

Preparation of carbon-supported PtRu nanoparticles for direct methanol fuel cell applications – a comparative study

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Abstract

Carbon-supported PtRu nanoparticles were prepared by different methods that involve the simultaneous chemical reduction of H_2PtCl_6 and RuCl_3 by NaBH_4 at room temperature (**PtRu-1**), by ethanol under reflux (**PtRu-2**), and by the thermal decomposition of a single-source molecular precursor [(bipy)₃Ru] (PtCl_6) (**PtRu-3**). Transmission electron microscopy (TEM) examinations show that the mean diameter of the PtRu nanoparticles is lowest for **PtRu-1** followed by **PtRu-2** and **PtRu-3**. Measurements of electrocatalytic properties, however, reveal a different trend, namely: **PtRu-3** > **PtRu-1** > **PtRu-2**. This is attributed to the formation of a more homogenous alloy nanoparticle system from the thermolysis of the single-source molecular precursor. All three catalysts are more active than commercially available E-TEK (20 wt.%) Pt catalyst. **PtRu-3** also displays the highest tolerance to carbon monoxide. Heat treatment of **PtRu-1** and **PtRu-2** only marginally affects their electrocatalytic performance, whereas the co-reduction of H_2PtCl_6 and RuCl_3 under alkaline conditions has more adverse outcomes.

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1. Introduction

Direct methanol fuel cells (DMFCs) are well poised to be convenient power sources for portable electronic products because of the possibility of instant recharge and the advantages of readily available fuel infrastructure, high specific energy, and low system weight and volume [1–5]. Nevertheless, there are still technological issues in areas such as insufficient room temperature catalyst activity, CO tolerance, and methanol cross-over in the polymer electrolyte membrane. While carbon-supported platinum nanoparticles have traditionally been the catalyst of choice for hydrogen fuel cell anodes, platinum is susceptible to deactivation by CO when a hydrocarbon fuel is used at room temperature. Alloys of

platinum and oxophilic metals are superior to platinum-only catalysts in this regard because they can operate through a bifunctional mechanism in which platinum activates the C–H bond cleavage in the surface adsorbed methanol while the oxophilic metal assists in the oxidation of CO to CO_2 [3,6–9]. The oxophilic metal may also alter the electron density of state of Pt, which leads to weakening of the Pt–CO bond. This electronic effect therefore enhances the electrocatalytic activities of the Pt alloys [10–12]. While there are ongoing efforts to improve the performance of various Pt alloy catalysts [13–16], the prevailing view still considers carbon-supported PtRu alloy nanoparticles to be the most efficient anode catalyst for methanol electrooxidation.

Catalytic activity is closely dependent on the method of preparation. Hence, it is of interest to explore new preparation methods to improve the performance of carbon-supported platinum alloy catalysts in DMFC applications. The

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simultaneous reduction of metal salts [17–19], microwave-assisted reactions [20,21], microemulsion-based synthesis [22–24] and the reduction of single-source molecular precursors [25–30] have been used to various extents. In principle, the molecular precursor approach has several intrinsic advantages, namely: assurance of molecular level mixing between the constituent metals and a predetermined stoichiometry based on the atomic composition in the precursor. Despite these apparent advantages, reports on single-source precursor synthesis of DMFC anode catalysts remain scarce because most of the single-source precursors are air and moisture sensitive so that their preparation and handling warrant special precaution. It is therefore useful to develop molecular precursors that are simple to synthesize and are atmospherically stable for subsequent processing. The only perceivable downside of the single-molecular precursor approach lies with the difficulty in controlling the alloy composition. This is because obtaining PtM alloy nanoparticles of different compositions involves the design and synthesis of new precursors, which may be cumbersome and in some cases not feasible.

This work reports a comparative study of carbon-supported PtRu nanoparticles obtained by three different preparation methods namely: (i) the co-reduction of H_2PtCl_6 and RuCl_3 by NaBH_4 at room temperature; (ii) the co-reduction of H_2PtCl_6 and RuCl_3 by ethanol at elevated temperature; (iii) a single-source molecular precursor approach. Borohydride reduction and reduction in ethanol are chosen as representative methods of the conventional approach because of their procedural simplicity and their proven effectiveness in producing smaller nanoparticles. The effect of pH in the co-reduction of individual metal salts and the influence of heat treatment on the catalysts are also investigated.

