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Review

Overview of the effects of rare-earth elements used as additive materials in molten carbonate fuel cell systems

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From the viewpoint of materials issues, there are some problems in molten carbonate fuel cell (MCFC) systems due to the corrosive and evaporative electrolytes and the high pressure caused by a stack in temperature of 650°C. The rare earth metals (RE) in as material additives primarily improve the creep resistance, corrosion resistance and high temperature resistance of materials. However, efforts to enhance the properties of MCFC materials using RE have not yielded the marked effects associated with their use in solid oxide fuel cells (SOFC). Therefore, we have conducted this review in order to describe and discuss the effects of RE as additive materials in the context of MCFC. This review also provides information regarding the development of MCFC materials using RE.

The incorporation of low concentrations of RE into previously RE-free materials may improve the stability of these materials to some degree, and also effect an increase in the cell efficiency of MCFC. La_2O_3-added cathode materials have primarily been applied as alternative materials, for the reduction of the dissolution of conventional NiO cathodes. Ce and Dy have both been theorized to possibly enhance the stability of anode electrode materials. Ce and La can both be employed as additives which enhance the stability of reforming catalysts. The addition of La_2O_3 to electrolytes has been previously shown to reduce the degree of dissolution in cathodes. Ce-based ceramics are thought to be promising coating materials, and it is believed that they may help to prevent the corrosion of the separator. However, future research into materials which exhibit long-term stability and low electrical conductivity is clearly warranted, as the field is in its infancy. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

The rare earth metals (RE) include the group IIIA elements, such as scandium, yttrium, and the lanthanide elements of the periodic table. The primary application of RE metals is in alloying, in which they are often utilized as additives. Materials to which RE elements are normally added include ductile iron (in which they alter the carbon morphology), super-alloys (in which they increase operating temperatures), Mg alloys (in which they enhance creep resistance), Al alloys (in which they improve tensile strength and corrosion resistance), oxygen-free high-conductivity copper (in which they improve oxidation resistance), and dispersion-strengthened materials (in which they improve high-temperature properties). In consideration of the useful effects of RE, the majority of recent research has focused on the uses of RE materials in fuel cells, in order to improve the performance of the fuel cells.

Among the variety of currently-developed fuel cell types it was shown, that a large variety of RE-added materials can be used in solid oxide fuel cells (SOFC), due principally to the high operating temperature of these cells, approximately 1000°C. Traditional electrode and electrolyte materials used in SOFC include Ni/Zr cermet

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and solid oxide/YSZ, respectively. RE additives used in SOFC materials, such as Nd, Gd, Y, Sm, La, and Ce, have proven not only to reduce the costs of the cells, but also to lower operating temperatures and increase power [1–6].

In molten carbonate fuel cells (MCFC), the application of RE is far more narrow than in SOFC, due to the lower operating temperature of these cells, which is around 650°C. From a materials standpoint, the MCFCs suffer from a variety of problems, including the corrosive and evaporative nature of the electrolytes, as well as the high stack pressure with the temperature of 650°C. However, MCFC materials have not benefited from adulteration with RE as much as have SOFC materials.

Therefore, in this review, we have introduced and discussed a few research projects which looked at the effects of the addition of RE to MCFC materials. This review also includes information regarding the development of more stable MCFC materials.

2. Molten carbonate fuel cell (MCFC)

The MCFC is a promising energy conversion device, which works by converting the chemical energy in fossil fuels into electricity, according to the reaction described by Equations. 1 and 2.

$$H_2 + CO_3^{2-} \Leftrightarrow H_2O + CO_2 + 2e^- \quad \text{(Anode)} \qquad (1)$$

$$1/2O_2 + CO_2 + 2e^- \Leftrightarrow CO_3^{2-} \quad \text{(Cathode)} \qquad (2)$$

In the case of direct internal reforming (DIR) MCFC systems, hydrogen is directly and continuously produced via the combination of the steam reformation of methane, which is shown in Equation 3, including a water-gas shift reaction which occurs in the catalytic reformer of the anode compartment.

$$CH_4 + 2H_2O \Leftrightarrow 4H_2 + CO_2 \qquad (3)$$

Fig. 1 is a schematic diagram of the traditional DIR-MCFC and the materials used in its construction.

