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SHORT COMMUNICATION

Surface modification of a MCFC anode by electrodeposition of yttrium

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1. Introduction

Porous nickel has been used as the anode for MCFCs; its performance is relatively satisfactory, but still not perfect. For example its electrocatalytic activity, sintering resistance, creep resistance etc., must be increased. To date, Ni–Cr, Ni–Co or Ni–Cu alloys have been considered as possible anode materials. On the other hand, the effective catalytic characteristics of rare earth metals have made them recognized as potent alloying elements; for example, the possibility of lanthanide–nickel alloy as a hydrogen occlusion material. In this study, an attempt has been made to modify nickel anode surfaces by electrodepositing yttrium, to improve the anodic polarization behaviour of the nickel electrode. The result shows that the anodic polarization performance of the electrodes can be improved significantly by electrodeposition of yttrium. The improvement of anodic polarization behaviour of the modified nickel electrode appears to derive from improvement of the wetting properties of the electrode.

2. Experimental details

The apparatus consisted of a stainless-steel container with gas-tight stainless steel cap. Inside the former was placed a high-density alumina crucible of circa 500 ml capacity. This crucible contained the electrolyte as well as the working, counter and reference electrodes. The whole system was heated by means of a vertical electric furnace. The Li_2CO_3 and K_2CO_3 powder for the electrolyte were guaranteed grade chemicals (Wako Chemical Co.).

Nickel wires of 99.7% purity (Japan Lamp Industries Co.) of 1.0 mm diam. were used for preparation of the working electrodes. The nickel wire was modified by depositing 0.23–0.92 mg cm^{-2} yttrium on its surface in 55LiCl-36KCl-9NaCl(mol %) eutectic mixture electrolyte containing 1.2 mol % anhydrous YCl_3 at 500 °C using a constant current of 50 mA cm^{-2}. The deposited yttrium diffuses into the nickel electrode to form solid solution alloy. If the amount of deposited yttrium increases Ni–Y intermetallic compounds can be also formed, such as NiY, Ni_2Y, Ni_2Y_3, etc., but these kinds of Ni–Y intermetallic compounds are not stable in molten carbonate. The details of the modification procedure are described in a previous paper [1]. The upper part of the wire was covered with an alumina tube and sealed with ceramic sealant as shown in Fig. 1.

The reference electrode was the so-called standard 'oxygen electrode' [2] to which all potential values are referred unless otherwise noted. The counter electrode was of gold.

The anodic polarization curves of the working electrodes were measured under a H_2–CO_2 gas mixture (H_2:CO_2 = 80 : 20) atmosphere at a scan rate of 1 mV s^{-1}.

3. Results and discussion

Figure 2 shows anodic polarization curves of nickel electrodes deposited with various amounts of yttrium. The height of the part of the electrode above the electrolyte surface level (h) was 23 mm, and the part of the electrode immersed in the electrolyte was 7 mm. The anodic polarization characteristics of the electrodes modified by yttrium are improved significantly compared with those of the bare nickel electrode. Furthermore, the degree of improvement increases with the increase in the amount of deposited yttrium. However, the experiments show that deposition of more than 1 mg cm^{-2} yttrium on nickel electrodes results in the dissolution of the deposited yttrium into the MCFC electrolyte.

The improvement may be attributed to (i) the increase in electrode surface area caused by the deposition of yttrium; (ii) the increase in catalytic activity of the electrode; and (iii) the increase in electrode reaction area due to the increase of the meniscus zone. Each of these possibilities will be discussed in turn.

3.1. *Increase in electrode surface area*

Due to the electrodeposition of yttrium, the surface of the nickel electrode becomes rougher compared with that of the nonmodified electrode. This situation can be shown by a comparison of the surface SEM images of two nickel discs, one of which has been modified by yttrium in the same way as above. The SEM image of the cross section of the modified disc also shows that the deposit layer is dense. To simplify the calculation two assumptions are made: (i) the deposition of yttrium produces semispherical grains with a radius r, and (ii) these grains are distributed over the entire surface of the electrode. Let the surface area of the electrode before and after the deposition be S and S_{after}. Then

$$S_{\text{after}} = (S - N\pi r^2) + N2\pi r^2 = S + N\pi r^2 \qquad (1)$$

where N is the number of grains. Since

$$S \geq N\pi r^2 \qquad (2)$$

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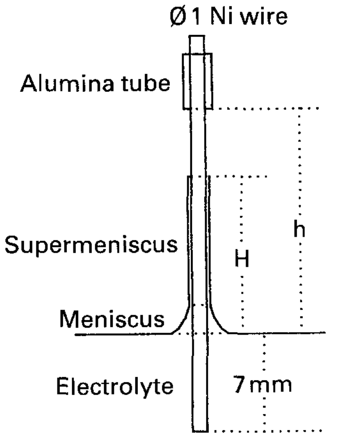

