

Short communication

One-step preparation and characterization of PtRu (1:1)/C electrocatalysts by polyol method for polymer electrolyte fuel cells

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Abstract

A one-step process is designed for the preparation of PtRu (1:1) electrocatalysts by the polyol method. Following investigations with an UV–vis spectrophotometer and an inductive-coupled plasma atomic emission spectrophotometer, it is found that an equimolar solution of Pt and Ru salts dissolved in ethylene glycol at temperatures above 190 °C is essential for the formation of the PtRu (1:1) solid solution. X-ray diffraction analysis is used to characterize the composition and size of the prepared electrocatalysts. The lattice parameter is 3.8663 Å, which corresponds to the value for a PtRu solid solution of equiatomic composition and this atomic ratio is confirmed by energy dispersive X-ray spectroscopy. Based on the Scherrer formula, the average particle size of the electrocatalysts is estimated to be 2.6 nm. It is confirmed by transmission electron microscopy that the nanoparticles are distributed uniformly on carbon, Vulcan XC 72. According to the results of unit cell test and CO-stripping voltammetry, the performance of the prepared electrocatalyst is comparable with that of a commercial one of the same composition.

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1. Introduction

In spite of the persistent efforts that have been made to develop reformate-tolerant electrocatalysts that can be employed in polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), PtRu is still considered as the electrocatalyst of choice [1]. The PtRu alloy generally shows CO and CO₂ tolerance, which is superior to that of pure Pt in PEMFCs and also exhibits high electrocatalytic ability for methanol in DMFCs. Moreover, the PtRu (1:1) solid solution has been reported to display better CO tolerance than PtRu electrocatalysts of other compositions [2].

Pt-based alloys are generally prepared by impregnation [3,4] and colloidal methods [5]. These methods require complex and time-consuming work, especially in the case of impregnation, where controllability of the particle shape, size and distribution does not meet the necessary requirements in terms of desired catalytic activity [6]. In this respect, preparation via alcohol reduction offers several advantages. That is, this method is much

simpler and allows the morphological properties of the particles to be controlled. The technique in which polyol is used as a solvent and reducing agent is referred to as the polyol method. Hirai et al. [7] attempted to perform alcohol reduction, in which a colloidal dispersion of noble metals was formed using polyvinylpyrrolidone (PVP) as a stabilizer and an aqueous solution of various kinds of alcohol as a solvent. Nano-sized powders of Co, Ni, Cu, and precious metals were prepared via the polyol method by Fievet et al. [8]. As interest in nano-sized catalysts increased, this method became adopted by more and more researchers [9–12]. Recently, for fuel cell applications, Pt/C or PtRu/C electrocatalysts were fabricated by traditional or modified polyol methods [13–15]. A stabilizing agent is used to prevent the agglomeration of nano-sized catalyst metals in the case of the colloidal method. This modification needs heat treatment to remove the surfactants and, therefore, does simple process. Also, the conditions under which the PtRu (1:1) solid solution is formed have not been totally elucidated.

This paper reports a one-step process for preparing PtRu (1:1)/C electrocatalysts via the polyol method without the use of a stabilizing agent. In contrast to the established polyol methods, wherein the reduction of metallic catalysts and the dispersion of the catalyst on carbon are carried out separately, the method

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employed in this work is designed so that the two processes can be conducted simultaneously. Moreover, no additional time is required to reduce the metal precursors or to support the reduced metals on carbon. In addition to the merit of providing a simple and low-cost process, the possibility that the distributional uniformity of the nano-sized electrocatalysts on carbon might be enhanced is also investigated. Attention is focused on the requirements to form the PtRu (1:1) solid solution and the physicochemical and electrochemical properties of the prepared electrocatalysts are evaluated.

2. Experimental section

2.1. Examination of two preconditions for a one-step process

An UV–vis spectrophotometer (UV–vis, Agilent 8453) was applied to monitor the reduction course of Pt, Ru, and PtRu from their salts in the region of 200–800 nm, using a quartz cuvette with a path length of 1 cm. For this analysis, 0.01 M ethylene glycol solutions of the Pt, Ru, and PtRu (1:1) salts were prepared and heated from room temperature to 190 °C at a rate of 2 °C/min. While they were being heated, 35 μ l samples of the solutions were drawn off using Pasteur pipettes starting from 50 °C and at 10 °C intervals. Eventually, 0.0001 M solutions were made from these samples for the purpose of analysis by diluting them in ethylene glycol. This monitoring was backed up by inductively-coupled plasma atomic emission spectrophotometric (ICP-AES) analysis of the samples at several selected temperatures.

