

Mechanism of *in situ* surface modification of molten-carbonate fuel cell anode

Gang Xie, Keiko Ema and Yasuhiko Ito*

Department of Nuclear Engineering, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606 (Japan)

(Received November 5, 1990)

Abstract

The performance of the anode of a molten-carbonate fuel cell (MCFC) is improved by the addition of tungstate ion to the electrolyte. This effect is due to reduction of tungstate ion to produce tungsten metal on the porous nickel electrode under a hydrogen atmosphere. The total anode reaction is the sum of the following consecutive reactions: $W(O) = W(II) + 2e^-$ and $W(II) + H_2 + CO_3^{2-} = W(O) + H_2O + CO_2$.

Introduction

A key point in the development of electrode materials for molten-carbonate fuel cells (MCFCs) is improvement in both the power output and the stability. Porous nickel has been used as the anode for MCFCs; its performance is relatively satisfactory, but still not perfect. For example, the 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. We have suggested a different approach, namely, to modify the surface of the nickel anode by electrodeposition of either tungsten or tungsten carbide from an LiCl-KCl eutectic melt containing K_2WO_4 . Polarization experiments reveal that the performance of the tungsten-modified electrode is superior to that of an unmodified one. Furthermore, the mechanical properties are improved by deposition of tungsten metal on the surface of the porous nickel anode. Studies have also shown [1] that the behaviour of nickel anodes can be enhanced remarkably by simply adding K_2WO_4 to the molten carbonate electrolyte. The subject of this work is to discuss the mechanism of this effect.

Experimental

The electrolyte consisted of an Li_2CO_3 - K_2CO_3 eutectic melt ($Li_2CO_3:K_2CO_3 = 62:38$). The Li_2CO_3 , K_2CO_3 , and K_2WO_4 powders used in

*Author to whom correspondence should be addressed.

this study were guaranteed-grade chemicals (Wako Chemical Co., Ltd.). The eutectic mixture was vacuum dried for at least 48 h at 300 °C, and then melted at 650 °C under pure CO₂. The whole apparatus was pumped down to the carbonate decomposition pressure for degassing and removal of water vapor. The melt was then saturated with CO₂ by bubbling, to neutralize any O²⁻ formed and to decompose any OH⁻ present. Prior to experimentation at each new gas composition, saturation of the melt by the gas atmosphere was normally conducted overnight.

A nickel disc of 7.0 mm dia. and 3.0 mm thickness was used as the working electrode. The reference electrode employed was the so-called standard 'oxygen electrode' [2]. This consisted of a coiled gold wire dipping into the electrolyte and blanketed with a P_{O₂}/P_{CO₂}=0.33/0.67 gas mixture. Potentials are reported against the 'oxygen electrode', unless otherwise stated. A gold electrode was used as the counter electrode. All electrodes were degreased with acetone, washed with distilled water, and finally dried in an oven.

A potentiogalvanostat (Model HA-301, Hokuto Denko Ltd.) coupled with a function generator (Model HB-105, Hokuto Denko Ltd.) was used to control the potential. The potentiogalvanostat was also interfaced with a 16-bit personal computer (Model PC9801VX21, Nippon Electric Co. Ltd.). All data were processed by this computer. The *i*-*E* curves were recorded on an X-Y recorder (Model 3025, Yokogawa Ltd.).

Results and discussion

Figure 1 shows the voltammogram for nickel in an electrolyte without K₂WO₄. Peaks A and B are the anodic and cathodic breakdown of the carbonate melt, respectively. The oxidation of carbon deposit, the product of the cathodic breakdown of electrolyte, gives rise to peak C. A previous study [3] revealed that peaks D and E account for the formation of nickel oxide and a higher nickel oxide, respectively.

