

— Communication —

Improvement in Corrosion Properties of Carbon-coated Fe-based Metals for PEFC Bipolar Plate

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Low cost metals are quite attractive as bipolar plate of polymer electrolyte fuel cell (PEFC). However, low cost metals easily corrode due to the absence of good passivation films. In order to give high electrical conductivity and corrosion resistance to low cost metals such as carbon steel (S25C), carbon-coat was carried out by plasma-assisted chemical vapor deposition. Carbon-coated samples were characterized by XRD, Raman spectroscopy, and interfacial contact resistance. Based on the results of polarization measurement, the combination of carbon-coat and electroless nickel plating was found to be effective for decreasing of anodic dissolution of base metal.

Key Words : PEFC, Bipolar Plate, Carbonaceous Thin Film, Corrosion

1 Introduction

Polymer electrolyte fuel cells (PEFCs) require high durability to achieve long cycle life. Moreover, the reduction of cost, mass, and space is necessary for the commercial application of PEFC, such as fuel cell vehicles (FCV), portable electronic devices etc. To obtain sufficient battery voltage for FCV use, stack of single cell by using bipolar plates is inevitable because of low voltage of single cell. Bipolar plates account for the large percent of mass and space in PEFC stack.^{1,2)} Hence, improvement of bipolar plates is essential to the commercial use of FCV. Requirements for bipolar plates are high electronic conductivity, high corrosion resistance, high mechanical strength, high gas impermeability, light materials, and low cost materials. So far, various carbonaceous materials have been used as bipolar plates in demonstration. However, due to their low toughness and gas permeability, thin carbon-based bipolar plates cannot be used. On the other hand, metallic materials are very attractive due to their high electronic conductivity in bulk, high mechanical strength, high gas impermeability, lightness, and low cost. There is a fatal flaw in metal bipolar plates, since most metals easily corrode in the PEFC operating condition. Dissolution of metal cation by corrosion impairs the performance of PEFC, such as degradation of polymer electrolyte membrane. Although novel metals, such as platinum and gold, are generally corrosion-free, they are very expensive. Stainless steel and titanium show high corrosion resistance because of their excellent passivation film. Although these high corrosion-resistance metals are desirable, passivation films composed of oxide layer decrease the surface electronic conductivity.^{3,4)} Since bipolar plates serve as current collector, high electron conductivity is essential. Therefore, most metallic materials without any pretreatment cannot satisfy both the high corrosion resistance and high elec-

tron conductivity.

So far, gold-coating on the surface of stainless steel, aluminum, and titanium have been extensively studied.^{3,4)} However gold-coating is very expensive and film thickness of gold is relatively large to give sufficient corrosion resistance. Hence, we focused on the carbon-coating. When carbon layer acts as barrier layer that cloaks active surface area of metals and gives high electronic conductivity, low-cost metal such as carbon steels can be used as the base materials for bipolar plate. Coating by electronic conductive carbon (sp²-type carbon) on metal has been thought to be not easy, since sp²-type carbonaceous thin film is porous, which cannot serve as barrier layer. We have prepared carbonaceous thin films for the negative electrode of lithium-ion batteries by plasma-assisted chemical vapor deposition (plasma CVD).^{5,6)} This carbonaceous thin film is mainly composed of sp²-type carbon and shows high electronic conductivity. Hence, carbon-coat by plasma-assisted CVD might be one of the candidate techniques for the practical use of metal bipolar plate.

In this communication, we report the preparation carbon-coated Fe-based metal by plasma-assisted CVD and their corrosion properties as bipolar plates of PEFCs.

2 Experimental

Carbon-coating on substrates was carried out by using plasma-assisted CVD from acetylene and argon. The detail procedure was shown in our previous papers.^{5,6)} Substrate materials are carbon steel (S25C containing C (0.26 %), Si (0.22 %), Mn (0.47 %), P (0.017 %), S (0.012 %), Cu (0.006 %), (Ni+Cr) 0.237 %, and Fe (balance)) and nickel-coated S25C prepared by electroless plating (Ni-P). Substrates were placed on a ground electrode whose temperature was kept at 1023 K and the applied rf power was set at 90 W. Coating time was selected to be

5 hours.

