

# Preparation of PtRu nanoparticles on various carbon supports using surfactants and their catalytic activities for methanol electro-oxidation

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## Abstract

In the anodes of direct methanol fuel cells (DMFCs), Pt poisoning by CO adsorption during methanol electro-oxidation has been a serious problem. Efforts to overcome or minimize this obstacle have largely involved investigations of PtRu bimetallic catalysts. In order to prepare fine PtRu alloyed hydrosols, we used non-ionic surfactants including L121, Pluronic P123, P65, Brij 35, and Tween 20 as stabilizers in this study. The sizes of the prepared metal particles change with the surfactant used. The finest metal hydrosol is obtained when Pluronic P123 and P65 are used. The resulting metal hydrosols with Pluronic P123, Brij 35 and Tween 20 are supported on Vulcan XC-72R. PtRu/XC-72R prepared with Pluronic P123 exhibits the best catalytic activity due to better dispersion of the alloyed metal. To improve further the activity of the PtRu catalyst, the commercial Vulcan XC-72R is replaced with carbon spherule (CS), a home-made carbon support. Electrochemical analyses such as cyclic voltammetry and galvanostatic-polarization tests are performed to evaluate the prepared catalyst. PtRu/CS has a superior performance to PtRu/XC-72R in methanol electro-oxidation when Pluronic P123 is employed as the stabilizer. The higher conductivity and larger inter-particle space of the CS appear to facilitate methanol electro-oxidation.

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**Keywords:** Direct methanol fuel cell; Methanol electro-oxidation; Platinum poisoning; PtRu or Platinum-ruthenium; Carbon spherule

## 1. Introduction

Direct methanol fuel cells (DMFCs) operating at low temperature are a promising power sources for a range of applications including transportation and portable power sources, since they do not require a separate hydrogen-generation system and use liquid methanol as fuel [1–5]. Even with the many advantages of DMFC, there are obstacles to overcome before commercialization will be possible. First of all, platinum, the electrode catalyst for DMFC, which is very active in hydrogen oxidation, methanol oxidation and oxygen reduction at relatively low temperature, is

very expensive. Numerous workers have addressed this problem [6–8]. Another drawback is platinum poisoning. When methanol electro-oxidation occurs in the DMFC anode, platinum is easily poisoned by CO adsorption [5,9–11]. To prevent or minimize this CO poisoning, many researchers have focused on secondary metal insertion in the platinum-loaded electrode. In this study, we chose ruthenium to improve a platinum-loaded electrode since this electrode generally shows the best performance when ruthenium is used as a secondary metal [12–17]. We have devised a novel method for synthesizing nano-sized metals and have evaluated the resulting catalysts for methanol electro-oxidation.

Traditionally, supported catalysts have been prepared by wet impregnation of the support material using water-soluble metal salts, followed by calcination and reduction. This method usually results in well-dispersed catalysts with reasonable activity and good thermal stability. The particle size-distribution of the active phase is, however, usually quite broad. Several other

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preparation methods have been investigated to prepare catalysts with fine particles and a narrower size-distribution [18–24]. Preparing hydrosols via stabilization of nano-sized metals by hydrophilic surfactants is one of the more promising techniques to achieve this goal. The main advantage of this technique, compared with others, is that the particles are formed at atmospheric pressure and room temperature, so that the procedure is not sensitive to the amount of surfactant. Bönnemann et al. [25] suggested a method for hydrosol preparation, but the process was somewhat complicated and made commercial production less feasible.

In this study, alloyed metal particles of platinum and ruthenium are prepared by a similar hydrosol method and deposited on a commercial carbon support, Vulcan XC-72R. This marks the first attempt to make PtRu hydrosols with a non-ionic surfactant; Bönnemann et al. [25] made Co, Rh, Pt, PtPd and PtRh hydrosols with surfactant, but not PtRu. In this study, PtRu hydrosols are prepared using various surfactants so that fine metal particles with a narrower size-distribution are obtained. Borohydride reduction is employed to reduce the metal precursors. In addition, a new type of carbon support material is used in place of Vulcan XC-72R to improve methanol electro-oxidation activity. This carbon support material is named ‘carbon spherule’ (CS) on account of its morphology. This carbon material has been investigated and performs well as the anode material for Li-ion secondary batteries [26–28].