An electrophoretic light-scattering spectrophotometer (ELS, Otsuka ELS-8000) was employed to measure the zeta potentials of the Vulcan XC 72 or PtRu nano particles with ethylene glycol as a background solution.

2.2. Preparation of PtRu (1:1)/C electrocatalysts

PtRu (1:1)/C (20 wt.% metal) electrocatalysts were prepared by a one-step process based on the polyol method and using the apparatus shown in Fig. 1. A camcorder attached to the apparatus enabled real-time observation of the transformation conditions as Pt, Ru, and PtRu were reduced. First, the Pt and Ru salts, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Wako chemicals), with a Pt:Ru molar ratio of 1:1 were placed in ethylene glycol and stirred for 10 min to achieve thorough dissolution. Then, a supporting carbon (Cabot, Vulcan XC 72) was added to the solution and, in this way, a starting suspension of the carbon–metal salts mixture was made and filled into a dropper. Meanwhile, ethylene glycol was placed in a reactor and heated to the reaction temperature, 195 °C, with refluxing under a stirring setting number 4 of a stirrer/hot plate (Corning, PC-420). The suspension being stirred in the dropper was dropped into the reactor at 195 °C at a rate of 2 ml per min and the reactor was maintained for 1 min at that temperature after the final drop. Following this, it was immediately returned to room temperature by means of a cooling fan. After, washing with distilled water, the resultant suspension was filtered through a nylon membrane (Nalgene, 0.2 μ m pore size) using an aspirator. Finally, after drying the

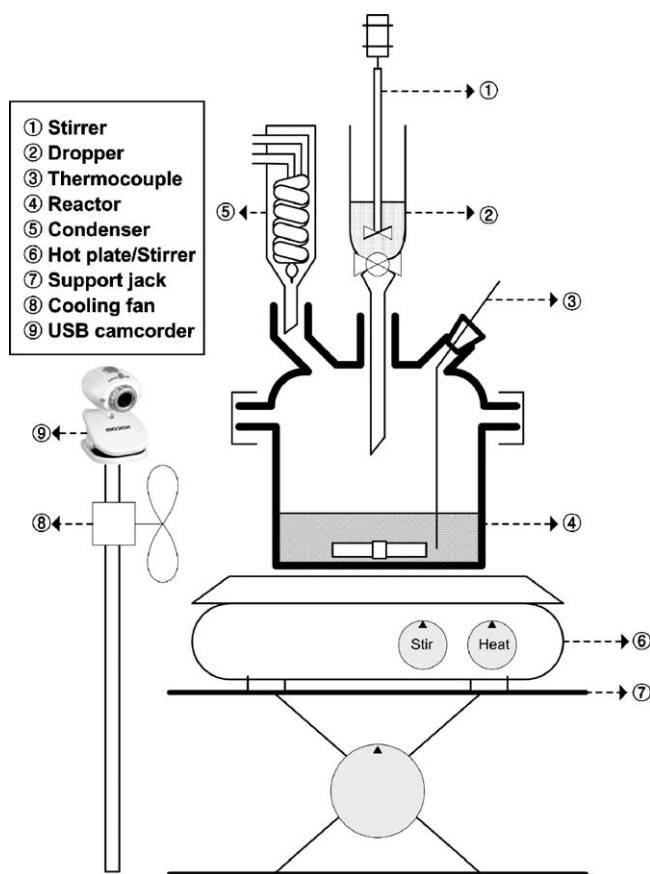


Fig. 1. Schematic diagram of apparatus used for one-step preparation of electrocatalysts.

filtered powders at 60 °C for several hours, carbon-supported PtRu (1:1) electrocatalysts were obtained.

2.3. Characterization of prepared electrocatalysts

To identify phases and estimate particle sizes, the prepared electrocatalysts were characterized using X-ray diffraction (XRD, Rigaku Geigerflex DMAX-IIA) at a scan rate of 4°/min, a voltage of 40 kV, and an output current of 30 mA. For observation of the dispersion state and reconfirmation of the particle size, an investigation with transmission electron microscopy (TEM, JEOL JEM-2010) was carried out at an accelerating voltage of 200 kV. Moreover, energy dispersive X-ray spectroscopy (EDS) using a beam size of 20 nm was coupled with TEM and ICP-AES (Jobin Yvon JY138 Ultrace) to analyze the composition of the electrocatalysts. The latter instrument was also used to examine the metallic residue in filtrate.

