Performance of a novel Ni/Nb cathode material for molten carbonate fuel cells (MCFC)

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Abstract

In this work the performance of NiO and a novel cathode material preoxidized nickel–niobium alloy were investigated. It is found that under a cathode atmosphere of $p(CO_2)/p(O_2) = 0.67$ atm/0.33 atm, the equilibrium solubility of nickel ions in $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C is about 17 ppm for the nickel oxide electrode and 8 ppm for the preoxidized nickel–niobium alloy electrode. The improvement in the stability of material in the melt may be attributed to the formation of a more dense nodular structure for the nickel–niobium alloy electrode when compared with a Ni electrode during preoxidation. The formation of a dense nodular structure for the nickel–niobium alloy electrode depresses the dissolution of NiO from the electrode into the carbonate melt and, accordingly, enhances the stability of the electrode material in the melt. The polarization performance of the NiO cathode was improved by electrodeposition of niobium. As far as the thermal stability and the polarization performance are concerned, the preoxidized nickel–niobium alloy can be considered as a candidate for the cathode material of MCFCs.

1. Introduction

The molten carbonate fuel cell (MCFC) is a highly efficient and environmentally clean means of power generation [1–6]. Nickel oxide, which is usually obtained by *in situ* oxidation of porous nickel, has been employed almost exclusively as cathode material in MCFCs since the 1970s [7, 8]. The performance of NiO is relatively satisfactory, but still needs some improvement. For example, its thermal stability (corrosion resistance) and polarization performance should be improved. In MCFC technology corrosion of NiO may cause the following problems: (i) cathode material loss, (ii) cell internal shorting and (iii) low total efficiency [9]. Many efforts have been made to improve the stability of the cathode material in the melt. One approach is choice of an alternative material which is more stable than NiO in the carbonate melt under MCFC operation conditions. To date, doped $LiFeO_2$, Li_2MnO_3 and $LiCoO_2$ have been considered as candidates for the cathode material [10–16], mainly to alleviate the concern of cell internal shorting associated with NiO dissolution. The electrical conductivity of these materials have been significantly improved by doping and may be considered acceptable. However, the porous cathode performance is usually lower than that of the baseline NiO.

Nickel–niobium alloys have been shown to have the properties required of insoluble anodes [17] as well as excellent catalytic activity [18, 19]. In addition, thermo-dynamic data indicate that oxides of niobium cannot be reduced by CO and H_2 in the anode atmosphere, that is, there will be no deposition of metal niobium in the matrix. Accordingly, the problem of cell internal shorting associated with the dissolution of the cathode material should be avoided. For these reasons a preoxidized nickel–niobium surface alloy was selected as a candidate for MCFC cathode material. The stability and the polarization performance of the preoxidized nickel–niobium surface alloy were investigated. For comparison, the stability and the polarization performance of NiO under the same operating conditions were also investigated.

2. Experimental details

The preparation of nickel–niobium surface alloy was carried out by electrochemical reduction of niobium(IV) ions on a nickel cathode in molten fluorides. Niobium

foils were used as the anode and the reference electrode. A eutectic mixture of 50 mol % NaF–50 mol % LiF was used as solvent for the electrochemical alloying of nickel with niobium at 750 °C. The melt purification was performed as follows: the bath was initially dehydrated by heating under vacuum (1 Pa) for 24 h at 500 °C, then melted under argon atmosphere at 750 °C. Niobium(IV) ions were generated *in situ* by addition of potassium heptafluoroniobiate(V) and metallic niobium to the bath. The following reaction occurs:

$$4\,Nb^{V} + Nb = 5\,Nb^{IV} \tag{1}$$

When an excess of metallic niobium was added to the bath, the equilibrium was shifted towards the right and a valence less than 4.2 of niobium ions was expected [20].