## 2. Experimental

### 2.1. Preparation of PtRu hydrosols

Surfactants including L121 (Synperonic polyethylene; ICI Surfactants America), Pluronic P123, P65 [poly(alkylene) oxide triblock copolymer; BASF], Brij 35 (polyoxyethylene lauryl ether; Aldrich), and Tween 20 (polyoxyethylenesorbitan monolaurate; Samchun) were used as stabilizers to synthesize PtRu hydrosol. Hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Kojima) and ruthenium trichloride ( $\text{RuCl}_3$ , Strem Chemicals) were used as Pt and Ru precursors, respectively.

The two metal precursors, 0.011 g ( $2.68 \times 10^{-5}$  mol)  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 0.0053 g ( $2.56 \times 10^{-5}$  mol)  $\text{RuCl}_3$ , were dissolved in de-ionized water at a 1:1 molar ratio of Pt:Ru. The solution was vigorously stirred for 2 h. After the precursors had dissolved, the solution was a semi-transparent dark purple. The chosen surfactant was then poured into the solution to stabilize the metal particles.

0.02 g  $\text{NaBH}_4$ , a strong liquid-phase reducing agent, was dissolved in 20 ml deionized water, and a small amount of  $\text{NaBH}_4$  solution was slowly injected into the previously prepared metal salt solution at a specific input rate using a 50-ml syringe. The metal salt solution gradually turned opaque black in less than 10 min after the  $\text{NaBH}_4$  solution was injected. The resulting solution was stirred for an additional 2 h. The prepared metal particles were named PtRu(P), PtRu(B), and PtRu(T), according to the surfactant used. Dynamic light scattering (DLS; Brookhaven Instruments Company photon correlation spectrometer equipped with a BI-200SM goniometer and a BI-

9000AT correlator) was performed to analyze the size of the metal particles stabilized by each surfactant.

### 2.2. Preparation of CS

CS was first prepared via hydrothermal synthesis and carbonization by Wu et al. [27]. Sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , Kanto) was selected as a precursor. After a stainless-steel autoclave was filled with 3 M sucrose solution, hydrothermal treatment was carried out at 190 °C for 5 h. The resulting black powder was washed with de-ionized water, dried at room temperature overnight, and carbonized in a tube furnace in flowing  $\text{N}_2$  at 35 ml  $\text{min}^{-1}$ . The heat was ramped at 5 K  $\text{min}^{-1}$ , and the final temperature of 1000 °C was applied.

The BET measurement was conducted at 77 K with a sorptometer (Micromeritics Instrument Corporation, ASAP 2010 series) to determine whether the carbon had sufficient BET surface area to support 20 wt.% of metal particles. The carbon samples were about 70–85 mg, and the samples were pretreated at 150 °C before analysis. The adsorption and carrier gases were  $\text{N}_2$  and He, respectively.

### 2.3. Deposition of PtRu nanoparticles on Vulcan XC-72R and CS

After the commercial carbon support, Vulcan XC-72R, was dispersed in *n*-butanol for 2 h, the metal particles were slowly added at a specific input rate using a 100-ml syringe while stirring vigorously for 2 h at 20 °C. Then, the PtRu/XC-72R catalyst sample was filtered, washed with ethanol and hot water, and dried under vacuum for 12 h. Heat treatment at 200 °C followed to remove impurities contained in the sample. The amount of metal in the catalyst was fixed at 20 wt.%, and the catalyst was named PtRu(S)/XC-72R [(S): (P) for Pluronic P123, (B) for Brij 35, or (T) for Tween 20]. The dispersion of metal particles on Vulcan XC-72R was analyzed by means of transmission electron microscopy (TEM, Jeol, JEM-2000EX II).

For preparation of PtRu nanoparticles on CS, only Pluronic P123 at half a critical micelle concentration (CMC) was used as a surfactant to synthesize fine metal particles since it produced much better results than Brij 35 and Tween 20 (Fig. 1). Other preparation procedures were similar to the PtRu/XC-72R samples.

### 2.4. Catalyst evaluation

All catalytic activities of the prepared PtRu samples were evaluated for methanol electro-oxidation by confirming the maximum current density in a half-cell test. The half-cell was a three-electrode cell system. A glassy carbon electrode, a Pt mesh electrode and an Ag/AgCl electrode served as the working electrode (BASi, MF-2012), the counter electrode (Princeton Applied Research, 219810) and the reference electrode (BASi, MF-2052 RE-5B), respectively.