In order to characterize carbon-coat on substrates, X-ray diffraction measurement (RIGAKU Rint-2100), Raman measurement (Jobin-Yvon T-64000), and Atomic force microscope (AFM) observation (Digital Instruments CP-II) were carried out. Interfacial contact resistance (ICR) of obtained carbon-coated metal was evaluated by the similar method reported by Wang *et al.*⁷⁾ Schematic illustration of ICR measurement is shown in Fig. 1. In this measurement, two carbon papers (TORAY TGP-H-120) were placed between the sample and two Au plates. The resistance was measured by using 4-probe resistance meter (TSURUGA model 3569). Applied compact force was 100 N cm^{-2} . Polarization measurement (HOKUTO-DENKO HSV-100F) was conducted by using a three-electrode cell. Carbon-coated samples and uncoated samples were used as working electrodes. A platinum wire was used as a counter electrode and an $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode was used as a reference electrode. Although simulated electrolyte condition for bipolar plate under PEFC operating have been reported in literature,⁸⁾ we selected $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ solution purged with N_2 as electrolyte to clarify the intrinsic effect of carbon-coat. Unless otherwise stated, the potential is referenced against $\text{Hg}/\text{Hg}_2\text{SO}_4$. Electrode potential was swept from immersion potential to 0.6 V at a scan rate of 20 mV min^{-1} . Electrochemical measurement was carried out at room temperature.

3 Results and Discussion

XRD patterns and Raman spectra of carbon-coated S25C and Ni-S25C are shown in Fig. 2. In XRD patterns, broad peaks are observed at about $2\theta = 26.4^\circ$. This result indicates that carbon-coat on S25C and Ni-S25C was composed of graphene layer. In Raman spectra, mainly three peaks around 1360 , 1580 and 1620 cm^{-1} were observed. The peak around 1580 cm^{-1} is well known to be related with crystallinity of carbonaceous materials, and is assigned to Raman active E_{2g} mode frequency (G band).⁹⁾ The peak around 1360 cm^{-1} is ascribed to Raman inactive A_{1g} mode frequency.⁹⁾ Peaks around 1360 and 1620 cm^{-1} appear in the case of finite crystal size and imperfection of carbonaceous materials, and the former is called as D band and the latter is as D' band. When we focus on the peaks around 1350 cm^{-1} , their intensities are higher than those of the peaks around 1580 cm^{-1} . Based on this result, surface of carbon-coat should be low crystallized carbon and the size of

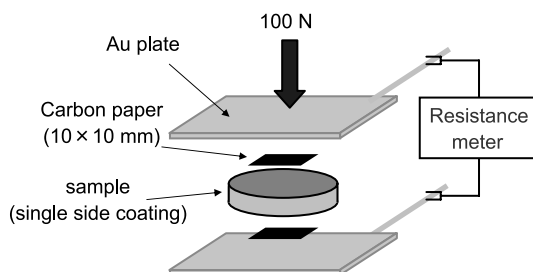


Fig. 1 Schematic illustration of ICR measurement.

crystallite would be small.

Values of ICR ($R_{\text{carbon paper}/\text{carbon-coated side of sample}} + R_{\text{carbon paper}/\text{uncoated side of sample}}$) of carbon-coated metals were below $10 \text{ m}\Omega\text{cm}^2$ under our experimental condition. On the other hand, ICRs ($2R_{\text{carbon paper}/\text{sample}}$) of S25C and Ni-S25C were over $50 \text{ m}\Omega\text{cm}^2$, and the value of SUS304 was about $300 \text{ m}\Omega\text{cm}^2$ due to the passivation film formed in air. This low resistivity is due to the sp^2 -type carbon observed in XRD measurement and Raman spectroscopy. It is noted that only single side of sample was coated by carbon. However, these ICR values are quite low compared to anticipated values. Although this phenomenon might be due to the surface change of uncoated side by coating process such as ultra-thin carbon coating by wraparound of plasma species or elimination of passivation film formed in air, the reason is not understood at this stage. Based on this result, carbon-coat gives high electronic conductivity without the formation of passivation film.

Next, polarization behavior was examined. Figure 3 shows anodic polarization curves of obtained metals. In S25C curve, large anodic current corresponding to Fe^{2+} dissolution was observed at the potential range from immersion potential to -0.2 V . After short passivation range, transpassive state was observed. Polarization curve for carbon-coated S25C was almost identical to that of S25C. This result shows that carbon-coat on the S25C could not prevent the contact between electrolyte solution and substrate. Polarization behavior of pristine

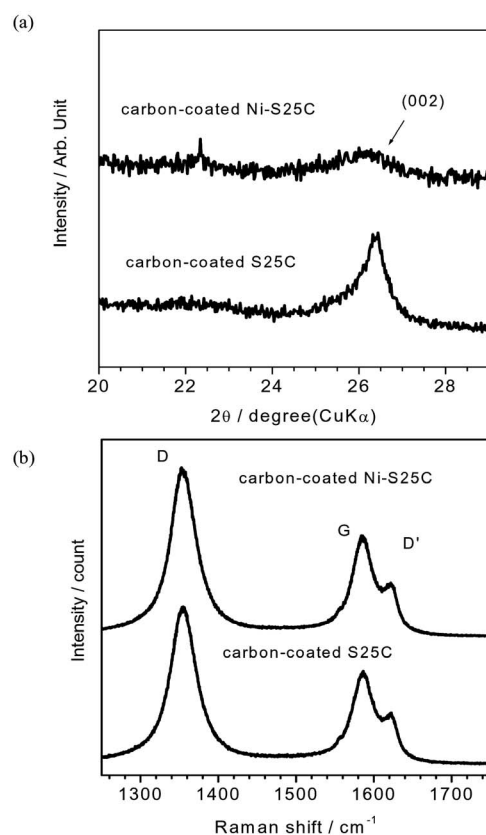


Fig. 2 XRD patterns (a) and Raman spectra (b) of carbon-coat on S25C and Ni-S25C.