2.4. Electrochemical measurement

An anode was prepared by means of the procedure proposed by Uchida et al. [16]. Nafion® perfluorinated ion-exchange resin (Aldrich, 5 wt.% solution) and normal butyl acetate (Aldrich) were used as the ionomer and the solvent, respectively, for the catalyst inks. The amount of ionomer on the carbon paper (SGL, GDL 10BB) that was used as a gas-diffusion layer (GDL) was

fixed at 1 mg cm^{-2} . Electrocatalyst layers were formed by brushing these inks on the carbon paper. The prepared electrode had a final PtRu electrocatalyst loading of 0.4 mg cm^{-2} . A commercial electrode purchased from E-TEK loaded with 0.4 mg cm^{-2} of Pt was employed as the cathode.

The electrocatalytic property of the catalyst was investigated by means of CO-stripping voltammetry using a potentiostat/galvanostat (EG&G, 263A) and a three-electrode cell. A saturated calomel electrode (SCE) and a Pt plate were used as the reference and counter electrodes, respectively. The prepared electrode was used as the working electrode. The tests were carried out in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte at a scan rate of 50 mV s^{-1} in the range of -0.3 to 0.56 V . Carbon monoxide was passed into the cell for 3 min through a bubbler that was located close to the working electrode.

A membrane electrode assembly (MEA) with an active area of 5 cm^2 was fabricated by pressing at 170 kg cm^{-2} the anode and cathode together to form a sandwich with an intermediate layer of Nafion[®] 117 pretreated with H_2O_2 and H_2SO_4 solutions at 140°C for 90 s.

The unit-cell was tested at 80°C under atmospheric pressure with two combinations of fuel/oxidant, namely H_2/O_2 and H_2 -100 ppm CO/O_2 , to investigate the effect of CO on the cell performance. Fuel and oxidant were injected into the cell through separate humidifiers at 90 and 80°C , respectively, at a flow rate of 200 ml per min , as determined by the mass flow controller/read out. The cell performance was measured with an electronic loader (Deagil Electronics, EL 200P).

3. Results and discussion

3.1. Formation of PtRu (1:1) solid solution

As mentioned above, it is necessary to form the PtRu electrocatalyst into an equi-atomic solid solution for the better tolerance to CO present in reformed fuel or produced as a by-product during the oxidation of methanol. Thus, investigation of the formation conditions of the PtRu (1:1) solid solution was conducted by monitoring the reduction course of Pt, Ru, and PtRu from their ethylene glycol solutions. The UV-vis spectra relating to each case are shown in Fig. 2.

In the case of Pt, the colour of the solution changed first to orange, and then to pale yellow, dark brown, and finally became transparent with a black precipitates as the temperature was increased. This colour change coincided with decay of the absorption peak of PtCl_6^{2-} at 267 nm [15], as shown in Fig. 2(a). In particular, in the temperature region of 120 – 150°C , the reaction takes place vigorously and the corresponding magnified UV-vis spectra are shown in the inset of Fig. 2(a). The characteristic absorption peak by PtCl_6^{2-} at 267 nm disappears and black precipitates begin to agglomerate when the temperature exceeds 150°C . The precipitate is identified as Pt by XRD analysis, as shown in Fig. 3(a).

In similar manner, the colour of the solution made with Ru salt changes to bluish green, pale green, brown, deep blue, black brown, and finally becomes transparent with black precipitates.

