SURFACE MODIFICATION OF NICKEL ELECTRODES
BY MOLTEN SALT ELECTROLYTIC PROCESSES

Yasuhiko Ito*, Hideki Yabe, and Keiko Ema

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

ABSTRACT

The surface of a porous nickel electrode has been modified by electrodeposition of either tungsten or tungsten carbide from molten halides. The electrode thus obtained shows high performance as an MCFC anode. The bare nickel electrode also operates well when a small amount of K₂WO₄ is added to the carbonate electrolyte, which is due to the result of in situ modification. High-performance hydrogen evolution cathode is also obtained by a similar modification process.

1. INTRODUCTION

It is well known that tungsten or tungsten carbide can be electrodeposited from molten halides [1 - 6]. In particular, electrodeposition of tungsten or tungsten carbide from halide melts containing WO₄²⁻ ion or the mixture of WO₄²⁻ ion and CO₃²⁻ ion seems so promising that several experimental studies of this reaction have been reported [7 - 9]. One of the applications of this electrodeposition reaction has been the surface modification of electrode materials, e.g., MCFC anode and hydrogen evolution cathode.

2. POROUS NICKEL ELECTRODE FOR MOLTEN CARBONATE FUEL CELLS

The molten carbonate fuel cell (MCFC) constitutes the second-generation of fuel cell technology and has many advantages in terms of fuel flexibility and system design[10-13]. The technology is directed towards large scale power generation that can utilize a wide variety of fossil fuels (including gasified coal, natural gas and alcohol) with high efficiency and low pollution.

In order to develop MCFC systems, many technological problems have to be solved through conducting strategic research programs. The development of suitable electrode
materials is vital: present materials severely limit both the lifetime and the performance of the cell. As a consequence, many investigations have been devoted to this area of endeavor. In order to develop an appropriate anode material for MCFCs, it is necessary to consider many factors, e.g., electrocatalytic activity, corrosion resistance, sintering resistance, creep resistance, etc. To date, Ni-Cr, Ni-Co, or Ni-Cu alloys have been considered as possible anode materials. A different approach, described here, is to modify the surface of the nickel anode by the electrodeposition of tungsten or tungsten carbide from molten halides [14].

2-1.EXPERIMENTAL

The experimental apparatus used to effect the electrodeposition is shown in Fig. 1. A gastight vessel, made of stainless steel, contained a high purity alumina or nickel crucible that could be raised or lowered. By this arrangement, electrodes that were fixed on the upper flange could be immersed in the molten electrolyte contained in the crucible. The electrolyte consisted of a LiCl-KCl eutectic melt (59 mol% LiCl, 41 mol% KCl) that was prepared under an argon atmosphere. All chemicals were of reagent grade (Wako Chemicals Co., Ltd.) and were dried under vacuum for several days at a temperature just below the melting point of the mixture. An Ag/Ag⁺ electrode or a platinum wire was used as the reference electrode. The former electrode comprised a silver wire and chloride that were both contained in a pyrex glass tube, which had a very fine tip. The potential of the electrode was calibrated against an alkali metal electrode, Li/Li⁺, that was electrodeposited on a nickel wire [15]. The electrode thus prepared exhibited good reproducibility. Unless otherwise stated, all potentials are reported with respect to the Li/Li⁺ reference electrode. The anode was made from glassy carbon. Sintered nickel-powder or nickel-fiber (porosity: 60-80%, mean pore size: 8 μm), placed inside an alumina tube, was employed as the cathode.

After melting the salt, vacuum-dried potassium tungstate or a mixture of potassium tungstate and potassium carbonate was added to a concentration of 0.02-0.1 mol%. The electrodeposition was conducted on the cathode at a temperature of 973 K and at a potential of 0.1-0.5 V or a current density of 100-300 mA cm⁻². After the electrolysis, 2-100 mg cm⁻² of tungsten or tungsten carbide was deposited on the electrode surface. The electrodeposited samples were removed from the vessel after several hours, washed with distilled water, dried, and kept in a desiccator. The samples were subjected to analysis using SEM, EPMA, EDX.
ESCA, RBS and X-ray diffraction techniques. The experimental apparatus used for polarization studies is shown in Fig. 2. The electrolyte comprised an Li$_2$CO$_3$-K$_2$CO$_3$ eutectic melt (62 mol% Li$_2$CO$_3$, 38 mol% K$_2$CO$_3$) contained in a high-purity alumina crucible. The electrolyte was dried under vacuum at just under its melting point for a few days. It was then melted under an argon atmosphere and maintained at the temperature of the experiment. An "oxygen electrode" [16] (O$_2$:CO$_2$=1:2) or platinum wire was employed as a reference electrode. The counter electrode was also an oxygen electrode. The working electrode (anode) was made from nickel (see above) and was housed in an alumina tube. Fuel gas (H$_2$:CO$_2$=4:1, after passing through water at 323 K) was introduced through the alumina tube. In order to effect in situ surface modification of the working electrode, K$_2$WO$_4$ was added to the molten carbonate electrolyte.

