

Transition Metal Carbides for New Cathode Material of Polymer Electrolyte Fuel Cell

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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 has a similar electronic structure with platinum and platinum-like behavior for hydrogen chemisorption.^{1,2} These reports have allowed many researchers to study the electrocatalytic properties of the transition metal carbides. However, because most of the transition metal carbides have very low corrosion resistance, it was very difficult to apply these carbides to the electrocatalyst in acidic media.

In order to apply the transition metal carbides to the cathode electrocatalyst of polymer electrolyte fuel cell (PEFCs), we have modified several carbides. Comparing with their pure carbides, the modified carbide catalysts were investigated with respect to the stability and the electrocatalytic activity for the oxygen reduction reaction (ORR)

Experimental

Pure and modified carbides were prepared by RF sputtering method. In order to modify the carbide, second metals were added into a pure carbide. All of carbide catalysts were deposited onto a glassy carbon rod substrate.

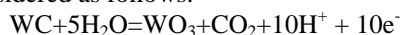
The microstructure of prepared carbide catalysts were confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The surface characterizations were conducted by X-ray photoelectron spectroscopy (XPS).

The electrochemical measurements were carried out in a solid-state cell with Nafion[®]117 as the electrolyte 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. The electrolyte membrane was sandwiched between the working electrode on the upper side and the counter electrode on the other side. Oxygen or nitrogen gas fed into the cell was humidified by passing it through a bubbler in order to attain a saturated relative humidity.

Results and discussion

Figure 1 shows the steady-state cyclic voltammograms for the pure carbide (WC) and its modified-carbide (Ta-added WC and Cr-added WC) on the Nafion[®] in a N₂ atmosphere. The pure WC catalyst showed a significant anodic current above 0.5V (versus DHE). However, the modified WC catalysts exhibited no large anodic current up to 1.0V (versus DHE). In particular, the Ta-added WC showed a significantly large corrosion resistance.

The oxidation of the WC by anodic polarization is considered as follows.³



The W in the WC oxidizes to WO₃ with the evolution of CO₂. In case of Ta or Cr, Ta oxide or Cr oxide is also formed in acidic media. Although these transition metal components might form the oxide films on the surface of the pure WC or the modified WC catalyst, it was found that the stability of WC is considerably increased by the addition of Ta or Cr. Based on the XPS analysis, it is considered that the enhanced stability might be related to the formation of W-Ta alloy or W-Cr alloy in the modified WC.

In order to investigate the electrocatalytic activity for ORR, the slow scan voltammetry (SSV) was carried out in N₂ and O₂ as shown in Fig.2. The apparent difference was shown between the both polarization curves in the N₂ and O₂ atmosphere in modified WC catalysts. This should be assigned to the cathodic current for ORR. In addition, the significant increases of onset potential in the ORR were observed in modified WC catalysts. The Ta-added WC showed ca.0.35V higher value than that of the pure WC.

From our study, it was proved that the modification of transition metal carbide by the addition of second metal such as Ta or Cr showed the significant improvement in the characteristics with respect to the stability in acidic media and the electrocatalytic activity for the ORR.

Acknowledgments

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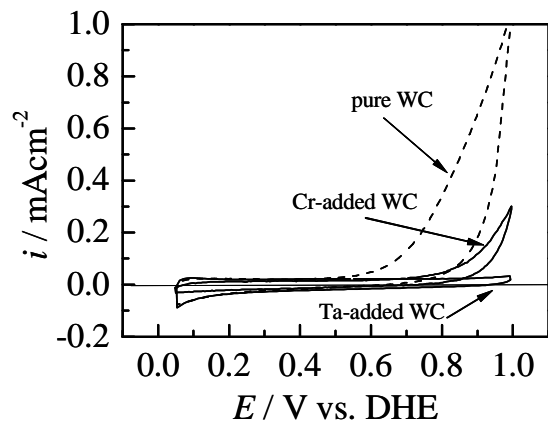


Fig. 1. Cyclic voltammograms in N₂ atmosphere; scan rate=100mV/s, 30°C.

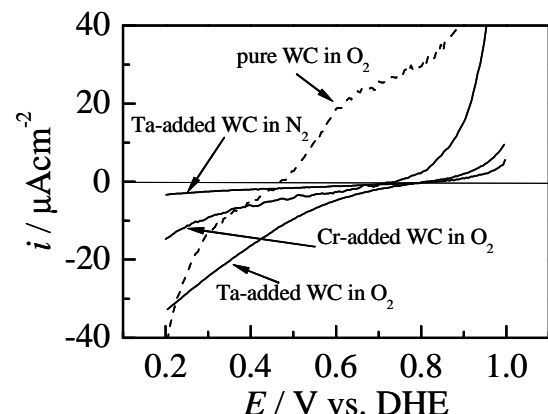


Fig. 2. Slow scan voltammograms for pure WC and modified WC catalysts; scan rate= 5mV/s, 30°C.