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Materials Chemistry and Physics 45 (1996) 238–242

MATERIALS
CHEMISTRY AND
PHYSICS

Oxygen reduction behavior with silver alloy catalyst in alkaline media

Hong-Ki Lee [a], Joong-Pyo Shim [b], Mi-Ja Shim [c], Sang-Wook Kim [d], Ju-Seong Lee [b]

[a] *Department of Chemistry, College of Natural Science, Woosuk University, 490 Hujeong-Ri, Samrye-Eup, Wanju-Kun, Chonbuk 565-701, South Korea*
[b] *Department of Industrial Chemistry, College of Engineering, Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul 133-791, South Korea*
[c] *Department of Life Science, College of Liberal Arts and Natural Science, Seoul City University, 90 Jeonnong-Dong, Dongdaemun-Ku, Seoul 130-743, South Korea*
[d] *Department of Chemical Engineering, College of Engineering, Seoul City University, 90 Jeonnong-Dong, Dongdaemun-Ku, Seoul 130-743, South Korea*

Received 16 December 1994; accepted 22 November 1995

Abstract

The electrochemical characteristics of silver catalyst impregnated on carbon black at the oxygen electrode for an alkaline fuel cell were studied. The electrode containing 30 wt.% silver catalyst showed a current density equivalent to that of Pt catalyst. To improve the catalytic activity and electrode performance, silver was bimetallized with Mg and the alloy state was confirmed by X-ray diffraction. When the atomic content of Ag–Mg alloy was 3:1, it showed the highest current density. A decrease in the corrosion potential at the electrode was found by the catalytic effect of silver. The contact of carbon and silver caused a decrease in the reaction sites of silver and the electrolyte, and hence the dissolution potential of silver was increased. Because the fuel cell was operated at an overpotential of 100–300 mV, the dissolution of silver was not important.

Keywords: Oxygen reduction; Silver catalyst; Electrode performance; Alkaline fuel cells; Silver alloy

1. Introduction

Since the first oil crisis in 1973, most developed countries have attempted to reduce their energy dependence on petroleum by diversification of their primary energy sources. In addition, clean energy systems are in demand as environmental interest has increased significantly; the automobile industry is particularly affected because NO_x emissions cause air pollution, including acid rain. The fuel cell is an electrochemical energy conversion apparatus for changing chemical energy into electrical energy directly. Whereas the energy efficiency of most power generation is about 30% due to the limitations of the Carnot cycle, the fuel cell system has a value of over 50–60%, and thus the total efficiency is increased around 80% if combination of waste heat is adapted [1–3].

The oxygen reduction kinetics is more rapid in alkaline electrolyte than in acid electrolyte, and the voltage is dependent on the concentration of hydroxide ions accumulated in the electrode. Because Pt or silver catalysts cause hydroxide ions to decompose rapidly, these metals are able to increase the potential of the oxygen electrode and approach the theoretical potential. The cost of the catalyst depends on the impregnated metals, and most studies have focused on the expensive Pt catalyst for the oxygen electrode materials in alkaline fuel cells. However, silver catalyst shows good oxygen reduction activity and causes rapid hydroxide ion decomposition, and it has been studied as a substitute for Pt because of the mild conditions of electrolyte and operating temperature in AFC [4–7]. Raney silver with gold or doped Ag with Bi, Ni, Ti has been reported to improve oxygen reduction performance. However, a large amount of silver is required because of its low catalytic activity [8,9]. Silver catalyst impregnated on carbon black has been utilized to diminish the amount of silver and to increase its catalytic surface area [10].

In this study, the characteristics of oxygen reduction at Ag/C (Ag impregnated on carbon) and Pt/C (Pt impregnated on carbon) electrodes in alkaline media were studied. To improve the oxygen reduction capability, Ag–M/C (impregnated Ag–M alloy on carbon) was mnufactured and the effects of the alloy on the electrode performance were investigated. In addition, the corrosion behavior of silver and carbon was studied at various potentials.