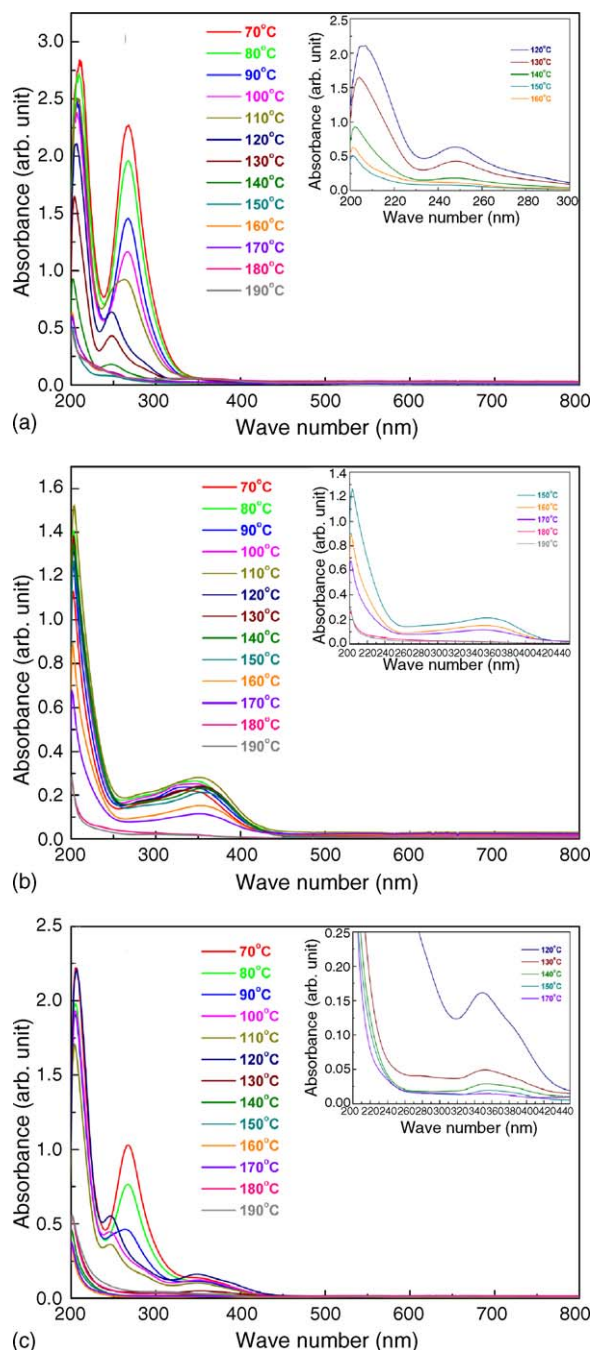


Fig. 2. UV-vis spectra of ethylene glycol solutions of (a) Pt salt, (b) Ru salt and (c) PtRu (1:1) salts heat-treated from room temperature to 190°C .

The UV-vis spectrum of the solution is given in Fig. 2(b) and exhibits a broad absorption peak at 360 nm , but no large shift in the peak to lower wavelengths is observed, although there is a decrease in the relative absorption intensity up to a temperature of 170°C . Unexpectedly, however, the reduction to black precipitates occurred as soon as the temperature exceeded 170°C . This black precipitate has also been identified by XRD analysis, as shown in Fig. 3(b), and is found to be Ru. It can be seen that the reduction path of Ru is very complex compared with that of Pt. Even though various Ru species are known to be present as intermediates during the reduction process [12], it is thought that

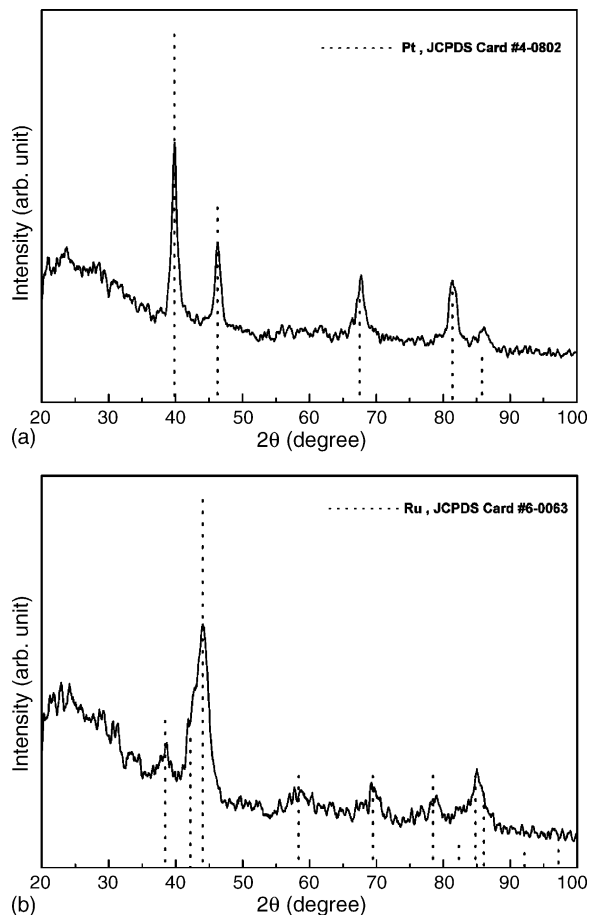


Fig. 3. XRD patterns of black precipitates obtained by reduction of ethylene glycol solutions with (a) Pt salt and (b) Ru salt.

