New Non-platinum Cathode Based on Chromium for PEFC

Jin-Hwan Kim, Akimitsu Ishihara, Shigenori Mitsushima, Nobuyuki Kamiya, and Ken-ichiro Ota*
Chemical Energy Laboratory, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501

(Received November 30, 2006; CL-061415; E-mail: ken-ota@ynu.ac.jp)

Chromium-based electrocatalysts which were prepared using an R.F. sputter with CrC target under Ar or Ar + N_2 atmosphere with or without heating a substrate at 1073 K were evaluated as a cathode of polymer electrolyte fuel cells (PEFCs). Heating the substrate during the sputtering was found to be very useful to enhance the catalytic activity for oxygen reduction reaction (ORR). It is considered that nitride (CrN) and/or carbonitride ($Cr_2C_{0.39}N_{0.61}$) may have high catalytic activity for the ORR.

Fuel cells have been widely studied as efficient and non-polluting electric power generators. In particular, the polymer electrolyte fuel cells (PEFCs) are expected to be alternative electrical sources for transportable and stationary applications because of their high power density and low operating temperature. However, PEFCs have many problems for their commercialization. The use of platinum as electrocatalysts at anode and cathode is one of the most serious problems, because platinum is expensive and the estimated amount of its resources is too small to supply a huge number of fuel cell vehicles. The other problem is that the slow reaction of oxygen reduction reaction (ORR) leads to a higher overpotential at the cathode.[1,2] In order to solve these problems, many researchers have investigated non-platinum compounds as the cathode of PEFCs.[3–9] Recently, the authors reported that Ta=C=N prepared using R.F. sputter with heating the sputtered materials had some catalytic activity for the ORR in acid media.[10] In this study, chromium(Cr)-based electrocatalysts, which had not been yet reported as a non-platinum cathode for the PEFCs, were prepared using R.F. magnetron sputtering. The electrochemical stability and catalytic activity for the ORR of Cr-based electrocatalysts were evaluated in acid solution. The Cr-based electrocatalysts were characterized using X-ray diffraction (XRD) analysis.

Cr-based electrocatalysts were prepared on bottom of a substrate (Glassy carbon rod: ϕ 5.2 mm) using R.F. magnetron sputtering. Cr_2C_3 (99%: Furuuchi Chemical Co., Ltd.) was used as a target. The chamber was vacuumed less than 1.0×10^{-3} Pa, and then the sputtering gas of Ar (30 sccm) or Ar (5 sccm) + N_2 (25 sccm) mixture was introduced. The Cr-based electrocatalysts prepared under Ar and Ar + N_2 are designated as Cr=C and Cr=C=N, respectively. The actual pressure was then 4.7×10^{-1} Pa. The R.F. magnetron sputtering was carried out for 30 min with an output power of 100 W. In order to examine the effect of heat treatment, the Cr=C and Cr=C=N electrocatalysts were formed at substrate temperatures of 343 (no heat treatment) and 1073 K during the sputtering.

The electrochemical measurements were carried out using a three-electrode cell at 303 K in 0.1 mol dm^{-3} H_2SO_4. A reversible hydrogen electrode (RHE) and a carbon plate were used as the reference and the counter electrode, respectively. The potential was expressed against the RHE. In order to evaluate the electrochemical stability, the cyclic voltammetry (CV) was performed at a scan rate of 50 mV s^{-1} from 0.05 to 1.0 V under N_2. Slow scan voltammetry (SSV) was performed under N_2 and O_2 to obtain the oxygen reduction current, after the cyclic voltammogram reached a steady state. The scan rate and the potential range of SSV were 5 mV s^{-1} and from 1.0 to 0.2 V, respectively. The difference in the current under the O_2 and under the N_2 was regarded as the oxygen reduction current. The current density was based on the geometric area. The catalysts were characterized using X-ray diffraction (XRD) (RIGAKU RINT2500) with Cu Kα radiation in the range from 10 to 90°. The specimens for XRD analysis were prepared on a quartz glass with a thickness of ca. 400 nm.

