A STUDY OF SURFACE MODIFICATION OF MCFC ELECTRODE

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ABSTRACT

In this study an attempt is made to produce nickel-niobium alloy films on nickel surface by an electrochemical process in molten fluoride. An investigation of the electrochemical behaviour of niobium ions in NaF- CaF$_2$ - K$_2$NbF$_7$ system has been conducted the following conclusions were drawn: The early stage of metal deposition is controlled by an instantaneous nucleation process, and higher applied potential is beneficial to the increase of the density of niobium nuclei. Thus a better quality of niobium coating can be obtained. The niobium-modified nickel electrode is used as MCFC anode; and the composite oxide formed by the preoxidation of Ni-Nb surface alloy is used as MCFC cathode. Some polarization experiments prove that corrosion resistance as well as electrocatalytic activity of the niobium-modified anode is superior than that of an unmodified one. The preoxidised Ni-Nb surface alloy is more stable than NiO cathode. Furthermore, the tests for electrocatalytic activity indicate that preoxidation Ni-Nb surface alloy is more effect than NiO on catalysis to the reduction of oxygen.

INTRODUCTION

The molten carbonate fuel cell (MCFC) is believed to be one of the most promising new energy conversion device that converts chemical energy in fossil fuels into electricity$^{[1-3]}$. Porous nickel has been used as the anode for MCFCs; its performance is relatively satisfactory, but still needs some improvements. For example, its corrosion resistance and electrocatalytic activity must be increased. Many efforts have been made to develop a novel anode material that is more stable than porous nickel. To date, Ni-Cr, Ni-Co or Ni-Cu alloys have been considered as possible anode materials$^{[4]}$. Nickel-niobium alloys have been shown to have the properties required of insoluble anodes$^{[5]}$ as well as excellent electrocatalytic activity$^{[6]}$. In this study, an attempt is made to produce
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 foil were used as anode and reference electrode. A eutectic mixture of NaF-CaF$_2$ (2:1 mol) was used as a solvent for electrochemical alloying of nickel with niobium at 900°C. Melt purification was performed as following: the bath was initially dehydrated by heating under a vacuum (1 Pa) for 24 h at 500°C, then melted under argon atmosphere at 900°C. Niobium (IV) ions were generated in situ by addition of potassium heptafluoro niobiate (V) and metallic niobium to the bath. The following reaction occurs:

$$4 \text{Nb}^V + \text{Nb} = 5 \text{Nb}^{IV}$$  \[1\]

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 could be expected [7].

The performance tests of nickel and nickel-niobium alloy were carried out in a melt of 62 mol% Li$_2$CO$_3$ - 38 mol% K$_2$CO$_3$ which is mostly used as electrolyte for MCFC at 650°C. In the test system, the electrode assemblies were composed of (i) a nickel-niobium surface alloy (working electrode), (ii) a gold foil (counter electrode), (iii) a platinum wire (reference electrode).

**RESULTS AND DISCUSSION**

**Preparation of Nickel-Niobium Surface Alloy**

Cyclic voltammetry can be employed to deduce whether one metal alloys with another one or not. It was found from the cyclic voltammogram of NbF$_7^{2-}$ in the fluoride melt (Fig.1) that the reduction wave corresponding to the formation of intermediate compound was observed at slightly positive potential (with respect to niobium...
reference electrode) on nickel compared with that on a molybdenum electrode. This revealed that niobium was unable to produce intermediate compound with molybdenum under existing condition. The experimental results were consistent with phase diagrams of nickel-niobium and molybdenum-niobium.

Niobium is more active than nickel in fluoride melt, therefore when the two metals were immersed in the bath and provided with a electrical connection, a galvanic cell occurred in which the reaction at the nickel cathode is the formation of the alloy Ni$_3$Nb. When the electrical circuit was closed the potential of the cathode versus the niobium reference was slight positive (5mV). According to the X-ray diffraction analysis, the composition of the surface alloy layer corresponds to Ni$_3$Nb compound. The result of SEM micrograph of the cross-section of the metallised nickel (see Fig.2) indicates that a uniform and adhesive surface alloy layer can be obtained on the nickel electrode by electrochemical alloying.

Corrosion Resistance of Nickel-Niobium Surface Alloy

In order to study corrosion resistance performance of nickel electrode modified by niobium (nickel-niobium alloy) in molten (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ at 650 °C, polarization measurements were employed to investigate the corrosion rates as well as reaction resistance of the two materials, nickel and nickel-niobium alloy. Fig.3 shows the cathodic and anodic polarization curves obtained at nickel and nickel-niobium alloy electrode respectively in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ at 650 °C. Fig.4 shows the micro-polarization measurements for nickel and nickel-niobium alloy carried out near their corrosion potentials. From the curves of Fig.3 and Fig.4 the reaction resistance, corrosion current density and corrosion rates of different materials in carbonate melt are shown in Table 1, in which abbreviated symbol mm/a means millimeter per year.

| Electrode | Corrosion current density / Am$^{-2}$ | Corrosion rate / mma$^{-1}$ | Reaction resistance /Ω |
|-----------|--------------------------------------|-----------------------------|-------------------------|
| Ni        | 0.16                                 | 0.17                        | 0.63                    |
| Ni-Nb     | 0.02                                 | 0.021                       | 21.7                    |

From Table 1 it is found that nickel-niobium alloy is superior to nickel in corrosion resistance in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ melt at 650 °C.
Electrocatalytic Activity of Nickel-Niobium Surface Alloy

In MCFC technology electrocatalytic activity for electrode materials is as important as corrosion resistance. Electrode materials utilized in MCFC are required to have good corrosion resistance and electrocatalytic activity. CO and H$_2$ have been employed almost exclusively as the fuel gas for MCFC in present, and at the negative electrode (anode), the fuel gas is oxidized, which may be written as:

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

$$CO + CO_3^{2-} \rightarrow 2 CO_2 + 2e \tag{3}$$

The anode functions as catalysts for the electrode reaction [2]-[3]. In this study, CO was selected as fuel gas to examine the electrocatalytic activity of anodic materials.