The catalyst ink was prepared by mixing the PtRu samples, ionomer (Nafion) and isopropyl alcohol for 12 h. Glassy carbon coated with the catalyst ink was used as the working elec-

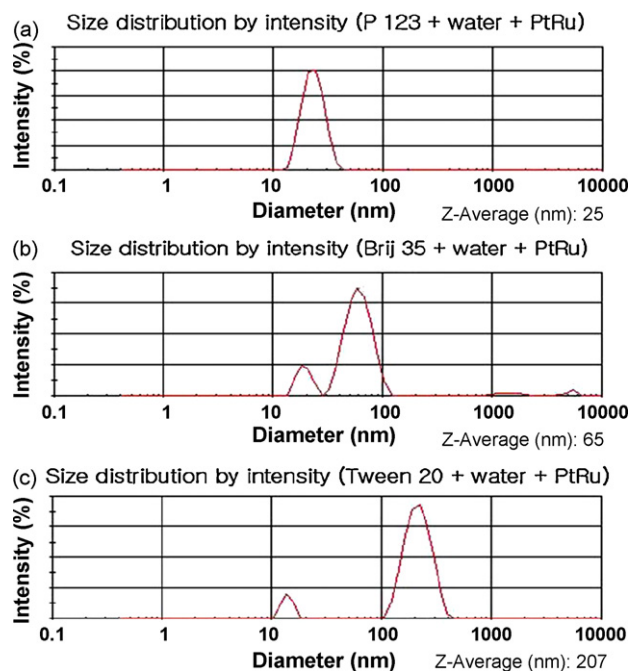


Fig. 1. Comparison of size-distribution of (a) PtRu(P), (b) PtRu(B), and (c) PtRu(T).

trode. All activity tests were performed in aqueous 0.5 M  $\text{H}_2\text{SO}_4$  solution and 1 M methanol after nitrogen purging to remove dissolved oxygen. Cyclic voltammograms were recorded with a potentiostat (Gamry Instruments, PC4/750) at a constant temperature of 40 °C in a water-jacketed reactor. The maximum current obtained from the potentiostat was converted into current density  $\text{mA mg}^{-1}$ .

### 3. Results and discussion

#### 3.1. Preparation and characterization of fine metal particles using various surfactants

Fine, well-dispersed metal particles on the support material are essential for effective metal loading in order for the same amount of catalyst material to result in greater activity. Several surfactants were used to synthesize the PtRu hydrosols, and the resulting hydrosols were combined with a mixture of pre-made Vulcan XC-72R and *n*-butanol to prepare the PtRu/XC-72R catalyst samples. The *n*-butanol not only dispersed the hydrophobic Vulcan XC-72R, but also destabilized the PtRu hydrosols. The dielectric constant was an important criterion for choosing the most appropriate solvent. Since *n*-butanol has a lower dielectric constant than water, PtRu hydrosols can be easily destabilized and deposited on the carbon support. Although other solvents with higher or lower dielectric constants than *n*-butanol such as methanol, ethanol, and heptanol were also tested, *n*-butanol resulted in the best PtRu/XC-72R sample in terms of metal dispersion on the carbon support and catalytic activity for methanol electro-oxidation.

Although a reverse micelle procedure has often been used to make fine metal particles [21,23,25], we prepared PtRu nanopar-

ticles by the hydrosol method. Deionized water was used as the solvent instead of a toxic organic solvent such as tetrahydrofuran (THF). In addition, the amount of surfactant used to stabilize the metal particles could be reduced through this process since hydrosol formation is not sensitive to the amount of surfactant, as previously mentioned. It was assumed that the PtRu nanoparticles could be stabilized although Pluronic P123 below CMC is used since the long hydrophobic chains (PPO group) of Pluronic P123 strongly attract one another in water. Actually, it is generally known that the CMC of Pluronic P123 is  $0.4 \text{ g L}^{-1}$  at room temperature. Thus, it was first attempted to stabilize PtRu nanoparticles with half a CMC of Pluronic P123 ( $0.2 \text{ g L}^{-1}$ ). An outstanding dispersion of the metal particles was obtained on the carbon support. Meanwhile, poor dispersion occurred when an even lower amount ( $0.1 \text{ g L}^{-1}$ ) of the surfactant was injected. Therefore, half a CMC of Pluronic P123 was used throughout the whole investigation. The minimum amount of the surfactant was not precisely defined, but half a CMC seems to be sufficient to stabilize the metal particles. Furthermore, if less surfactant is used to stabilize the metal particles, it will be easier to remove the surfactant after the catalyst is prepared.

