Ni-5Dy and Ni-10Dy, on which small amounts of Dy₂O₃ formed. Dy₂O₃ resulted from the preferential oxidation of the intermetallic phase Ni₁₇Dy₂, which was oxidized into a mixture of nickel and Dy₂O₃. In order to investigate the lithiation reaction of NiO in the melt the scales formed on nickel, Ni-1Dy and 3-Dy, respectively, were further analyzed by XPS. Fig. 6 shows the spectra of Ni $2p_{3/2}$. The binding energies of Ni $2p_{3/2}$ corresponding to NiO and Ni₂O₃, respectively, are 854.3 and 855.8 eV. It is clear from Fig. 6 that the nickel oxides formed on pure nickel and on Ni–Dy alloys are mixtures of Ni³⁺/Ni²⁺, and the content of Ni³⁺ is higher than that of Ni²⁺, suggesting that Ni²⁺ has been partly oxidized into Ni³⁺ by lithiation reaction, whilst the effect of Dy on the lithiation of NiO in the melt was not clearly observable. However, the XRD analysis confirmed



Fig. 6. XPS spectra of Ni $2p_{3/2}$ for pure nickel, Ni–1Dy and Ni–3Dy exposed for 100 h to molten (0.62Li,0.38K)₂CO₃ at 650 °C after argon sputtering for 600 s.

the beneficial effect of Dy less than 5 wt.% on the lithiation reaction to some extent. In fact, the presence of Dy displaced the diffraction peak of NiO at $2\theta = 37^{\circ}$ to a higher angle due to the introduction of Li⁺ ions into the NiO lattice, resulting in a partial transformation of Ni²⁺ ions into Ni³⁺, thus decreasing the lattice parameter.

3.3. Discussion

The NiO cathodes dissolve in molten carbonates during fuel cell operation by an acidic dissolution mechanism, resulting in the formation of Ni²⁺ ions in solution, which diffuse from the cathode toward the anode under a concentration gradient, and are reduced to metallic Ni at a certain distance away from the cathode by dissolved H₂ proceeding from the anode side, eventually giving rise to the short-circuit of the cell. The dissolution reaction of the NiO cathode occurs according to the following reaction:

$$NiO = Ni^{2+} + O^{2-}$$
(4)

The solubility of NiO in molten (0.62Li,0.38K)₂CO₃ at $650 \,^{\circ}\text{C}$ was clearly decreased by the addition of 0.5-3% Dy, with a maximum effect for a Dy content of 1%. Because Dy₂O₃ does not react with NiO to form complex oxides, Dy mainly exists as independent Dy₂O₃ besides forming a solid solution in NiO. The XRD analysis confirmed the presence of small amounts of Dy_2O_3 in the samples containing 3% Dy. The improvement of the stability of NiO in molten (Li,K)₂CO₃ by Dy₂O₃ may be ascribed to the following reasons. Firstly, Dy₂O₃ tends to increase the basicity of the melt, resulting in a corresponding decrease of the NiO solubility. Matsuzawa et al. [14] found that the solubility of La₂O₃ in molten (Li,K)₂CO₃ was significantly higher than that of NiO and proposed that La caused the melt to be more basic, producing a decrease of the solubility of NiO in the melt. In the present study, the Dy_2O_3 solubility in the melt was not measured, but it is expected that the addition of Dy and La has similar effects. Huang et al. [13] examined the effect of four types of RE oxides (CeO₂, La₂O₃, Pr₂O₃, Nd₂O₃) on the electrochemical behavior of new cathodes, and observed that the solubility of the RE-modified NiO cathodes was one order of magnitude lower than that of the RE-free NiO cathodes. This lower solubility was due to the fact that the solubility of RE oxides in molten carbonates was significantly higher than that of NiO, and as a result the concentration of O²⁻ was increased in the micro-region containing RE oxides and NiO due to the preferential dissolution of RE oxides, inhibiting the dissolution of NiO in the melt. Based on this mechanism, it is expected that the solubility of NiO in the melt tends to decrease with increasing the content of Dy, which, however, was not supported by the experimental results. In the present study, the lower solubility was observed in the samples of 1% Dy-modified NiO. Daza et al. [5] examined the solubility of the NiO cathodes modified with different contents of CeO₂ ranging from 0.3 to 5.0 wt.%, and also observed a minimum corrosion in the samples with 0.3–1 wt.% cerium oxide content. Dy₂O₃ could react with Li₂O to form the double oxide $LiDyO_2$ ($Dy_2O_3 + Li_2O = 2LiDyO_2$). The formation of LiDyO₂ probably inhibited the preferential dissolution of Dy₂O₃ to a certain extent, and thus was disadvantageous to decreasing the solubility of NiO. Secondly, it has been accepted that NiO incorporates lithium cations from molten carbonates during fuel cell operation. The lithiation process modifies the surface composition of NiO that is converted partly into more stable $\text{Li}_x \text{Ni}_{1-x} \text{O}_2$ (Ni²⁺ ions are substituted by Ni³⁺), and probably affects the stability of NiO in the melt. Although the phase $Li_xNi_{1-x}O_2$ was not detected by XRD, the XPS analysis confirmed the presence of higher Ni³⁺ content with respect to Ni²⁺ in the surface of NiO scale. The presence of Dy could promote the lithiation process of NiO in molten (Li,K)₂CO₃, and thus decrease the solubility of NiO.

