Pt-Ru Bimetallic nanoparticles loading on activated carbon fibers without using reducing agents

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Platinum-ruthenium (Pt-Ru) bimetallic catalyst system is being used as catalyst materials of DMFCs anode due to its high tolerance for carbon monoxide poisoning. Recently, activated carbon fiber (ACF) is reported as a useful catalyst support because it has several advantages such as high dispersion of impregnated metals and low mass transfer resistance due to its uniformly developed micropores. Therefore, Pt-Ru nanoparticles loading on ACF without using reducing agents is carried out to develop an effective bimetallic catalyst. PtCl62− and Ru3+ are impregnated on ACF, and heated up to 800°C in N2. TG, XRD, TEM and EDS analyses are carried out to confirm Pt/Ru particles loading and distribution on ACF. The amount of PtCl62− impregnation is average 75% larger than that of Ru3+ at pH upto 3.5 and increases after pH 3.5 by crossing that of PtCl62−, while Ru3+ impregnation is much affected by pH. There are uniformly distributed Pt and Ru nanoparticles, which means simple impregnation and heating the PtCl62− and Ru3+ complexes up to 400°C is enough to obtain pure Pt-Ru nanoparticles on ACF without using reducing agents.

Keywords: Platinum-ruthenium alloyed nanoparticles, Activated carbon fiber, Co-impregnation

The direct methanol fuel cells (DMFCs) have been considered as a reasonable power source for portable and transportation applications1−3. Platinum (Pt) particles are known as having a high catalytic activity for the oxidation of methanol. However, catalyst poisoning was caused by carbon monoxide under low-temperature reaction and this can be solved by using binary or multi-component anode catalysts4,5. Ruthenium (Ru) is recommended as a second catalyst that promotes effective methanol electrooxidation. Therefore, Pt-Ru bimetallic catalyst system is now being used as catalyst materials of DMFCs anode due to its high tolerance for carbon monoxide poisoning6−8. Bimetallic catalyst of high surface area is generally prepared by co-impregnation, co-precipitation, or absorbing colloids which use reducing agents6,10.

Activated carbon (AC) has been used as DMFC supported material because of high specific surface area, high adsorption capacity, and good mechanical strength1,11,12. However, uniform distribution of Pt-Ru nanoparticles on activated carbon is not easy due to the different pore size distribution. Recently, activated carbon fiber (ACF) was reported as a useful catalyst support because it has several advantages such as high dispersion of impregnated metals and low mass transfer resistance due to its uniformly developed micropores13−15. Therefore, easy and uniform dispersion process is now being surveyed for the effective catalyst impregnation on ACF. Ryu et al.16 have studied the Pt loading on ACF without using reducing agents, and easily obtained uniformly distributed Pt nanoparticles. Therefore, Pt-Ru nanoparticles loading on ACF without using reducing agents was carried out to develop an effective bimetallic catalyst for using in DMFCs electrode. To obtain the purpose, (i) Pt and Ru compounds were dissolved in distilled water and ACF was added to the solution, (ii) the PtCl62− and Ru3+ complexes co-impregnated ACF were heat treated in N2 surrounding and (iii) TG, XRD, EDS analyses were carried out to confirm Pt-Ru particles loading on ACF, and TEM observations were carried out to study the distribution of metals.

Experimental Procedure

Materials
Activated carbon fiber (ACF, Toyobo KF-1500, Japan, BET specific surface area: 1435 m²/g) was chopped, washed in distilled water and dried for over
night at 110°C in a vacuum dryer. H$_2$PtCl$_6$·5.7H$_2$O (Kojima Chemicals Co.) and RuCl$_3$·3H$_2$O (Aldrich) were used as the Pt and Ru sources. H$_2$PtCl$_6$·5.7H$_2$O was dissolved in distilled water, produced PtCl$_6^{2-}$ and 2H$^+$, and named Pt solution. RuCl$_3$·3H$_2$O was also dissolved in distilled water, produced Ru$^{3+}$ complexes such as [Ru(H$_2$O)$_6$]$_{3+}$, RuCl$_3$(H$_2$O)$_3$, [RuCl(H$_2$O)$_5$]$_{2+}$, and named Ru solution.

