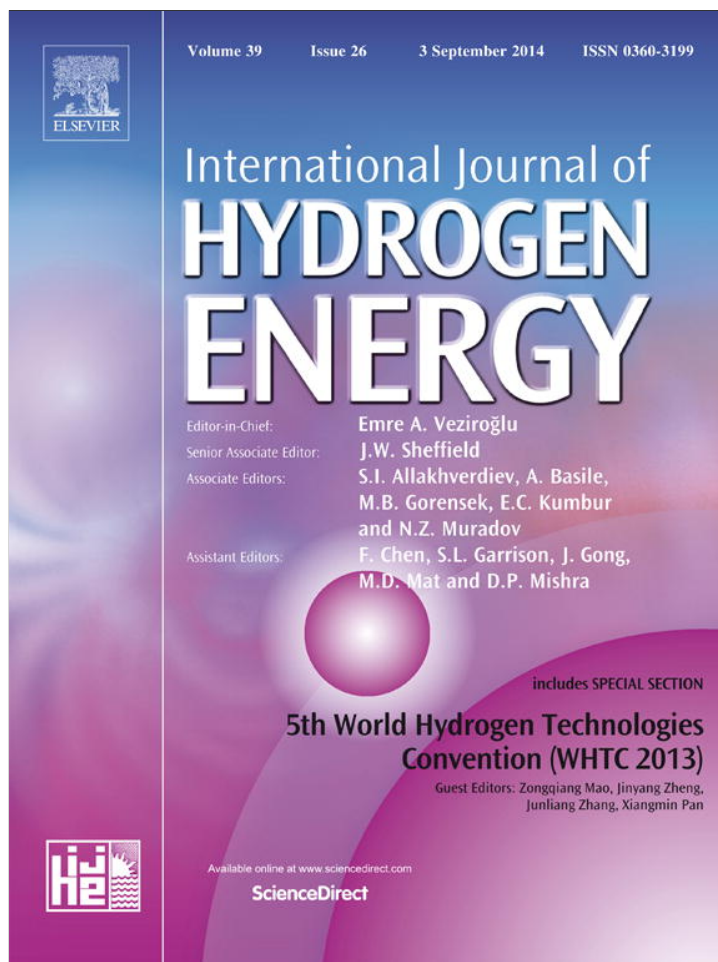


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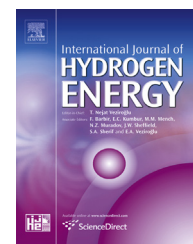
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# Flame aerosol synthesis of carbon-supported Pt–Ru catalysts for a fuel cell electrode

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## ABSTRACT

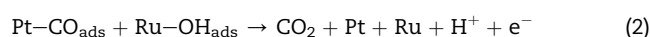
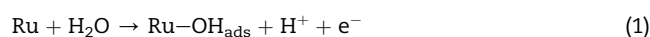
This study describes how a flame spray pyrolysis method was successfully used to synthesize PtRu catalysts supported by carbon agglomerates. Nearly spherical catalysts composed of metallic Pt and Ru with molar ratio of 1:1 were produced in the flame and their size was about 1.9 nm. X-ray diffraction measurements revealed that amorphous-like Ru was well mixed into the Pt crystalline lattices. Through cyclic voltammetry for methanol oxidation reaction and CO stripping, it was found that the electrochemical activities of the catalysts produced from this process are comparable to or slightly better than those of an equivalent commercial sample with the same composition.

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## 1. Introduction

Platinum (Pt) is widely used as an electrochemical catalyst for low-temperature fuel cells due to its excellent catalytic performance; however, Pt catalysts are often degraded by trace levels of CO produced during the reforming process of fossil fuels. The adverse effect of CO, well known as CO poisoning, is the result of CO molecules binding with the Pt surface stronger than the hydrogen. This CO binding inhibits the catalytic reaction of hydrogen. Platinum-ruthenium (Pt–Ru) composite nanoparticles are generally considered as one of the most promising catalysts to circumvent the CO poisoning [1].

