

SURFACE MODIFICATION OF NICKEL ELECTRODES FOR MOLTEN CARBONATE FUEL CELLS

HIDEKI YABE, YASUHIKO ITO*, KEIKO EMA and JUN OISHI

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

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Summary

The surface of a porous nickel electrode is modified by electrodeposition of either tungsten (from an LiCl-KCl eutectic melt containing K_2WO_4) or tungsten and tungsten carbide (from a mixture of K_2WO_4 and K_2CO_3 at 973 K). Polarization curves show the performance of the tungsten-modified electrode to be superior to that of its bare counterpart. However, the bare nickel electrode operates well as an anode for molten carbonate fuel cell systems when a small amount of K_2WO_4 is added to the electrolyte. This behaviour is considered to be the result of *in situ* modification of the electrode surface

Introduction

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 [1 - 4]. 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 programmes. 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 endeavour (*e.g.*, refs. 4, 5). 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.

*Author to whom correspondence should be addressed

A different approach, described here, is to modify the surface of the nickel anode by electrodeposition of tungsten or tungsten carbide from molten halide

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 an 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 a reference electrode. The former electrode comprised a silver wire and silver 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 [6]. 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.

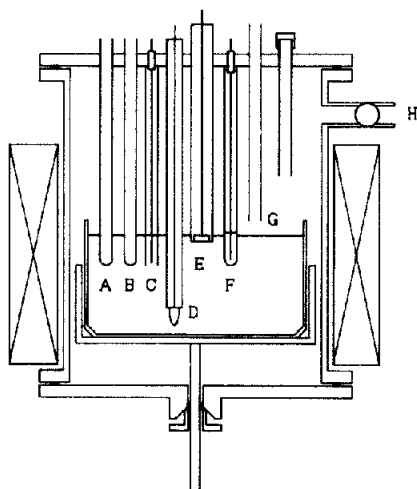


Fig 1 Experimental apparatus for electrodeposition studies. A thermocouple, B zirconia electrode, C Li/Li⁺ electrode, D counter electrode (anode), E working electrode (cathode), F reference electrode, G gas inlet, H gas outlet

After melting the salt, vacuum-dried potassium tungstate or a mixture of potassium tungstate and potassium carbonate was added at 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 Li₂CO₃-K₂CO₃ eutectic melt (62 mol% Li₂CO₃, 38 mol% K₂CO₃) contained in a high-purity alumina crucible. The electrolyte was dried under vacuum at just under the 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" [7] (O₂/CO₂ = 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 (H₂/CO₂ = 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, K₂WO₄ was added to the molten carbonate electrolyte.

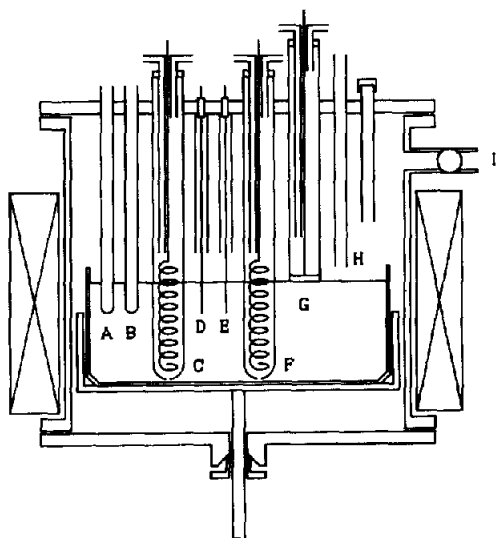


Fig 2 Experimental apparatus for polarization studies in molten carbonate. A thermocouple, B zirconia electrode, C counter electrode ("oxygen electrode"), D platinum wire, E nickel wire, F reference electrode ("oxygen electrode"), G working electrode (MCFC anode), H gas inlet, I gas outlet

Results and discussion

Figure 3 shows an electron micrograph of a typical tungsten-coated electrode obtained at 0.1 V in an LiCl–KCl melt containing 0.1 mol% of K_2WO_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). Note, the deposit was identified as tungsten by X-ray diffraction analysis.