The anode and the cathode are both relatively low-priced, the anode being a Ni-based porous electrode, and the cathode being a NiO-based porous electrode. The electrolyte, which is composed of an alkaline carbonate mixture (generally, 62 mol% Li_2CO_3-38 mol% K_2CO_3), is contained within a porous $LiAlO_2$ matrix. The separators or housing which contain the gas flow channels are constructed of stainless steel, i.e. SUS316L and SUS310S. The typical operating temperature of MCFC is approximately 650°C. The technology inherent to the construction of these cells has already partially entered the commercial demonstration phase. However, a question still exists as to how long the lifespan of such a cell would be. In order for the technology to be commercially viable, an MCFC must last approximately 40,000 h. The known lifespan-limiting phenomena, which are caused by the corrosive electrolyte, the relatively high operating temperatures, and stack pressure in the MCFC, include the following:

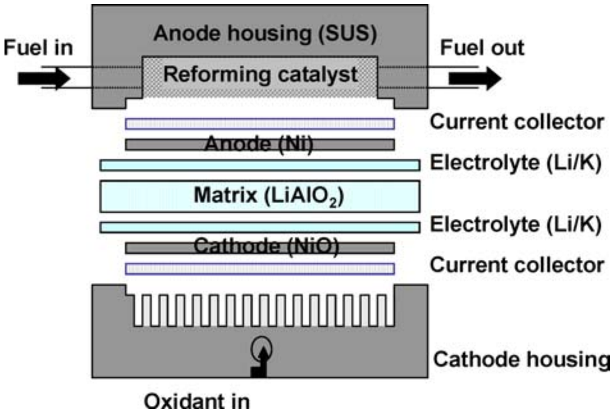

Figure 1 Schematic diagram of the components of the DIR-MCFC unit cell.

1. Dissolution of the NiO cathode.
2. High-temperature creep and sintering of the porous components.
3. Reforming catalyst deactivation.
4. Electrolyte losses and electrolyte retention capacity.
5. Corrosion of the separator plate.
6. Matrix cracking

These problems have also led to a great deal of research which has been conducted into the development of RE-supplemented MCFC materials. The RE-added materials used in the construction of MCFC over recent years are listed in Table I.

2.1. Cathode electrode for MCFC

2.1.1. Method to improve the stability of cathode material without RE

NiO has, since the 1970s, been the most commonly used material in the construction of MCFC cathodes [7]. However, the dissolution of the NiO cathode into an electrolyte, and the structural degradation of the cathode during the high-temperature operation of the cells, are among the most serious of the factors which limit the lifespan of these cells. Therefore, a great deal of research regarding MCFC cathode materials has been conducted since the 1970s. Recently, significant advances in the materials used in the construction of MCFC cathodes have been made, and this particular field has advanced more quickly than has research into the improvement of the other materials used in MCFC construction.

There are two ways to improve cathode stability by altering the cathode materials themselves. One is to substitute completely new materials for NiO in the construction of cathodes, and the other involves the modification of the

TABLE I Effects of RE addition on the component materials for MCFC

Composition of material	Comments	Reference
Cathode		
CeO_2 (1–3 wt.%)/NiO	Lower dissolution rate than NiO; needed lithiation controlling.	[29]
La_2O_3/lithited NiO	Reduced nickel dissolution and improved cell efficiency; long-term tests are required	[30]
$La_{0.8}Sr_{0.2}CoO_3$/NiO	Lower Ni dissolution than that of the conventional nickel oxide cathode.	[31]
CeO_2, La_2O_3, Pr_2O_3, Nd_2O_3/NiO	The solubility was about one order of magnitude lower than that of RE-free NiO	[32]
Anode		
CeO_2/Ni-Cr	Performance equivalent to the Ni-Cr anodes; however, it suffered some chemical instability	[47]
Dy/Ni–Dy (Dy_2Ni_{17})	Corrosion was significantly lower than that of pure Ni, forming a scale mainly composed of NiO	[48]
La_2O_3/Sm_2O_3 with Ti	Performed well over a period of 144 h following an initial decrease of open circuit voltage	[50]
Catalysts		
La-Ni/γ-Al_2O_3	Decreased the stability of the reforming catalyst	[63]
Ni-RE/Al_2O_3	Elevated the catalyst activities and resisted the formation on $NiAl_2O_4$.	[64]
Ni/Ce-ZrO_2/θ-Al_2O_3	High activity and stability	[65]
Electrolyte		
La_2O_3/NiO	Reduced the solubility of NiO by one-tenth, cell performance being studied	[66, 67]
Separator		
Ce based ceramic/SUS	Promising coating materials	[68]

NiO, with stabilizing additives. Another method which could be used to improve the cathode would involve the addition of alkali earth metal oxides or carbonates to the electrolytes.

Several lithiated materials, including $LiCoO_2$, $LiFeO_2$, Li_2CoO_2, and Li_2MnO_3, have been investigated fairly extensively with regard to their possible use as modifying (or coating) materials for these NiO cathodes, due principally to their extremely low solubility in carbonate melt electrolytes [8–20]. Other metals or metal oxides, including Nb [21], Ni-Al alloy [22], Ni-Ti alloy [23], and MgO [24], have also been coated, doped, or otherwise added to NiO in order to improve the performance of the cathode material. Other candidates for NiO additives, including ZnO [25], $MgFe_2O_4$ [26], and Co_3O_4 [27], have also been introduced, and research has been conducted on ternary systems, such as $(Li_{0.52}Na_{0.48})_{2-2x}AE_xCO_3$ (AE = Ca, Sr and Ba) [28] since 2004.