2. Experimental

2.1. General

H_2PtCl_6 , RuCl_3 and 2,2' bipyridine (bipy) were purchased from Aldrich. $[(\text{bipy})_3\text{Ru}]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ was prepared according to the method of Broomhead and Young [31]. Carbon black (Vulcan XC 72) with a surface area of $250 \text{ m}^2 \text{ g}^{-1}$ was supplied by Cabot and was used as the catalyst support. All chemicals were used as received without further purification. Distilled de-ionized water was employed throughout the study and all glassware was washed with chromic acid and distilled water in succession and oven-dried before use. A JEOL JEM2010 microscope was used to obtain all transmission electron microscopy (TEM) images of the nanoparticles, while a JEOL MP5600LV provided scanning electron microscopy and energy dispersive analysis by X-rays (SEM/EDX) of the catalysts. Powder X-ray diffraction patterns of the samples were recorded on a Rigaku D/Max-3B diffractometer using $\text{Cu K}\alpha$ radiation.

2.2. Electrochemical measurements

The electroactivities of the catalysts for methanol oxidation were evaluated in a three-electrode cell by cyclic voltammetry at 50 mV s^{-1} on an EG&G 273 potentiostat/galvanostat. A Pt gauze and a standard calomel electrode served as the counter and reference electrode, respectively, while a thin film of Nafion impregnated PtRu/carbon composite cast on a vitreous carbon disk electrode was the working electrode. The Nafion impregnated PtRu catalyst ink was prepared by mixing 10 mg of the catalyst with 200 mg of 5 wt.% Nafion solution and 500 mg of distilled water. The electrolyte was 2 M CH_3OH in 1 M H_2SO_4 for all cyclic voltammetric runs. For all samples, the voltammograms were recorded after 20 activation cycles. Current densities were normalized with repeat to the electrode geometrical area. The Pt content in each of the prepared catalysts was kept at 20 wt.% so as to allow fair comparisons with a commercial E-TEK catalyst (20 wt.% nominal).

2.3. Preparation of PtRu-1

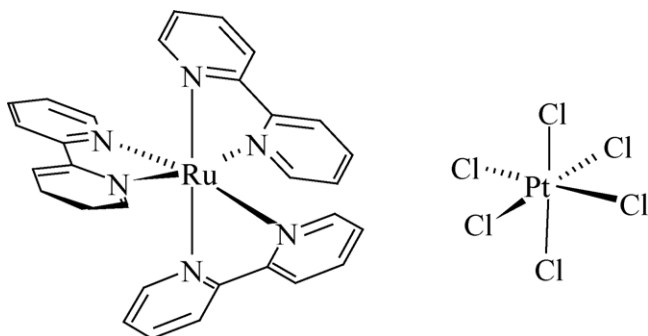
After adding 25 mg of carbon black (Vulcan XC 72) to 15 mL of distilled water, the resultant suspension was sonicated for 15 min. An amount of 5.3 mg RuCl_3 in 10 mL distilled water and 0.52 mL of 50 mM solution of H_2PtCl_6 were added to this suspension and stirred well. Then 40 mg of NaBH_4 , dissolved in 25 mL distilled water was introduced. Stirring was continued for 2 h before the solution was centrifuged. The recovered solid was washed with water and dried under vacuum.

2.4. Preparation of PtRu-2

Carbon black (25 mg; Vulcan XC 72), RuCl_3 (5.3 mg) and 0.52 mL of 50 mM H_2PtCl_6 solution were mixed in 50 mL ethanol and sonicated for 15 min. The resulting mixture was refluxed under constant stirring for 2 h. The reaction mixture was then allowed to cool to room temperature and centrifuged. The solid phase was washed with ethanol and water and vacuum dried.