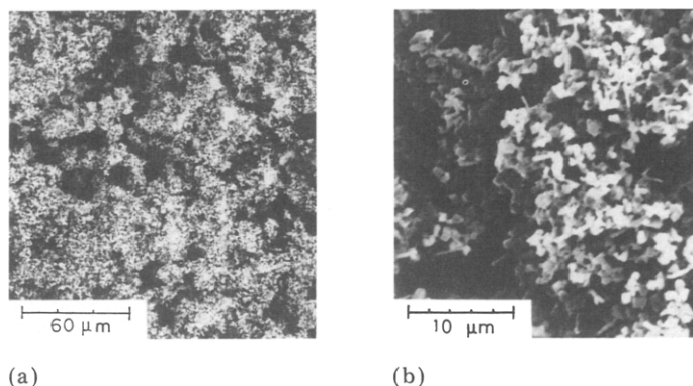


Fig. 3 Electron micrograph of electrodeposited tungsten on sintered nickel powder substrate

Figure 5 presents an electron micrograph of a typical tungsten carbide sample obtained at 0.2 V in an LiCl–KCl melt containing 0.1 mol% of K_2WO_4 and 0.1 mol% of K_2CO_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_2C , WC and W. The results from EDX and RBS further confirmed that both tungsten and tungsten carbide were electro-deposited 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 “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-fibre substrate (porosity 80%) coated with tungsten. It can be seen that when modified by tungsten the MCFC exhibits good performance.

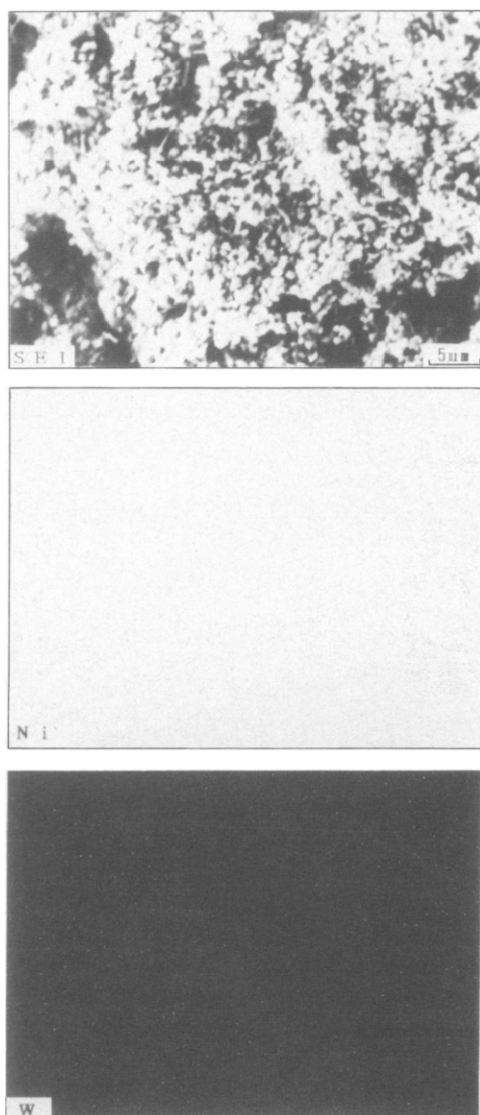
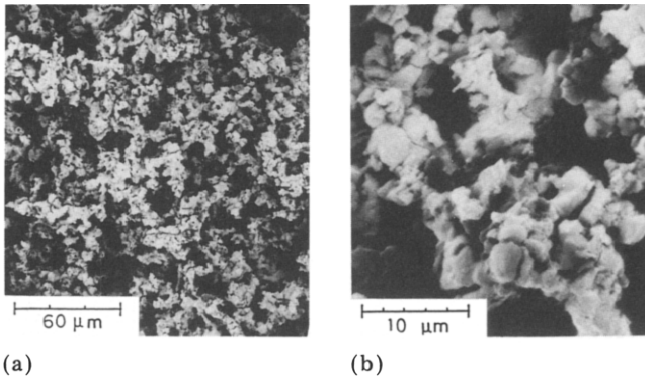


Fig 4 EPMA of electrodeposited tungsten sample shown in Fig 3

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.