2.1.2. Method to improve the stability of cathode materials using RE

Many research projects focused on improving the stability of NiO cathodes using RE elements have been conducted since 2000 [29–33]. In comparison with other MCFC component materials, NiO cathodes tend to dissolve more readily in corrosive and evaporative electrolytes. Therefore, the effects of RE additives to NiO have been the subject of substantially more attention than have any of the other components of MCFC.

In 2000, Daza *et al*. constructed a modified NiO cathode via Ce impregnation, and evaluated its properties via both surface and bulk analyses. The Ce-impregnated cathodes exhibited the same pore size distribution curves and morphology as did the reference NiO cathodes. The presence of Ce also exerted some effects on nickel oxidation; this process was faster in cases in which Ce had been incorporated. At low CeO_2 contents, between 0.3–1 by wt.%, the corrosion process was noticeably retarded. However, according to the published report, the synergistic effect of Ce and Li resulted in a ready lithiation of the cathode, generating marked modifications to the cathode surfaces, which appeared more prominent for the Ce-free samples, and also resulted in variations in the volume of the cathode. Therefore, additional research into the control of lithiation is clearly required [29].

In 2002, cathode materials based on lithium-nickel mixed oxides and modified via La impregnation were investigated for their ability to potentially yield an alternative MCFC cathode. According to the author of this study, La_2O_3 was selected on the basis of the consideration that it could be utilized as a catalyst support in both industrial and technological applications. It was also believed that the incorporation of La might create an oxygen buffer, thereby facilitating the lithiation of NiO. In this report [30], the cathode material was prepared via *ex situ* NiO lithiation, with a high Li content and La impregnation. The electrochemical behavior of this material was evaluated in a eutectic Li/K mixture at 650°C, via electrochemical impedance spectroscopy (EIS), with regard to La content, immersion time, and gas composition. The final results of this study suggested that the incorporation of low concentrations of La into the lithiated NiO reduced nickel dissolution (Table II) and improved the overall efficiency of the cell.

The impedance spectra were analyzed in order to gain insight into the structural changes occurring in the electrode over the first 100 h. These changes involved a

TABLE II Chemical analyses of the samples before and after electrochemical tests, and the nickel and lanthanum content in the eutectic [30]: L_{40}: lithiated NiO without lanthanum; $L_{40}La_{0.3}$: 0.3 wt.% of La_2O_3; $L_{40}La_{0.5}$: 0.5 wt.% of La_2O_3; $L_{40}La_{0.8}$: 0.8 wt.% of La_2O_3

	Sample				Eutectic	
	wt.% Li (before)	wt.% Li (after)	wt.% L_2O_3 (before)	wt.% L_2O_3 (after)	Ni (ppm)	La (ppm)
L_{40}	4.40	3.10			12	
$L_{40}La_{0.3}$	4.40	3.40	0.26	0.18	1.3	26
L_{40} $La_{0.5}$	4.40	3.00	0.50	0.42	6.6	33
L_{40} $La_{0.5}$	4.50	2.70	0.81	0.69	2.0	34

marked loss of Li, and a low degree of Ni and La dissolution. La was also determined to exert a positive influence on the charge-transfer processes associated with oxygen reduction. However, long-term tests should be conducted in this regard in the future.

In the 2003 study of Popov *et al.* [31], a doped La ternary system, $La_{0.8}Sr_{0.2}CoO_3$, was coated onto sintered NiO electrodes via a sol-gel process, and the electrochemical performance of this construction was evaluated on a laboratory scale, with 3 cm^2 half-cells at the conventional conditions of MCFC performance. As a result, this coated cathode was determined to exhibit a potential of over 109 mV at an applied current density of 160 mA/cm^2. Dissolution studies conducted with molten Li/K at 650°C revealed a lower rate of Ni dissolution than was observed in conventional NiO cathodes. Impedance analysis revealed that the behavior of the coated cathode was similar to that of NiO. Therefore, they reported that this cathode had great promise with regard to its possible use as an alternative MCFC cathode. However, more studies regarding the control of cathode pores is still required, in order to establish minimum values for cathode polarization.