further chemical analyses are necessary to clarify the mechanism completely. Finally, the reduction course of the solution of PtRu with a 1:1 molar composition was followed by UV–vis spectroscopy. The spectra of the solutions continuously heat-treated from room temperature to 190 °C are shown in Fig. 2(c). No traces of any chemical reaction between the Pt and Ru salts are observed, but only combinations of the previous UV–vis results for Pt or Ru. The new XRD pattern of the final black precipitates is presented in Fig. 4(a). The face-centered cubic phase is identified as a PtRu solid solution and the lattice parameter is estimated to be 3.9034 Å from the (2 2 0) peak at $2\theta \approx 69^\circ$. The Ru content in this solid solution is estimated to be about 20 at.% from the calibration curve produced from the lattice parameters of the PtRu bulk alloys [17]. The deficiency of Ru in the solid solution compared with that in the initial composition may be caused by the difference in the full-scale reduction temperature of Pt and Ru. The ICP-AES results listed in Table 1 strongly support this speculation.

From the above findings, it can be concluded that when using multiple components, the conditioning of the simultaneous reduction is important to form the desired solid solution. This is one of the two preconditions for making the one-step process possible. For the purpose of comparison, a solution with a PtRu molar composition of 1:1 was dropped into ethylene

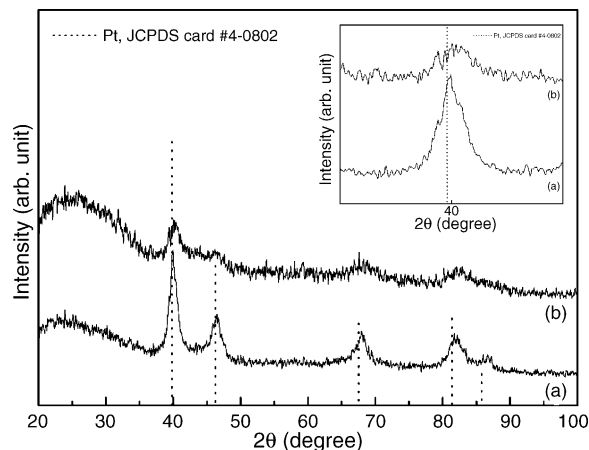


Fig. 4. XRD patterns of PtRu precipitates prepared by (a) continuous heat-treatment from room temperature to 190 °C and (b) dropping at 190 °C.

Table 1

ICP-AES results for ethylene glycol solution of PtRu (1:1) salts heat-treated from room temperature to 190 °C

	Room temperature	50 °C	90 °C	130 °C	170 °C
Pt (10^{-8} mol)	6.59	5.42	5	0.075	0.15
Ru (10^{-8} mol)	6.59	6.52	5.96	3.62	0.97

glycol maintained at 190 °C, which is a sufficiently high temperature for the simultaneous reduction of the two metals, and then the resulting black precipitates were analyzed by XRD (see Fig. 4(b)). Comparison with the former XRD pattern, reveals that, from the (1 1 1) peak, the peaks shifts to higher angles.

To examine the other essential precondition, namely the possibility of a spontaneous supporting mechanism, the average zeta potentials of the Vulcan XC 72 and PtRu nanoparticles in ethylene glycol were measured and found to be 55 and 25 mV, respectively. Consequently, it can be said that the PtRu nanoparticles are supported spontaneously on Vulcan XC 72 by the electrostatic force that arises from the difference in the relative potentials.