2-2. RESULTS AND DISCUSSION

Figure 3 shows an electron micrograph of a typical tungsten-coated electrode obtained at 0.1 V in a LiCl-KCl melt containing 0.1 mol% of K$_2$WO$_4$ at 973 K. Analysis showed that 13.2 mg cm$^{-2}$ of tungsten was deposited on the surface. An EPMA investigation revealed that small amounts of tungsten were uniformly deposited on the nickel substrate (Fig. 4). The deposit was identified as tungsten by X-ray diffraction analysis.

Figure 5 presents an electron micrograph of a typical tungsten carbide sample obtained at 0.2 V in a LiCl-KCl melt containing 0.1 mol% of K$_2$WO$_4$ and 0.1 mol% of K$_2$CO$_3$ at 973 K. A coating of 2.6 mg cm$^{-2}$ was found on the surface. EPMA studies showed (Fig. 6) small amounts of tungsten and carbon to be uniformly dispersed across the surface. Using X-ray diffraction, it was found that the deposit was composed of W$_2$C, WC and W. The results from EDX and RBS further confirmed that both tungsten and tungsten carbide were electrodeposited from the chloride melt onto the porous nickel substrate.

The results of polarization measurements conducted on an MCFC anode, modified by tungsten and tungsten carbide and immersed in molten carbonate, are presented in Fig. 7. In this figure, the apparent current density is plotted along the abscissa and the potential of the MCFC anode (vs. the oxygen electrode) on the ordinate. Curve (a) was obtained on a bare, sintered nickel-powder substrate (porosity: 60%), curve (b) on a sintered nickel-powder substrate (porosity: 60%) coated with tungsten, and curve (c) on a sintered nickel-fiber substrate (porosity: 80%) coated with tungsten. It can be seen that when modified by tungsten the MCFC exhibits good performance.
The polarization characteristics of a bare, sintered nickel-powder substrate (porosity: 60%) in molten carbonate containing 0.1 mol% tungstate ion are given by curve (d) in Fig. 7. This system was examined in order to study the effects of in situ surface modification in the MCFC electrolyte. The data show that this very simple treatment enhances the performance of the electrode.

After this in situ surface modification, a small amount of tungsten is deposited on the nickel powder substrate as shown in Fig. 8, which might explain the high performance of the electrode.

Curve (e) represents the polarization characteristics of the MCFC anode when modified by tungsten and tungsten carbide by adding 1.0 mol% of tungstate ion to the molten carbonate. This anode was obtained at 0.2 V in a LiCl-KCl melt containing 0.1 mol% $K_2WO_4$ and 0.02 mol% $K_2CO_3$ at 973 K. After the electrolysis, about 10 mg cm$^{-2}$ of tungsten plus tungsten carbide were deposited on the surface. This anode shows good electrical performance, greater durability, and enhanced resistance to corrosion. Other studies demonstrated that the electrodeposition of tungsten carbide alone increased the electrode durability, but did not improve the polarization characteristics.

2-3. CONCLUSIONS

The principal results obtained from the above experiments are summarized as follows.

(i) The electrodeposition of tungsten and tungsten carbide from molten chloride on porous nickel substrates has been achieved.

(ii) Polarization measurements show that the performance in molten carbonate electrolyte of an MCFC anode modified by tungsten is superior to that of its bare, porous nickel counterpart. However, similar improvement was not observed when the anode was modified by tungsten carbide.

(iii) The porous nickel electrode itself gives excellent performance as an MCFC anode when $K_2WO_4$ is added to the electrolyte. This may be due to the exertion of a catalytic effect by tungsten.

The above electrodes showed similar improvements in polarization and durability when tested with the electrolyte over a period of more than several hundred hours.
3. HYDROGEN EVOLUTION CATHODE

The development of a low overvoltage hydrogen evolution cathode is still an important research subject in the field of hydrogen energy systems, as well as the soda electrolysis industry. Namely, the development of a hydrogen cathode which shows low overvoltage and high corrosion resistance at high temperatures in high concentrations of caustic soda is still desired. In order to obtain new-type low overvoltage hydrogen evolution cathode, we have tried to apply our molten salt electrodeposition method to the surface modification of a cathode to be used for the hydrogen evolution reaction.

3-1. EXPERIMENTAL

The experimental apparatus used to effect surface modification is almost the same as that described before. Nickel and mild steel were used as electrode substrates onto which tungsten or tungsten carbide were electrodeposited. LiF-KF eutectic melt was used as the electrolyte. For an electrodeposition experiment, 0.1 mol% K₂WO₄ or a mixture of 0.1 mol% K₂WO₄ and 0.1 mol % K₂CO₃ were added to the electrolyte. Furthermore, for some experiments, 0.001 - 0.01 mol % of K₂PtCl₆ was added in an attempt to lower the hydrogen overvoltage. The experimental temperature was 973K.

The electrolytic cell used for overvoltage measurements is shown in Fig. 9. Aqueous 9N-NaOH was used as the electrolyte and the experimental temperature was kept at 60 - 80 °C. To minimize the concentration change or the effect of contamination, 50 % of the electrolyte was changed every few days.