In 2004, Huang *et al.* presented a series of papers [32] focusing on the effects of the four types of RE oxides on the electrochemical behavior of new cathodes, using electrochemical impedance spectroscopy, X-ray diffraction, and scanning electron microscopy. These cathode materials were prepared on the basis of the modification of NiO via impregnation with 0.3–1.0 wt.% RE oxides (CeO_2, La_2O_3, Pr_2O_3, Nd_2O_3). In this paper, the RE oxide-impregnated nickel cathodes exhibited comparable porosity, pore sizes, and morphology as were observed in the nickel cathode. The solubility of this cathode in the melts was one order of magnitude lower than that of the RE-free NiO cathodes. The author explained this low solubility as follows: "The solubility of RE oxide in the carbonate melts was far more than that of NiO. Consequently, concentration of O^{2-} was increased in the micro region containing RE oxide and NiO due to the preferential dissolution of RE oxide. That was to say, increase of concentration of O^{2-} was disadvantageous for the formation of Ni^{2+} ion from the standpoint of view of dissolution equilibrium of NiO." It was also reported in this study that the impedance spectra for all of the cathode materials revealed important variations in charge transfer resistance over the 200 h of immersion. These variations showed that dissolution and charge transfer processes were occurring under the conditions of the RE-modified cathode surface at the time of carbonate exposure. The dissolution of NiO was attributed to the RE-modified surface of the cathode. Therefore, a dramatically low NiO dissolution rate was observed in the RE oxide-modified cathode materials. These cathode materials also enhanced the charge transfer processes associated with oxygen reduction, with better results being observed with higher RE oxide contents. The cathode to which 1.0 wt.% of RE oxide had been added exhibited lower dissolution and charge transfer resistance values. Consequently, it was reported that the 1.0 wt.% RE oxide/NiO cathode material might prove to be a viable alternative to the NiO normally used in the construction of the MCFC cathodes.

2.2. MCFC anode

2.2.1. Method to improve the stability of the anode material without RE

Another hindrance to the development of MCFCs is the creep and sintering occurring in the Ni anode. In order to solve these problems, a variety of metals, including Cr, Al and Cu, have been used as additives. Among these, Ni–Cr has been frequently used in the construction of an anode, and constitutes the current material of choice for commercialization [33]. However, further research has been recently conducted in an attempt to generate better creep resistance greater cost-effectiveness than can be achieved with Ni–Cr anodes, resulting in the development of alternative anode materials, as well as protocols which reduce the amount of material used, and improved manufacturing methods.

The most significant research and development of anode materials has involved the addition of highly creep and sintering-resistant pure metals, metal oxides, and intermetallic compounds to Ni [34–44]. Furthermore, several papers have been presented regarding the coating or electro-deposition of Al and Nb onto the surface of Ni anodes [45, 46].

2.2.2. Method to improve the stability of anode materials using RE

Fewer papers have been submitted regarding the effects of RE-addition to anodes than on the effects of RE-addition to cathodes. In 1993, one such paper revealed that the proper doping of CeO_2 onto Ni–Cr anodes might yield a performance equivalent to that of Ni–Cr anodes [47]. However, post-test analyses indicated that this technique caused an unacceptable degree of chemical instability.

In 2004, Zeng *et al.* assessed the corrosion behavior of binary Ni–Dy alloys containing 1, 3 and 5 wt.% Dy in a eutectic $(Li/K)_2CO_3$ mixture at 650°C [48]. The alloys used in this trial had a two-phase structure, consisting

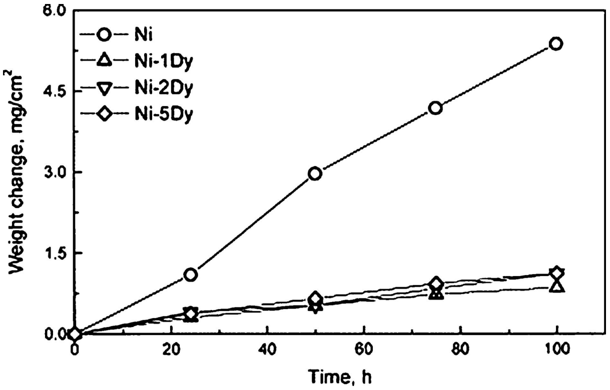

Figure 2 Corrosion kinetics of the pure and Ni–Dy alloys in molten $(0.62Li,0.38K)_2CO_3$ at 650°C in air [48]: Ni-1Dy:1 wt.% of Dy; Ni-3Dy: 3 wt.% of Dy; Ni-5Dy: 5 wt.% of Dy.

of an α-Ni solid solution and an intermetallic Dy_2Ni_{17} compound. The results of these experiments showed that the corrosion rates of the three types of Ni–Dy alloys were all substantially lower than the corrosion rate of pure Ni (Fig. 2), and that corrosion rates decreased with increasing Dy concentrations, forming a scale composed primarly of NiO, combined with a small amount of dysprosium oxides.

The weight gain exhibited by the alloys changed only slightly with increasing Dy concentrations, whereas the thickness of the scale decreased with increasing Dy contents. According to the paper, these results may be attributed to the following factors. First, Dy ions may function as barriers which block the diffusion of Ni along grain boundaries, as has been observed in other RE elements. Second, the formation of Dy-rich oxides may serve to block Ni diffusion, resulting in lower corrosion rates. Additionally, the two-phase structure of these alloys may also contribute to their lower corrosion rates.

