

Performance of direct methanol fuel cell using carbon nanotube-supported Pt–Ru anode catalyst with controlled composition

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Abstract

The performance of a single-cell direct methanol fuel cell (DMFC) using carbon nanotube-supported Pt–Ru (Pt–Ru/CNT) as an anode catalyst has been investigated. In this study, the Pt–Ru/CNT electrocatalyst was successfully synthesized using a modified polyol approach with a controlled composition very close to 20 wt.%Pt–10 wt.%Ru, and the anode was prepared by coating Pt–Ru/CNT electrocatalyst on a wet-proof carbon cloth substrate with a metal loading of about 4 mg cm⁻². A commercial gas diffusion electrode (GDE) with a platinum black loading of 4 mg cm⁻² obtained from E-TEK was employed as the cathode. The membrane electrode assembly (MEA) was fabricated using Nafion[®] 117 membrane and the single-cell DMFC was assembled with graphite endplates as current collectors. Experiments were carried out at moderate low temperatures using 1 M CH₃OH aqueous solution and pure oxygen as reactants. Excellent cell performance was observed. The tested cell significantly outperformed a comparison cell using a commercial anode coated with carbon-supported Pt–Ru (Pt–Ru/C) electrocatalyst of similar composition and loading. High conductivity of carbon nanotube, good catalyst morphology and suitable catalyst composition of the prepared Pt–Ru/CNT electrocatalyst are considered to be some of the key factors leading to enhanced cell performance.

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1. Introduction

Fuel cells are clean, efficient, and noiseless. There is increasing interest in the development of fuel cell systems [1] due to their profound commercial applications. Particularly, direct methanol fuel cells (DMFCs) [2,3] can be used as dependable and long-lasting portable power sources to replace batteries, which suffer from low energy capacities and short runtimes, in various electronic equipments. Although significant advances have been achieved for DMFC systems in recent years, considerable efforts are still needed to make them commercially practical.

DMFCs strongly depend on the use of Pt electrocatalyst for effective oxygen reduction and Pt–Ru electrocatalyst for methanol fuel electrooxidation. The use of bi- or multi-

component anode catalysts for methanol electrooxidation is an effective way to solve the catalyst poisoning problems caused by CO and other reaction intermediates under low-temperature reaction conditions. Conventionally, highly conductive carbon blacks, such as Vulcan[®] XC72 (Cabot) and Shawinigan[®] (Chevron), with high surface areas are used as supports for electrocatalysts to ensure large electro-reaction surfaces and good electronic conduction. Although such carbon black-supported electrocatalysts have exhibited quite moderate performances on DMFCs so far, a new generation of electrocatalyst carbon supports, such as carbon spheres [4], graphite nanofibers [5], carbon nanohorns [6] and carbon nanotubes [7–9], are actively being sought and tested with attempts to significantly improving membrane fuel cell performances. In particular, more and more carbon nanotubes (CNT) have been investigated [10–19] recently as advanced electrocatalyst supports due to their distinctive characteristics.

Formation of electrocatalysts on CNT for membrane fuel cell applications is commonly conducted using reductive deposition

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methods. A variety of conventional reducing agents, e.g., HCHO, HCOOH, NaBH₄, N₂H₄, etc., have been tested but only with poor deposition results. At present, reductive preparation of CNT-supported Pt (Pt/CNT) electrocatalyst using ethylene glycol (EG) as a reducing agent, i.e. a polyol approach, is the most popular method [7–10]. Good electrocatalyst formations can be readily obtained. The main functions of EG are: (a) to work as a chelating agent for complexation and dispersion of metal ions in the reduction process leading to small particle sizes and (b) to serve as a reducing agent to convert metal ions into metal or alloy nanoparticles. In a general polyol process, CNTs were generally first subjected to oxidation pretreatment [20] using a strong acid, such as HNO₃ or a mixture of HNO₃ and H₂SO₄, solution so as to remove impurities and generate sufficient amounts of functional groups, e.g., –OH, –COOH, –C=O, etc., on the surfaces. These surface functional groups have stronger attraction forces toward metal ions than bare carbon nanotube surfaces and some even have ion exchange capabilities, such as carboxylic acid groups. Therefore, they are believed to work as metal-anchoring sites in order to facilitate metal nuclei formation and electrocatalysts deposition. The preparation of Pt/CNT electrocatalyst using a polyol method is, in fact, very simple and straightforward.