Preoxidized Ni and nickel–niobium alloy served as candidates for MCFC cathode material. The procedures for preoxidation of nickel foil and nickel–niobium surface alloy were as follows: the electrodes were washed with hot alkaline solution, rinsed with acetone and distilled water. After being dried in the oven at 80 °C for at least an hour, the electrodes were placed into $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C under oxygen atmosphere. This process lasted for 48 h. The stability of the materials was examined by determination of the nickel ions content in a melt of 62 mol % Li_2CO_3–38 mol % K_2CO_3 under various operating conditions. Nickel ions content in the carbonate melt was determined by atomic adsorption spectroscopy (AAS) after the melt sample was taken out and dissolved with HCl acid. The polarization performance of the electrode materials was investigated using polarization curve measurements.

3. Results and discussion

3.1. Preparation of nickel–niobium surface alloy

Niobium is more active than nickel in fluoride melt. When the two metals were immersed in a bath with electrical connection, a galvanic cell occurred in which the reaction at the nickel cathode was the formation of the alloy Ni_xNb. According to X-ray microprobe analysis, the composition of the surface alloy layer corresponds to Ni_3Nb.

3.2. Preoxidization of nickel and nickel–niobium surface alloy

According to the procedures described previously, nickel and nickel–niobium surface alloy electrodes were oxidized in the carbonate melt under oxygen atmosphere. After preoxidation the electrode materials were examined by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD results indicate that the main product is NiO for the oxidation of nickel and is a composite oxide $NiO \cdot Nb_2O_5$ for the oxidation of the nickel–niobium surface alloy. SEM images show a more

dense nodular structure for the oxidized nickel–niobium electrode when compared with the nickel oxide electrode.

3.3. Stability tests for NiO and preoxidized nickel–niobium surface alloy

In research on MCFCs the most frequently used cell operating temperature is 650 °C and the cathode atmosphere consists of CO_2 and O_2 ($p(CO_2)/p(O_2) = 2:1$). For this reason, an atmosphere with a composition of CO_2 partial pressure of 0.67 atm and O_2 partial pressure of 0.33 atm was selected to determine the equilibrium content of nickel ions in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C for NiO and the preoxidized nickel–niobium surface alloy.

Dissolution curves in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C of NiO and the preoxidized nickel–niobium surface alloy are shown in Figure 1. Under the selected operating condition it took the NiO electrode around 80 h to reach the dissolution equilibrium and the equilibrium solubility of nickel ions in the melt was about 17 ppm. For the preoxidized nickel–niobium alloy it took around 90 h to reach the dissolution equilibrium and the equilibrium solubility of nickel ions in the melt was 8 ppm. The stability of nickel oxide in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt was greatly improved after the formation of the nickel–niobium surface alloy. The improvement in the stability of the cathode material may be attributed to the formation of a more dense nodular structure for the nickel–niobium alloy electrode when compared with the Ni electrode during preoxidation. The formation of a dense nodular structure for the nickel–niobium alloy electrode depresses the dissolution of NiO from the electrode into the carbonate melt and enhances the stability of the electrode material in the carbonate melt.

3.4. Polarization performance of NiO and preoxidized nickel–niobium surface alloy

The reduction of oxygen dissolved in molten alkali carbonates is one of the major electrode processes occurring in MCFCs. The kinetics of oxygen reduction
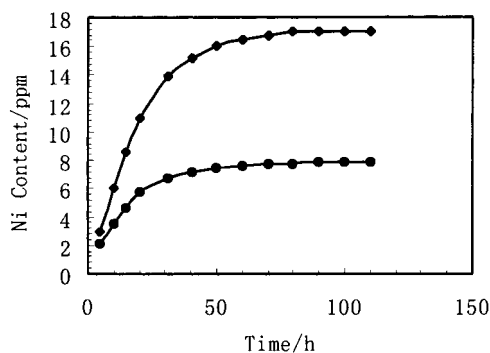

Fig. 1. Nickel ions content in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt as a function of time, $T = 923$ K, $p(CO_2) = 0.67$ atm, $p(O_2) = 0.33$ atm. Key: (◆) NiO; (●) preoxidized nickel–niobium surface alloy.

have important effects on the polarization loss of the cathode.