The resulting samples were named PtRu(P), PtRu(B), and PtRu(T), corresponding to the surfactants, Pluronic P123, Brij 35, and Tween 20, respectively. Dynamic light scattering was used to confirm the formation of hydrosols (Fig. 1). Among the surfactants, Pluronic P123 resulted in the finest PtRu hydrosol formation with a narrow size-distribution. This implies that Pluronic P123 stabilizes the metal particles most effectively.

Pluronic P123 is a polyoxyalkylene (POA) type triblock copolymer, while Brij 35 and Tween 20 are polyoxyethylene type polymers that have been widely used in catalyst preparation through micelles (Fig. 2). It is postulated that Pluronic P123 forms a more densely packed micelle structure than the other surfactants due to its relatively large hydrophobic tails. Therefore, it can stabilize metal particles and thereby more effectively make metal hydrosols. The criterion of hydrophilic–lipophilic balance (HLB) appears to support this idea. HLB is a criterion that briefly indicates hydrophilicity (high HLB value) or lipophilicity (low HLB value) of various surfactants. The smallest (0) and largest (20) HLBs define the highest lipophilicity and hydrophilicity, respectively. The HLB values for Pluronic P123, Tween 20, and Brij 35 are 6.0, 16.7, and 16.9, respectively [29–31], and are shown in Fig. 3. Pluronic P123 has

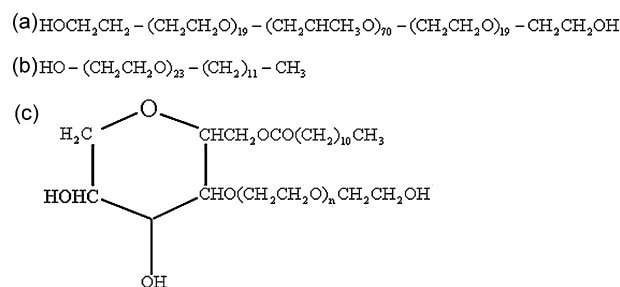


Fig. 2. Chemical formulae of (a) Pluronic P123, (b) Brij 35, and (c) Tween 20.



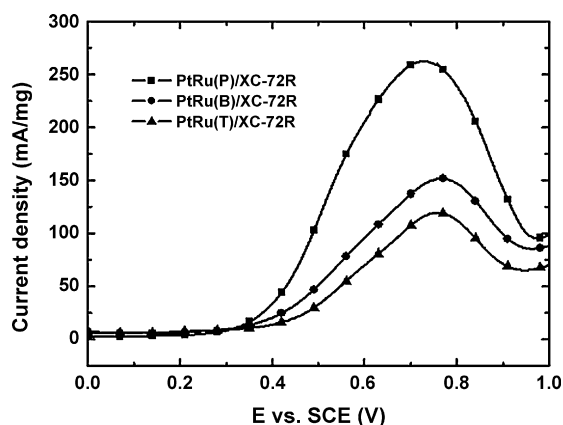


Fig. 5. Linear sweep voltammograms of PtRu(S)/XC-72R catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  solution at 40 °C. Sweep rate = 50  $\text{mV s}^{-1}$ .

shown) to that obtained with Pluronic P123. Although it is suspected that non-ionic surfactants with HLB values of 6–10 are best for good dispersion in water, choosing the best surfactants in this system based on such values is still under investigation.

Nano-sized metal particles prepared with Pluronic P123, Tween 20, and Brij 35 were supported on Vulcan XC-72R, and the resulting materials were designed PtRu(S)/XC-72R [(S): (P) for Pluronic P123, (B) for Brij 35, or (T) for Tween 20]. The materials were then filtered, washed, dried, and heat-treated as described in Section 2. Particle sizes and dispersions of the catalysts prepared with the three surfactants were confirmed by TEM (Fig. 4). PtRu(B)/XC-72R and PtRu(T)/XC-72R, which have a much larger size-distribution (Fig. 1), display a high level of metal particle aggregation, while PtRu(P)/XC-72R displays a high dispersion of 1- to 3-nm metal particles. The activities of these three catalysts for methanol electro-oxidation are shown in Fig. 5. The performance of PtRu(P)/XC-72R is superior to that of the other two samples. Better dispersion directly results in higher activity.