Different from the cathode Pt electrocatalyst, the anode Pt–Ru electrocatalyst must have a right composition, e.g., Pt:Ru = 1:1 in atomic ratio, in order to obtain high electrocatalytic activity and high poisoning resistance with respect to methanol electrooxidation. However, in the preparation of Pt–Ru/CNT, difficulties arise that platinum and ruthenium ions or salts cannot be reduced simultaneously at the same pH of the reaction solution with competitive reduction rates. This is due to different reduction capabilities and reaction conditions for the platinum and ruthenium ions. For example, the pH value for platinum deposition can be as high as 12 but ruthenium salts will form and precipitate under this condition. Thus, Pt–Ru/CNT cannot be readily prepared using a simple polyol approach with satisfactory results. Common drawbacks that are encountered including undesirable electrocatalyst compositions overly rich in Pt element, low metal deposition efficiency, large particle sizes and non-uniform particle dispersion resulting in poor electrocatalyst activity and cell performance.

Recently, we have successfully developed a modified polyol method that allows us to prepare Pt–Ru/CNT anode electrocatalysts with high metal deposition efficiencies, excellent nanoparticle morphology and, in particular, desired electrocatalyst compositions. This depended mainly on the creation of a suitable deposition environment on the CNT surfaces near the isoelectric point (IEP) [21,22], i.e., the polarity of zeta (ζ) potential turns from negative to positive or vice versa, where both complexed platinum and ruthenium ions have almost equal specific adsorption rates. Thus, at this particular point, the composition of formed Pt–Ru catalyst can be controlled by the composition of metal ions in the deposition solution. In this study, we investigate the performance of a single-cell DMFC using in-house prepared Pt–Ru/CNT with controlled composition as an anode catalyst.

2. Experimental

2.1. Preparation of Pt–Ru/CNT electrocatalyst and DMFC anode

Multi-walled carbon nanotubes were obtained from Advance Nanopower Inc., Taiwan having diameters of 8–15 nm and an average surface area of 233 m² g⁻¹. The length of the carbon nanotubes was found to be 1–2 μ m. The as-received carbon nanotubes were first oxidized in a hot solution, composed of 8 M HNO₃ and 2 M H₂SO₄, for several hours under refluxing conditions to remove impurities and generate surface functional groups. Purification of CNT surfaces prevents self-poisoning by foreign impurities while functional group generation enhances electrocatalyst formation. To determine the CNT surface charge conditions, the zeta potential as a function of pH of the EG solution for acid-treated CNT before and after Pt–Ru electrocatalyst formation was measured using a Zetasizer Nano ZS meter (Malvern Instruments) and the IEPs were determined. Each specimen was prepared by adding a specific amount of acid-treated CNT or Pt–Ru/CNT (0.01 wt.%), respectively, into an EG solution, which contained 2.5 wt.% of water. The mixture was well-mixed by high-speed stirring and then ultrasound sonicated for 15 min. The pH of the solution was adjusted in situ during zeta potential measurement using HCl and NaOH aqueous solutions.

Reagent grade reducing agents, i.e., ethylene glycol and sodium hydrogen sulfite (NaHSO₃) solution, were obtained from Merck and electrocatalyst precursor salts, i.e., H₂PtCl₆·6H₂O and RuCl₃, were purchased from Alfa Aesar. They were used as received without further purification. Preparation of the Pt–Ru/CNT anode electrocatalyst was intended to have a composition of about 20 wt.%Pt–10 wt.%Ru, i.e., an atomic ratio of Pt:Ru = 1:1. As an example, a known amount (0.70 g) of acid-oxidized CNT was added to 50 ml EG aqueous solution. The above mixture was ultrasound sonicated for 10 min, followed by high-speed stirring for 30 min, using a high-speed stirrer (Heidolph, Silent Crusher M) to form a homogeneous paste so that EG was able to completely cover the carbon nanotube surfaces. Then, 0.54 g of H₂PtCl₆·6H₂O and 0.21 g of RuCl₃ as Pt–Ru electrocatalyst precursors were dissolved in 10 ml EG, together with addition of 1 ml of 1 M NaHSO₃ aqueous solution as a modifier, forming complexed salts or ions. After that, the catalyst precursor salt/EG/NaHSO₃ solution was slowly added to the prepared CNT/EG paste and the pH was adjusted to about 4 by dispensing a suitable amount of 4N NaOH using a metering pump into the above mixture. The solution was subjected to high-speed stirring for the complexed metal salts or ions to adhere to the surfaces of carbon nanotubes. In the meantime, the resultant mixture was heated at 130 °C using a microwave heater for 60 min to form Pt–Ru/CNT with the pH monitored. The microwave system was an Ethos microwave lab station (Milestone, model: MPR-600/6S) equipped with a temperature controller that controlled the functioning of the microwave generator. The reaction solution was refluxed during reaction.