Excellent CO tolerance of Pt–Ru catalyst was described by the bifunctional mechanism [2–4] of Ru as:



Eqs (1) and (2) explain how hydroxyl groups adsorbed on the surface of Ru regenerate the CO-contaminated Pt surface. For maximizing performance, the Ru must be exposed to the surrounding H<sub>2</sub>O vapor and be in contact with the surface Pt. On the other hand, Pt-encapsulated Ru core–shell nanostructures

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are expected to be least active because the Ru has no chance to contact the atmosphere. Thus, microstructure control of Pt and Ru is of particular interest in order to improve the catalytic performance while maintaining the CO tolerance. Moreover, the Pt–Ru catalyst provides another benefit in reducing the cost of the precious electrode catalyst, as the price of ruthenium is about one eleventh the price of platinum [5].

Many researchers have proposed various methods such as chemical reduction method<sup>1</sup>, chemical vapor deposition [6], and thermal reduction [7] for synthesis of the catalysts. However these methods require a long time and multistep processes. Here, we recently proposed a novel method using flame which offers great benefits relative to the other methods: a continuous single-step production [8] of such catalysts and easy scale up. In the process, the flame was used not only as a precursor for carbon agglomerates but also as a heat source to pyrolyze Pt precursor vapor toward metallic Pt spheres in a size range of 1–10 nm. The key was to make carbon agglomerates form prior to the inception of Pt particle in flame. As a result, the size and surface coverage of Pt particles on carbon agglomerates were both controllable and the Pt/C catalysts had a similar electrochemical activity to a commercial (E-TEK) Pt/C sample [8].

In this study, we attempted to extend this flame method to a continuous production of well-designed Pt–Ru/C catalysts with a single step. However, there is another big challenge as compared to the synthesis of Pt/C catalysts. Ru species should be well mixed with Pt in a scale of 1–10 nm so as to maximize the function of Ru to relieve CO poisoning. Another requirement is that such tiny Pt–Ru nanoparticles are made to form on surface of carbon agglomerates with good dispersion conditions. Hence, the purpose of this study is to resolve the issues using the flame method.

As-produced carbon-supported Pt–Ru (PtRu/C) particles are characterized by transmission electron microscopy, energy-dispersive spectroscopy, thermogravimetric analysis, X-ray diffraction and X-ray photoelectron spectroscopy. The electrocatalytic properties of the PtRu/C particles are examined by cyclic voltammetry and CO-stripping, and compared to an equivalent commercial catalyst.

## 2. Experimental section

As aforementioned, there would be two important timings: one is the formation of carbon agglomerates prior to the formation of Pt or Ru [8]; the other is the simultaneous nucleation of Pt and Ru in flame for better mixing of them. As the nucleation of the Pt or Ru is initiated by the pyrolysis of the precursor in flame, it is of great importance to find a good pair of precursors of Pt and Ru which have a similar pyrolysis reaction kinetics. For this purpose, the reaction temperatures of platinum and ruthenium precursors were estimated running a thermogravimetric analyzer (TGA; Z50, TA Instruments) with a dynamic mode: a constant rampling rate of 10 °C min<sup>-1</sup> in air. After a series of preliminary TGA experiments for several types of those precursors, platinum(II) acetylacetonate (Pt(acac)<sub>2</sub>, Aldrich, 97%) powder and ruthenium(III) acetylacetonate (Ru(acac)<sub>3</sub>, Aldrich, 97%) powder were finally chosen for the catalyst precursors. In Fig. 1, the two precursors