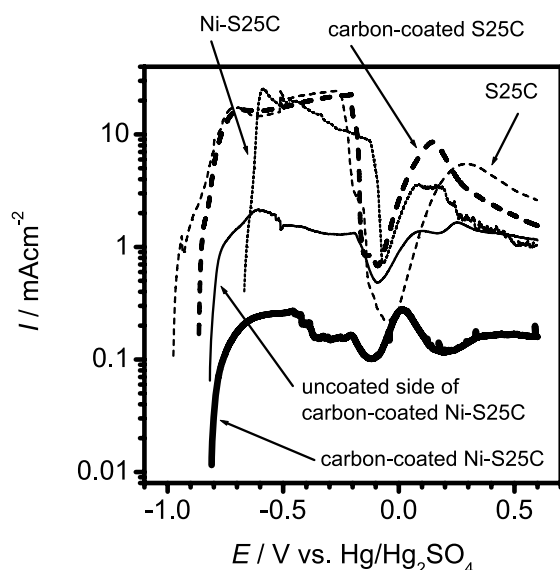


Fig. 3 Anodic polarization curves of S25C, Ni-S25C, carbon-coated S25C, carbon-coated Ni-S25C, and uncoated side of carbon-coated Ni-S25C. Initial potential was immersion potential and sweep rate was 20 mV min^{-1} .

Ni-S25C was not so different from that of S25C. This is because that Ni layer formed by electroless plating in this study was amorphous phase and possessed intergranular defect, leading to the access of electrolyte on the S25C. Anodic current between immersion potential to -0.2 V of carbon-coated Ni-S25C was decreased by about $1/10$ compared to uncoated side of the same sample. This is because carbon-coat on the Ni-S25C prevents the contact between electrolyte solution and substrate, leading to the decrease of active surface area of Ni-S25C. In addition, anodic current of uncoated side of carbon-coated Ni-S25C was decreased compared to that of bare Ni-S25C. This might be due to the flattening of intergranular defect of Ni layer by heating at 1023 K . Moreover, formation of Fe-Ni alloy¹⁰⁾ and Ni_3P ¹¹⁾ was confirmed by XRD measurement. Correlation between the decrease of anodic current of uncoated side and the formation of Fe-Ni alloy and Ni_3P was not clarified at this time. The difference of carbon-coat is considered from SEM and AFM observation. Surface morphology of carbon-coat on S25C was similar to that of carbon nanowalls from SEM image.¹²⁾ The detail of this structure will be reported elsewhere. Anodic current of carbon-coated S25C was not suppressed due to this porous structure. On the other hand, surface morphology of carbon-coat on Ni-S25C was quite dense from AFM image (Fig. 4). This morphological difference influenced the prevention of electrolyte penetration. Although corrosion properties obtained in this study did not satisfy the requirement of metal bipolar plate,⁸⁾ optimization of the condition of electroless nickel plating and plasma-assisted CVD would bring the sufficient corrosion properties.

4 Conclusion

Carbon-coating on Fe-based materials was carried out by plasma-assisted CVD. Based on the results of XRD

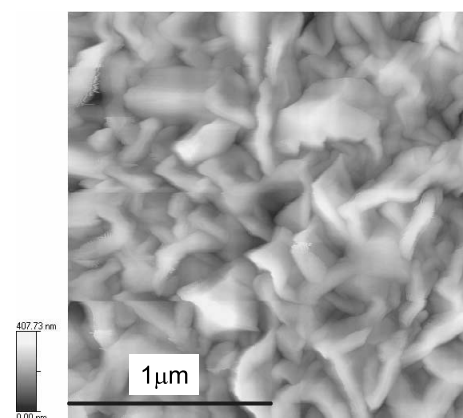


Fig. 4 AFM image (tapping mode) of carbon-coated Ni-S25C.

measurement and Raman measurement, carbon-coat mainly consisted of sp^2 -type carbon. Carbon-coated materials showed high electrical conductivity compared with raw materials and SUS304. Although anodic polarization behavior of carbon-coated S25C in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ was not improved, anodic current of carbon-coated Ni-S25C was decreased by about $1/10$ compared to uncoated side of the same sample. It is concluded that carbon-coating on the Fe-based materials might be candidate technique for the improvement of metal bipolar plates. Investigation of corrosion properties under the PEFC operating condition and coverage properties of carbon-coating was undergoing. Results will be reported in the future.

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