2. Experimental

2.1. Materials

Polytetrafluoroethylene (PTFE) for the binder was Teflon 30J from Du Pont, and KOH from Shinyo Co. was used as

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the electrolyte. $AgNO_3$, the surfactant, and other reagents were obtained from Aldrich. The carbon paper for the gas diffusion layer was type TGP-H-060 (thickness: 0.2 mm; porosity: 72%) from Toray, and the carbon black was Vulcan XC-72 (specific surface area: 254 m^2 g^{-1}) obtained from Cabot.

2.2. Preparation of the catalyst

Platimum impregnated on carbon black (Pt/C) was prepared by the reduction of $H_2PtCl_6 \cdot 6H_2O$ to Pt metal with a reducing agent ($Na_2S_2O_4$), which is known as the colloidal method. The reduced Pt particles combined with free sulfur from the reducing agent to form sulfur sol of the Pt–S type. These compounds were adsorbed on carbon to prepare Pt catalysts a few angstroms in size. The amount of Pt impregnated on carbon black was 10 wt.%.

For the preparation of Ag/C, as shown in Fig. 1, a silver colloidal solution was obtained from the mixture of $AgNO_3$ and reducing agent ($NaBH_4$) to which was added sodium dodecylbenzenesulfonate (SDBS). The silver colloidal solution obtained was added to the carbon dispersion solution, and silver was impregnated on carbon black by agitation. The amount of impregated silver catalyst was 30 wt.% on carbon black.

For the alloy of silver with Mg, $AgNO_3$ and $MgCl_2$ were dissolved in NH_3 solution before being added to the carbon dispersion solution. Silver and metals were impregnated on carbon black as salts by the above-mentioned procedure. In a reducing atmosphere, Ag–Mg was sintered at 900 °C for 1 h to be impregnated as the Ag–M alloy on carbon black. After the impregnation on carbon black, the silver alloy catalyst was treated for 24 h in alkaline solution to eliminate the unreacted metals.

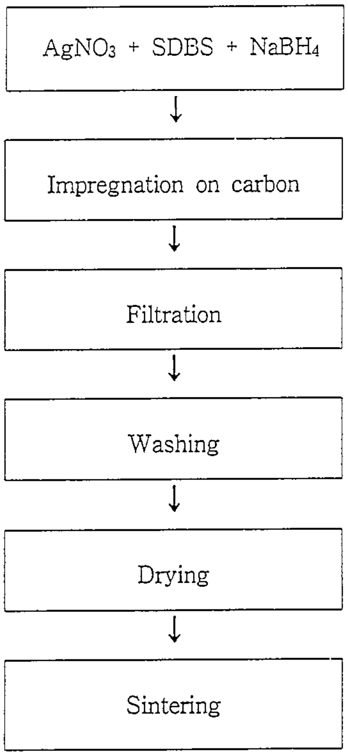

Fig. 1. Diagram of the manufacturing process of Ag/C by the colloidal method.

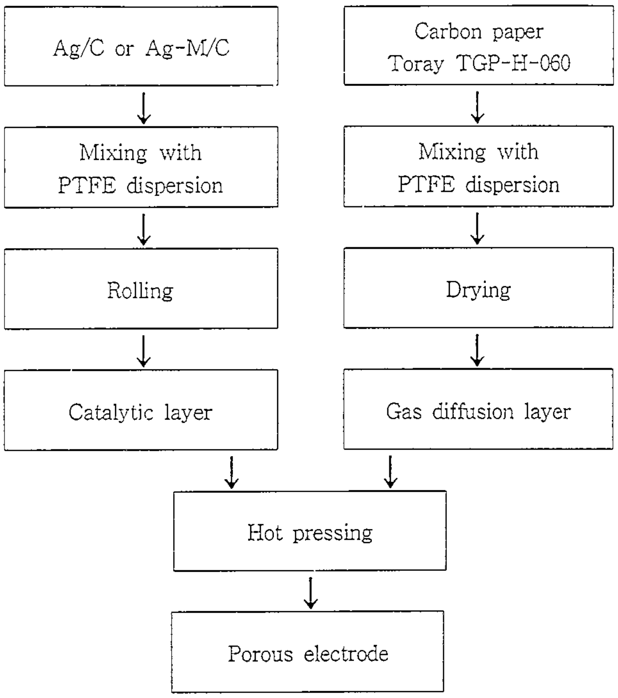

Fig. 2. Diagram of the manufacturing process of the porous electrode.