2.5. Preparation of PtRu-3

A single-source precursor $[(\text{bipy})_3\text{Ru}](\text{PtCl}_6)$ (Scheme 1) was prepared in a slightly different way from the procedure reported in the literature [32,33]. In brief, to a well-stirred 10 mL aqueous solution containing 0.37 g (494 $\mu\text{ moles}$) of $[(\text{bipy})_3\text{RuCl}_2] \cdot 6\text{H}_2\text{O}$, H_2PtCl_6 (0.2 g, 488 $\mu\text{ mol}$) dissolved in 5 mL water was added drop by drop. The resulting solution was stirred for 30 min and the precipitate was filtered and washed with methanol (2 mL) and diethyl ether and dried at 70°C for about 2 h. The yield was 0.32 g (66%). Elemental analysis showed the following results: calculated for $\text{C}_{30}\text{H}_{24}\text{N}_6\text{Cl}_6\text{RuPt}$ (molecular weight,



Scheme 1. Proposed structure of single-source precursor.

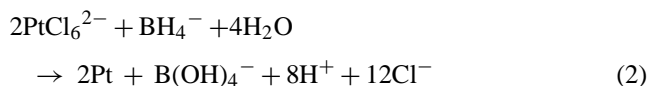
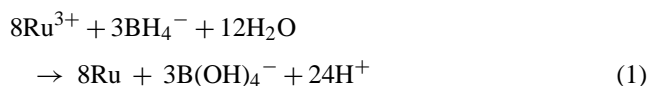
977.43); C, 36.87%; H, 2.47% and N, 8.60%; observed: C, 36.44%; H, 2.46% and N, 8.36%.

The single-source precursor and Vulcan Carbon XC 72 (25 mg each) were ball-milled together and the homogenized mixture was heated in a horizontal tube furnace in 5% H₂/95% Ar at 550 °C for 2 h.

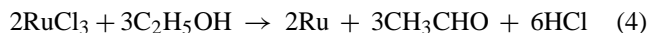
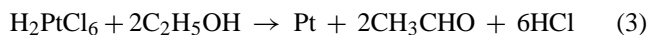
3. Results and discussion

3.1. Synthesis of PtRu catalysts

Preparation of metal and metal alloy nanoparticles by borohydride reduction of the corresponding metal salts is a well-recognized practice (**PtRu-1**). The reaction is facile even at room temperature and forms small particles easily. The stoichiometry of the reduction reactions can be summarized as follows [34]:



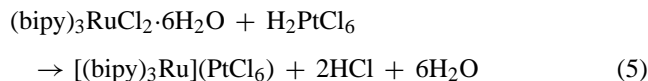
The electrocatalyst **PtRu-2** was prepared by the reduction of H₂PtCl₆ and RuCl₃ in ethanol, which can be represented by the following equations [35]:



These two reactions are common methods for the preparation of metal nanoparticles. The borohydride reduction is particularly adept at producing small and highly uniform metal particles, and many noble-metal-based DMFC catalysts have been obtained via this route. There are also reports suggesting that the NaBH₄ reduction of cobalt and nickel salts could lead to predominantly the formation of metal borides instead of the metal nanoparticles, which might adversely affect the performance of the electrocatalysts [36,37]. By contrast, ethanol reduction of H₂PtCl₆ and RuCl₃ is free from such competing

side-reactions, and forms relatively pure PtRu alloy nanoparticles.

The precursor [(bipy)₃Ru](PtCl₆) was prepared by a simple metathesis reaction between *tris*-bipyridyl ruthenium(II) chloride hexahydrate and chloroplatinic acid in methanol or water. The probable structure of the adduct is shown in Eq. (5). The precursor was found to be extremely stable and sparingly soluble in acetonitrile, DMSO and DMF:

