TRANSITION METAL CARBIDES FOR NEW CATHODE MATERIAL OF POLYMER ELECTROLYTE FUEL CELL

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ABSTRACT

In this study, the applicability of the transition metal carbides to the cathode catalyst of polymer electrolyte fuel cell (PEFC) was investigated. The tungsten carbide was modified by the addition of second metal such as Ta or Cr in order to improve its stability in corrosive atmosphere. Comparing with its pure carbide, the modified tungsten carbides were evaluated with respect to the stability and catalytic activity for ORR. Based on the electrochemical measures, it was proved that the modification of tungsten carbide by the addition of second metal such as Ta or Cr showed that the significant improvement in the characteristics with respect to the stability in cathode atmosphere of PEFC and the catalytic activity for the ORR.

INTRODUCTION

Transition metal carbides have been widely studied as electrocatalysts, because of their electrochemical properties and electrical conductivities. In particular, it has been reported that tungsten carbide (WC) has a similar electronic structure with platinum and platinum-like behavior for hydrogen chemisorption (1, 2). Trassatti et al. found that WC is superior to the other transition metal carbides concerning the electrocatalytic activity for the oxygen reduction reaction (ORR) (3). These results allowed many researchers to study the electrocatalytic properties of WC. However, the WC has very low corrosion resistance in acid electrolytes. This makes difficulty in the application of this material as an electrocatalyst.

In this study, we have modified WC in order to increase its low stability in corrosive atmosphere. The pure WC was modified by the addition of transition metal such as Ta or Cr. Comparing with pure WC, the modified WCs were investigated with respect to the stability and the electrocatalytic activity for the ORR, and the applicability of WC to cathode material was discussed.

EXPERIMENTAL

The modification of WC was made by RF sputtering method, which sputters Ta or Cr together with WC. All of the pure and modified WCs were deposited onto a glassy...
carbon rod substrate.

The microstructure of the sputter-deposited samples was confirmed by X-ray diffraction (Shimadzu, XRD-6000) and transmission electron microscopy (Hitachi, HF2000). The surface characterizations of the samples were conducted by X-ray photoelectron spectroscopy (Shimadzu, ESCA3200) using Mg Kα radiation before and after the electrochemical measurements.

The electrochemical measurements were carried out in a solid-state cell with Nafion®117 as the electrolyte as shown in Fig. 1 in order to conduct the experiment under the same environment as PEFCs. A dynamic hydrogen electrode (DHE) and a platinum foil with Pt black were used as the reference electrode and the counter electrode, respectively.

RESULTS AND DISCUSSION

Electrochemical measurements

Figure 2 shows the steady-state cyclic voltammograms for the pure WC and modified WC (Ta-added WC, Cr-added WC) on the Nafion® under a N₂ atmosphere. A significant anodic current above 0.5V (vs. DHE) is observed in the pure WC according to the anodic polarization, while the modified WC catalyst shows no large anodic current up to 1.0V (vs. DHE). In particular, the Ta-added WC showed a significantly large corrosion resistance.

The oxidation of the tungsten carbide by the anodic polarization is considered as follows (4, 5).

\[ \text{WC} + 5\text{H}_2\text{O} = \text{WO}_3 + \text{CO}_2 + 10\text{H}^+ + 10\text{e}^- \]  

According to the anodic polarization, the W in WC oxidizes to WO₃ with the evolution of CO₂. In the case of Ta or Cr, it is considered that Ta oxide or Cr oxide are also formed by polarization in acidic media. Although these transition metal components (W, Ta, Cr) form the oxide films on the surface of the modified WCs as well as the pure WC, the enhanced stability in the modified WC by the addition of Ta or Cr was observed.

In order to evaluate the electrocatalytic activity for the ORR, the slow scan voltammetry (SSV) was carried out in N₂ and O₂ as shown Fig. 3. While the pure WC shows oxidation behavior above 0.45V (vs. DHE) in the polarization curve of O₂ atmosphere, the Cr-added WC and Ta-added WC exhibit cathodic current up to 0.7V and 0.8V (vs. DHE), respectively. The onset potentials of the modified WCs are significantly increased compared with that of the pure WC. Especially, the Ta-added shows ca. 0.35V higher than value than that of the pure WC. It is considered that the cathodic current observed in the modified WC must be corresponded to the ORR current in comparison with their cathodic current in N₂ atmosphere. It appears that the addition of Ta or Cr to the pure WC increases the catalytic activity for ORR as well as the stability. Especially, the effect of Ta is superior to that of Cr.