Fig. 1. Meniscus and supermeniscus film on a wire electrode.

the following relation is obtained:

$$S \leq S_{\mathrm{after}} \leq 2S \quad (3)$$

This means that the surface area of the nickel electrode increases as yttrium deposition proceeds and approaches twice the value compared with that before deposition if the grains completely occupy the whole surface. As shown later in Fig. 4, the surface increase factor caused by yttrium deposition is about 1.5–1.8. However, the increase in the anodic polarization current is much more than twice, as shown in Fig. 2. Therefore, it may be concluded that the improvement in anodic polarization behaviour results not only from the increase in electrode surface area.

3.2. *Increase in catalytic activity*

Considering the effective catalytic characteristics of rare earth metal and the possibility of lanthanide–nickel alloy to be a hydrogen occlusion material, it is very plausible that the modified nickel electrode surface possesses more active characteristics compared with the pure nickel electrode. For an electrode, the anodic current can be expressed in the form:

$$I = knFAC_{\mathrm{s}}e^{-E/RT}\left(e^{(1-\alpha)nF\eta/RT} - e^{-\alpha nF\eta/RT}\right) \quad (4)$$

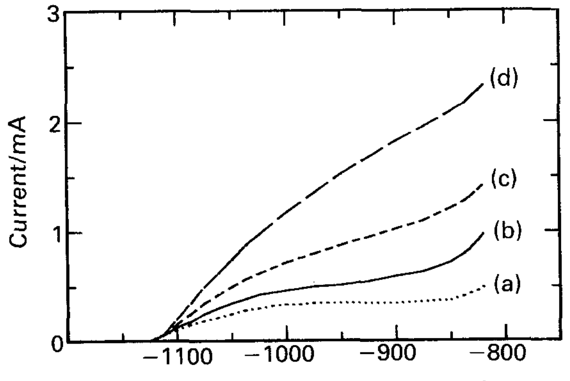

Fig. 2. Anodic polarization curves of modified nickel electrode and pure nickel electrode. Key: (a) ϕ1Ni, (b) ϕ1Ni + 0.23 mg Y cm^{-2}, (c) ϕ1Ni + 0.46 mg Y cm^{-2} and (d) ϕ1Ni + 0.92 mg Y cm^{-2}.

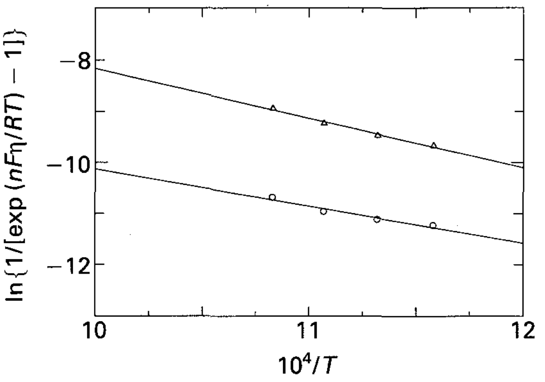

Fig. 3. The relationship between anodic polarization current and temperature for modified nickel electrodes. Key: (△) Ni + 0.92 mg Y cm^{-2} and (○) Ni.

where n, F, R, T and α have their usual significance. E, η, k, A and C_{s} are the activation energy, anodic polarization potential, the frequency factor, the surface area of the electrode and the concentration, respectively [3]. Equation 4 can also be written as an Allen–Hickling expression:

$$\ln\left[I/(e^{nF\eta/RT} - 1)\right] = \ln(knFAC_{\mathrm{s}}) - (\alpha nF\eta + E)/RT \quad (5)$$

Assuming that $\alpha = 0.5$ and does not change, even after deposition of yttrium, the value of activation energy, E, can be estimated from the slope $-(\alpha nF\eta + E)/R$ of the $\ln[I/(e^{nF\eta/RT} - 1)] - 1/T$ plot. The experiments were carried out at 650, 630, 610 and 590 °C, respectively. η was chosen as 220 mV. The results are shown in Fig. 3. The slopes for the pure nickel electrode and the modified nickel electrode with 0.92 mg cm^{-2} yttrium are -7.217×10^3 and -9.697×10^3 K, respectively. From the slopes, the activation energies E are calculated as 49.3 and 70.0 kJ mol^{-1}, respectively. It appears that the contribution to the improvement of the anodic polarization by the modified electrode does not derive entirely from the improvement of the catalytic activity by yttrium deposition. However, the proper situation might be more complicated, because the modification of the nickel electrode can cause a change in reaction mechanism, for example, from a consecutive reaction mechanism