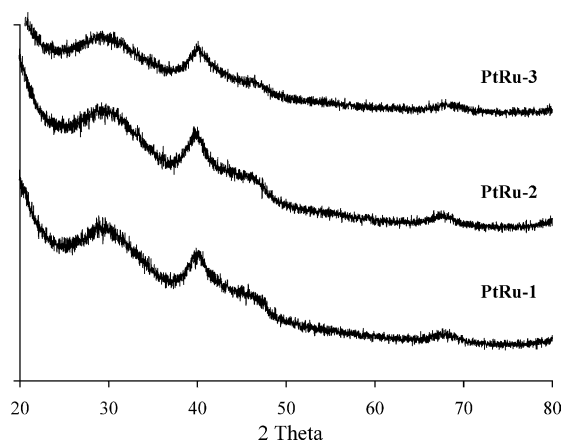


Upon heating the precursor complex–carbon composite in a H₂/Ar gas mixture, the precursor complex underwent reductive decomposition to yield carbon-supported PtRu alloy particles. The clean thermolysis of the single-source precursor in hydrogen is expected to result in a purer metal catalyst for the DMFC reactions.

3.2. Characterization of carbon-supported PtRu nanoparticles

EDX analyses of the carbon-supported PtRu alloy catalysts showed a Pt to Ru ratio of 1:1, which agrees well with the starting stoichiometric ratio of the metals. EDX also confirmed that the materials were devoid of common contaminations such as B, Cl and Na.

The catalysts **PtRu-1**, **PtRu-2** and **PtRu-3** were characterized by powder X-ray diffraction (XRD). The resulting XRD patterns show only the very broad peaks of f.c.c. Pt without any peaks that can be assigned to h.c.p. Ru or its oxides (Fig. 1). The f.c.c. Pt structure was inferred from the three different peaks at $2\theta = 39.9^\circ$ (1 1 1), 46.2° (2 0 0) and 67.9° (2 2 0). The absence of peaks due to ruthenium suggests the formation of solid solutions of Ru in Pt without any phase segregation. It has been reported that PtRu alloys containing up to 52 wt.% Ru would show only peaks due to Pt f.c.c. [38]. The peak-broadening in the XRD pattern is a characteristic of the nanometer length scale and validates the effectiveness

Fig. 1. X-ray powder diffraction of **PtRu-1**, **PtRu-2** and **PtRu-3** catalysts.

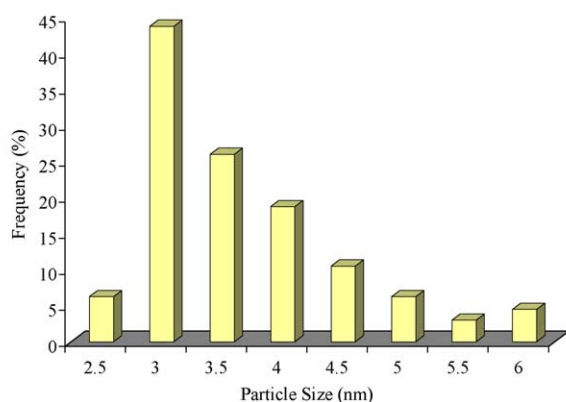
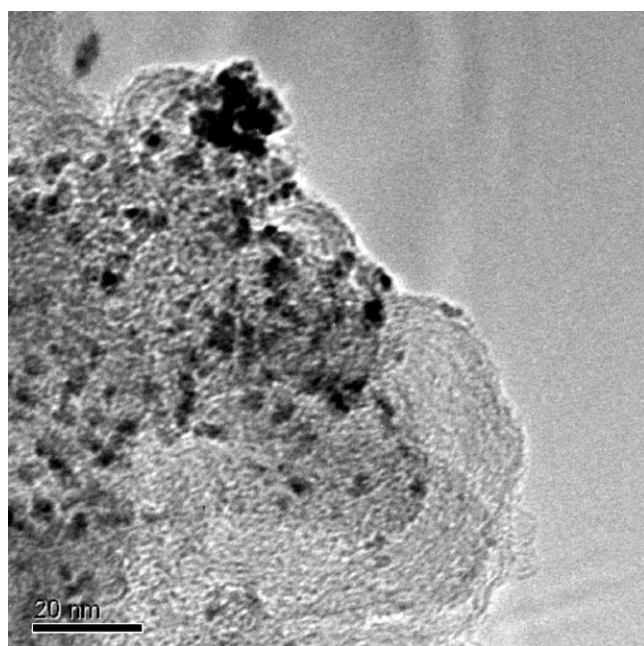


Fig. 2. TEM image of **PtRu-1** and histogram of the particle-size distribution.

of the experimental protocols in producing nanosize metal particles.

