

Tungsten-based Carbides as Anode for Intermediate-Temperature Fuel Cells

Hiroki Muroyama,^{*,z} Koji Katsukawa, Toshiaki Matsui,^{*} and Koichi Eguchi^{*}

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Tungsten carbides were prepared from ammonium paratungstate via temperature-programmed carburization under flowing a gaseous mixture of CH_4/H_2 to employ as anode catalysts in fuel cells consisting of CsH_2PO_4/SiP_2O_7 -based composite electrolyte operative at 200°C. The resulting materials were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. The heat-treatment at high temperatures promoted the reduction and carburization of tungsten component. The single phase of WC was observed for the samples subjected to the carburization at and above 800°C. The single cell employing the catalyst prepared at 850°C attained the best performance. The anode material containing the metallic W exhibited low stability under the power generation condition. With nickel or cobalt additives, the carburization of tungsten species was initiated at low temperatures. The samples with the additives heat-treated at high temperatures were composed of several tungsten carbides including WC. When these samples were applied as anode catalysts, the additive species lowered the cell performance. These results indicated that the WC phase was the most effective electrocatalyst for the hydrogen oxidation.

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Manuscript submitted April 7, 2011; revised manuscript received June 3, 2011. Published July 1, 2011.

Fuel cells are one of the promising energy conversion devices due to their high efficiency and low emissions. Recently, polymer electrolyte fuel cells (PEFCs) have attracted a great deal of attention for stationary and transportation applications, and have been developed for commercialization. Operating temperature of PEFCs is limited up to 100°C because water plays an important role in proton conduction in perfluorosulfonic acid membrane electrolytes. Such low operating temperatures induce some issues, e.g. CO poisoning of Pt electrocatalysts, and complicated fuel processing and water management. Thus, electrolytes operating above 100°C under low humidified conditions are expected to overcome these problems, and considerable efforts have been directed for the development of such electrolyte materials.^{1–8}

We have reported a new proton-conductive electrolyte of CsH_2PO_4/SiP_2O_7 -based composite. The CsH_2PO_4/SiP_2O_7 composite with a molar ratio of 1/2 exhibited 44 mS cm⁻¹ at 266°C under 30% H₂O/Ar atmosphere.³ In this composite, the solid acid of CsH_2PO_4 reacted with a part of SiP_2O_7 at the contacting interface to form $CsH_5(PO_4)_2$, which served as a new proton-conductive phase. Fuel cell employing this composite electrolyte was operated successfully at around 200°C, indicating its high stability under fuel cell operating conditions.⁶ For such fuel cells, the platinum catalyst supported on carbon (Pt/C) was used as an electrocatalyst as for PEFCs.

Many studies on development of electrode materials with low Pt loading or without Pt metal have been extensively conducted so far due to high cost of noble metals. Among them, carbides of transition metals have been paid attention as prospective alternative electrocatalysts, since molybdenum and tungsten carbides showed catalytic activity comparable to noble metals for several reactions.^{9–13} Moreover, considerable efforts have been devoted to improving insufficient catalytic activity of these materials for hydrogen oxidation. Several preparation methods have been tried to enlarge the catalytic surface area of carbide compounds.¹⁴⁻²² Addition of other metal species to molybdenum carbide or tungsten carbide has been also studied to enhance the catalytic activity. The hydrogen oxidation was facilitated by the formation of oxycarbide species in cobalttungsten carbide.²³ These approaches, however, were less effective for the enhancement of catalytic activity. These carbide materials have been examined in the low temperature range below 100°C, while the use of carbides at higher temperature can be considered as a possible factor for the promotion of catalytic reactions. In this study, therefore, we prepared tungsten compounds via temperatureprogrammed carburization and evaluated their catalytic performance as the anode in fuel cells operating at 200°C. Temperatureprogrammed carburization is known as a suitable process for the preparation of the carbide compounds with high surface area.^{17,22} In addition, additive effects of Ni and Co components on the carburization reaction and the catalytic activity of tungsten-based carbides were also investigated.