Curve (e) represents the polarization characteristics of the MCFC anode when modified by tungsten and tungsten carbide by adding 1.0 mol% of



(a) (b)
Fig 5 Electron micrograph of electrodeposited tungsten carbide on sintered nickel powder substrate

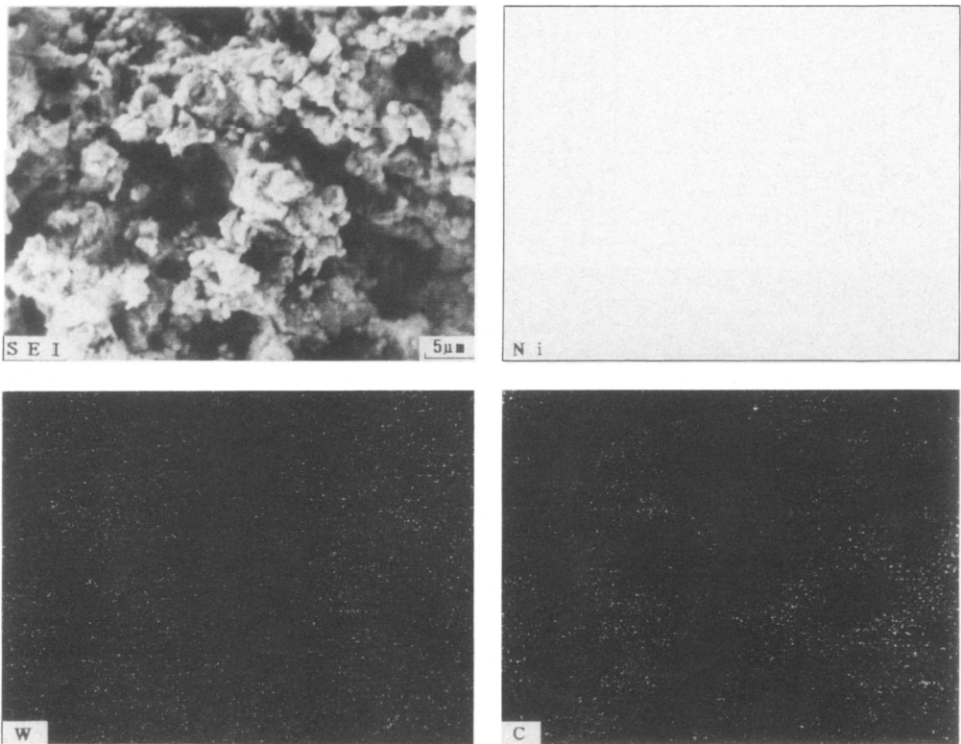


Fig 6 EPMA of tungsten carbide sample shown in Fig 5

tungstate ion to the molten carbonate. This anode was obtained at 0.2 V in an 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

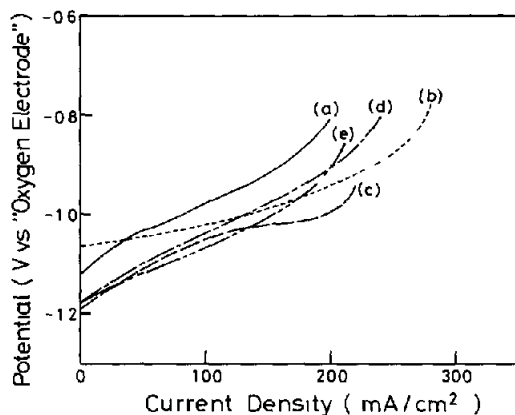


Fig 7 Polarization curves for electrodes in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic, 923 K (a) Sintered nickel powder, (b) sintered nickel powder modified by tungsten (Fig 3), (c) sintered nickel fiber modified by tungsten, (d) sintered nickel powder, (e) sintered nickel powder modified by tungsten and tungsten carbide

performance, greater durability, and enhanced resistance to corrosion. Other studies demonstrated that electrodeposition of tungsten carbide alone increased electrode durability but did not improve the polarization characteristics

Conclusions

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

(i) 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 tungsten exerting a catalytic effect.

The above electrodes when tested with the electrolyte showed similar improvement in polarization and durability over more than several hundred hours [8].

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