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Effect of thermal treatment on structural change of anode electrocatalysts for direct methanol fuel cells

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ABSTRACT

Commercially available carbon-supported Pt, PtCo and PtRu catalysts from E-TEK are heat-treated in turn at 600 °C and 800 °C each for an hour. The as-received and as-heated catalysts are used as anode catalysts for direct methanol fuel cells. Structural and surface composition changes induced by heating are analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. For the Pt catalyst, heating the catalysts caused only the mass activity decrease due to particle sintering, whereas the specific activity and CO tolerance remained unchanged. The performance of the PtCo and PtRu catalysts is affected differently by heating. Heating the PtRu catalyst adversely affects its catalytic activity and its CO tolerance due to Pt depletion at the surface. In contrast, although Pt depletion also takes place for the heated PtCo catalysts, these catalysts show an even higher specific activity and approximately the same CO tolerance. The observed difference is likely due to the optimum atomic ratio difference for Ru/Pt and Co/Pt; an increased atomic ratio on the surface for Co/Pt results in an activity enhancement, which is contrary to the effect of the increase of Ru/Pt atomic ratio.

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1. Introduction

The most likely polymer electrolyte membrane fuel cells for portable power source applications are direct methanol fuel cells (DMFCs), which have obvious advantages due to the elimination of a fuel-processor subsystem (Liu et al., 2006; Wee & Lee, 2006; Serov & Kwak, 2009). One of the pending issues hindering the development of DMFCs is the poor catalytic performance at the anode (Li, Zheng, Liao, & Zeng, 2011). Pt catalysts are active for methanol electrooxidation but are also self-poisoned by the reaction by-products such as CO-like species (Long, Ohtaki, Hien, Randy, & Nogami, 2011; Zhao et al., 2011). It is well known that, in addition to the chemical composition of the catalyst system, the performance of the catalyst is also very much dependent on its preparation method, the type of support materials used and the pretreatment procedures (Wasmus & Kuver, 1999). Structural changes can also result in changes in the catalytic activity. One crucial factor that must be taken into account is the surface depletion/enrichment upon thermal treatment for binary catalysis. Unfortunately, many of the published works involving heat treatment failed to provide this evidence (Castro Luna, Camara, Paganin, Ticianelli, & Gonzalez, 2000;

Li et al., 2004; Min, Cho, Cho, & Kim, 2000; Watanabe, Tsurumi, Mizukami, Nakamura, & Stonehart, 1994). In this work, we specifically studied the effects of structural changes of the catalysts and correlated the effects with the catalysts' activity. The typical catalysts used in a DMFC were selected, including Pt and PtRu catalysts. Because transition metals such as Fe, Co and Ni are often abducted with Pt to form alloyed catalysts for DMFC applications, we also selected PtCo catalysts in this study.

2. Experimental

Commercially available Pt, PtCo and PtRu catalysts supported on XC-72 Vulcan carbon with a metal loading of 20 wt% were sourced from E-TEK. The nominal Pt-to-M (M=Co and Ru) atomic ratio is 1 to 1. The catalysts were heat treated in a tubular furnace for one hour at 600 °C and 800 °C, at a heating rate of 5 °C/min. (Note that in our experiments, the catalysts were heat treated at different temperatures with 100 °C as the interval. The catalysts heated at 600 °C and 800 °C were selected for this study because they have distinct properties.) High-purity Ar (0.5 sL/min) was flushed for one hour before heating and was then cooled to room temperature. The as-heated catalysts are denoted as Pt/C-X, where X represents the heating temperature (for example, Pt/C-600 is the catalyst heated at 600 °C), and Pt/C represents the as-received catalysts without heat treatment.

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The X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Rigaku D/Max-3B diffractometer (Shimadzu) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ angles were scanned from 20° to 85° at $4^\circ/\text{min}$. The diffraction data were curve-fitted using a least square program provided by the equipment manufacturer. The elemental compositions were determined by an energy-dispersive X-ray (EDX) analyzer attached to a JEOL MP5600LV scanning electron microscope (SEM) operating at 15 kV. The surface compositions were obtained by X-ray photoelectron spectroscopy (XPS). The XPS data were obtained using an ESCALAB MKII spectrometer (VG Scientific) using Al-K α radiation (1486.71 eV). The spectral correction was based on the graphite C1s level at 284.5 eV (Gurau et al., 1998). The vendor-supplied XPSPEAK version 4.1 was used to deconvolute all of the XPS data using fixed half widths and fixed spin-orbit splitting in the first trials.