denoted very similar kinetics of decomposition reaction which was ended at ~250 °C starting from 170 °C. A 1:1 mole ratio mixture of Pt(acac)<sub>2</sub>: Ru(acac)<sub>3</sub> was dissolved in xylene with a concentration of 0.12 wt %. After mixing, the solution was ultrasonicated for 10 min at 10 °C. The Pt–Ru/xylene precursor was sprayed as droplets from an ultrasonic atomizer by compressed air at 50 psi, and then fed to the center of the burner through a heated tube as shown in Fig. 2. The carrier gas (air) containing the solution droplets flowed at 1.33 L min<sup>-1</sup>. Next to the center tube, a shield gas of Argon flowed at a rate of 0.36 L min<sup>-1</sup>. As a carbon source, acetylene (C<sub>2</sub>H<sub>2</sub>) and dry air were injected through the third and fourth concentric annuli at 0.105 and 1.35 L min<sup>-1</sup>, respectively, forming a coflow diffusion flame. On the edge of the burner, argon gas was injected at 30 L min<sup>-1</sup> to stabilize the flame. The injection speed of the shield gas was 10 times larger than that of the C<sub>2</sub>H<sub>2</sub>, so as to retard the decomposition of both the Pt(acac)<sub>2</sub> and Ru(acac)<sub>3</sub> precursors to after carbon inception. More details of material preparation and instrumentation are described in our previous work [8].

As such, carbon-supported Pt–Ru composite particles were thermophoretically deposited to a water-cooled quartz tube as depicted in Fig. 2, then collected and dried for further characterization of the samples. Mass fraction of Pt–Ru metallic species in the dried sample was determined by measuring the mass difference before and after burning the carbon species in TGA machine. This experiment was repeated upon changing the stoichiometry ratio of the flame until the mass fraction of Pt–Ru in the sample denoted 20 wt%. It should be noted that the gas flow rates described above were the final result from these preliminary experiments. As-deposited PtRu/C particles were then dispersed in ethanol with an ultrasonicator. A few milliliters of PtRu/C-ethanol suspension were dropped onto a carbon-coated grid and then dried at room temperature. Morphology and size of PtRu/C particles were characterized with a transmission electron microscopy (TEM; JEOL 2010, JEOL). The Pt and Ru mole ratio was confirmed through the energy dispersive spectroscopy (EDS; JEM 2100F, JEOL). Crystalline phases of the dried powder samples were verified by X-ray diffraction (XRD; D/Max-2400, Rigaku). The XRD measurement was performed by scanning the angle of 2θ in a range of 30–90° with 0.1° min<sup>-1</sup>, while irradiating Cu Kα X-ray (30 kV, 40 mA, 0.15218 nm). The PtRu/C particle size was

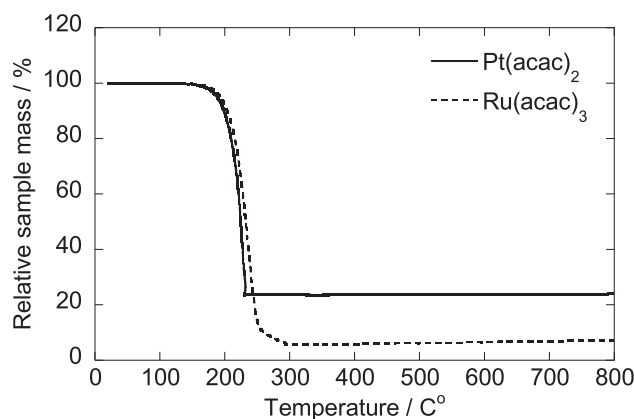
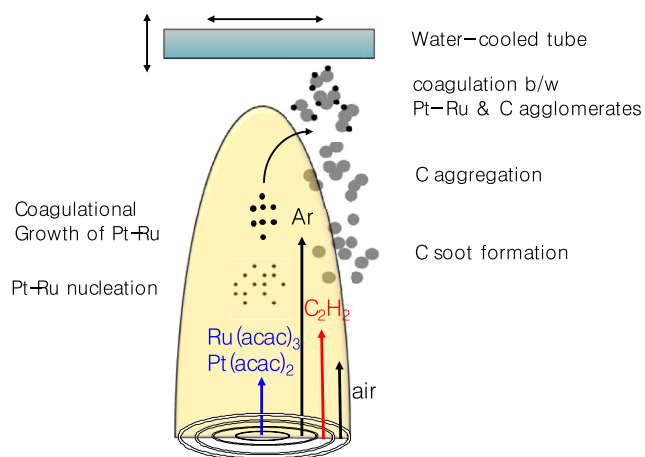


Fig. 1 – TGA profiles of Pt and Ru precursors.