The cyclic voltammograms (CVs) reached immediately steady state, indicating that the drastic surface charge did not occur due to the potential cycling. Figure 1 shows the steady state CVs of Cr=C and Cr=C=N prepared at 1073 K. As shown Figure 1, there were no specific anodic and cathodic peaks due to the anodic dissolution and cathodic deposition. The anodic electric charge (Q_a) and cathodic charge (Q_c) were calculated using the steady state CVs. When no one-sided reaction based on oxidation and reduction of the catalysts occurred, the ratio of Q_a to Q_c was closed to unity. Both ratios, Q_a/Q_c, of Cr=C and Cr=C=N prepared at 1073 K were 0.96. In addition, the ratios of Cr=C and Cr=C=N prepared at 343 K were 1.02 and 0.97, respectively. These results indicated that all the Cr=C and Cr=C=N prepared at 343 and 1073 K had high electrochemical stability in 0.1 mol dm^{-3} H_2SO_4 in the potential range of 0.05 to 1.0 V. The real surface area of the electrocatalysts was assumed to be proportional to the capacity of an electric double layer. The capacity was estimated using the electric quantity for charge/discharge of the layer. Therefore, the ratio of the real surface area may be assumed to be equal to that of the charge/discharge current of the specimens. Using the values of the

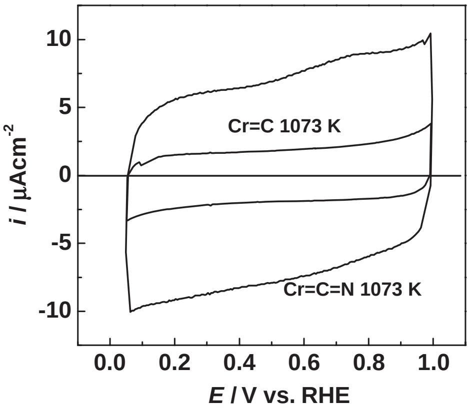

Figure 1. Cyclic voltammograms for the Cr-based electrocatalysts in 0.1 mol dm^{-3} under N_2 at 303 K, scan rate: 50 mV s^{-1}, scan range: 0.05–1.0 V.

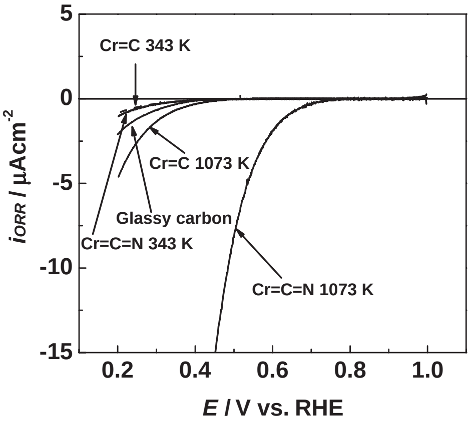

Figure 2. Potential–ORR current density curves for the Cr-based electrocatalysts prepared at 343 and 1073 K.

anodic currents at 0.4 V in the CVs, the ratio of the real surface area between the Cr=C=N and Cr–C prepared at 1073 K calculated to be approximately 3.8.

Figure 2 shows the potential–ORR current density curves for the Cr=C and Cr=C=N. The catalytic activities for the ORR on the Cr=C and Cr=C=N prepared with out heat treatment (at approximately 343 K) were the same and low. Both the C=C and Cr=C=N prepared at 1073 K had higher catalytic activity for the ORR than those at 343 K. This indicated that the heating sputtered material during the sputtering served to enhance the catalytic activity for the ORR. The increase in the catalytic activity for the ORR on the Cr=C=N prepared at 1073 K was much larger than that on the Cr=C prepared at 1073 K. For instance, the i_{ORR} at 0.4 V of the Cr=C=N prepared at 1073 K was approximately 2343 times greater than that of the Cr=C prepared at 343 K. The effect of the real surface area on the i_{ORR} must be considered to compare the catalytic activity. Because the ratio of the real surface area between Cr=C=N and Cr=C prepared at 1073 K was approximately 3.8, the difference of i_{ORR} at 0.4 V was much greater than the ratio of the real surface area. This revealed that the increase in the i_{ORR} was responsible for the increase in the catalytic activity for the ORR. Therefore, the sputtering under gas atmosphere containing nitrogen was found to be very useful for increasing the catalytic activity for the ORR. The electrode potential at the i_{ORR} of $-0.2\,\mu A\,cm^{-2}$, which was designated as E_{ORR}, was regarded as the onset potential where the i_{ORR} started to flow. The E_{ORR} of the Cr=C=N prepared at 1073 °C, which had the highest catalytic activity for the ORR in this experiment, was 0.72 V. This value was nearly the same as that of the Zr=O=N prepared using reactive R.F. sputtering at 1073 K, that is, 0.73 V, and that of the Ta=C=N prepared at 1073 K, i.e., 0.73 V.[10,11]