In 2002, a study was undertaken in order to verify that Ce could be used as an MCFC electrode material. The characteristics of the Ce species, including the thermodynamic, chemical, and surface properties of metallic Ce when used as candidate anode materials, were analyzed in molten Li/Na under the anodic and cathodic conditions inherent to the construction of MCFCs. The solubility of the Ce was determined via absorption spectro-photometry, and the electrochemical stability domains were established at different temperatures, predicated on the relevant thermo-chemical calculations [49].

In 2004, Tagawa *et al.* [50] employed a composite anode material consisting of La_2O_3/Sm_2O_3 with Ti fine powder (to provide electronic conductivity), which served as the anode electrode in a dry methane type of MCFC, in which methane was directly charged to the anode as a fuel. These researchers had selected La_2O_3/Sm_2O_3 on the basis of the findings they had obtained in a series of screening experiments involving TPD, TG, and a tubular reactor. This anode, when assembled into a cell unit, was reported to perform quite well over a period of 144 h, following an initial reduction in the voltage of the open circuit.

2.3. Reforming catalyst in DIR-MCFC

In the case of DIR-MCFC or direct dry methane (methane catalytic partial oxidation; CPOX) MCFC systems [51], the reforming catalyst or the partial oxidation catalyst is positioned in the anode compartment. Ni-based catalysts are normally used in DIR-MCFC, and an Rh-based catalyst has been implicated as the optimal CPOX catalyst [52, 53]. The supports of both catalysts are known as MgO or Al_2O_3. Due to their direct contact with the anodes, both of the catalysts were deactivated via the sintering of the carrier material, or by the migration and evaporation transport of the electrolyte. This deactivation results in a reduction of the specific activity of the catalysts [54].

In order to render the catalyst more resistant to deactivation during this operation, the catalyst support was replaced with a variety of elements, including Al_2O_3, SiO_2, Cr_2O_3, SiO_2, γ-$LiAlO_2$, and α-$LiAlO_2$, and small amounts of metals such as Li, K, Cs, Ru, or Rh were added as promoters [55–62].

In 1996, Berger *et al.* prepared a Ni catalyst containing La via co-precipitation for DIR-MCFC. The reactivity and alkaline resistance of this catalyst were evaluated. In Berger's subsequent paper, he revealed that the addition of La to the co-precipitated Ni/γ-Al_2O_3 catalyst had effected a diminution of its stability [63]. According to this paper, this was probably attributable to the interaction of Ni–La with alumina.

Another study conducted in 1999 attempted to characterize the reaction performances of methane partial oxidation to syngas over Ni-RE/Al_2O_3 catalysts [64]. That study reported a lifespan of up to 500 h for some of the tested catalysts. As a result, It was demonstrated that the RE additives could elevate the catalyst activities and resist the formation on $NiAl_2O_4$.

In 2003, Jun *et al.* conducted a study investigating the properties of the Ni/Ce-ZrO_2/θ-Al_2O_3 reforming catalyst [65]. In this study, the catalyst exhibited a high degree of activity and stability under the typical steam reforming of methane for 200 h at 750°C (Fig. 3).

The authors reported that these higher levels of activity and stability were attributable to the pre-coating of a Ce-ZrO_2 layer on the θ-Al_2O_3. According to this study, a chemical interaction occurring between Ni and Al_2O_3 results in the inactivation of $NiAl_2O_4$, and this process occurs more rapidly in the presence of steam. However, Ce-ZrO_2 was also shown to effectively prevent the phase transformation of Ni/Al_2O_3 into $NiAl_2O_4$, and was also shown to play a role in the formation of stable NiO_x species in the presence of steam. This NiO_x formation was visualized via TPR. It was then further speculated that populations of NiO_x may perform crucial functions in both the activity and stability of the catalysts. Therefore, Ce-ZrO_2 clearly enhanced the metallic Ni sites which had been reduced from the NiO_x species, which strongly interact with the support, thereby becoming active sites for methane-reforming reactions, and conferring a high degree of coke resistance.

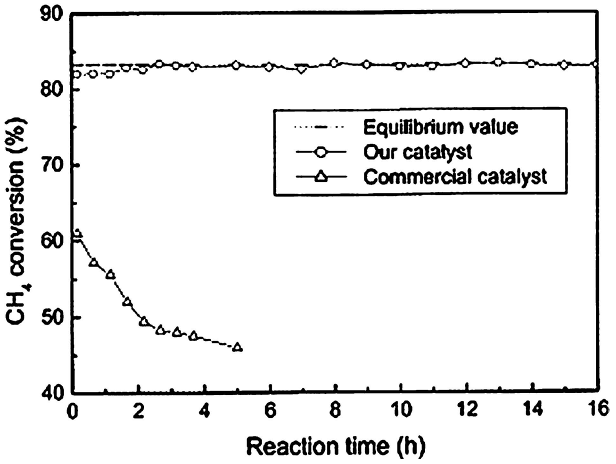

Figure 3 Comparison of stability in the stoichiometric steam reforming of methane (reaction conditions: $P = 1$ atm, $T = 1023$ K, $H_2O/CH_4 = 1.0$, GHSV = 72,000 ml/g$_{cat}$ h) [65]. "Our catalyst" in the figure refers to Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$.