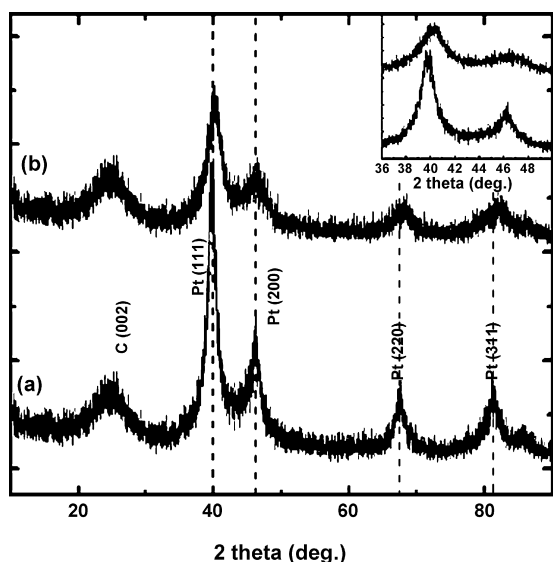


Fig. 6. XRD patterns of (a) Pt/XC-72R and (b) PtRu(P)/XC-72R.

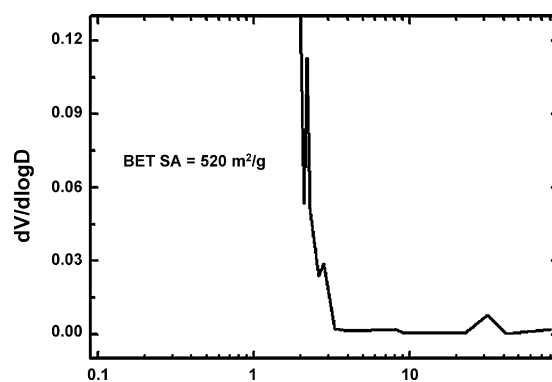


Fig. 7. Specific BET surface area and pore size distribution of CS.

### 3.2. Characterization of PtRu(P)/XC-72R and PtRu(P)/CS

Whether an alloyed catalyst of Pt and Ru with a 1:1 molar ratio shows the best activity for methanol electro-oxidation remains controversial, but it is becoming generally accepted [13]. The PtRu catalysts were thus prepared at a molar ratio of 1:1. In order to verify the formation of a Pt and Ru alloy, XRD analysis was carried out; the patterns from 10 to 90° for Pt/XC-72R and PtRu(P)/XC-72R are shown in Fig. 6. The pattern of Pt/XC-72R exhibits the diffraction peaks of (1 1 1), (2 0 0), and (2 2 0) planes at  $2\theta$  values of 39.7, 46.5 and 67.6°, respectively. These data indicate that Pt was present with a face-centered cubic (fcc) structure. The PtRu(P)/XC-72R prepared with a 1:1 molar ratio of Pt to Ru has an almost identical diffraction peak pattern to that of Pt/XC-72R, except that the peaks are slightly shifted to higher angles and are of much lower intensity. The peak shift is generally understood as a sign of alloy formation between Pt and Ru. Similar observations have been reported by Lee et al. [32] and Guo et al. [33]. Peaks associated with the hexagonal

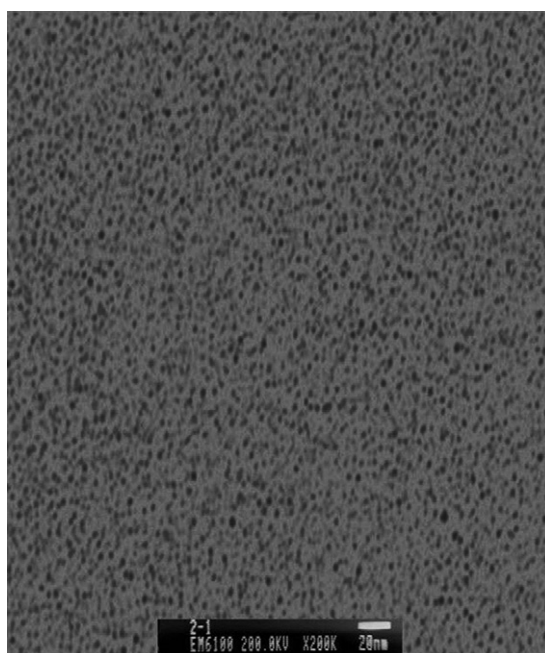


Fig. 8. TEM image of PtRu(P)/CS.