2.3. Manufacture of the porous electrode

The electrodes were manufactured by adhering the catalytic layer and the gas-diffusion layer. The catalytic layer served as the reaction site at the three-phase zone consisting of the electrolyte, supplied gas and catalysts. The gas-diffusion layer supplies the gas to the catalytic layer. The catalytic layer was prepared by binding the catalyst with PTFE using the rolling method, and the gas-diffusion layer was prepared with carbon paper containing 40 wt.% PTFE. The process for manufacturing the porous electrode is illustrated in Fig. 2.

3. Results and discussion

3.1. Electrode performance of Pt/C and Ag/C

The catalytic activity of Pt/C and Ag/C was compared with the electrode performance. The time required to reach the equilibrium electrode potential is shown in Fig. 3. The Pt/C electrode showed a saturation potential at an early stage, before 1 h, by its good catalytic activity, and the Ag/C electrode showed an equivalent value after 2 h. The fact that the electrode manufactured with Pt/C was faster than the Ag/C electrode indicates that the catalytic activity of Pt/C was higher than that of Ag/C. To confirm the possibility of substituting silver catalyst instead of platinum catalyst, the current density of each electrode was investigated, and the results

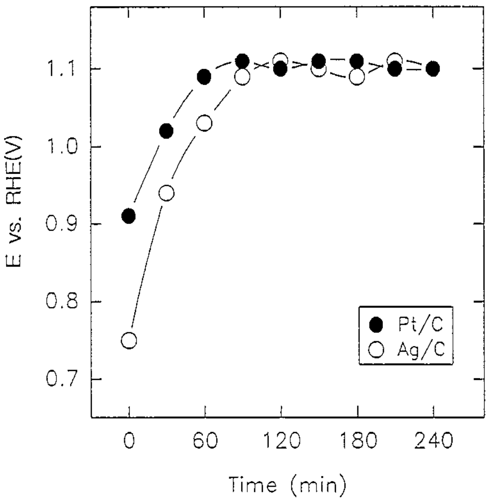

Fig. 3. Potential of the oxygen electrode according to the operating time for Pt/C (10 wt.%) and Ag/C (30 wt.%).

are given in Fig. 4. At an overpotential of 300 mV, the Pt/C electrode and the Ag/C electrode showed the same current density after 2 h.

3.2. Effect of sintering and electrode thickness

The effect of sintering on electrode performance was studied (Fig. 5). By the agglomeration of silver particles on carbon during heat treatment at 1000 °C, lower electrode performance was found owing to an increase in the silver particle size and a decrease in the surface area. Using the same electrode manufacturing process, the electrode thickness can be affected only by the catalyst loading amount. An increase in the amount of catalyst led to the creation of more reactive sites, and the current density should show a higher value. However, the electrode performance showed the highest current density for a 0.8 mm electrode and diminished again despite the large catalyst amount. The increase in the electrode thickness prevented the diffusion of fuel gas and the diluted electrolyte at the electrode (Fig. 6).

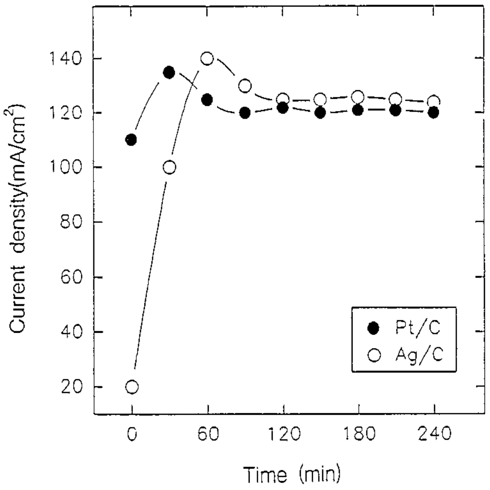

Fig. 4. Current density of the oxygen electrode according to the operating time. Overpotential: −300 mV, Pt/C (10 wt.%), Ag/C (30 wt.%).