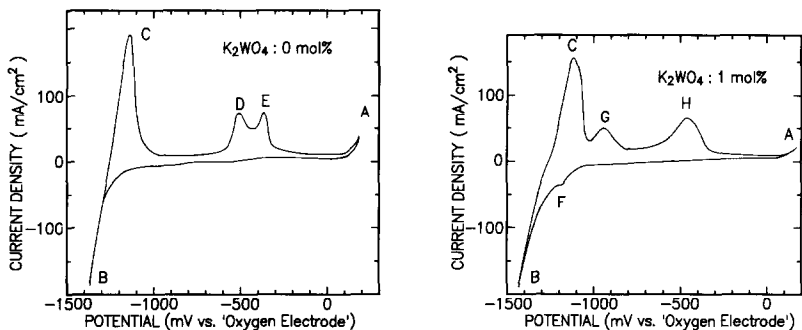


Fig. 1. Voltammogram for nickel under $P_{Ar}/P_{CO_2}=0.99/0.01$ at 650 °C (scan rate: 50 mV s⁻¹).

Fig. 2. Voltammogram for nickel under $P_{Ar}/P_{CO_2}=0.99/0.01$ at 650 °C with addition of 1 mol% K₂WO₄ (scan rate: 50 mV s⁻¹).

The voltammogram for nickel in the presence of 1 mol% K_2WO_4 is given in Fig. 2. Two new peaks, F and G, appear at about -1200 and -950 mV, respectively. Compared with the results of Fig. 1, it appears that these two new peaks are associated with reduction of tungstate and oxidation of the reduction product, respectively. In order to confirm this assertion, an investigation was made of the relationship between the limiting current density at peak F and (a) the square root of the scan rate, (b) the concentration of added K_2WO_4 . The data given in Figs. 3 and 4 show that the limiting current density is proportional to both these parameters. These observations indicate that peak F is indeed due to the reduction of tungstate. Furthermore, the results of Fig. 4 reveal that the saturation concentration of K_2WO_4 in molten carbonate is about 0.4 mol l^{-1} .

An XPS investigation was implemented to identify the reduction product of tungstate. Two samples were prepared under the same atmosphere (namely, $P_{Ar}/P_{CO_2} = 0.99/0.01$) by potentiostating nickel electrodes at -1200 and -1450 mV for 29 and 26 h, respectively. The findings (summarized in Table 1) confirm that peak F represents the deposition of tungsten metal. Consequently, peak G in Fig. 2 must correspond to oxidation of the tungsten deposit. Tungsten oxide was also detected because tungsten metal is easily oxidized to WO_3 in an oxygen atmosphere if the temperature is higher than 300°C . When samples were withdrawn from the electrolyte, some of the tungsten on the surface of the samples was oxidized to WO_3 in air. This is verified by the fact that the ratio of WO_3 to W decreases with increase in the sputtering period. X-ray diffraction patterns did not reveal the presence of either tungsten metal or tungsten oxide (Figs. 5 and 6). This suggests that the deposited tungsten layer is rather thin. The data also indicate that graphite can deposit along with tungsten in this potential range.

The voltammogram for a tungsten metal electrode obtained under the above mentioned atmosphere is shown in Fig. 7. Clearly, tungsten metal is quite unstable and starts to dissolve at a potential of about -1100 mV. From the relation between mass change and the charge passed during anodic

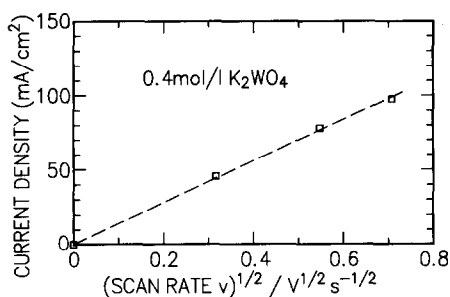


Fig. 3. Peak current density vs. square root of scan rate at peak F.