Table 1

Mean particle sizes and mean crystallite sizes of the PtRu(P)/XC-72R and PtRu(P)/CS obtained from TEM and XRD

	Average particle size from TEM (nm)	Average crystallite size from XRD (nm)
PtRu(P)/XC-72R	2.0	2.0
PtRu(P)/CS	2.6	2.5

close-packed (hcp) structure of pure Ru and RuO<sub>2</sub> are not identified in the peak pattern of PtRu(P)/XC-72R, which indicates the absence of metallic Ru and its oxides in the PtRu alloy.

The BET surface area and the pore size distribution of CS are shown in Fig. 7. This carbon material has a specific BET surface area of 520 m<sup>2</sup> g<sup>-1</sup>. This is more than twice that of the commercial carbon support, Vulcan XC-72R with 250 m<sup>2</sup> g<sup>-1</sup>.

The PtRu(P) hydrosols were deposited on CS and designated PtRu(P)/CS. The PtRu(P)/CS sample was also characterized by TEM (Fig. 8). The metal particle size ranges from 1 to 3 nm and its dispersion is as high as that of PtRu(P)/XC-72R. The crystallographic information for PtRu(P)/CS is obtained by XRD and compared with that of PtRu(P)/XC-72R. Changing the support carbon from Vulcan XC-72R to CS does not seem to affect the peak patterns of the supported PtRu particles. However, the graphitization peak area for the carbon support, located between 20 and 30°, is larger for CS than for Vulcan XC-72R, which implies a larger degree of graphitization in CS due to the higher carbonization temperature during its preparation. One may expect that more graphitized carbon should have higher conductivity, which would increase the electrochemical performance of the electrode. It was intended to use CS to enhance the conductivity of the support carbon. The average crystallite sizes of metal particles supported on both carbon supports were calculated from line broadening of the (2 2 0) peak according to Scherrer's equation. The particle sizes obtained by TEM are provided for comparison (Table 1). The similarity of the particle sizes and the crystallite sizes suggests that most of the existing particles are single crystallites.

The electrochemical activities of the prepared samples were evaluated with cyclic voltammetry and galvanostatic experi-

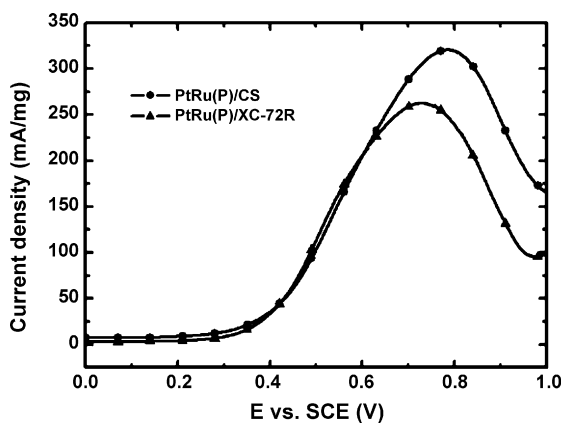


Fig. 9. Linear sweep voltammograms of 20 wt.% PtRu(P)/XC-72R and PtRu(P)/CS in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution at 40 °C. Sweep rate = 50 mV s<sup>-1</sup>.