**Preparation and characterization of Pt/Ru loaded ACF**

Figure 1 shows the schematic flow diagram of Pt-Ru loading on ACF. Chopped (4-6 mm) ACF was added to (i) Pt and Ru mixed solution, (ii) Pt solution following Ru solution, (iii) Ru solution following Pt solution, and agitated for different time intervals at 100 rpm, pH 5.0, and 25°C. Then, the PtCl$_6^{2-}$ and Ru$^{3+}$ complexes co-impregnated ACFs were removed from the solutions. Absorbancies of filtrates were measured with UV-spectrophotometer (Shimadzu V-1700, Pharma Spec. Japan) at 325 µm, and the residual metal concentrations were measured with ICP (Optima 3300DV, Perkin-Elmer Inst.). The impregnation amounts of PtCl$_6^{2-}$ and Ru$^{3+}$ complexes on ACFs were calculated from the standard curves and the results were compared before and after impregnation. TG analyses of metal ion impregnated ACFs were carried out to investigate the degradation of PtCl$_6^{2-}$ and Ru$^{3+}$ complexes in nitrogen surrounding. Then, one set of ampoules was heated up to 800°C, simultaneously. When the ampoules were raised up to desired temperature, the corresponding ampoule was quenched and sealed off for further XRD (D/MAX2000 Ultima/PC, Rigaku Co.) and energy dispersive spectroscopy (EDS, ThermoNoran co.) study. The average particle size was estimated from the broadening of the (220) reflection for the Pt-Ru/ACF samples following the Endo’s method.

The structural characteristics of Pt-Ru nanoparticles loaded ACF were investigated by N$_2$ adsorption at 77 K (Micromeritics ASAP-100). TEM (JEOL, JEM-2010) observations were carried out to study the morphology and distribution of Pt/Ru nanoparticles on ACFs.

**Results and Discussion**

**Impregnation of PtCl$_6^{2-}$ and Ru$^{3+}$ on ACF**

Figure 2 shows the impregnation amounts of PtCl$_6^{2-}$ and Ru$^{3+}$ complexes on ACFs from solution as a function of ion concentration. The impregnated amounts of both ions increased as the increase of ion concentration. The amount of PtCl$_6^{2-}$ impregnation was average 75% larger than that of Ru$^{3+}$ complexes for each concentration at pH 5.0 for 30 min.

Figure 3 shows the co-impregnation of PtCl$_6^{2-}$ and Ru$^{3+}$ complexes on ACFs from mixed solution (Pt/Ru) and step by step impregnation (PtCl$_6^{2-}$ following Ru$^{3+}$, Ru$^{3+}$ following PtCl$_6^{2-}$). The co-impregnation amount of PtCl$_6^{2-}$ from Pt-Ru was larger than that of mixed
solution. However, the total amounts of both competitive ion impregnation were similar between Pt/Ru and Pt-Ru, while the amount of Ru\(^{3+}\) impregnation alone was a little smaller than that of competitive impregnation with PtCl\(_6^{2-}\). This was due to the formation of complexes such as [Ru(H\(_2\)O)\(_6\)]\(^{3+}\), and which resulted in the decrease of impregnation.

Figure 4 shows the impregnation of PtCl\(_6^{2-}\) (1000 ppm) and Ru\(^{3+}\) (1000 ppm) complexes on ACFs as a function of pH. The amount of PtCl\(_6^{2-}\) impregnation was not affected below the pH 5.0, however Ru\(^{3+}\) (1000 ppm) complexes impregnation was deeply affected by solution pH between 3.0 to 5.0, which was due to the variety of Ru\(^{3+}\) complexes in low pH solution.