2.4. Others

2.4.1. Electrolyte

Ota *et al.* presented a series of papers regarding the results of tests conducted to evaluate the solubility of NiO as a function of CO_2 partial pressure in La_2O_3-added electrolytes. The addition of La_2O_3 to molten carbonate (Li/Na) was determined to 10% more effective in reducing NiO solubility (Fig. 4) than was observed in the MgO-added electrolytes.

According to report submitted by Ota *et al.*, this effect on NiO solubility could be attributed primarily to the acid-base equilibria of the melts, as well as the fact that NiO solubility was smaller in basic melts of the practical use region [66].

In 2005, the same researchers also presented papers regarding the feasibility of La as an MCFC electrolyte additive [67]. In that paper, they asserted that the molten carbonates might be rendered more basic via the inclusion of the La as an additive, as the stable phase of the La oxide in the molten carbonates was determined to be $La_2O_2CO_3$. Therefore, the more basic molten carbonate with the La additive generated a reduction in the solubility of pure NiO. This effect was also attributed to the acid-base equilibrium, which is known to be related to the solubility of NiO in molten carbonates. In this case, that equilibrium was found to be 1–2 orders of magnitude greater than that observed with the alkali and alkali earth metals.

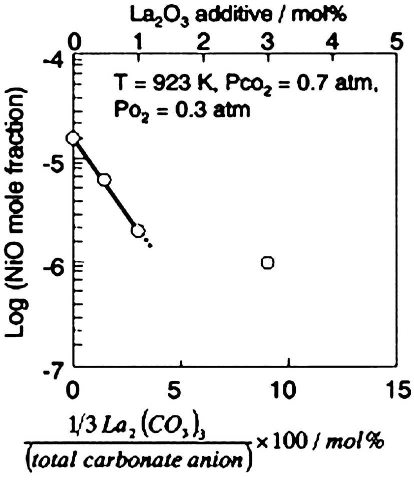

Figure 4 NiO solubility as a function of La_2O_3 concentrations in the Li/Na eutectic melts [66].

2.4.2. Separator plate and current collector

The stainless steel separator plates in the MCFCs also require protection against corrosion. Keijzer *et al.* submitted a report regarding the corrosion resistance of SUS-separator plates coated with a variety of metallic components, including Ti, Y, Nb, La, Ce, Nd, Hf, and Ta. Among these, they reported that the results of their stability experiments indicated that Ce-based ceramics constituted promising coating materials, which could prevent the separator from corroding when used in the construction of MCFCs [68].

3. Conclusions

In considering the effects of the addition of RE to the materials used in MCFCs, La_2O_3-added cathode materials were primarily utilized in order to find an material alternative to the conventional NiO cathode in the MCFCs. Apparently, the addition of RE to the NiO cathode reduced the solubility of the cathodes in the carbonate melts. This is due to the fact that the more soluble RE (as compared to NiO) increased the O^{2-} concentrations, and reduced the rates of NiO dissolution. The addition of La_2O_3 to the electrolytes also proved far more effective in the reduction of NiO solubility. This effect was attributed to the increasing basicity of the electrolyte.

Anodes constructed with Ni–Dy alloys may exhibit even lower corrosion rates. In this study, we also confirmed the possibility of using Ce as an alternative anode material.

Ce and La were both found to be viable additives which improved the stability of both the reforming catalyst and the separator. In the reforming catalyst, RE appears to effectively prevent the phase transformation of Ni/Al_2O_3 into $NiAl_2O_4$, and thus improves both the stability and activity of the reforming catalyst, in the presence of steam.

Finally, the incorporation of low RE concentrations into RE-free materials might reduce the dissolution of materials induced by the carbonate melts of the electrolyte at high temperatures, thereby enhancing the efficiency of the cells. However, the majority of these results were predicated on short-term stability tests. Therefore, further research into the long-term stability of these materials is clearly warranted.