A typical TEM image of carbon-supported PtRu nanoparticles, prepared from the NaBH_4 reduction of H_2PtCl_6 and RuCl_3 (**PtRu-1**), is given in Fig. 2. A mean diameter of the particles of about 3.75 nm (S.D. = 1.01 nm) was obtained by counting over 100 particles in randomly chosen areas. The TEM also indicates that the nanoparticles are uniformly dispersed on the carbon surface.

The alcoholic reduction of platinum and ruthenium salts results in slightly larger particles (mean diameter = 6.96 nm) and a broader size distribution (S.D. = 1.55 nm). It is also observed that the addition of 0.2 mL of 1 M NaOH to the reaction mixture leads to further agglomeration of the nanoparticles (mean diameter = 10.2 nm, S.D. = 1.87 nm). These results contrast strongly with the polyol (ethylene glycol) reduction of metal salts, in which smaller and more uniform Pt nanoparticles are formed in the presence of a base (KOH or NaOH) [39,40]. Representative TEM images of carbon-

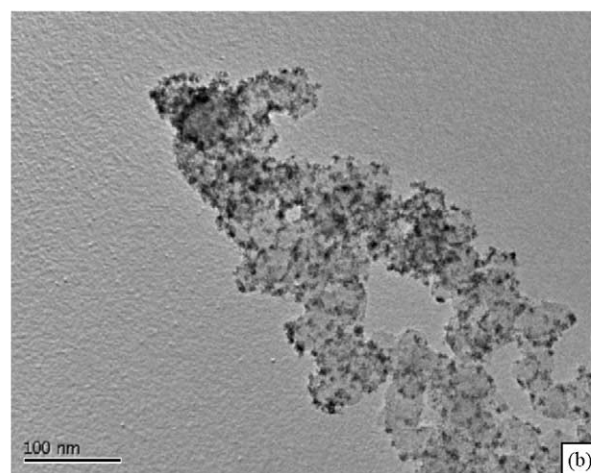
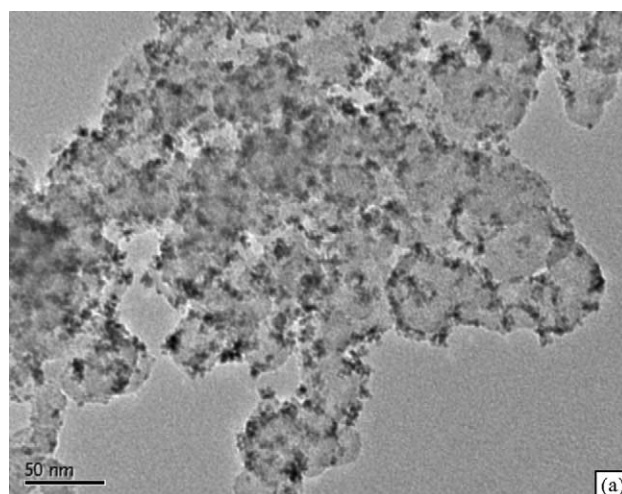


Fig. 3. TEM images of **PtRu-2** nanoparticles prepared in the (a) absence and (b) presence of NaOH.

supported **PtRu-2** nanoparticles prepared with and without NaOH are presented in Fig. 3(a) and (b), respectively. Histograms of the particle-size distributions for these two cases are given in Fig. 4.

It is also observed that PtRu nanoparticles prepared by the NaBH_4 and alcoholic reductions without XC-72 agglomerate within minutes of their formation and salt out easily. The presence of a suitable stabilizing agent such as PVP is needed to maintain the nanoparticles in suspension. The use of PVP during the reduction reactions also leads to the formation of smaller nanoparticles (<4 nm) with a more uniform size-distribution. The PVP-protected nanoparticles are not catalytically active and thermal activation is required to remove the organic shells. In fact, thermally activated particle-size enlargement could be a significant side-effect. Subsequently, these protected particles were not used in this study. In the presence of carbon, no sign of agglomeration of the PtRu particles is detected by TEM. The carbon surface can satisfactorily bind the nanoparticles through chemical and mechanical interlocking effects, which result in an increase in the activation