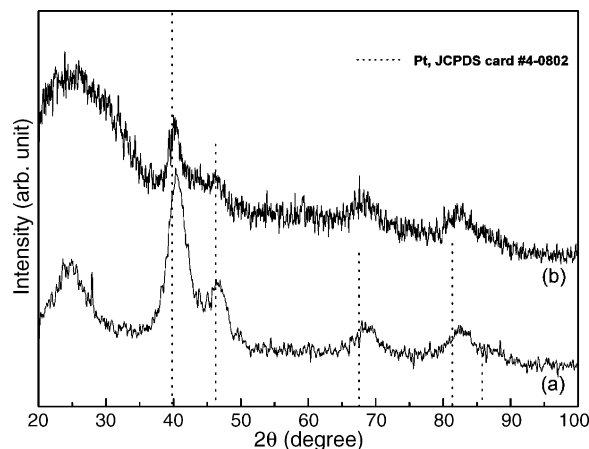


Fig. 5. XRD patterns of (a) PtRu/C electrocatalysts prepared by one-step process and (b) PtRu precipitates prepared by dropping at 190 °C.

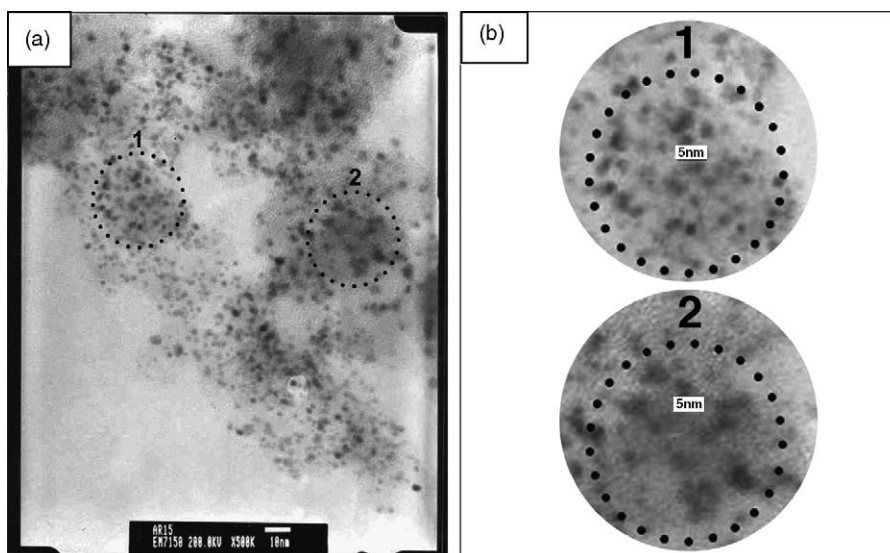


Fig. 6. TEM images of (a) PtRu (1:1)/C electrocatalyst prepared by one-step process and (b) magnified view of areas 1 and 2.

3.2. Characterization of PtRu (1:1)/C electrocatalyst

The XRD pattern of the PtRu (1:1)/C electrocatalyst is shown in Fig. 5(a), where the peaks appear to be shifted to a high angle side compared with the positions (dotted line) expected for pure Pt, as demonstrated by the XRD pattern of the PtRu particles shown in Fig. 5(b).

The lattice parameter is estimated to be 3.8663 Å, which corresponds to the value for a PtRu solid solution of equi-atomic composition [17,18]. Antolini [18] reported that the lattice parameter of a PtRu 1:1 carbon-supported catalyst was higher than that of the bulk alloy because only part of the Ru present in the carbon-supported catalyst was alloyed with Pt. Also, this result was confirmed by a decrease in the lattice parameter following thermal treatment. Taking into consideration these results and those in the previous section, it can be concluded that the one-step process is successful from the viewpoint of the formation of a solid solution. The atomic composition of the filtrate and electrocatalysts prepared using this process have been analyzed by EDS and ICP-AES for the sake of confirmation. The results are listed in Table 2 and are found to correspond to those obtained from XRD analysis. No metallic residue is detected in the filtrate.

Using the Scherrer formula the average particle size of the catalyst is estimated from the (2 2 0) peak as 2.6 nm. A TEM image of the electrocatalyst is given in Fig. 6. This shows that the average particle size is about 2.5 nm, which corroborates the above estimation. A uniform distribution of the electrocatalyst is also confirmed by the image. In conclusion, therefore two pre-conditions demanded for the one-step preparation of the catalyst

Table 2
Atomic composition of PtRu (1:1)/C electrocatalyst

	EDS at. %	ICP-AES at. %
Pt	50.66	47.5
Ru	49.34	52.5

using the polyol method have been successfully satisfied. On the basis of these results, it is thought that other Pt-based alloys, in addition to the PtRu composition used here, could be prepared by this method.