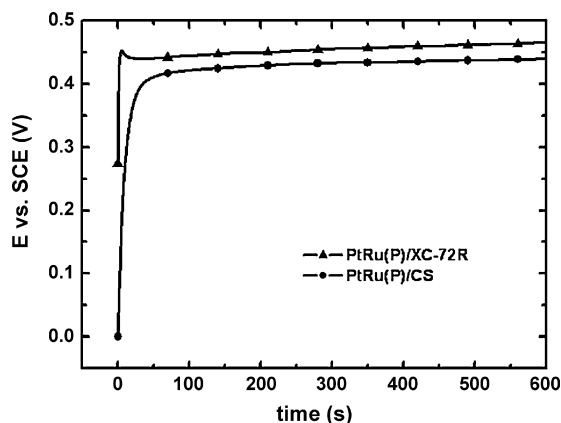


Fig. 10. Galvanostatic curves of 20 wt.% PtRu(P)/XC-72R and PtRu(P)/CS in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution at 40 °C under a constant current condition ( $i_{\text{const.}} = 0.7 \text{ mA}$ ). Sweep rate = 50 mV s<sup>-1</sup>.

ments for methanol electro-oxidation as shown in Figs. 9 and 10, respectively. The maximum current density of PtRu(P)/CS is higher than that of PtRu(P)/XC-72R by 15% while their onset voltages are similar (Fig. 9). Galvanostatic curves are supplied to substantiate these results. This experiment is designed to evaluate the degree of catalyst deactivation under a constant-current condition ( $i_{\text{const.}} = 0.7 \text{ mA}$ ). The curve indicates the potential

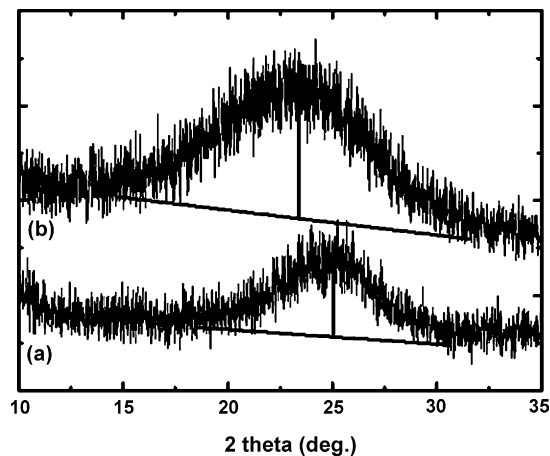


Fig. 11. Graphitization peaks of (a) Vulcan XC-72R and (b) CS.

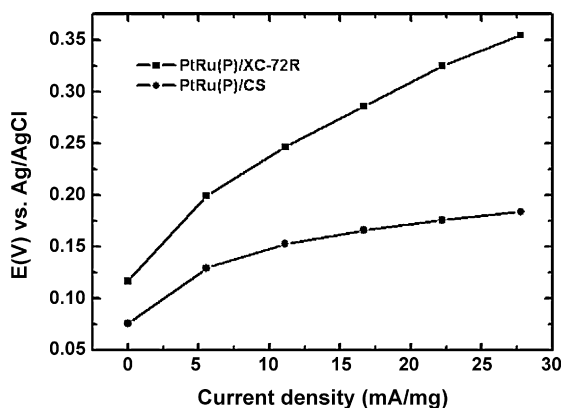


Fig. 12. Galvanostatic-polarization profile of PtRu(P)/XC-72R and PtRu(P)/CS.

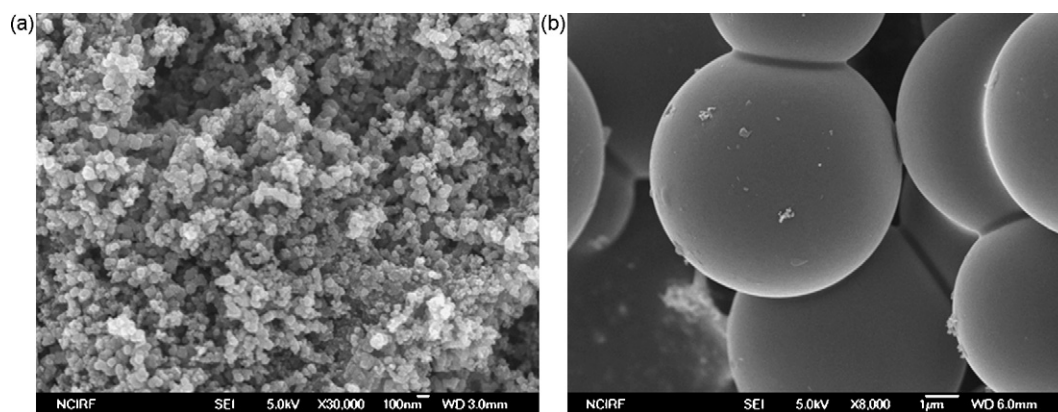


Fig. 13. SEM images of (a) Vulcan XC-72R and (b) CS.

required to sustain a constant current for a specific time during methanol electro-oxidation. Therefore, a catalyst with a lower potential has a higher methanol electro-oxidation activity. Based on these results, PtRu(P)/CS is more active than PtRu(P)/XC-72R. The activity difference between PtRu(P)/XC-72R and PtRu(P)/CS must come from the difference in the carbon support since the same metal preparation technique is used for both catalysts. To characterize both of these carbon support materials, conductivity and galvanostatic-polarization experiments were performed.