X-ray analysis; XRD and XPS

Figure 4(a) shows the X-ray diffraction (XRD) pattern and the transmission electron micrograph (TEM) of the Ta-added WC. Two crystalline peaks were observed.
in the XRD pattern. A large peak of $2\theta=35.8^\circ$ is assigned to the stoichiometric tungsten carbide (WC) $<100>$ plane (6). A very small peak of $2\theta=41^\circ$ might correspond to Ta (6), but its crystallinity is very low. The XRD result indicates that the Ta-added WC is mostly composed of amorphous phases with low crystallinity. The TEM of the Ta-added WC shows that the ultrafine particles of ca. 1nm are uniformly distributed with a nano-crystalline phase as shown in Fig. 4(b). The nano-crystalline phase might be assigned to WC. The nano-particles should be amorphous phases and be composed of alloys containing W, C and/or Ta, because no crystalline peaks except for a large WC crystalline peak were observed in the XRD pattern.

Since the alloy condition of the modified WCs consisting of mostly amorphous nanoparticles is difficult to identify by using XRD, the characterization was carried out through X-ray photoelectron spectroscopy (XPS). Figure 5 shows XPS peaks of the Ta-added WC after surface Ar$^+$ etching. As shown in Fig.5 (a), there exist two types W with different electron states corresponding to W4f7/2=31.6 and 31.2eV, respectively. The former should be assigned to the carbidic W (B.E=31.6eV). This carbidic W may be a stoichiometric WC, because a crystalline peak of the WC was detected in XRD pattern. On the other hand, the latter (B.E=31.2eV) was different from that of WC or W metal. This result suggests the existence of a W alloy with another metal in the Ta-added WC (7, 8). In the case of Ta, three Ta types with different electron state are observed, i.e., carbidic state, metallic state and intermediate state (between carbidic and metallic states) as shown in Fig. 5(b) (9, 10). Since whether or not the Ta of the carbidic state bonds to carbon in a stoichiometric state is not proved, the carbidic Ta is referred to as TaCx. The Ta with an intermediate electron state exhibits higher binding energy than that of Ta metal and is probably associated with the Ta alloy with another metal.

Based on the presence of W and Ta with electron states different from their carbidic and metallic state, we can conjecture the formation of W-Ta alloy in the Ta-added WC. From Hiasimoto’s report (11), the shifts of W and Ta peaks in W-Ta alloy were also confirmed and their result is in good agreement with our result. Therefore, the shifted peaks of W and Ta compared with their metallic state should be due to the charge transfer from Ta to W according to the formation of W-Ta alloy in Ta-added WC. Moreover, it is well known that the W-Ta alloy increases the corrosion resistance in its alloy (11). The enhanced stability observed in the Ta-added WC should be related to the formation of W-Ta alloy. It has been reported that the W-Cr alloy also play an important role in the increase of corrosion resistance (12), and the enhanced stability of the Cr-added WC should be also caused by the presence of W-Cr alloy.

Figure 6 shows a comparison of the ORR catalytic activity between W-Ta, TaC, TaC and Ta-added WC. Although W-Ta alloy shows very high stability, its catalytic activity for ORR is considerably lower than Ta-added WC. The activities in TaC and Ta is also inferior to that of the Ta-added WC. This result indicates that the W-Ta alloy, TaC and Ta are not related to the enhanced catalytic activity in the Ta-added WC. On the other hand, we found that the presence of WC not oxidized in the Ta-added WC after the electrochemical measurements by the XPS analysis as shown in Fig. 7. The Ta-added WC shows apparent XPS peaks corresponding to WC in comparison with the pure WC. The WC observed in the Ta-added WC should exist on surface and/or sub-surface, and it is considered that its oxidation may be restrained by the addition of Ta,

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i.e. the formation of W-Ta alloy. Therefore, the enhanced activity observed in the Ta-added WC should be related to carbidic tungsten (WC), which remains on surface and/or sub-surface.

CONCLUSION

In this study, we have investigated WC as a non-Pt cathode material for a PEFC. The WC was modified in order to increase its low stability in corrosive atmosphere. From above results, it was proved that the modification of WC by the addition of second metal such as Ta or Cr showed the significant improvement in the characteristics with respect to the stability in an acid medium and the catalytic activity for the ORR.

It is considered that the new applicability of an electrocatalytic design based on the carbide materials was confirmed by our study. This electrocatalyst design concept through the modification of carbide materials will be expected to increase the application of the transition metal carbide to the electrocatalyst material (cathode and anode) of PEFC.

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Reference electrode (DHE)

Working electrode

WC+Ta or WC deposited G/C electrode

Nation®

Counter electrode

Figure 1. Schematic drawing of electrochemical cell.

Figure 2. Cyclic voltammograms in N₂ atmosphere; scan rate=100mV/s, 30°C.
Figure 3. Slow scan voltammograms for pure WC and modified WC catalysts; scan rate = 5mV/s, 30°C.
Figure 4 X-ray analysis of Ta-added WC.

(a) XRD pattern

(b) TEM image

Nanocrystalline phase

Ultrafine nanoparticle
Figure 5. XPS spectra for WC+Ta catalyst after Ar⁺ surface etching.
Figure 6. Slow scan voltammograms under O₂ atmosphere; scan rate=5mV/s, 30°C.

Figure 7. XPS spectra of WC+Ta and pure WC catalysts after electrochemical measurements.