**Fig. 2 – Schematic of the experimental setup for flame aerosol synthesis of PtRu/C catalysts.**

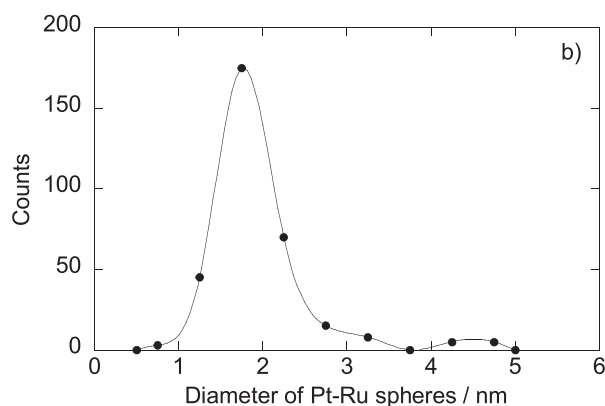
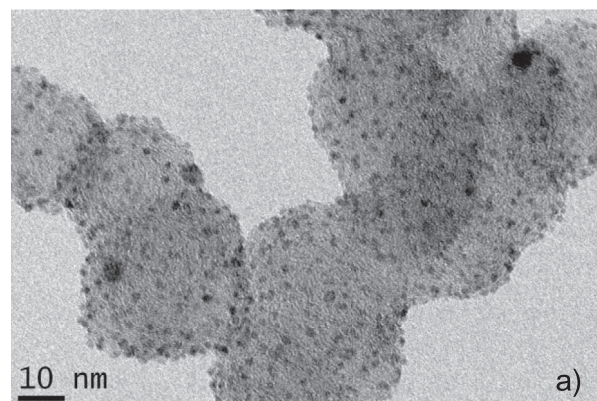
obtained from the Scherrer equation using the full width of half maximum (FWHM) value and compared to the particle size measurements from TEM. Surface chemical states of Pt and Ru particles were characterized by X-ray photoelectron spectroscopy (XPS; ESCALAB 250 XPS spectrometer, VG Scientifics) upon irradiating Al-K $\alpha$  X-ray with a resolution of 0.45 eV.

The electrochemical measurements were performed using an EC-Lab electrochemical analyzer and a conventional three-electrode electrochemical cell (Biologic VSP). The working electrode was prepared as follows. A glassy carbon electrode (5 mm in diameter; electrode area of 0.19635 cm<sup>2</sup>) was polished with diamond solution and Al<sub>2</sub>O<sub>3</sub> slurries and then washed in DI water with sonication before the experiments. 2.5 mg of PtRu/C catalyst and 2 ml of DI water was mixed in vial, and ultrasonicated for 20 min. 20  $\mu$ L of the solution was dropped on the polished glassy carbon surface with a micropipette to afford a PtRu loading of 20  $\mu$ g cm<sup>-2</sup> on the electrode, and then dried in an oven for 60 min at 70 °C. Nafion solution (0.025 wt.%, 20  $\mu$ L) was dropped onto a suspension-dried glassy carbon electrode and dried in a vacuum oven at 70 °C for 30 min. A Pt foil and a silver chloride electrode (Ag/AgCl sat. 3.5 M KCl) were used as the counter electrode and reference electrode, respectively. The Ag/AgCl reference electrode was calibrated on a daily basis using a Pt disk electrode and H<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> electrolyte to ensure that its potential did not drift. All potentials were converted to the reversible hydrogen electrode (RHE) scale. Cyclic voltammetry for the methanol oxidation was performed in a solution of H<sub>2</sub>SO<sub>4</sub> (0.5 mol) and CH<sub>3</sub>OH (1 mol) purged with pure nitrogen gas for 15 min. The electrodes were cycled in the potential range between 0.05 and 1.2 V (versus RHE) at a scan rate of 50 mV s<sup>-1</sup>. For the CO stripping voltammetry, the electrolyte of 0.5 mol H<sub>2</sub>SO<sub>4</sub> was purged with CO for 30 min while the electrode potential was fixed at 0.1 V. After the measurement with CO-purged electrolyte, the electrolyte was saturated by CO and thus purged again for 30 min with nitrogen gas to remove the CO in the electrolyte, and the measurement was repeated.