Experimental

Tungsten carbide was obtained by temperature-programmed reaction as follows.²² Ammonium paratungstate, $(NH_4)_{10}W_{12}O_{41}$ ·5H₂O, (APT, Ardrich) was loaded into an alumina boat and placed into a quartz tube inside a furnace. Temperature was raised up to 200°C with a supply of pure nitrogen and subsequently up to target temperatures of 650–900°C in 50% CH₄/H₂ with a heating rate of 0.2°C min⁻¹. The sample was heat-treated at the desired temperature for 5 h and then exposed to 2% O₂/N₂ for 6 h after cooling to room temperature. The resultant tungsten compound was denoted as APT-*T* (*T* = 650–900), which was prepared by the heat-treatment at *T*°C. A mixture of carbon black (Vulcan XC72R) and the obtained tungsten compound in a weight ratio of 1.5:1 was prepared for electrochemical measurements and represented as APT-*T*/C (*T* = 650–900). Commercial WC (Aldrich) mixed with carbon black was also used as an electrocatalyst and denoted as commercial WC/C.

For the synthesis of tungsten carbide containing nickel or cobalt species, Ni(NO₃)₂·6H₂O or Co(NO₃)₂·6H₂O and APT were used as starting materials. The metal nitrate hydrate and ATP were dissolved in distilled water. The carbon black was also added to the solution in a weight ratio of 1.5:1 to total metal components (W, Ni, Co). This solution was stirred during evaporation to dryness. The resulting precursor was carburized by temperature-programmed reaction as mentioned above. APT M_x C-T (M=Ni, Co; x=0.01, 0.5; T=650, 750, 850) denotes tungsten compound containing M component with a molar ratio of 1:x, which was heat-treated at T° C.

 \overline{C} rystal structure of the samples was analyzed by X-ray diffraction (XRD, Rigaku, Rint 1400 X-ray diffractometer). Crystallite size of the tungsten compounds was evaluated by Sherrer equation. Specific surface area was measured by BET method with N₂ adsorption (Shimadzu, Gemini 2375). Binding energy of W 4f for the samples was obtained by X-ray photoelectron spectroscopy (XPS) with Mg Kα radiation (Shimadzu, ESCA-3400). Ag 3d electron binding energy corresponding to metallic silver was referenced at 368.3 eV for calibration.

Performance of a single cell employing the resultant electrocatalyst (APT-T/C, APT M_xC -T, and commercial WC/C) was evaluated at 200°C. For the fabrication of anode, the resultant catalyst was

^{*} Electrochemical Society Active Member.

^z E-mail: muroyama.hiroki.5c@kyoto-u.ac.jp

ultrasonically dispersed in 1-methyl-2-pyrrolidone (Wako Pure Chemical Industries) to form paste. Subsequently, the obtained paste was applied on teflon-coated carbon paper (Toray) and heated to dryness. The loading of electrocatalyst was fixed at 2.5 mg cm⁻². A commercial Pt/C supported on carbon paper (BASF Fuel Cell, Inc., phosphoric acid fuel cell, Pt loading: 1.0 mg cm⁻²) was used for cathode. The composite electrolyte of CsH₂PO₄/SiP₂O₇ was prepared as mentioned in previous reports.^{3,6} Membrane electrode assembly (MEA) was fabricated by uniaxial pressing of the composite powder with electrodes (diameter: 13 mm, thickness: ca. 1.3 mm, electrode area: 0.283 cm²). Then, the resulting MEA was heattreated at 220°C for 1 h and placed in apparatus. Gaseous mixtures of 30% H₂O/H₂ and 30% H₂O/O₂ were supplied to anode and cathode, respectively, with a flow rate of 50 ml min⁻¹. A current-voltage (I-V) characteristic was examined using a potentiostat (Solartron 1287 potentiostat). For a single cell employing APT-T/C, the I-V curves were iteratively recorded to evaluate the stability of catalysts. After the first *I-V* measurement (1st), the single cell was held under 30% H₂O/N₂ atmosphere for 1 h, and subsequently the measurement was carried out again (2nd). This sequence of operation was repeated in some cases.