All of the electrochemical evaluations were performed at room temperature. A conventional three-compartment electrochemical cell was used to evaluate the catalysts by cyclic voltammetry (CV). An Autolab PGSTAT12 served as the potentiostat/galvanostat. A rotating disk electrode (RDE, EG & G PARC, Model 616) was used as the working electrode. The catalyst layer on the RDE was fabricated by casting $10 \mu\text{L}$ of catalyst ink by micropipette (10 mg of catalysts + 1 mL of ethanol + 0.1 mL of Nafion (5 wt% from Aldrich)) onto a 5 mm diameter vitreous carbon disk electrode to a metal loading of $0.92 \text{ g}/\text{m}^2$. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively, whereas 1 M CH_3OH (Merck) in 0.5 M H_2SO_4 (Merck) was the electrolyte for the catalytic activity test. A stationary electrode was used except for the CO-stripping measurements, in which the electrode was kept at 400 rpm to avoid the formation of gas bubbles. The electrochemical active surface area measurements and the CO-stripping CV tests were performed in a 0.5 M H_2SO_4 electrolyte. All reported potentials were referenced to the SCE. The catalysts were cycled between 0 and 1 V at $20 \text{ mV}/\text{s}$ until a stable response was obtained before the cyclic voltammograms were recorded. For CO stripping, 10% CO in argon gas was employed. The electrolyte was saturated with the gas while the electrode was held at -0.15 V for 30 min. After CO adsorption, the bulk CO was removed, and the electrolyte was thoroughly purged by high-purity Ar. The CO-stripping CVs were collected from -0.15 V (starting potential) with two potential vertices at 1 and -0.2 V . The completed oxidation of the adsorbed species was accomplished in the first scan, and no oxidation was found in the second scan.

3. Results and discussions

3.1. Physicochemical characterization of the catalysts

The metal loadings in the catalysts were confirmed to be 20 wt% by EDX. The atomic ratio of Pt-to-Ru was also confirmed to be 1 to 1, whereas the Pt-to-Co ratio was 1 to 1.2, in contrast with the nominal ratio of 1 to 1.

XRD is a conventionally employed bulk analysis technique by which information about the crystal structure, lattice parameters and crystal orientation of the supported catalysts can be obtained. Figs. 1–3 show the XRD patterns of the as-received and as-heated catalysts for Pt, PtRu and PtCo, respectively. The reflection centered at $2\theta = 25^\circ$ in Figs. 1 and 3 is the graphite (002) diffraction from the XC-72 carbon support (Liu, Qiu, Chen, & Zhu, 2002; Liu, Yang, Han, Chen, & Gan, 2002). The expected sharper and more intense diffraction peaks that are observed upon increasing the heating temperature, as seen in Figs. 1–3, are caused by an increase in the degree of crystallization and particle sintering, particularly at 800°C . For the Pt/C catalysts seen in Fig. 1, the strong diffraction

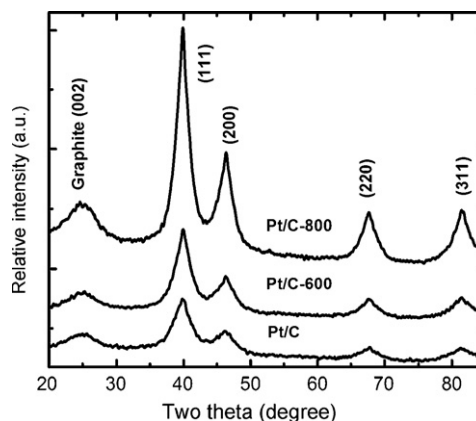


Fig. 1. XRD patterns of the Pt/C, Pt/C-600 and Pt/C-800 catalysts.

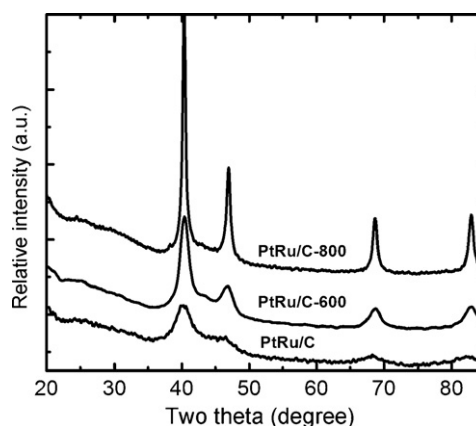


Fig. 2. XRD patterns of the PtRu/C, PtRu/C-600 and PtRu/C-800 catalysts.

peaks at Bragg angles of 39.8° , 46.3° , 67.5° and 81.3° can be indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of face-centered cubic platinum. The same pattern was also observed for all heat-treated catalysts, indicative of an f.c.c Pt structure. The XRD patterns shown in Fig. 2 for the PtRu catalysts match the Pt f.c.c structure but are shifted to higher 2θ values. There were no observable lines corresponding to those of the hexagonal structure of pure Ru. The shift in the 2θ value corresponds to a decrease in the lattice parameter due to the incorporation of smaller Ru atoms into the Pt lattice (Zhang & Chan, 2003). The diffraction peak positions at the (1 1 1) facet for PtRu/C-600 and PtRu/C-800 shifted to 40.4° . This result can be

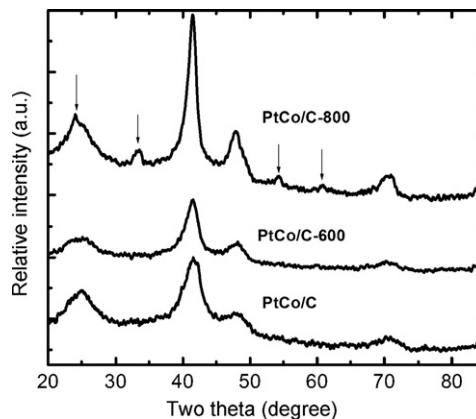


Fig. 3. XRD patterns of the PtCo/C, PtCo/C-600 and PtCo/C-800 catalysts.

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