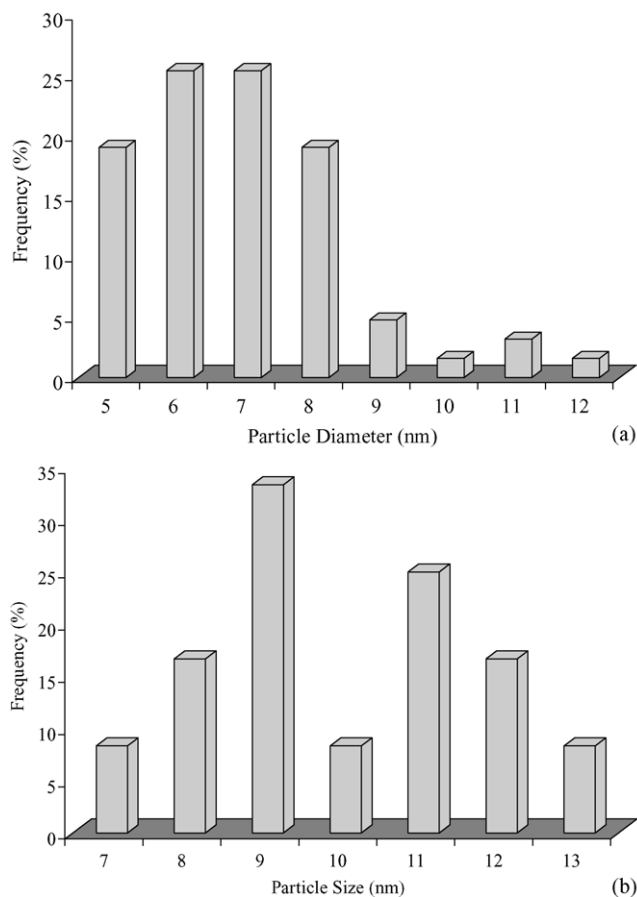


Fig. 4. Histogram of the particle-size distribution in **PtRu-2** prepared (a) without and (b) with NaOH addition.

energy required for particle agglomeration through surface diffusion.

In order to obtain carbon-supported PtRu nanoparticles from single-source molecular precursors, researchers often resort to a solution adsorption or deposition method to load the carbon black with the precursor compound. This is followed by decomposition at elevated temperatures in a reducing atmosphere to form small and nearly monodisperse nanoparticles. Due to the poor solubility of the [(bipy)₃Ru](PtCl₆) precursor in common organic solvents, ball-milling is used to load the precursor on to the carbon black. **PtRu-3** is the result of the thermolysis of a carbon homogenized precursor in a H₂/Ar mixture at 550 °C. The molecular precursor decomposes under these conditions to form metal alloy particles with well-defined stoichiometry and uniform mixing at the atomic level. The mean particle diameter, as measured by TEM, is 8.4 nm (S.D. = 3.3 nm). A TEM image of **PtRu-3** and a histogram of the particle-size distribution are given in Fig. 5.

In all of the above preparations leading to the carbon-supported PtRu nanoparticles, almost all of the nanoparticles are bound to the carbon surface and repeated TEM examinations do not indicate the presence of any isolated nanoparticles or metal agglomerates outside of the carbon matrix.

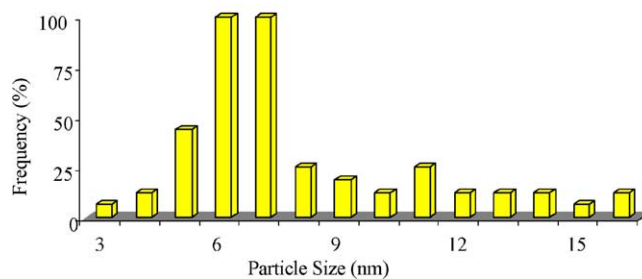
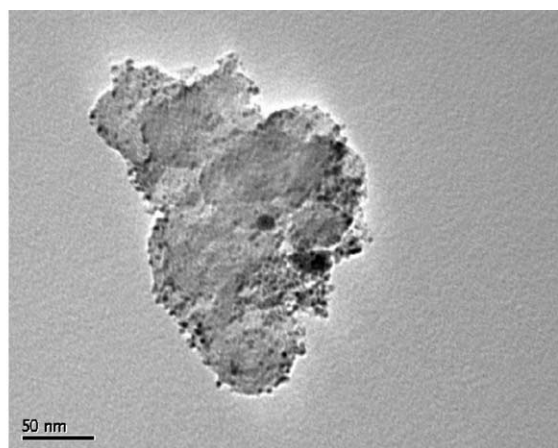