Results and Discussion

Influence of carburization temperature on the properties of tungsten compounds.-- The XRD patterns of the tungsten compounds synthesized by the heat-treatment of APT with a supply of 50% CH₄/H₂ are shown in Fig. 1. Single phases of WO₂ and metallic W were observed in the diffraction patterns of APT-650 and APT-700, respectively. As the heat-treatment temperature was further raised, tungsten carbide species such as WC and W2C were formed. The diffraction pattern of APT-750 suggested the presence of W as well as W₂C and WC, whereas the samples heat-treated at and above 800°C were composed of single phase of WC. This change in tungsten compounds approximately agreed with the result of thermogravimetric analysis reported previously.²² According to this literature, the starting material of APT was decomposed to WO₃ at 350°C, accompanied with evolution of water and ammonia. With elevating temperature under 50% CH₄/H₂ atmosphere, WO₃ was gradually reduced to WO₂ in the range of 660-690°C. Subsequently, the TG profile exhibited a maximum weight loss at 760°C, indicating the

formation of metallic W. Upon heating beyond this temperature, a weight gain was observed corresponding to the carburization of tungsten species and the deposition of graphitic carbon. Diffraction peaks of deposited carbon were not observed in the XRD pattern of all samples in the present study.

XPS measurements were carried out to examine electronic state of tungsten. The XPS spectra of W 4f for APT-T (T = 650-800) are shown in Fig. 2. The spectrum of APT-650 consisted of three peaks at 32.8, 35.4, and 37.7 eV, which was quite analogous to that of bulk WO₃ reduced at 500°C in hydrogen.²⁴ This report indicates that tungsten species were in the oxidation states of WO₃, W₂O₅, and WO₂. Considering the diffraction pattern was identical to that of WO₂ phase, the surface of APT-650 was partially oxidized. The APT-700 sample exhibited four specific peaks at 31.3, 33.4, 35.6, and 37.8 eV attributable to W(0) $4f_{7/2}$, W(0) $4f_{5/2}$, W(VI) $4f_{7/2}$, and W(VI) $4f_{5/2}$, respectively.^{24–26} This result revealed the existence of WO₃ as well as metallic W on the surface. For the samples heattreated at 750–900°C in a gaseous mixture of CH_4/H_2 , two noticeable peaks corresponding to tungsten carbide were observed in the ranges of 31.6–31.7 and 33.7–33.8 eV. Judging from the broad peak at 36.5–38.7 eV in the spectra of these samples, tungsten species in the oxidation state was present on the surface. The tungsten oxide might be ascribable to partial oxidation of the tungsten carbide by the exposure to diluted oxygen gas at the final processing stage.

Figure 3 shows the *I-V* characteristics of a single cell employing the resultant electrocatalyst at 200°C. The measurement was repeated for the evaluation of the stability. For all cells, open circuit voltage achieved (0.87-0.98 V) was comparable to that for the system using CsH_2PO_4/SiP_2O_7 composite electrolyte with Pt/C electrodes under the same condition reported previously.⁶ The single cell with APT-850/C exhibited the best performance among the samples investigated. Thus, the WC catalyst was more active for the hydrogen oxidation than WO₂ and W, which were main tungsten species in APT-650/C and APT-700/C catalysts, respectively. The heat-treatment at 750°C under a CH₄/H₂ atmosphere led to insufficient carburization of tungsten component, resulting in the slightly lower performance at 1st measurement as compared with the heat-treatment at 850°C. The APT-900/C catalyst did not attain the activity level of the APT-850/C, although the WC phase was observed as the major one in these catalysts. The carburization at higher temperature is expected to promote agglomeration of WC particle and concomitant carbon deposition over the catalyst. For the single cell employing



Figure 1. XRD patterns of (a) APT-650, (b) APT-700, (c) APT-750, (d) APT-800, (e) APT-850, and (f) APT-900.



Figure 2. XPS spectra of W 4f for (a) APT-650, (b) APT-700, (c) APT-750, and (d) APT-800.



Figure 3. *I-V* characteristics of a single cell employing (a) APT-650/C, (b) APT-700/C, (c) APT-750/C, (d) APT-850/C, and (e) APT-900/C at 200 $^{\circ}$ C.