Ni-Dy alloys, except Ni-3Dy, had lower passive current than pure nickel, indicating the formation of a more compact scale on Ni–Dy alloys than on nickel. As compared with pure nickel, the growth of NiO on two-phase Ni-Dy alloys, especially the alloys with higher Dy content, was inhibited significantly. Dy ions may act as barriers to block the diffusion of nickel along grain boundaries, inhibiting the growth of NiO, as observed in some studies on other rare-earth elements [25,26]. Ni-Dy alloys are composed of a solid solution of Dy in nickel plus the intermetallic phase $N_{17}Dy_2$. During corrosion in molten $(Li,K)_2CO_3$, the intermetallic phase Ni₁₇Dy₂ was partly oxidized in situ into a mixture of metallic nickel and Dy₂O₃. The formation of Dyrich oxides may block the outward diffusion of nickel, thus decreasing the growth of NiO. Meanwhile, it was noted that because of the preferential oxidation of Ni₁₇Dy₂ through the inward diffusion of oxygen, the distribution of Dy₂O₃ followed approximately that of Ni₁₇Dy₂ in the original alloys. As a result the alloys could form an external scale composed of NiO incorporating some Dy₂O₃ instead of a Dy₂O₃ scale, as observed in air oxidation of Ni–Dy alloys [27], which avoided the decrease in the electrical conductivity of the scale to some extent. Additionally, the incorporation of lithium ions with lower valence than Ni²⁺ decreases the defect concentration in NiO and thus tends to reduce the corrosion rate of nickel. The presence of Dy helps to promote the lithiation reaction of NiO in the melt, and thus offers further improvement in the protection of the NiO scale.

4. Conclusions

The incorporation of 0.5-3 wt.% dysprosium into nickel oxide decreased clearly its solubility in molten (0.62Li,0.38K)₂ CO_3 from 19.4×10^{-6} (mole fraction) for pure NiO to 13.3×10^{-6} , 11.8×10^{-6} and 15.9×10^{-6} for a Dy content of 0.5, 1 and 3 wt.%, respectively. This improvement was ascribed to the fact that the preferential dissolution of Dy₂O₃ increased the basicity of the melt, and thus decreased the solubility of NiO in the melt. Meanwhile, the formation of $Li_x Ni_{1-x}O_2$ (where Ni²⁺ ions are partly substituted by Ni³⁺ ions) by a lithiation reaction increased the stability of NiO in the melt, which was further enhanced by the addition of Dy. The presence of Dy decreased the passive current density of Ni in the melt, and inhibited the growth of NiO. This effect was related to the fact that Dy inhibited the outward diffusion of nickel, and thus the formation of NiO. Meanwhile, the addition of Dy tends also to facilitate the lithiation reaction of NiO in the melt, reducing the defect concentration of NiO.

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