Fig. 5 shows anodic polarization curves obtained at different materials. It was evident that the polarization current obtained at nickel-niobium alloy was larger than that obtained at nickel electrode. For an electrode, the polarization current can be expressed as following:

$$I=knFACe^{-\frac{E_A}{RT}}(e^{-\frac{1+\alpha nF\eta}{RT}}, e^{-\frac{\alpha nF\eta}{RT}}) \tag{4}$$

Where $n$, $F$, $R$, $T$ and $\alpha$ have their usual significance. $k$, $A$, $C_n$, $E_A$ and $\eta$ are the frequency factor, the surface area of the electrode, the concentration, the activation energy and polarization overpotential respectively. Equation (4) can also be written in the form:

$$\ln \left[ \frac{I}{(e^{\frac{\alpha nF\eta}{RT}} - 1)} \right] = \ln (knFACe^{-\left(\frac{E_A}{RT}\right)}) - (\frac{\alpha nF\eta}{RT}) \tag{5}$$

The value of activation energy, $E_A$, can be estimated from the slope of the $\ln \left[ \frac{I}{(e^{\frac{\alpha nF\eta}{RT}} - 1)} \right] - 1/T$ plot. Fig.6 shows the relations between polarization current and temperature for different materials. From the curves of Fig.6 the activation energy $E_A$ are calculated as 52.5 and 41.5 kJ/mol for nickel and Ni-Nb surface alloy respectively. The activation energy decreases obviously with the deposition of niobium. It indicates that the deposition of niobium indeed caused the increase of the catalytic activity of the electrode. Thus it can be seen that as catalysts for the oxidation of CO nickel-niobium surface alloy is more effective than nickel.
Stability of Cathode Materials

The cleaned nickel foil and Ni-Nb surface alloy immersed in molten \((\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3\) at 650 °C, surrounded by oxygen atmosphere are preoxidized for 48 hours. The post preoxidation material analyzed by X-ray diffraction shows that the nickel electrode is oxidized and forms NiO, while the Ni-Nb surface alloy is also oxidized and forms the composite oxide NiO-Nb$_2$O$_3$. The p(CO$_2$)=0.67 atm, p(O$_2$)=0.33 atm are used for the cathode atmosphere of MCFC. The equilibrium solubility of the NiO electrode in molten carbonate at 650 °C is studied. Fig.7 shows the solubility curves of the two materials in molten \((\text{Li}_{0.62}\text{K}_{0.38})_2\text{CO}_3\) at 650 °C. From Fig.7 a and b the time for the dissolution of preoxidation Ni electrode (NiO electrode) in molten carbonate to reach to equilibrium needs 80 hours, and the equilibrium solubility is approximate 17 ppm, while the dissolution of post preoxidation Ni-Nb surface alloy electrode (NiO-Nb$_2$O$_3$ electrode) in molten carbonate to reach to equilibrium needs nearly 100 hours and the equilibrium solubility is only 8 ppm. This indicates that due to the nickel electrode surface modification, the Ni-Nb surface alloy is formed, so under preoxidation the formed composite oxide NiO-Nb$_2$O$_3$ can effectively inhibit the dissolution of NiO. It shows that not only the equilibrium solubility of NiO is largely reduced, but also the time required for NiO to reach to equilibrium is also delayed. Furthermore, the tests for electrocatalytic activity indicate that the oxidized Ni-Nb surface alloy is more effect than NiO on catalysis to the reduction of oxygen.

CONCLUSIONS

Polarization experiments reveal that corrosion resistance as well as electrocatalytic activity of the niobium-modified electrode (nickel-niobium surface alloy) is superior to that of an unmodified one. Surface modification of a MCFC anode by electrochemical alloying can be employed to improve the performance of the electrode material. The composite oxide formed by prexidation of Ni-Nb surface alloy can depress effectly the dissolution of nickel ions from NiO.

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Fig. 1  Voltammograms of NaF-CaF$_2$-K$_2$NbF$_7$ obtained at 900 °C on different cathode materials.
- Mo; ... Ni. scan rate=10mVs$^{-1}$.

Fig. 2  SEM micrograph of the cross-section of the metallided nickel.

Fig. 3  Cathode and anodic polarization curves for nickel and Ni-Nb alloy electrode in (Li$_{0.62}$K$_{0.38}$)$_2$CO$_3$ at 650 °C.
Fig. 4 Micro-polarization curves for different materials in the same system as Fig. 3 at 650 °C, area = 0.345 cm².

Fig. 5 Anodic polarization curves obtained at different electrode materials.

Fig. 6 Relations between polarization current and temperature for different electrode materials.

Fig. 7 The solubility curves of the post preoxidation of Ni and Ni-Nb surface alloy electrodes in molten in the same system as Fig. 3 at 650 °C.

\[ p(\text{CO}_2) = 0.67 \text{ atm} \quad \text{and} \quad p(\text{O}_2) = 0.33 \text{ atm} \]