Acknowledgments

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References

1. A. TSOGA, A. NAOUMIDIS, W. JUNGEN and D. STÖVER, *J. Eur. Ceram. Soc.* **19** (1999) 907.
2. T. SHIMONOSONOA, Y. HIRATAA, Y. EHIRAA, S. SAMESHIMAA, T. HORITAB and H. YOKOKAWAB, *Solid State Ionics* **174** (2004) 27.
3. T. SHIMADAA, C. WEN, N. TANIGUCHIC, J. OTOMOD and H. TAKAHASHIA, *J. Power Sources* **131** (2004) 289.
4. T. S. ZHANG and J. MA, *Scripta Mater.* **50** (2004) 1127.
5. J. B. WANGA, J. C. JANGB and T. J. HUANG, *J. Power Sources* **122** (2003) 122.
6. Y. OKAWA and Y. HIRATA, *J. Eur. Ceram. Soc.* **25** (2005) 473.
7. C. IACOVANGELO, *J. Electrochem. Soc.* **133** (1986) 1359.
8. R. C. MAKKUS, K. HEMMES and J. H. W. DE WIT, *ibid.* **141** (1994) 3429.
9. W. LADA, A. DEPTULA, B. SARTOWSKA, T. OLCZAK, A. G. CHMIELEWSKI and M. CAREWSKA, *J. New Mat. Electro. Sys.* **6** (2003) 33.
10. L. PLOMP, J. B. J. VELDHUIS, E. F. SITTERS and S. B. V. D. MOLEN, *J. Power Sources* **39** (1992) 369.
11. T. FUKUI, H. OKAWA and T. TSUNOEKA, *ibid.* **71** (1998) 239.
12. E. FONTES, M. FONTES and D. SIMONSSON, *Electrochimica Acta* **41** (1996) 1.
13. L. GIORGI, M. CAREWSKA, S. SCACCIA, E. SIMONETTI, E. GIACOMETTI and R. TULLI, *Int. J. Hydrogen Energ.* **21** (1996) 491.
14. E. ANTOLINI and L. GIORGI, *Ceram. Int.* **24** (1998) 117.
15. S. T. KUK, Y. S. SONG and K. KIM, *J. Power Sources* **83** (1999) 50.
16. T. FUKUI, S. OHARA, H. OKAWA, T. HOTTA and M. NAITO, *ibid.* **86** (2000) 340.
17. A. LUNDBLAD, S. SCHWARTZ and B. BERGMAN, *ibid.* **90** (2000) 224.
18. TH. BRENSCHEIDT, F. NITSCHKÉ, O. SÖLLNER and H. WENDT, *Electrochim. Acta* **46** (2001) 783.
19. S. G. KIM, S. P. YOON, J. HAN, S. W. NAM, T. H. LIM, I. H. OH and S. A. HONG, *ibid.* **49** (2004) 3081.
20. L. GIORGI, M. CAREWSKA, M. PATRIACA, S. SCACCIA, E. SIMONETTI and A. DIBARTOLOMEO, *J. Power Sources* **49** (1994) 227.
21. B. FANG and H. CHEN, *J. Electroanal. Chem.* **501** (2001) 128.
22. M. MOHAMEDI, Y. HISAMITSU, K. KIHARA, T. KUDO, T. ITOH and I. UCHIDA, *J. Alloy Compd.* **315** (2001) 224.
23. C. BELHOMME, E. GOURBA, M. CASSIR and C. TESSIER, *J. Electroanal. Chem.* **503** (2001) 69.
24. H. J. CHOI, S. K. IHM, T. H. LIM and S. A. HONG, *J. Power Sources* **61** (1996) 239.
25. B. HUANG, F. LI, Q. YU, G. CHEN, B. ZHAO and K. HU, *ibid.* 128 (2004) 135.
26. H. OKAWA, J. H. LEE, T. HOTTA, S. OHARA, S. TAKAHASHI, T. SHIBAHASHI and Y. YAMAMASU, *ibid.* **131** (2004) 251.
27. M. J. ESCUDERO, T. RODRIGO, L. MENDOZA, M. CASSIR and L. DAZA, *ibid.* **140** (2005) 81.
28. K. TANIMOTO, T. KOJIMA, M. YANAGIDA, K. NOMURA and Y. MIYAZAKI, *ibid.* **131** (2004) 256.
29. L. DAZA, C. M. RANGEL, J. BARANDA, M. T. CASAIS, M. J. MARTÍNEZ and J. A. ALONSO, *ibid.* **86** (2000) 329.
30. M. J. ESCUDERO, X. R. NÓVOA, T. RODRIGO and L. DAZA, *ibid.* **106** (2002) 196.
31. P. GANESAN, H. COLON, B. HARAN and B. N. POPOV, *ibid.* **115** (2003) 12.
32. B. HUANG, G. CHENA, F. LIA, Q. C. YUB and K. A. HUA, *Electrochim. Acta* **49** (2004) 5055.
33. D. JUNG, I. LEE, H. LIM and D. LEE, *J Mater Chem.* **13**(7) (2003) 1717.
34. C. LEE, D. JUNG, I. LEE, K. BYUN and H. LIM, *Metals Mater Int.* **9**(6) (2003) 605.
35. C. G. LEE, K. S. AHN, H. C. LIM and J. M. OH, *J. Power Sources* **125** (2004) 166.
36. S. A. HONG, S. W. NAM, T. H. LIM, I. H. OH and S. P. YOON, *Hwahak Konghak* **33** (1995) 640.