Niobium is a typical valve metal with good catalytic activity and improves the catalysis of base materials as an alloying element. In fact, nickel–niobium alloy has been shown to have excellent catalytic activity to the oxidation of CO in the carbonate melt [18]. For this reason, the preoxidized nickel–niobium surface alloy was selected as a candidate MCFC cathode material and its polarization performance was investigated. For comparison, the polarization performance of NiO under the same operating conditions was also investigated.

3.4.1. Voltammetric characteristics of oxygen reduction

To examine the polarization performance of the cathode material under MCFC operating conditions, it is necessary to understand the characteristics of oxygen reduction. Appreciable effort has been made to elucidate the kinetics and mechanism of oxygen reduction reaction, most work having been done on gold, which is the most stable material in molten carbonate among all metallic electrodes and does not react with the melt. In the present work we restricted our experimental conditions to $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C and to an atmosphere of $p(O_2)/p(CO_2) = 0.9$ atm/0.1 atm, to compare our results with previous work [21, 22].

Typical cyclic voltammograms for oxygen reduction on gold in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C are shown in Figure 2. There is a reduction peak at around 50 mV. This reduction peak disappeared on the curves recorded for the melt saturated with CO_2 or Ar, which were often considered as the background baselines. This indicates that the reduction peak in Figure 2 resulted from the reduction of oxygen.

The relation between peak current (I_p) and square root of sweep rates $(v^{1/2})$ is shown in Figure 3. This is linear which indicates that the reduction of oxygen is under diffusion-control. The results are in agreement with those of Uchida and Appleby [21, 22]. Because the peak potential does not show clear scan rate depen-
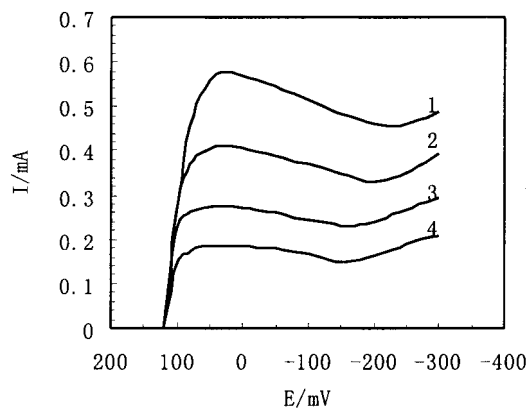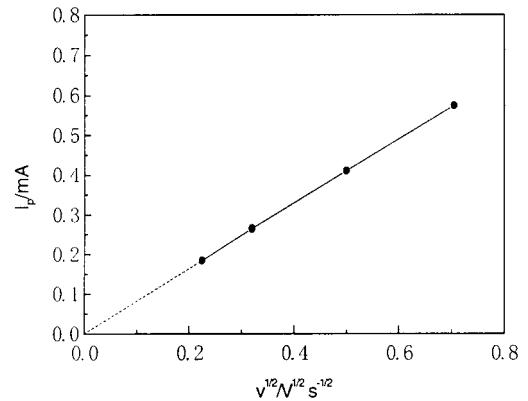
Fig. 3. Peak current (I_p) shown as a function of square root of sweep rates $(v^{1/2})$.

dence, it is difficult to apply the conventional analysis of cyclic voltammetry to obtain kinetic information. For this reason, polarization curve measurements were carried out to examine the performance of different cathode materials.

3.4.2. Polarization performance of cathode materials

Vogel et al. reported that the diffusing species during oxygen reduction is mainly the superoxide ion (O_2^-) according to the determination of the equilibrium constants for the formation of peroxide (O_2^{2-}) and superoxide (O_2^-) and the reduction is a three-electron process in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C [23]. The process of oxygen reduction can be written as follows:

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

$$O_2^- + 2\,CO_2 + 3\,e^- = 2\,CO_3^{2-} \tag{3}$$
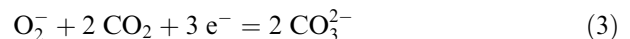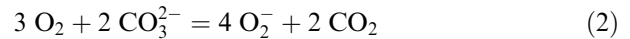
Polarization curve measurements were carried out under various cathode atmospheres. Figure 4 shows the curves obtained on different electrodes in the $(Li_{0.62},$