### 3. Results and discussion

Fig. 3 shows the TEM micrograph of PtRu/C catalyst and size distributions of PtRu particles prepared from the one-step continuous flame spray pyrolysis method. The sampling height is 80 mm from the burner top. Many tiny darker PtRu spheres obviously form on the surface of bigger gray carbon agglomerates in the figure. PtRu particles are observed to have a good dispersion with average particle size of about 1.9  $\pm$  0.6 nm. The EDS spectra for the particles revealed that the darker small particles are composed of the mole ratio of 1:1.05 (Pt:Ru).

Those carbon-supported PtRu catalyst samples were also examined by XRD. Fig. 4a) shows XRD patterns of PtRu/C catalyst with four major peaks at 40.3°, 46.8°, 68.1°, and 81.6° in 2 $\theta$  unit. Those peak positions are pretty close to those of face-centered-cubic structured metallic Pt: 2 $\theta$  values of 39.8°, 46.4°, 67.7°, and 81.5° from JCPDS (No. 870640), corresponding to the crystallographic planes of (111), (200), (220) and (311) of Pt. It is worth noting that all the peak positions observed are slightly shifted to the higher 2 $\theta$  values, suggesting that the Pt lattice might be contracted by any means as summarized in Table 1. Higher angles, i.e. lower lattice parameter indicates formation of solid solution of PtRu with Pt lattice contracted due to the replacement of some Pt atoms by the smaller Ru atoms ( $r_{\text{Ru}} = 0.133$  nm and  $r_{\text{Pt}} = 0.138$  nm) [9–11]. The possible presence of Ru in form of solid solution rather than crystalline phase can explain why there is no apparent peak of



**Fig. 3 – a) TEM image, b) size distribution of PtRu/C catalysts.**



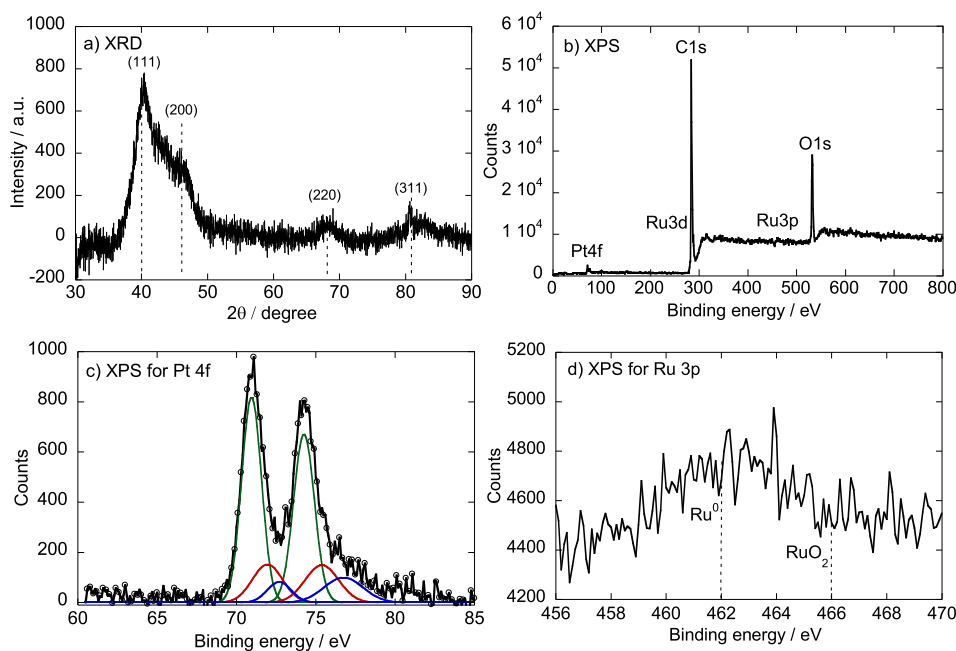


Fig. 4 – a) XRD and b) XPS profile of PtRu/C catalysts : c) XPS for Pt 4f peak and d) Ru 3p peak.

ruthenium or its crystalline oxide. The crystallite size calculated through the Scherrer equation is about  $\sim 1.5$  nm, fairly consistent with that from the TEM measurement.