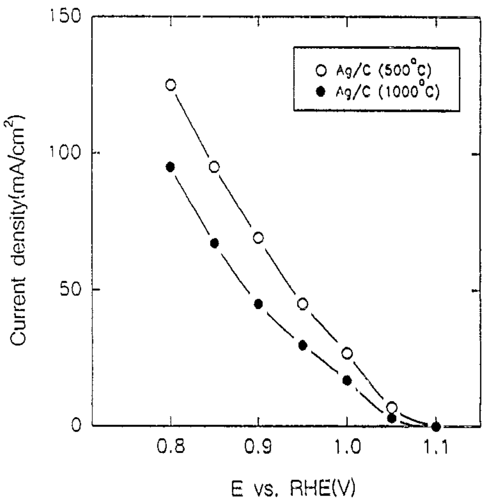

Fig. 5. Polarization curve of the Ag/C electrode according to the sintering temperature.

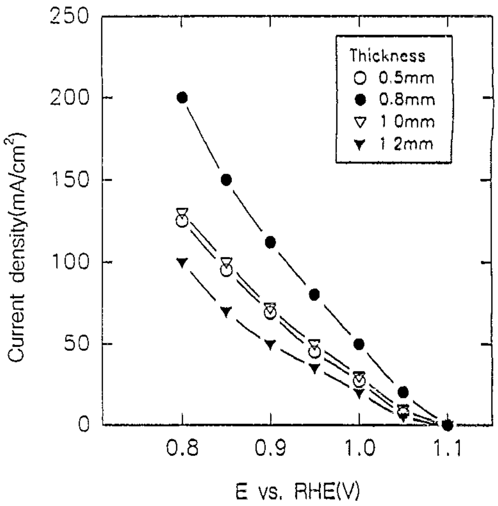

Fig. 6. Polarization curve of the Ag/C electrode for various electrodes.

3.3. Catalytic activity of Ag–M alloy/C

Ag–Mg alloy was impregnated on carbon black at different Ag:Mg ratios (1:1, 3:1, 1:3) and the characteristic peaks of the X-ray diffraction pattern were distinguished; the results are shown in Fig. 7. In addition, the results for the alkaline treatment to eliminate unreacted materials are illustrated in Fig. 8. In Ag–Mg (1:1), the characteristic peak of AgMg appeared at 43.28°. In Ag–Mg (3:1), the peaks of Ag_3Mg overlapped with the Ag peaks. In Ag–Mg (1:3), the peaks of $AgMg_3$ were seen at 43° and 62.44°. After the alkali treatment, the $AgMg_3$ peaks disappeared but the peaks corresponding to AgMg and Ag_3Mg remained.

3.4. Electrode performance

The electrode performance depends on the activity and the structure of the catalyst material itself. In order to compare the characteristics of the Ag–M alloy catalyst, the catalytic activity improvement and the structure of the silver catalyst according to the alloy of Ag–M should be investigated. As

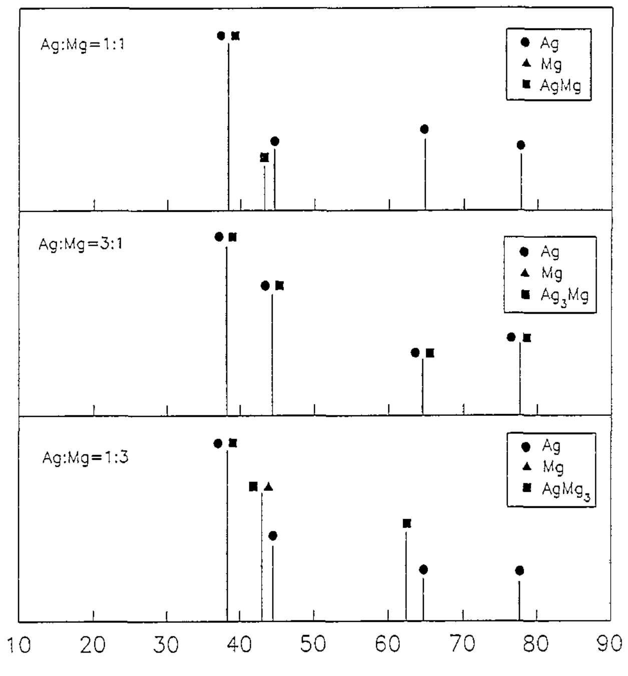

Fig. 7. XRD patterns of Ag–Mg/C (before alkali treatment).