APT-850/C, the maximum power density was 4.1 mW cm⁻², which was 7.3% of that in the case of Pt/C anode (56 mW cm⁻²).⁶ As a result, the WC catalyst was much inferior in the activity to the Pt catalyst even at 200°C. According to the previous report, electrochemical measurement at 50°C revealed that hydrogen adsorption on WC surface was rate-determined by slow dissociation of hydrogen molecule.^{10,18} Thus, it was considered that the high operating temperature of 200°C could not significantly enhance the rate of this step. Note that the cell performance decreased during the consecutive measurement for APT-700/C and APT-750/C containing metallic W. The proton conductive phase of $CsH_5(PO_4)_2$ in the electrolyte was in the molten state under the operating condition. Considering the electrocatalysts was exposed to the acidic molten salt, the corrosion of W metal by the electrolyte should be responsible for the deterioration of performance. On the other hand, the single cells exhibited highly-reproducible I-V curves for APT-650/C, APT-850/C, and APT-900/C. This result clarified that the electrocatalysts consisting of WO₂ and WC were stable under this operating condition. Consequently, the WC phase was the most favorable among tungsten compounds with respect to the activity for hydrogen oxidation and the stability in acidic condition at 200°C.

Additive effect of nickel and cobalt species on the properties of tungsten-based compounds.— The typical XRD patterns of the tungsten-based compounds containing nickel or cobalt are shown in Fig. 4. For both systems with additives, the diffraction patterns revealed that reduction and carburization of tungsten species were promoted with increasing heat-treatment temperature, as in APT-*T* samples. In the case of the heat-treatment at 650°C, crystalline



Figure 4. XRD patterns of (a) APTNi_{0.01}C-650, (b) APTNi_{0.01}C-750, (c) APTNi_{0.5}C-650, (d) APTNi_{0.5}C-850, (e) APTCo_{0.5}C-650, and (f) APTCo_{0.5}C-850.

phases of metallic W and tungsten carbide were detected regardless of the additive species, while the sample without additives exhibited a single phase of WO₂ as shown in Fig. 1a. Moreover, as can be seen in Figs. 4a and 4c, an increase in the amount of additives led to rapid carburization of the tungsten component. These results indicated that the addition of nickel and cobalt facilitated the reduction and carburization reactions. The samples heat-treated at 750 and 850°C were composed of W2C as well as WC despite the heat-treatment at relatively high temperatures. Considering graphitic carbon was deposited at 850°C over the samples with the large amount of nickel or cobalt, methane should be decomposed to carbon by the additive components before the reaction with tungsten species. Thus, the carburization of tungsten species to form WC could not proceed completely at high temperatures. The XRD patterns also clarified that the added nickel and cobalt species existed as metallic Ni and Co₃W₃C, respectively. Hereafter, when the characteristics of the samples with additives were evaluated, the APT $M_{0.01}$ C-650 (M = Ni, Co) catalysts containing metallic W were excluded due to instability in the fuel cell operating condition as mention above.

The crystallite size of the tungsten carbide observed in Fig. 4 was calculated by Sherrer equation as summarized in Table I. The crystallite size tended to increase either with increasing heat-treatment temperature or with increasing amount of additive component. The grain growth was more noticeable for nickel than cobalt.

Electronic state of tungsten, nickel, and cobalt elements was examined by XPS measurement. No specific peaks were detected in Ni 2p and Co 2p spectra due to a small amount of these components. The W 4f spectra of all samples showed definite and broad peaks attributed to carbide and oxide species, respectively. Difference between the spectra of the sample with and without additive species was not remarkable.

The observed crystalline phases and maximum power density of the single cell for the samples are also summarized in Table I. The result of APT-850/C is shown for comparison. The maximum power density for all electrocatalysts investigated was not specifically related with the crystallite size of the major phase. The cell

Table I. Crystallite size and phase, and maximum power density of single cell for APT M_x C-T (M = Ni, Co; x = 0.01, 0.5; T = 650-850) and APT-850/C.