Fig. 4b) shows the overall XPS result for the PtRu/C catalyst composed of Pt-4f, C-1s, and Ru-3d peaks at 70–80 eV, 280–290 eV, and 460–470 eV, respectively. Fig. 4c) shows that the Pt-4f core-level XPS spectrum of the PtRu/C catalyst is mainly composed of three pairs of doublets. The highest doublet (at 70.8 and 74.2 eV) is the signal of metallic Pt. The second highest doublet (at 71.9 and 75.4 eV) is assigned to Pt[III] states as in PtO or Pt(OH)<sub>2</sub>. The weakest third doublet at 72.7 and 76.8 eV suggests the minor level of Pt[IV] as in PtO<sub>2</sub> exists in the present catalysts. Based on the peak heights of the three doublets, the surface fraction of the metallic Pt is estimated to  $\sim 77\%$ . The high oxidative states in the sample are probably due to the high-temperature heating of PtRu/C particles in flame where oxygen is rich. Though Ru3d and Ru3p peaks can exist, the Ru3d peak overlaps with the carbon peak C1s. Fig. 4d) shows a broad and little, but still discernable Ru-3p peak of PtRu/C catalyst at  $\sim 462.5$  eV which is close to the value (462 eV) of metallic Ru (Ru<sup>0</sup>) [12]. Due to the relatively large noise level, the existence of a small peak of RuO<sub>2</sub> at 466 eV can not be ruled out. Nevertheless, it seems clear that the ruthenium mostly exist in a metallic form. The surface mole fractions of Pt and Ru are estimated from the intensities of Pt 4f and Ru 3p with atomic sensitivity factors of 4.4 and 1.30, respectively. As a result, a mole ratio of Pt:Ru is 1.1:1 which is fairly consistent with our EDS result and the literature value [12].

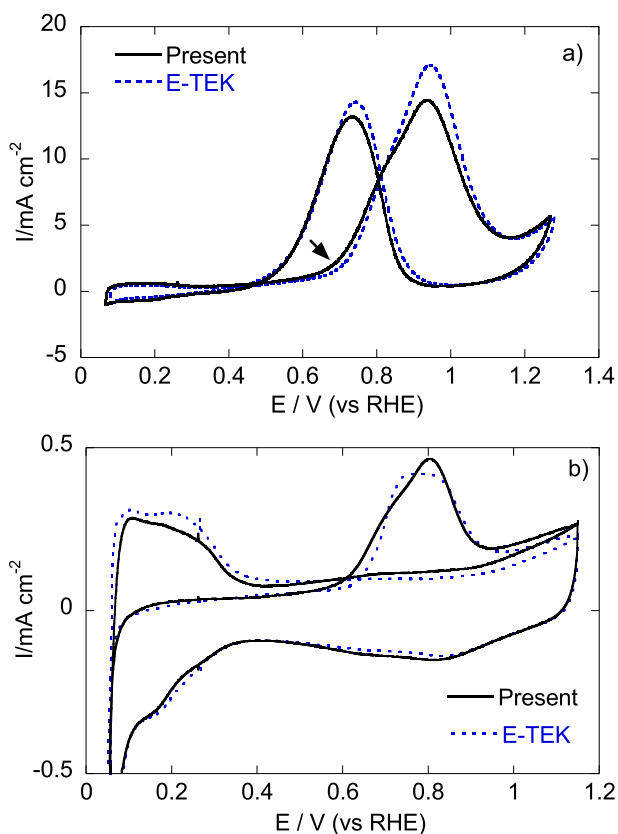
Fig. 5a) shows the stationary cyclic voltammograms (CV) for the methanol oxidation reaction (MOR) of the present 20 wt % PtRu/C catalyst and an equivalent commercial E-TEK sample with the same composition. The solid line and dotted line correspond to the present sample and the commercial one, respectively. In the positive scan, the adsorption and dehydrogenation of methanol result in the formation of CO–Pt at