37. G. B. KIM, Y. J. MOON and D. Y. LEE, *J. Power Sources* **104** (2002) 181.
38. L. SUSKI and J. WYRWA, *J. Appl. Electrochem.* **20** (1990) 625.
39. J. C. WITHERS, H. C. SHIAO, R. O. LOUTIFY and P. WANG, *JOM.* **43** (1991) 36.
40. E. R. HWANG, J. W. PARK, Y. D. KIM, S. J. KIM and S. G. KANG, *J. Power Sources* **69** (1997) 55.
41. J.-H. WEE, D.-J. SONG, C.-S. JUN, T. H. LIM, S. A. HONG, H. C. LIM and K.-Y. LEE, *J. Alloy Compd.* **390** (2005) 155.
42. J.-H. WEE, D.-J. SONG, C.-S. JUN, T. H. LIM, S. A. HONG, H. C. LIM and K.-Y. LEE, *J. Alloy. Compd.* **390** (2005) 161.
43. H.-S. CHOO, K.-Y. LEE, Y.-S. KIM and J.-H. WEE, *Intermetallics* **13** (2005) 157.
44. Y. S. KIM, K. Y. LEE and H. S. CHUN, *J. Power Sources* **99** (2001) 26.
45. B. FANG, X. LIU, X. WANG and S. DUAN, *J. Electroanal. Chem.* **441** (1998) 1.
46. *Idem., ibid.* **441** (1998) 65.
47. K. MYLES, M. KRUMPELT, G. KUCERA, M. ROCHE and E. INDACOCHEA, in Proceedings of Joint Contactors Meet: Advanced Turbine System, Fuel Cells and Coal-Fired Heat Engines Conf., Morgantown, WV, USA (1993) p. 386.
48. C. L. ZENG, T. ZHANG, P. Y. GUO and W. T. WU, *Corros. Sci.* **46** (2004) 2183.
49. V. CHAUVAUT, V. ALBIN, H. SCHNEIDER, M. CASSIR, H. ARDELEAN and A. GALTAYRIES, *J. Appl. Electrochem.* **30** (2000) 1405.
50. T. TAGAWA, A. YANASE, S. GOTO, M. YAMAGUCHI and M. KONDO, *J. Power Sources* **126** (2004) 1.
51. S. FRENI and S. CAVALLARO, *Int. J. Hydrogen Energy* **24** (1999) 75.
52. D. HICHMAN, E. UAUPFER and L. SCHUMDT, *Catal. Lett.* **17** (1993) 223.
53. D. QIN, J. LAPSZEWICZ and X. JIANG, *J. Catal.* **159** (1996) 140.
54. J.-H. WEE and K.-Y. LEE, *J. Appl. Electrochem.* **35** (2005) 521.
55. J. R. ROSTRUP-NIELSEN and L. J. CHRISTIANSEN, *Appl. Catal. A* **126** (1995) 381.
56. R. J. SELMAN, *Energy (Oxford)* **11** (1986) 153.
57. K. KISHIDA, E. NISHAYAMA, M. MATSUMURA, T. TANAKA, S. KANEKO, Y. MORI and S. NAKAGAWA, in Extended Abstracts of the International Seminar on Fuel Cell Technology and Applications, Scheveningen (The Netherlands, 1987) p. 40.
58. N. GIORDANO, F. FRUSTRERI, P. TSIAKARAS, A. MEZZAPICA and A. PARMALIANA, in Abstracts of the Fuel Cell Seminar (Tuscon, USA, 1986) p. 230.
59. R. J. BERGER, E. G. M. DOESBURG, J. G. VAN OMMEN and J. R. H. FOSS, *Catal. Sci. Technol.* **1** (1991) 455.
60. V. A. SOBANYIN, I. I. BODROVA, E. Y. TITOVA, O. V. BAZHAN, V. D. BELYAEV and N. N. BODROV, *React. Kinet. Catal. Lett.* **39** (1989) 443.
61. M. TARJANYI, L. PAETCH, R. BERNARD and H. GHEZEL-AYAGH, in Proceedings of International Seminar on Fuel Cells (Tuscon, USA, 1985) p.177.
62. M. ITO, T. TAGAWA and S. GOTO, *Appl. Catal. A* **184** (1999) 73.
63. R. J. BERGER, E. B. M. DOESBURG, J. G. VAN OMMEN and J. R. H. ROSS, *Appl. Catal. A* **143** (1996) 343.

64. J. WAN, *Tianranqi Huagong (In Chinese)* **24** (1999) 28.
65. H. S. ROH, K. W. JUN and S. E. PARK, *Appl. Catal. A* **251** (2003) 275.
66. S. MITSUSHIMA, K. MATSUZAWA, N. KAMIYA and K. I. OTA, *Electrochim. Acta* **47** (2002) 3823.
67. K. MATSUZAWA, T. MIZUSAKI, S. MITSUSHIMA, N. KAMIYA and K. OTA, *J. Power Sources* **140** (2005) 258.
68. M. KEIJZER, K. HEMMES, P. J. J. M. VAN DERPUT, J. H. W. DE WIT and J. SCHOONMAN, *Corros. Sci.* **39** (1997) 483.

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