3-2. RESULTS AND DISCUSSION

Figure 10 shows the overvoltages measured with bare nickel and mild steel electrodes. The results are in fair agreement with the results reported by other researchers. In this figure, large overvoltages of about 300 or 400 mV are observed in the high current density range.

Figure 11 shows the scanning electron micrograph of tungsten electrodeposited on the mild steel substrate. With this electrode, hydrogen overvoltage was measured. The result is shown in Fig. 12.

Compared with the results shown in Fig. 10, a drastic decrease of overvoltage is realized. Figure 13 shows the result obtained with the use of nickel electrode modified by
tungsten carbide. This modification was conducted by electrodepositing tungsten carbide from LiF-KF eutectic melt containing 0.1 mol% K$_2$WO$_4$ and 0.1 mol% K$_2$CO$_3$ at 200 mA/cm$^2$. The polarization characteristics are better than those obtained with the use of bare nickel substrates but worse than those obtained with mild steel substrates. From these results, although some improvement can be effected by surface modification with tungsten or tungsten carbide, much more improvement is still required. So, in anticipation of some significant improvement in overpotential, a small amount of K$_2$PtCl$_6$ was added to the electrolyte. As shown in Fig. 14, a drastic change in morphology is observed. Hydrogen overvoltage was measured by using this electrode. The result is shown in Fig. 15.

Much improvement in performance is observed in this figure. From a duration test, the high performance of the tungsten-platinum modified electrode was confirmed for a longer-term electrolysis. Figure 16 summarizes the polarization characteristics obtained by using electrodes prepared by several methods.

The practical effect of platinum addition (1/100 of tungsten) is significant even though the mechanism leading to this improved performance is not so clear yet.

3-3. CONCLUSIONS

The principal results obtained from the above experiments are summarized as follows.

(i) The polarization characteristics of nickel and mild steel cathodes were improved by electrodepositing tungsten film on the surfaces of the materials from LiF-KF eutectic melt containing WO$_4$$^{2-}$.

(ii) A drastic morphology change was observed when very small amounts of platinum are codeposited during the electrodeposition of tungsten.

(iii) The tungsten-platinum modified electrode thus obtained showed significantly improved performance as a low overvoltage hydrogen evolution cathode.

4. CONCLUSIONS

As described above, the surface modification of electrodes by molten salt electrolytic processes (including in-situ surface modification in a molten salt system) is promising, though there remains further problems for the implementation of this process on an industrial scale.

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Fig. 1. Experimental apparatus for electrodeposition studies. A: thermocouple; B: zirconia electrode; C: Li/Li+ electrode; D: counter electrode(anode); E: working electrode(cathode); F: reference electrode; G: gas inlet; H: gas outlet.

Fig. 2. Experimental apparatus for polarization studies in molten carbonate. A: thermocouple; B: zirconia electrode; C: counter electrode("oxygen electrode"); D: platinum wire; E: nickel wire; F: reference electrode("oxygen electrode"); G: working electrode(MCFC anode); H: gas inlet; I: gas outlet.

Fig. 3. Electron micrograph of electrodeposited tungsten on sintered nickel powder substrate.
Fig. 4. EPMA of the electrodeposited tungsten sample shown in Fig. 3.

Fig. 5. Electron micrograph of electrodeposited tungsten carbide on sintered nickel powder substrate.

Fig. 6. EPMA of the tungsten carbide sample shown in Fig. 5.
Fig. 7 Polarization curves for electrodes in the Li$_2$CO$_3$-K$_2$CO$_3$ eutectic, 923K.
(a) Sintered nickel powder;
(b) Sintered nickel powder modified by tungsten (Fig. 3);
(c) Sintered nickel fiber modified by tungsten;
(d) Sintered nickel powder;
(e) Sintered nickel powder modified by tungsten and tungsten carbide.

Fig. 8. Electron micrograph of the electrode

(a) Sintered nickel powder (b) After in situ surface substrate (porosity 60%, modification mean pore size: 8μm).

Fig. 9. Schematic diagram of the cell used for hydrogen overvoltage measurements.

A: Ar Outlet
B: Stirrer
C: Thermometer
D: Counter Electrode
E: Reference Electrode
F: H$_2$ Outlet
G: H$_2$ Inlet
H: Working Electrode
I: Ar Inlet
J: Water Bath
Fig. 10. Hydrogen overvoltage at several electrodes (9N NaOH, 80°C).

Fig. 11. Electron micrograph of tungsten

Fig. 12. Hydrogen overvoltage of the nickel electrode modified by tungsten under various conditions.

Fig. 13. Hydrogen overvoltage of the nickel electrode modified by tungsten carbide (9N NaOH, 80°C).
Fig. 14. Electron micrograph of tungsten-platinum (LiF-KF, K$_2$WO$_4$:0.1mol%, K$_2$PtCl$_6$:0.001mol%, deposition potential:0.2V vs. Li,K/Li$^+$/K$^+$ at 973K).

Fig. 15. Hydrogen overvoltage of the nickel electrode modified by tungsten-platinum under various conditions (9N NaOH, Fig. 13. sample).

Fig. 16. Hydrogen overvoltage at several electrodes (9N NaOH, 80°C).