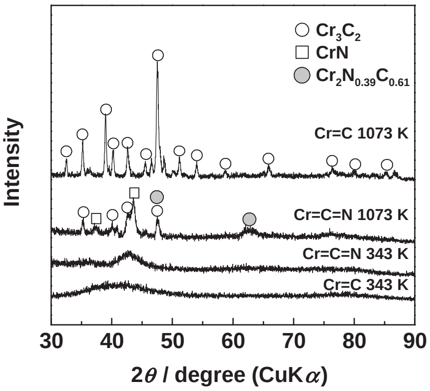

Figure 3. XRD patterns for the Cr–C and Cr–C–N prepared at 343 and 1073 K.

Figure 3 shows the XRD patterns for the Cr=C and Cr=C=N prepared at 343 and 1073 K. Each Cr=C and Cr=C=N prepared at 343 K showed a broad peak at near 43°. This indicates that Cr=C and Cr=C=N prepared at 343 K were composed of amorphous phase or nanocrystals. The sharp peaks of the Cr=C and Cr=C=N prepared at 1073 K demonstrated that the crystallization or the growth of nanocrystals proceeded. The XRD peaks of the Cr=C prepared at 1073 K corresponded to those of Cr_3C_2 (JCPDS; 35-0804). The XRD peaks of the Cr–C–N prepared at 1073 °C showed not only Cr_3C_2 (JCPDS; 35-0804) but also CrN (JSPDS; 11-0065) and $Cr_2C_{0.39}N_{0.61}$ (JSPDS; 19-0325). The sputtering under gas atmosphere containing nitrogen resulted in the formation of nitride and carbonitride. Because the catalytic activity for the ORR on the Cr=C and Cr=C=N prepared at 1073 K was higher than that prepared at 343 K, the crystallization or the crystal growth may increase the catalytic activity. In addition, because the catalytic activity on the Cr=C=N prepared at 1073 K was much greater than that on the Cr=C prepared at 1073 K, nitride (CrN) and/or carbonitride ($Cr_2C_{0.39}N_{0.61}$) may have high catalytic activity for the ORR. It seems that nitrogen in the electrocatalyst strongly affects the catalytic activity.

Chromium-based compounds prepared using R.F. magnetron sputtering with or without heat treatment at 1073 K were investigated at the non-platinum cathode for PEFCs. Heating the substrate during the sputtering served to enhance the catalytic activity for the ORR. The sputtering under gas atmosphere containing nitrogen was found to be very useful for increasing the catalytic activity. It seems that Cr=C=N electrocatalysts prepared at high temperature have the possibility as the substitute materials of the cathode for PEFCs.

References

1 R. Cote, G. Lalande, G. Faubert, D. Guay, J. P. Dodelet, G. Denes, *J. New Mater. Electrochem. Syst.* **1998**, *1*, 7.
2 B. Wang, *J. Power Sources* **2005**, *152*, 1.
3 D. Villers, X. Jacques-Bedard, J. Dodelet, *J. Electrochem. Soc.* **2004**, *151*, A1507.
4 S. Marcotte, D. Villers, N. Guillet, L. Roue, J. P. Dodelet, *Electrochim. Acta* **2004**, *50*, 179.
5 Y. Liu, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *Electrochem. Solid-State Lett.* **2005**, *8*, A400.
6 V. Mentus, *Electrochim. Acta* **2004**, *50*, 27.
7 M. Azuma, M. Kashihara, Y. Nakato, H. Tsubomura, *J. Electroanal. Chem.* **1988**, *250*, 73.
8 A. Ishihara, K. Lee, S. Doi, S. Mitsushima, N. Kamiya, M. Hara, K. Domen, K. Fukuda, K. Ota, *Electrochem. Solid-State Lett.* **2005**, *8*, A201.
9 K. Lee, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *Electrochim. Acta* **2004**, *49*, 3479.
10 J. Kim, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *Electrochemistry*, in press.
11 S. Doi, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, *J. Electrochem. Soc.* **2007**, *154*, B362.