3.3. Electrochemical properties

The electrocatalytic activity of the PtRu (1:1)/C electrocatalyst for CO was investigated by means of CO-stripping voltammetry. The resulting voltammogram is given in Fig. 7.

The onset of CO oxidation for the electrocatalysts prepared in this work occurs at a lower potential than that of a commercial Pt/C catalyst and, also, the onset potential is at a similar value to that of the PtRu electrocatalysts prepared by the conventional colloidal method [19].

The cell voltage versus current density characteristics of a unit cell with the PtRu (1:1)/C electrocatalyst under atmospheric pressure and using the two combinations of fuel/oxidant, H₂/O₂ and H₂-100 ppm CO/O₂ are shown in Fig. 8. In both cases, the cell performance is close to that of a cell with a commercial PtRu

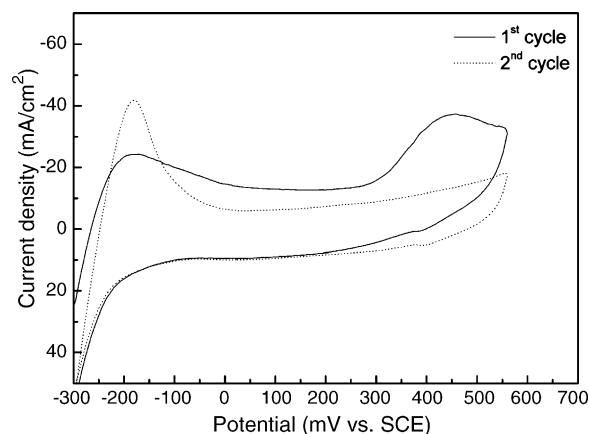


Fig. 7. CO-stripping voltammograms for PtRu (1:1)/C electrocatalyst prepared by one-step process; scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄.

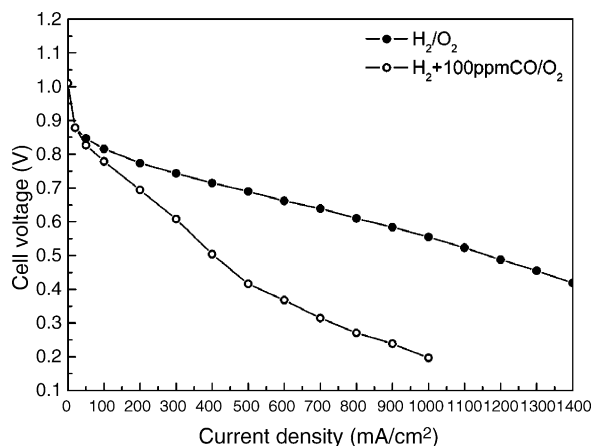


Fig. 8. Unit cell performances with PtRu (1:1)/C electrocatalyst at 80 °C using H₂ (solid circle) and H₂-100 ppm CO (open circle) as fuel.

(1:1)/C catalyst (E-TEK, 20 wt.% PtRu (1:1)/Vulcan XC 72) and Nafion[®] 115 at cell temperature of 85 °C [20]. For example, the cell voltages are 0.69 and 0.42 V at 500 mA cm⁻² for the H₂ and H₂-100 ppm CO fuels, respectively.

4. Conclusions

PtRu (1:1)/C (20 wt.% metal) electrocatalysts have been prepared by a one-step process based on the polyol method. The two preconditions for the one-step process, namely the formation of a PtRu solid solution of equi-atomic composition and the existence of a spontaneous supporting system, are investigated by UV-vis, XRD, ICP-AES, and ELS. In addition, XRD and TEM-EDS analyses have been conducted to verify the particle size, distribution and composition of the electrocatalyst. The electrocatalytic properties have been investigated by means of CO-stripping voltammetry and unit cell tests. The following conclusions are reached:

1. dropping addition of an equimolar solution of Pt and Ru salts dissolved in ethylene glycol at a temperature above 190 °C is essential for the formation of the PtRu (1:1) solid solution.
2. PtRu nanoparticles can be supported spontaneously on Vulcan XC 72 by the electrostatic force arising from the relative potential difference.

3. An electrocatalyst of the PtRu (1:1)/C form can be produced by a one-step process with an average particle size of 2.6 nm and a uniform distribution.
4. The cell performance of the electrocatalyst is comparable with that of a commercial counterpart of the same composition.

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