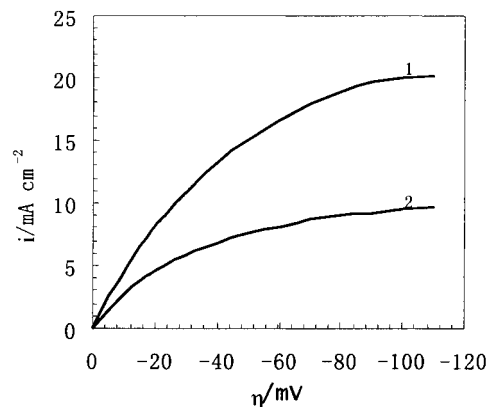Fig. 2. Cyclic voltammograms for oxygen reduction on gold in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C under $p(O_2)/p(CO_2) = 0.9$ atm/0.1 atm. Sweep rates: (1) 0.5; (2) 0.25; (3) 0.1; (4) 0.05 V s^{-1}.

Fig. 4. Polarization curves obtained on different electrodes in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C with a gas composition of $p(O_2)/p(CO_2) = 0.9$ atm/0.1 atm. Key: (1) preoxidized nickel–niobium alloy; (2) NiO.
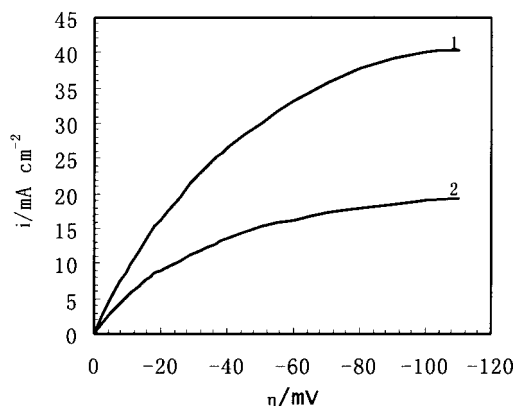
Fig. 5. Polarization curves obtained on different electrodes in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C with a gas composition of $p(O_2)/p(CO_2) = 0.33$ atm/0.67 atm. Key: (1) preoxidized nickel–niobium alloy; (2) NiO.

Table 1. Exchange current density i_0 of oxygen reduction reaction on different electrodes

Electrodes	Exchange current density i_0/mA cm^{-2}	
	$p(O_2)/p(CO_2) = 0.9/0.1$	$p(O_2)/p(CO_2) = 0.33/0.67$
NiO	17.67	11.04
NiO · Nb$_2$O$_5$	24.10	13.25

$K_{0.38})_2CO_3$ melt at 650 °C with a gas composition of $p(O_2)/p(CO_2) = 0.9$ atm/0.1 atm. Figure 5 shows the curves obtained on different electrodes in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C with a gas composition of $p(O_2)/p(CO_2) = 0.33$ atm/0.67 atm.

In the region $|\eta| < 10$ mV the following equation holds.

$$i_0 = \frac{di}{d\eta} \frac{RT}{nF}$$

Here i_0 is exchange current density and η the polarization overpotential. Linear regression was carried out in this small polarization region and i_0 values were calculated assuming an electron transfer number $n = 3$. The results are listed in Table 1. It can be seen that there is a slight increase in the exchange current per unit geometric area for the preoxidized nickel–niobium cathode. The increase in the exchange current may be attributed to the increase in the electrode effective surface area and/or the increase in catalytic activity of the electrode. The mechanism for this requires further investigation.

4. Conclusions

The following conclusions can be drawn. (i) Under a cathode atmosphere of $p(CO_2)/p(O_2) = 0.67$ atm/0.33 atm, the equilibrium solubility of nickel ions in the $(Li_{0.62}, K_{0.38})_2CO_3$ melt at 650 °C is about 17 ppm

for a NiO electrode and 8 ppm for a preoxidized nickel–niobium alloy electrode. The cathode stability of the nickel electrode was improved significantly by the deposition of niobium. (ii) The polarization performance of the NiO cathode was improved by the electrodeposition of niobium. As far as the thermal stability and the polarization performance are concerned, the preoxidized nickel–niobium alloy can be considered as a candidate material for MCFC cathodes.