Fig. 5. TEM image of **PtRu-3** and histogram of the particle-size distribution.

3.3. Electrocatalytic properties

Cyclic voltammetry was used to evaluate and benchmark the activities of the three differently prepared catalysts for room temperature electrooxidation of methanol against a commercial (E-TEK) Pt catalyst. For a fair comparison, the Pt loadings in **PtRu-1**, **PtRu-2** and **PtRu-3** were pegged at the nominal Pt level in the commercial catalyst, i.e., at about 20 wt.%. A voltage range of 0–1 V was swept at the rate of 50 mV s⁻¹ (Fig. 6). The peak current densities due to methanol oxidation are shown in Table 1. The voltammetric features are consistent with literature reports and are typical of the electrooxidation of methanol on Pt-based bimetallics [21–24,39–42] namely: a methanol oxidation peak during the forward scan (from 0 to 1 V) at about 700 mV (versus SCE)

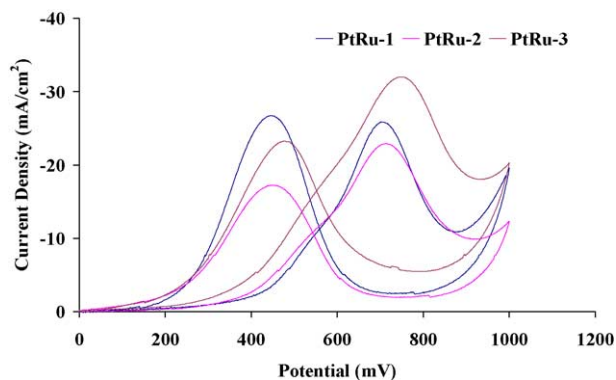


Fig. 6. Cyclic voltammograms for **PtRu-1**, **PtRu-2** and **PtRu-3**.

Table 1
Comparison of electrocatalytic properties of various catalysts

| Catalyst | Details of preparation | Peak current density ^a (mA cm ⁻²) | Activity figure of merits ^b | I_f/I_b |
|---------------|-----------------------------------------------------|----------------------------------------------------------|----------------------------------------|-----------|
| PtRu-1 | As prepared | -25.78 | 111% | 0.96 |
| | After heat treatment ^c | -21.83 | 94% | 1.05 |
| PtRu-2 | As prepared | -23.65 | 102% | 1.29 |
| | After heat treatment ^c | -22.77 | 98% | 1.32 |
| | Reduction with addition of 0.2 mL NaOH ^d | -20.63 | 89% | 1.0 |
| | Reduction with addition of 0.4 mL NaOH ^d | -9.46 | 41% | 1.11 |
| | Reduction with addition of 0.6 mL NaOH ^d | -9.41 | 40% | 1.13 |
| PtRu-3 | As prepared | -31.81 | 137% | 1.40 |
| E-TEK | – | -23.28 | 100% | 1.04 |

^a Normalized to the electrode geometrical area.

^b With respect to the E-TEK (20 wt.%) Pt catalyst.

^c Heated in a constant flow of H₂ (5%)–Ar (95%) gas mixture.

^d 1 M NaOH solution.

and another anodic peak on the reverse scan (~450 mV versus SCE) due to the removal of incompletely oxidized carbonaceous species formed in the forward scan [43,44].