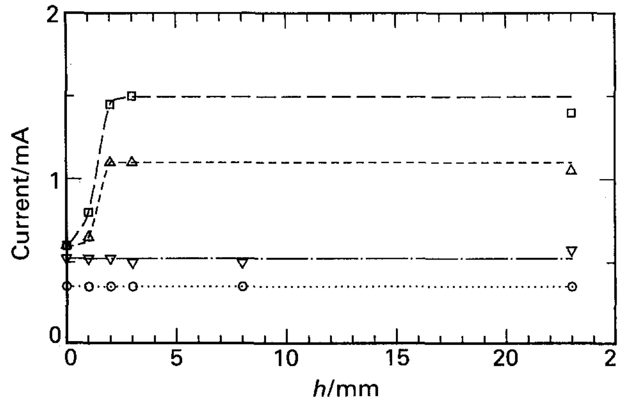

Fig. 4. The relationship between the current and the height of electrode above electrolyte. Key: (□) ϕ1Ni + 0.92 mg Y cm^{-2}, (△) ϕ1Ni + 0.46 mg Y cm^{-2}, (▽) ϕ1Ni + 0.23 mg Y cm^{-2} and (○) ϕ1Ni.

to a parallel reaction mechanism [4–9]. This would result in a change in α, and a change in α would affect the activation energy plot. But even a case of $\alpha = 1$, results in the activation energy E to be $59.4\,\mathrm{kJ\,mol^{-1}}$, which is still larger than that of the pure nickel electrode. The results given here will not be fully supportive for the catalytic energy change although further consideration is yet required.

3.3. *Increase of electrode reaction areas due to increased meniscus zone*

This is the probable reason for the improvement in anodic polarization behaviour of the modified nickel electrode. The wetting properties of electrode materials in molten carbonate are highly relevant to the performance of the porous electrodes. Pure nickel cannot be wetted well in molten carbonate: the contact angle is 50–60° in reducing atmosphere [10, 11]. The wettability of metals is influenced by their surface state and may be changed by addition of alloy elements [10]. Fisher and coworkers have reported that addition of proper alloy elements can improve the wettability of nickel effectively [10].

As shown in Fig. 1, a meniscus of electrolyte forms at the three phase interface when an electrode is partially immersed in an electrolyte, and it is possible that the electrolyte extends above the visible meniscus on the surface of the partially immersed electrode in the form of a very thin invisible film, i.e. a supermeniscus [12, 13]. The electrode surface in contact with the meniscus and the supermeniscus, if it exists, will contribute appreciably to the anodic reaction. Thus if the height of the electrode above the electrolyte surface level (h) is reduced to less than H, the total intrinsic height of two menisci (the meniscus and the supermeniscus), the formation of such menisci will be disturbed, then the reaction area will decrease, and so will the faradaic current. By adjusting the position of the alumina cover, and measuring the anodic current, I, of the electrode as a function of the height, h, of the electrode above the electrolyte surface level, the total height, H, of the menisci can be estimated from the breakpoint of the I–h plot. To eliminate the contribution from the part of the electrode immersed in the electrolyte, the length of that part was fixed at 7 mm. A full discussion of the distinction and determination of the meniscus and the supermeniscus is outside the scope of this work.

The I–h plots are shown in Fig. 4. The heights of menisci of the modified nickel electrodes with 0.92, 0.46 and $0.23\,\mathrm{mg\,cm^{-2}}$ yttrium deposition are 3, 2.5 and 0 mm, respectively. The effect of improvement in the wettability of nickel electrodes increases with increase in the amount of deposited yttrium. In the case of pure nickel electrodes, no meniscus was measured. When electrodes are completely immersed, the anodic polarization current for the modified nickel electrode was higher than that for pure nickel, due to the increase in surface area caused by yttrium deposition and the increase factor was about 1.5–1.8. In the case of partial immersion, above the level of the electrolyte, the most important factor for the increase in the anodic polarization current is the increase in the reaction surface area due to the formation of the menisci.

Special care must be taken in seeking to improve the wettability of porous nickel electrodes by depositing yttrium on its surface. If the porous electrode is wetted too much, all the pores will be filled with electrolyte, and the reaction area will decrease rather than increase. So the amount of deposited yttrium should be carefully controlled.

4. Conclusion

The anodic polarization behaviour of nickel electrodes can be improved by electrodepositing yttrium from molten chloride. The behaviour increases with increase in the amount of deposited yttrium in the range $0.23–0.92\,\mathrm{mg\,cm^{-2}}$. The improvement in anodic polarization behaviour is caused predominantly by improvement in the wettability of the electrode. The heights of meniscus of the modified nickel electrodes were measured indirectly and determined to be 2.5–3 mm, whereas the pure nickel electrode was found to be wetted poorly in molten carbonate under a H_2–CO_2 gas mixture ($H_2 : CO_2 = 80 : 20$).

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