Sample	Crystallite size ^a /nm	Crystalline phase	Maximum power density/mW cm ⁻²
APTNi001C-750	15 (W ₂ C)	W ₂ C, WC	1.6
APTNi _{0.01} C-850	16 (WC)	W_2C, WC	1.7
APTNi _{0.5} C-650	19 (W ₂ C)	W ₂ C, WC, Ni	0.27
APTNi _{0.5} C-750	20 (W ₂ C)	W ₂ C, WC, Ni, C	0.50
APTNi _{0.5} C-850	24 (WC)	W ₂ C, WC, Ni, C	0.58
APTCo _{0.01} C-750	$12 (W_2C)$	W_2C , WC	1.9
APTCo _{0.01} C-850	12 (WC)	W_2C , WC	1.8
APTCo _{0.5} C-650	12 (W ₂ C)	W ₂ C, WC, Co ₃ W ₃ C	1.6
APTCo _{0.5} C-750	13 (W ₂ C)	W ₂ C, WC, Co ₃ W ₃ C, C	0.42
APTCo _{0.5} C-850	19 (WC)	W ₂ C, WC, Co ₃ W ₃ C, C	0.31
APT-850/C	12 (WC)	WC	4.1

^aThis value was calculated from the strongest diffraction peak, which was attributed to the compound in parenthesis.

performance for the APT $M_{0.01}$ C-T (M = Ni, Co, T = 750, 850) samples was comparable despite the heat-treatment temperature and the additive species. The increase in amount of the additive components lowered power density. These additives promoted the formation of carbon, which covered active sites of the catalyst. In addition, it was noted that the cell performance for APTCo_{0.5}C-750 and APT-Co_{0.5}C-850 was much lower than that for APTCo_{0.5}C-650. Considering the peak intensity of Co₃W₃C phase increased with the heattreatment temperature as shown in Fig. 4, the catalytic activity of this compound should be low for hydrogen oxidation. The maximum power density for all samples containing the additive species was not as high as that of APT-850/C. The additives gave rise to the formation of W₂C and Co₃W₃C as well as WC, while APT-850/C was composed of the single phase of WC. Thus, it could be concluded that the WC phase was the most effective for hydrogen oxidation among the tungsten carbide species observed in the present study. This conclusion agreed with the previous literature, which mentioned that W₂C was less active than WC for electrochemical hydrogen oxidation in a H₂SO₄ solution at room temperature.¹⁴

Comparison of the fuel cell performances employing APT-850 and commercial WC.—Influence of crystallite size and specific surface area on electrocatalytic activity of WC was evaluated by comparing the characteristics of APT-850 and commercial WC. The crystallite sizes of WC phase in APT-850 and commercial WC were calculated to be 12 and 37 nm, respectively, from the line-broadening analysis of the diffraction peak. N₂ adsorption measurement revealed that APT-850 and commercial WC possessed specific surface area of 8.3 and 0.6 m² g⁻¹, respectively. The maximum power density of single cell using commercial WC/C was 1.3 mW cm⁻², which was 32% of that in the case of APT-850/C. Accordingly, the fabrication of WC particle with small size and large surface area is desirable for the improvement of catalytic activity for hydrogen oxidation.

Conclusions

We prepared tungsten-based compounds from ammonium paratungstate via temperature-programmed carburization. Fuel cell performance was evaluated by employing the CsH₂PO₄/SiP₂O₇

electrolyte and these carbide catalysts for anode at 200°C. X-ray diffraction and X-ray photoelectron spectroscopy revealed that reduction and carburization of tungsten species proceeded readily during heat-treatment at higher temperatures. The additive nickel or cobalt component promoted the formation of tungsten carbide species, and mixtures of tungsten-based carbide phases were confirmed in the samples with additives. The best single cell performance was achieved by using APT-850/C consisting of WC. Accordingly, the key factor for high catalytic activity is the fabrication of singlephase WC.

The current density for a single cell using APT-850/C as an anode electrocatalyst was lower than that for the conventional Pt/C. However, the obtained APT-850 was more active than commercial WC sample for hydrogen oxidation due to higher surface area and smaller crystallite size. Consequently, it is important to synthesize fine and highly-dispersed WC particles for the enhancement of catalytic activity.

Acknowledgment

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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