After reduction reaction, the reacted mixture was filtered and the collected carbon nanotubes were washed and rinsed with a sufficient amount of Millipore water (resistivity $>16.0\text{ M}\Omega\text{ cm}$). The filtrate and wash wastewater were analyzed using an inductively coupled plasma-optical emission spectroscope (ICP-OES) (Jobin Yvon, Ultima-2) to determine the total amounts of unreacted metal ions as well as washed out metal ions and particles. Then, the actual amount of each metal supported on CNTs was calculated. Finally, the electrocatalyst loaded carbon nanotubes were dried in an oven at 100°C under vacuum condition for several hours.

The prepared Pt–Ru/CNT was used as a DMFC anode electrocatalyst with a loading of about 4 mg cm^{-2} . The electrocatalyst was first well-mixed with a suitable amount of 5 wt.% Nafion[®] solution (e.g., 1 g carbon nanotube-supported electrocatalyst with 3 g Nafion[®] solution in dry basis) and then applied to a wet-proof carbon cloth (Electrochem Inc.) by brushing followed by a leveling procedure. Then, the coated electrode was put in a holder to keep the flat shape and then dried in an oven at 60°C for several hours before being hot pressed into a membrane electrode assembly (MEA).

2.2. Characterization of prepared Pt–Ru/CNT electrocatalyst and DMFC anode

Physical characterization of the prepared Pt–Ru/CNT electrocatalysts was conducted using a transmission electron microscope (TEM) (JEOL, JEM 2010 operating at 200 kV) for morphology and particle-size analyses. X-ray diffraction (XRD) spectroscopy was used to examine the formation of Pt–Ru on CNT surfaces and to compare the pattern with that of a Pt–Ru black alloy (Pt:Ru = 1:1 in atomic ratio) obtained from Alfa Aesar. A Siemens Diffractometer (D 5000) was used to record the patterns. Scans were acquired with a 0.02° step size over 2θ range of $20\text{--}90^\circ$. Diffraction peaks of crystalline phase were compared with those of standard species reported in the JCPDS Data File. A scanning electron microscope (SEM) (JEOL, JSM-T330A operating at 8 kV) with a backscattering electron detector was employed to examine the prepared DMFC anode with coating of Pt–Ru/CNT electrocatalyst and the result was compared to that of a commercial anode (E-TEK) coated with Pt–Ru/C.

2.3. Electrochemical investigation on methanol electrooxidation

Electrochemical investigation on the prepared Pt–Ru/CNT electrocatalyst with respect to methanol electrooxidation was carried out using cyclic voltammetry. A commercial Pt–Ru/C electrocatalyst (Alfa Aesar) was also tested for comparison. For all the electrochemical tests, the same amount of electrocatalyst (0.5 mg) was used each time. Each sample was mounted on a glassy carbon electrode (0.196 cm^2) and fixed with 0.1 ml of 5 wt.% Nafion solution. A three-electrode system was employed with Pt as a counter electrode and Ag/AgCl as a reference electrode. Methanol electrooxidation experiments were performed at room temperature in 0.5 M H_2SO_4 aqueous solution contain-

ing 1.0 M CH_3OH using a linear-sweep method with a sweep rate of 10 mV s^{-1} .