High conductivity of the carbon support is essential for improving electrochemical activity of the supported catalyst. The conductivity of the CS and Vulcan XC-72R are approximately  $1.32$  and  $1.19 \text{ S cm}^{-1}$ , respectively. CS shows higher conductivity compared with Vulcan XC-72R by almost 10%; the calculated experimental errors are  $\pm 2\%$  for both supports after 10 replicates. It is thought that this higher conductivity originates from the higher degree of graphitization in CS. This can be identified from the graphitization peak in XRD, as shown in Fig. 11. The quantitative height and area of the graphitization peak for CS are 99 and 742, respectively, while the corresponding values for Vulcan XC-72R are 64 and 309. Although these differences in height and area cannot be directly correlated to the conductivity difference, it is obvious that CS is graphitized more than Vulcan XC-72R.

PtRu(P)/XC-72R and PtRu(P)/CS were then characterized by galvanostatic-polarization (Fig. 12). PtRu(P)/CS exhibits higher activity than PtRu(P)/XC-72R, given that the overpotential of PtRu(P)/CS for each current density is lower than that of PtRu(P)/XC-72R. In other words, there is more polarization for PtRu(P)/XC-72R than PtRu(P)/CS, which results in a decrease in activity of PtRu(P)/XC-72R. It is considered that this polarization difference between the two catalysts is due to the difference in methanol transport. From a comparison of the SEM images of Vulcan XC-72R and CS in Fig. 13, CS contains much larger particles than Vulcan XC-72R. CS must have a larger inter-particle space than Vulcan XC-72R, which facilitates methanol transport to the catalyst surface, so that more of the metal particles deposited on CS participate in methanol electro-oxidation. According to these images, the particle size of CS is ca.  $6\text{--}7 \mu\text{m}$ , while that of Vulcan XC-72R is ca.  $50\text{--}100 \text{ nm}$ —the

images are presented with the different scale due to the huge difference in size of the carbons. This is somewhat consistent with the report by Liu et al. [34] where a PtRu catalyst supported on mesocarbon microbeads (MCMB) displayed lower polarization characteristics than a catalyst supported on Vulcan XC-72R. Liu et al. suggested, with evidence from polarization curves, that the lower polarization was due to larger pores and channels in MCMB that facilitated methanol transport.

#### 4. Conclusions

Non-ionic surfactants such as L121, Pluronic P123, P65, Brij 35, and Tween 20 have been employed as stabilizers to prepare PtRu alloyed hydrosols. Among these surfactants, only Pluronic P123 and P65 are found to be useful stabilizers for obtaining relatively uniform and fine hydrosols. Nano-sized metal particles prepared with Pluronic P123, Brij 35, and Tween 20 have been supported on Vulcan XC-72R, and the resulting materials are designed PtRu(S)/XC-72R [(S); (P) for Pluronic P123, (B) for Brij 35, or (T) for Tween 20]. The average PtRu particle size in the prepared PtRu(P)/XC-72R is ca.  $2 \text{ nm}$  with a narrow size-distribution. On the other hand, PtRu particle aggregation is observed for PtRu(B)/XC-72R and PtRu(T)/XC-72R. Consequently, PtRu(P)/XC-72R reveals the best catalytic activity due to better dispersion of the alloyed metal.

Carbon spherule (CS) is used successfully as a support material that improves the activity of the PtRu catalyst for methanol electro-oxidation and gives superior performance to the commercial carbon support, Vulcan XC-72R. The fine PtRu metal particles with Pluronic P123 are successfully supported on CS, and highly dispersed PtRu(P)/CS is achieved. The higher conductivity and the larger inter-particle space of the CS results in better performance of PtRu(P)/CS for methanol electro-oxidation than that of PtRu/XC-72R prepared with Pluronic P123.

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