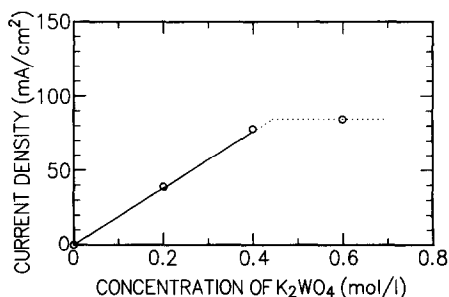
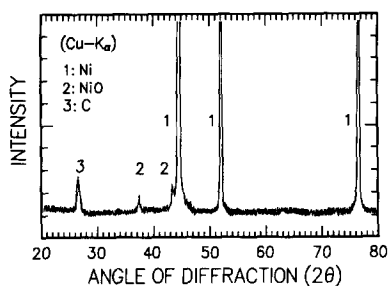
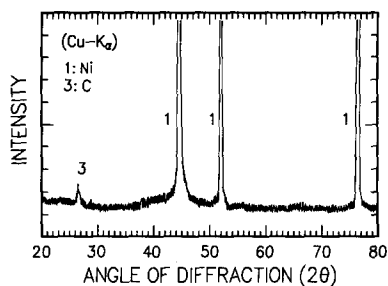
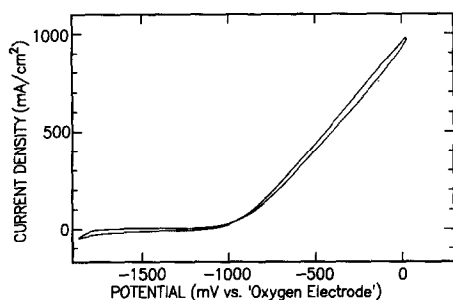


Fig. 4. Peak current density vs. concentration of added K_2WO_4 at peak F (scan rate: 300 mV s^{-1}).

TABLE 1

Results of XPS measurements

Sample no.	Preparation conditions	Sputtering period (min)	WO ₃ :W
1	Ar:CO ₂ : 100:1 potential: -1200 mV period: 29 h	2	82:18
		9	64:36
		15	61:39
		30	54:46
		50	53:47
2	Ar:CO ₂ : 100:1 potential: -1450 mV period: 26 h	0	100:0
		2	83:17
		7	59:41
		9	46:54
		15	40:60

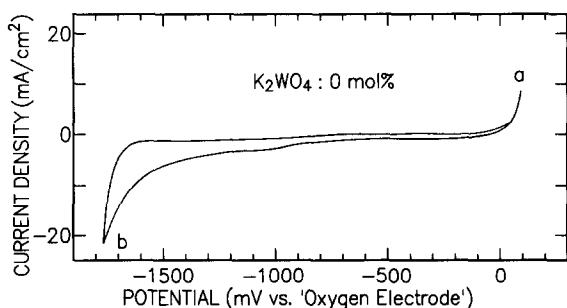
Fig. 5. XRD spectrum for nickel prepared at -1200 mV at 650 °C with addition of 3 mol% K₂WO₄.Fig. 6. XRD spectrum for nickel prepared at -1450 mV at 650 °C with addition of 3 mol% K₂WO₄.Fig. 7. Voltammogram for tungsten under $P_{Ar}/P_{CO_2}=0.99/0.01$ at 650 °C (scan rate: 50 mV s⁻¹).

dissolution of tungsten metal, tungsten is assumed to exist in molten carbonate in several valence states, from +2 to +6, with a potential dependency, Table 2. Unfortunately, the exact forms of these tungsten ions are not known.

TABLE 2

Relation between potential and valency of dissolved tungsten

Sample no.	Potential (mV)	Mass change (mg)	Charge passed (C)	Valency
1	-500	-209	630	5.8
2	-700	-470	1318	5.3
3	-800	-184	491	5.1
4	-1000	-19	37	3.6
5	-1100	-15	22	2.7

Fig. 8. Voltammogram for gold under $P_{Ar}/P_{CO_2}=0.99/0.01$ at $650\text{ }^\circ\text{C}$ (scan rate: 50 mV s^{-1}).

Similar to that found above for nickel, only one oxidation peak is detected for tungsten. By virtue of the influence of the reaction of the nickel electrode, there is a possibility that the other peaks concerned with the reaction of tungsten ions may be masked by the peaks associated with the nickel electrode. In order to simplify the situation, in place of nickel, a gold wire electrode was used to investigate the mechanism of the reaction of tungsten ions in molten carbonate. Figure 8 presents the background voltammogram for gold. The peaks, a and b, are due to the anodic and the cathodic breakdown of molten carbonate, respectively.