Figure 5 shows the TG curves (a) PtCl\(_6^{2-}\), (b) Ru\(^{3+}\) complexes, (c) PtCl\(_6^{2-}\) and Ru\(^{3+}\) complexes coimpregnated ACF, and (d) the as-received ACF as a function of temperature in N\(_2\) surrounding, with which the degradation of PtCl\(_6^{2-}\). Ru\(^{3+}\) complexes, especially simultaneous change of the PtCl\(_6^{2-}\) and Ru\(^{3+}\) complexes on ACF can be studied. The TG curve of the as-received ACF shows constant up to 500°C after evaporation of water and then slowly declined. The weight of both PtCl\(_6^{2-}\) and Ru\(^{3+}\) complexes impregnated ACF was slowly decomposed between 100°C to 400°C, following the rapid declination. The single phase degradation means Pt and Ru atoms became alloyed nanoparticles. Wang\(^6\) and Kawaguchi\(^8\) reported the similar degradation of Pt and Ru coimpregnated carbon black.

Figure 6 shows the XRD patterns of PtCl\(_6^{2-}\) and Ru\(^{3+}\) complexes co-impregnated ACF which were heated up to 400°C. The four characteristic peaks at 20 values of ca. 39.8, 46.5, 67.8, and 81.2°, respectively, corresponding to (111), (200), (220), and (311) planes of the face-centered cubic (fcc) crystalline of Pt were observed in the XRD pattern. This result was the same as many other researchers have reported\(^4,6,8,12\). The absence of the Ru peaks in Pt-Ru/ACF was believed principally single phase disordered structures, indicating the formation of alloy nanoparticles\(^6\). Kawaguchi\(^8\) also reported that relative small size of Ru atom was embedded in the Pt-Ru crystalline structure. Therefore, EDX analysis was necessary to confirm the Ru nanoparticles in ACF.

Figure 7 shows the EDS graph of PtCl\(_6^{2-}\) and Ru\(^{3+}\) complexes impregnated ACF, heated up to 400°C. It indicates that all peaks in the EDS graph were
associated with the carbon support, platinum and ruthenium. Therefore, Ru particle size was also loaded on ACF by this simple impregnation and heating the Ru\textsuperscript{3+} complexes.

Figure 8 shows the TEM observation of Pt and Ru loaded ACF, which was heated at 400°C. There were uniformly distributed Pt-Ru alloyed particles and the average particle size was about 5-8 nm, which was very similar to Wang\textsuperscript{6} and Kawaguchi’s result\textsuperscript{8}. The average Pt particle size on ACF was 2.0 nm through the same impregnation and heating method\textsuperscript{16}. This means the average particle size of metal increased by the aggregation of two metal particles\textsuperscript{6}, and the size was enlarged as the increase of heat treatment temperature\textsuperscript{8}. In spite of growth of particle size, Pt and Ru alloyed nanoparticles on ACF can be obtained by simple impregnation and heating the metal ions without using reducing agents.

Table 1 shows the textural properties of the Pt and Ru nanoparticles loaded ACF determined by N\textsubscript{2} adsorption at 77 K. The BET specific surface area and total pore volume decreased due to the Pt-Ru nanoparticles loaded on ACF. The ratio of micropore volume to total pore volume also reduced, while average pore diameter was enlarged. These indicated that Pt-Ru nanoparticles were mainly loaded at the entrance of micropores.

**Conclusions**

Pt-Ru alloyed nanoparticles loading on activated carbon fiber (ACF) can be easily carried out by co-impregnation of PtCl\textsubscript{6}\textsuperscript{2-} and Ru\textsuperscript{3+} complexes from solution and heating the ion impregnated ACF up to 400°C in N\textsubscript{2} without using reducing agents for developing an effective bimetallic catalyst. However, the total amount of co-impregnated ions were no difference between mixed ion solution and step by step solution. The amount of PtCl\textsubscript{6}\textsuperscript{2-} impregnation was about 75% larger than that of Ru\textsuperscript{3+} complexes up to 3.5 and increases after pH 3.5 by crossing over PtCl\textsubscript{6}\textsuperscript{2-}. The XRD, TEM and EDS analysis confirmed the Pt-Ru alloyed nanoparticles loading and uniform distribution on ACF, which means that heating up the PtCl\textsubscript{6}\textsuperscript{2-} and Ru\textsuperscript{3+} complexes to 400°C is enough to obtain pure Pt-Ru bimetallic nanoparticles loading on ACF without using reducing agents.

**References**