low overpotential. It is observed an anodic current peak around ca. 0.93 V (max. current density  $I_f$  of 14.4 mA cm<sup>-2</sup>), where surface water associated with Ru might react with adsorbed CO on the electrode containing the present sample and produce CO<sub>2</sub>, proton (H<sup>+</sup>), electron, a vacant site on the Pt surface. At higher potential, the current decreases due to the formation of hydroxide on the electrode surface. On the negative scan, it is seen an anodic peak ( $I_b$ ) at 0.73 V associated with the oxidation of species formed due to the methanol oxidation. Finally, the current decreases due to surface blocking by CO [13]. Overall, the MOR characteristics of the present sample are very similar to those of the commercial sample (E-TEK). As denoted by an arrow in the figure, the onset potential of methanol oxidation on the present catalyst is slightly lower than that of the commercial catalyst. This might indicate the present sample is slightly more active than the commercial one. The ratio between the two peak heights obtained by positive and negative scans, i.e.,  $I_f/I_b$  is around 1.01 for the present sample, which is quite smaller than that for the E-TEK sample (1.20). This suggests that the present catalyst has a higher catalytic activity for the methanol oxidation and thereby reacts with carbonaceous materials better than the commercial catalyst [14].

Fig. 5b) shows the CO stripping voltammograms obtained from the present and the commercial catalysts. The electrochemically active surface areas ( $S_{EAS}$ ) of the PtRu/C catalysts are calculated by using Eq. (3). [10]

Table 1 – Comparison of lattice parameters and lattice spacings of Pt between Pt/C and PtRu/C samples.

(220) Plane	$2\theta$	d-Value/nm	Lattice parameter/nm
Pt/C	67.73	0.13873	0.3924
PtRu/C	68.1	0.13752	0.3889



**Fig. 5 – Cyclic voltammograms for a) methanol oxidation reaction and b) CO stripping of the present catalysts in comparison with the E-TEK sample.**

$$S_{\text{EAS}} = \frac{Q_{\text{CO}}}{G_{\text{Pt-Ru}} \times 420 (\mu\text{C}/\text{cm}^2)} \quad (3)$$

, where  $Q_{\text{CO}}$  is the charge for CO desorption electro-oxidation in units of  $\mu\text{C}$ ,  $G_{\text{Pt-Ru}}$  represents the PtRu metal loading ( $\mu\text{g}$ ) in the electrode, and  $420 \mu\text{C cm}^{-2}$  is the charge required to oxidize a monolayer of CO on the PtRu/C catalyst. Through Eq. (3), the electrochemically active area of the present catalyst is found to be  $72.9 \text{ m}^2 \text{ g}^{-1}$ , a little greater than that of the commercial catalyst ( $65.7 \text{ m}^2 \text{ g}^{-1}$ ). The onset potential of present catalyst is also lower than of the commercial catalyst: 0.60 V vs 0.64 V. The catalyst obtained from the present one-step continuous flame spray pyrolysis method seems to have the more competitive electrochemical activity.

#### 4. Conclusion

In this article, we demonstrated the flame spray pyrolysis method could be successfully applied to produce PtRu/C catalyst at a single step. The size of spherical PtRu particles formed on the surface of carbon agglomerates was around  $1.9 \pm 0.6 \text{ nm}$  with a good dispersion. The XRD and XPS analysis manifested that Ru species most likely exists in form of solid solution in a crystalline Pt lattice, and the two species are both metallic and quite well mixed in the nanoscale with a mole ratio of 1:1. Finally, the cyclic voltammetry measurements for the MOR and

CO stripping showed that the present catalyst denoted a good electrochemical activity which is at least comparable to that of the commercial catalyst from E-TEK with the same composition.

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