The voltammogram for gold in the presence of 3 mol% K_2WO_4 is shown in Fig. 9. Obviously, peak R is caused by the reduction of tungstate to tungsten, and peak A by the oxidization of tungsten. Peak T presents two possibilities: (1) the oxidation of tungsten carbide, the latter may deposit together with tungsten during the reduction reaction; (2) the oxidation of tungsten ion of an intermediate valence state. If case (1) is true, the same behavior should be observed when using a tungsten carbide electrode. Figures 10 and 11 show, respectively, the voltammograms for W_2C and WC under the same experimental conditions. Clearly, the behaviour is markedly different from that observed in Fig. 9. Thus, peak T is probably due to case (2), namely, the oxidation of some species of tungsten ion.

Reduction of tungstate is more difficult on gold than on nickel because of the higher overpotential for the reduction of tungsten ions. The potential

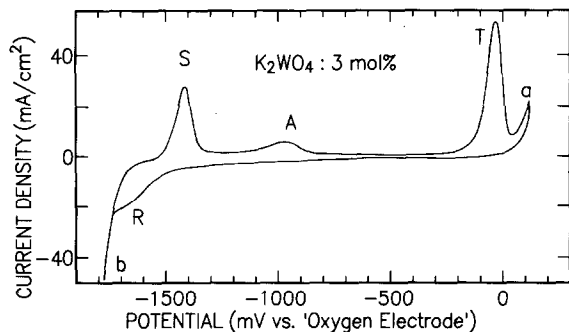


Fig. 9. Voltammogram for gold under $P_{Ar}/P_{CO_2} = 0.99/0.01$ at $650\text{ }^\circ\text{C}$ with addition of 3 mol% K_2WO_4 (scan rate: 50 mV s^{-1}).

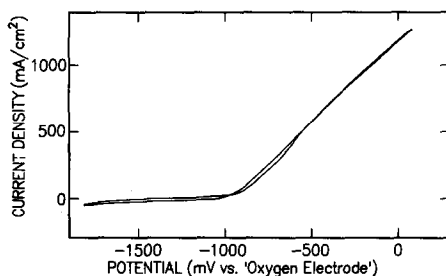
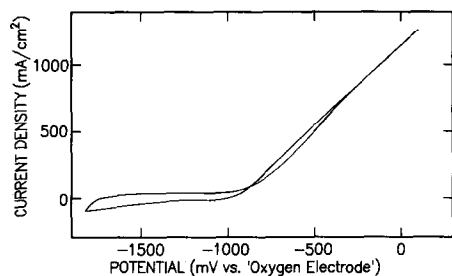


Fig. 10. Voltammogram for tungsten carbide under $P_{Ar}/P_{CO_2} = 0.99/0.01$ at $650\text{ }^\circ\text{C}$ (scan rate: 50 mV s^{-1}).

Fig. 11. Voltammogram for tungsten under $P_{Ar}/P_{CO_2} = 0.99/0.01$ at $650\text{ }^\circ\text{C}$ with addition of 3 mol% K_2WO_4 (scan rate: 50 mV s^{-1}).

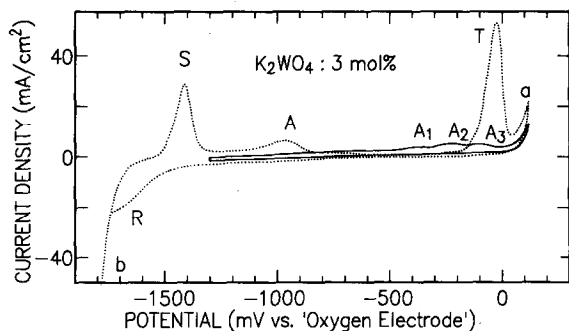


Fig. 12. Voltammogram for gold after electrolysis at -1300 mV under $P_{Ar}/P_{CO_2} = 0.99/0.01$ at $650\text{ }^\circ\text{C}$ with addition of 3 mol% K_2WO_4 (scan rate: 50 mV s^{-1}).