The onset potentials for methanol oxidation on **PtRu-1** and **PtRu-2** are around 350–400 mV. By contrast, the onset of methanol electrooxidation on **PtRu-3**, prepared from the single-source molecular precursor, occurs much earlier, at around 280 mV. This indicates that the catalyst is able to reduce significantly the overpotential in methanol oxidation. The peak current densities due to methanol oxidation (at ~700 mV) for **PtRu-1**, **PtRu-2**, **PtRu-3** and the 20 wt.% E-TEK catalyst are -25.78, -23.65, -31.8 and -23.28 mA cm⁻², respectively. The catalyst activities can therefore be ranked in the following order E-TEK ~ **PtRu-2** < **PtRu-1** < **PtRu-3** (see Table 1). This ranking does not follow the order of decreasing particle size, for which **PtRu-1** < **E-TEK** < **PtRu-2** < **PtRu-3**. It should be mentioned that the E-TEK catalyst has Pt particles in the range of 2–10 nm and a mean diameter of 5.1 nm [39]. Based on particle-size analysis alone, the activity of **PtRu-3** would be expected to be lower than those of the other prepared catalysts and also the commercial E-TEK catalyst. Perhaps the homogeneity in mixing the two metals at the atomic scale (which is excellent for single-source molecular precursor) results in a higher performance for **PtRu-3**.

Heat treatment of **PtRu-1** and **PtRu-2** is expected to lower catalyst activity through a sintering-induced increase in the particle size. The decrease is, however, very marginal (2–6%) and this can be attributed to surface stabilization offered by the carbon support. A similar effect has been reported recently by Liu et al. [44]. On the other hand the addition of NaOH during the reduction reaction influences the electrocatalytic properties adversely to a very large extent. This agrees well with the TEM results that show a large increase in the particle size and extensive agglomeration when NaOH is present in the ethanolic reduction of H₂PtCl₆ and RuCl₃.

Yet another method to benchmark the catalyst performance is to compare the ratio of current densities associated with the anodic peaks in the forward (I_f) and reverse

(I_b) scans. Such a ratio has been used to infer the CO tolerance of the catalysts [43,44]. A lower I_f/I_b value signifies poor oxidation of methanol to CO during the anodic scan and excessive accumulation of carbonaceous species on the catalyst surface. In other words, a greater extent of CO poisoning. Hence a higher I_f/I_b value is indicative of improved CO tolerance. The I_f/I_b values of the three differently prepared catalysts are listed in Table 1. Heat treatment of the catalysts does not significantly alter the I_f/I_b values; more important is the effect of the pH used in the syntheses. It can be clearly seen that **PtRu-3**, prepared from the single-source precursor, has the best CO resistance among the prepared catalysts. It also compares favourably with the E-TEK catalyst.

A comparison of all the data presented in Table 1 reveals that **PtRu-3** had the best application performance as an anode catalyst, i.e., a 37% increase in electrocatalytic activity relative to the E-TEK catalyst as well as enhanced CO tolerance. This behaviour is due to the relatively large particle size of the PtRu nanoparticles in **PtRu-3**. This enhancement may be related to the high level of homogeneity of bimetallic mixing in catalysts obtained via from the single-source precursor approach.

4. Conclusions

Carbon-supported PtRu nanoparticles are prepared through: (i) room temperature NaBH₄ reduction of H₂PtCl₆ and RuCl₃ (**PtRu-1**); (ii) ethanol reduction of H₂PtCl₆ and RuCl₃ under reflux (**PtRu-2**); (iii) thermolysis of a single-source precursor (**PtRu-3**). Carbon is introduced as suspended solids in the first and second methods but through ball-milling in the third method. Despite the fact that **PtRu-3** from the single-source molecular precursor has the largest average particle diameter, it displays the lowest onset potential and the highest current density for methanol oxidation at room temperature. It is also the most CO tolerant among the three differently prepared catalysts. Heat treatment of these catalysts only reduces their activities marginally. By

comparison, a higher pH used in the preparation has a more significant adverse effect on catalyst performance. The results from this work highlight the advantages of the single-source molecular precursor approach in catalyst preparation, notwithstanding the fact that the catalyst composition may not be easily adjusted when using this procedure.

Acknowledgement

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