Acknowledgement

References

1. L. Blomen and M. Mugerwa (Eds), 'Fuel Cell System' (Plenum, New York, 1993).
2. A.J. Appleby and F.R. Foulkes, 'Fuel Cell Handbook' (Van Nostrand Reinhold, New York, 1990).
3. J.R. Selman and T.D. Claar (Eds), 'Molten Carbonate Fuel Cell Technology' (The Electrochemical Society, Pennington, NJ, 1982).
4. K. Kinoshita, F.R. Mc Larnon and E.J. Cairns, 'Fuel Cell', (National Fuel Cell Coordinating Group, Washington DC, 1988).
5. K.I. Ota, B.T. Kim, H.Y. Take and N. Kamiya, 'High Temperature Corrosion of Metals with Molten Carbonate', Proc. 5th China–Japan bilateral conference on 'Molten Chemistry and Technology', Kunming, China, Sept. 28–Oct. 2 (1994), p. 42.
6. C. Yuh, R. Johnsen, M. Farooque and H. Maru, *J. Power Sources* **56** (1995) 1.
7. J.R. Selman and H.C. Maru, *in* Mamantov and J. Braustein (Eds), 'Advances in Molten Salt Chemistry' Vol. **4** (Plenum Press, New York, 1983), p. 308.
8. J.R. Selman and L.G. Marianowski, *in* D.G. Lovering (Ed), 'Molten Salt Technology' (Plenum Press, New York, 1982), p. 323.
9. C. Iacovangelo, *J. Electrochem. Soc.* **133** (1986) 1359.
10. G. Kucera, K. Myles, A. Brown, M. Roche, D. Chu and E. Indacochea, Proc. 4th Annual Fuel Cells Contractors Review Meeting, Morgantown, WV, USA, 31 July (1992).
11. K. Myles, M. Krumpelt, G. Kucera, M. Roche and E. Indacochea, Proc. Joint Contractors Meeting: 'Advanced Turbine Systems, Fuel Cells and Coal-Fired Heat Engines' Conference, Morgantown, WV, USA, 3–5 Aug (1993), p. 386.
12. L. Plomp, J. Veldhuis, E. Sitters, F. Van Berkel and S. Van der Molen, Proc. International Fuel Cell Conference, Makuhari, Japan (1992), Paper III-B-1.
13. J. Smith, G. Kucera and A. Brown, Proc. 2nd Symposium on Molten Carbonate Fuel Cell Technology', Seattle, WA, USA, Oct. 1990, Proc. Vol. **90-16** (The Electrochemical Society, Pennington, NJ, 1990), p. 225.
14. L. Plomp, J.B.J. Veldhuis, E.F. Sitters and S.B. Van der Molen, *J. Power Sources* **39** (1992) 369.
15. L. Giorgi, M. Carewska, M. Patriaca, S. Scaccia, E. Simonetti and A. Dibartolomeo, *J. Power Sources* **49** (1994) 227.
16. N. Kamiya, Y. Takeishi, S. Shibata, H. Yoshitake and K-I. Ota, Proc. 5th China–Japan bilateral conference on 'Molten Salt Chemistry and Technology', Kunming, China, Sept. 28–Oct. 2 (1994), p. 58.
17. T. Fujii and H. Baba, *Boshoku Gijutsu* **29** (1980) 457.
18. B. Fang, X. Liu, X. Wang and S. Duan, *J. Electroanal. Chem.* **441** (1998) 1.

19. B. Fang, X. Liu, X. Wang and S. Duan, *J. Electroanal. Chem.* **441** (1998) 65.
20. G.W. Mellors and S. Senderoff, *J. Electrochem. Soc.* **112** (1965) 266.
21. I. Uchida, T. Nishina, Y. Mugikura and K. Itaya, *J. Electroanal. Chem.* **206** (1986) 229.
22. A.J. Appleby and S.B. Nicholson, *J. Electroanal. Chem.* **112** (1980) 71.
23. W.M. Vogel, S.W. Smith and L.J. Bregoli, *J. Electrochem. Soc.* **130** (1983) 574.