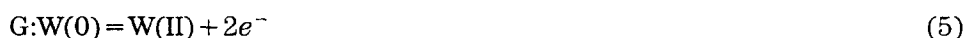
to reduce tungstate is about 500 mV more negative on gold than on nickel.

In order to obtain more information about tungsten ions of intermediate valence state, a linear stripping voltammetric technique was used. Figure 12

shows the typical cyclic voltammetric response after constant potential electrolysis at -1300 mV for 6 h with addition of 3 mol% K_2WO_4 to the electrolyte. For the purposes of comparison, the normal voltammogram recorded under identical experimental conditions (Fig. 9) is also given (dotted line). It can be seen that three anodic oxidation peaks (shown as A1, A2 and A3) are present at about -400 , -250 and -50 mV, respectively. These peaks are due to the formation of three kinds of tungsten ion of different valency. Clearly, peak A3 is identical with peak T. Taking into consideration that tungsten can exist in molten carbonate in several valence states, i.e., $+2$, $+3$, $+4$, and $+6$, and from the results above, the anodic oxidation of tungsten can be summarized as follows:



With a nickel electrode, it is reasonable to assume that oxidation of the tungsten deposit (peak G, Fig. 2) results in the formation of bivalent tungsten ions, as expressed by eqn. (1) above, i.e.,



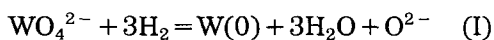
An MCFC anode usually works at a potential of about -900 mV. From Figs. 2, and 5, it can be seen that at, or around, this potential, tungsten will be oxidized to bivalent ions. Another fact is that tungstate ions are quite difficult to reduce electrochemically. For oxidation of hydrogen at the MCFC nickel anode, the anode reaction:



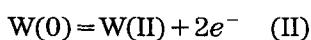
takes place slowly, and tends to be the controlling step of the whole process. This disadvantage limits the performance of the anode and therefore the power output of the MCFC. Experiments confirm that hydrogen gas can readily reduce tungstate to tungsten in molten carbonate, i.e.,



As a matter of fact, these results may represent the mechanism of the *in situ* catalytic activation effect described above. That is, first, tungstate is reduced by hydrogen:



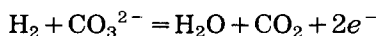
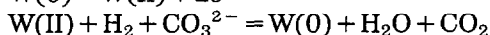
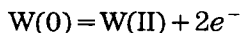
Then, the reduced tungsten is oxidized at the nickel anode to produce bivalent ions:



Next, the bivalent tungsten ions are again reduced to tungsten by hydrogen:



The anode reaction will be a cycle of steps of (II) and (III), and the total anode reaction may be expressed by:



The sequence also holds for a nickel electrode with a surface modified by the deposition of tungsten. The only difference is that step (I) is unnecessary.

Conclusions

The following conclusions can be drawn from the above investigations.

- (i) Tungsten dissolves in molten carbonate in several valence states from +2 to +6 with a potential dependency.
- (ii) Reduction of tungstate is quite irreversible.
- (iii) With addition of tungstate, the performance of an MCFC anode can be improved through indirect oxidation of hydrogen.
- (iv) Deposition of tungsten metal on the surface of a porous nickel anode also improves the mechanical properties of the anode.

Acknowledgement

The work was supported by a Grant-in-Aid from the Japanese Ministry of Education, Science, and Culture.

References

- 1 H. Yabe, Y. Ito, K. Ema and J. Oishi, *J. Power Sources*, 24 (1988) 207.
- 2 A. Borucka and C. M. Sugiyama, *Electrochim. Acta*, 13 (1963) 1887.
- 3 G. Xie, Y. Sakamura, K. Ema and Y. Ito, *J. Power Sources*, 32 (1990) 125.