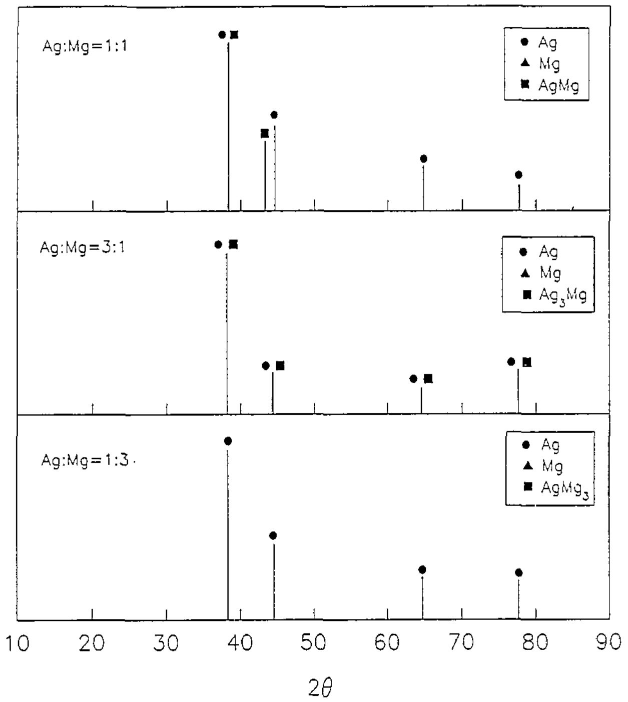

Fig. 8. XRD patterns of Ag–Mg/C (after alkali treatment).

shown in Fig. 9, the current densities of the Ag–Mg electrodes manufactured from the different silver alloy formations, which were obtained for various ratios of silver and Mg, showed the order 3:1 > 1:1 > 1:3; there was an almost similar tendency shown by the results for Ag–Ba, but the electrode of Ag–Mg (3:1) showed higher a current density than the Ag–Ba (5:1) electrode. From these results, it is assumed that the silver catalyst containing Mg shows the highest catalytic activity at the oxygen electrode in an alkaline fuel cell.

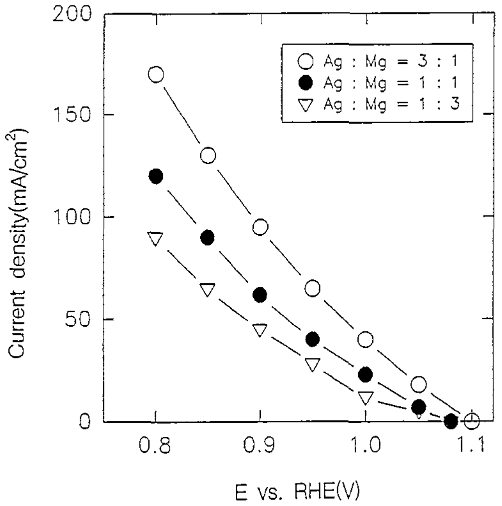

Fig. 9. Polarization curve of the Ag–Mg/C electrode.

3.5. *Effect of PTFE on the corrosion of the Ag/C electrode*

The polarization curve of silver electrode and the effect of PTFE, which was mixed in as a binder to serve the appropriate structure of the electrode, were investigated in 6 N KOH solution at 25 °C, and the results are shown in Fig. 10. If dissolved oxygen exists in solution, the following reactions could occur [11]:
anode reaction:

$$4Ag + 6OH^- = 4Ag(OH)_2^- + 4e^- \qquad (1)$$

cathode reaction:

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (2)$$

total reaction:

$$4Ag + O_2 + H_2O + 4OH^- = 4Ag(OH)_2^- \qquad (3)$$

The equilibrium electrode potential was 1.075 V (versus RHE), and as the amount of dissolved oxygen was increased,

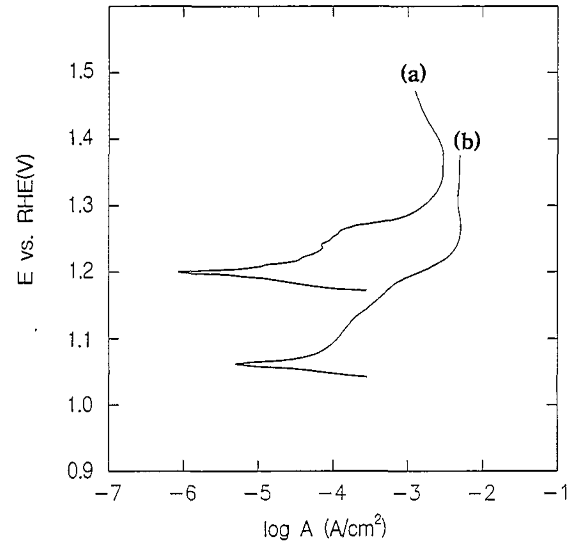

Fig. 10. The potentiodynamic anodic polarization curves of the Ag and Ag + PTFE electrodes: (a) Ag + PTFE; (b) Ag.

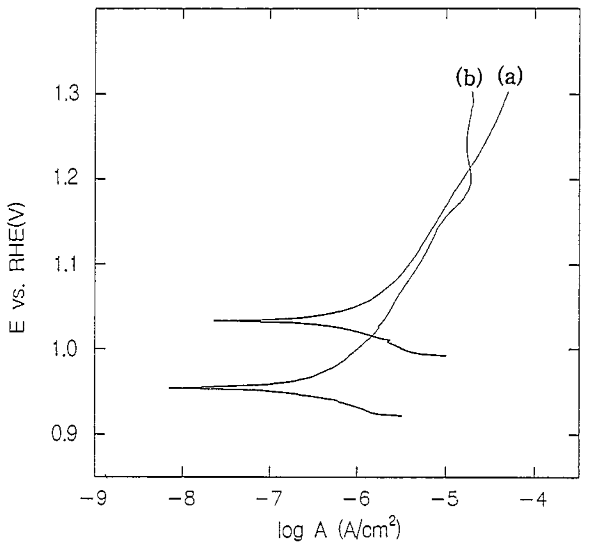

Fig. 11. The potentiodynamic anodic polarization curves of carbon and Ag/C: (a) carbon; (b) Ag/C.

the corrosion potential increased. The corrosion potential increased and the corrosion current decreased upon addition of PTFE. The reaction sites decreased because the silver powder came into partial contact with PTFE, and the dissolution potential of silver increased because the electrolyte permeation was hindered by the hydrophobicity of PTFE.

In Fig. 11, the polarization curves of electrodes prepared with carbon or Ag/C are shown. The corrosion potential of Ag/C is lower than that of the carbon electrode, because silver on carbon plays a catalytic role, and thus the corrosion potential of carbon can be decreased. Also, the dissolution potential of silver metal increases, because the reaction sites of silver decreased due to the contact with carbon and PTFE. Since the fuel cell was operated at an overpotential of 100–300 mV, dissolution of silver was not important.

4. Conclusions

From the studies of the Ag–Mg alloy catalyst in alkaline media, the following conclusions can be drawn.

(1) The Ag/C electrode manufactured by the Ag (30 wt.%) catalyst impregnated on carbon showed a saturation value after 2 h that was equivalent to the current density of Pt/C (10 wt.%).

(2) The Ag/C electrode showed the highest current density at a thickness of 0.8 mm with a PTFE content of 30 wt.%.

(3) The highest current density compared with that of Ag/C was obtained for the electrode of Ag–Mg(3:1)/C catalyst (240 mA, at an overpotential of 300 mV).

(4) The corrosion potential of Ag/C was lower than carbon, and the corrosion current was decreased because of the decrease in reaction sites due to contact with the silver catalyst.

Acknowledgements

This work has been supported by the basic research program of the Agency for Defence Development, Korea. The authors express their appreciation to the ADD.

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