2.4. Investigation on DMFC performance using Pt–Ru/CNT anode electrocatalyst

The anode was prepared by coating Pt–Ru/CNT electrocatalyst on a wet-proof carbon cloth substrate with a metal loading of about 4 mg cm^{-2} . A commercial gas diffusion electrode (GDE) with a platinum black loading of 4 mg cm^{-2} , obtained from E-TEK, was employed as the cathode. Both catalyst loadings were applied as absolute masses and did not include the weight of carbon support materials. In the preparation of MEA, the prepared anode and the GDE cathode were hot-pressed onto both sides of a Nafion[®] 117 membrane at 130°C with an applied pressure of 0.5 kN cm^{-2} for 5 min. Then, the MEA was fabricated into a single-cell DMFC using two graphite endplates and fasten with bolts and nuts. The single-cell DMFC was first activated at 40°C and 0.3 V for 2 h. It was then tested between 40 and 60°C by feeding 1 M methanol solution (40 ml min^{-1}) with circulation through the anode compartment, and by flowing oxygen (250 ml min^{-1} , 20 psi back pressure) through the cathode compartment. Performance tests of DMFCs were conducted using a fuel cell test station developed by Lynntech Inc. A comparison cell was also fabricated and tested using a commercial carbon-supported Pt–Ru (Pt–Ru/C) anode (E-TEK) with a similar composition and loading (i.e., 4 mg cm^{-2} in absolute mass) to the prepared Pt–Ru/CNT anode. The cell performance curves, i.e., plots of cell voltage (V) versus current density (A), as well as power density versus current density curves were collected and compared.

3. Results and discussion

3.1. Preparation of Pt–Ru/CNT using a modified polyol approach

The measured zeta potentials as a function of pH of EG solution are shown in Fig. 1. As expected, the acid-treated CNT exhibited zeta potentials at a higher pH range while the catalyst-

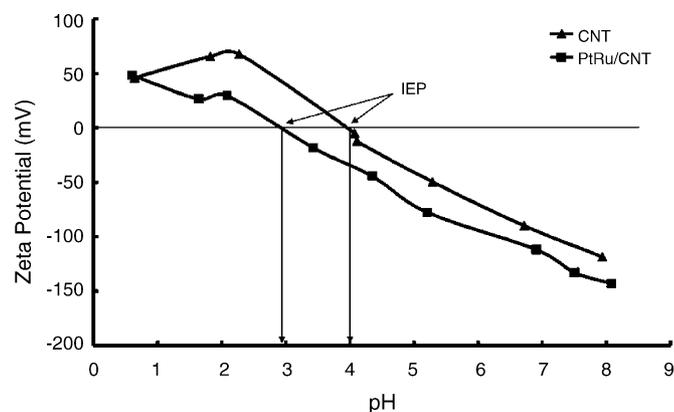


Fig. 1. Zeta (ζ) potential as a function of pH for both CNT (bare, acid-treated CNT) and Pt–Ru/CNT (electrocatalyst-deposited CNT) in ethylene glycol solutions containing 2.5 wt.% H_2O .

coated Pt–Ru/CNT showed zeta potential at a lower pH range. It can be seen that the IEP of the former falls at around pH 4. This is the initial pH value of the reaction solution that was employed in the electrocatalyst preparation experiments. It is thought to be the suitable condition for formation of a large number of particle nuclei that will ensure formation of small particles. However, the IEP for Pt–Ru/CNT has shifted negatively to about pH 2.9. It is clear that the IEP during catalyst formation is not fixed and changes with the reaction environment. Thus, the suitable reaction condition should cover a pH range, e.g., pH 3–4, that is close to the ever-changing IEP during Pt–Ru/CNT electrocatalyst formation. It is clear that the difference in the locations of two IEPs was caused by two different zeta potential versus pH curves. The zeta potential was in general strongly dependent on the surface charge condition of the CNT surface. Since the Pt–Ru catalyst, which occupied about 20–25% of the total CNT surfaces after reaction, had quite different surface characteristics from the uncoated CNT, therefore Pt–Ru/CNT exhibited a different zeta potential curve, and, in turn, gave rise to a different IEP.

With the additions of electrocatalyst precursor salts and sulfite species, the initial pH of reaction solution was found to be about 1. At the start of catalyst formation, the reaction solution was thus adjusted to pH 4 that is close to the initial IEP of CNT surface. The solution pH decreased gradually during the deposition process. After deposition reaction, the pH decreased back to around 3 or a lower value mainly due to the release of protons from carboxylic acid functional group, platinum precursor salt and EG reducing agent. It should be noted that EG is a very weak acid ($pK_a \approx 15$). Therefore, it most likely remains intact during

the complexation process with metal ions at a low pH environment. In addition, the Pt(+IV) and Ru(+III) precursor salts may also not fully ionize to Pt^{4+} and Ru^{3+} in the EG solution with a small content of water. This modified process, however, is unique in that it undergoes Pt–Ru electrocatalyst deposition on CNT surface in a fairly low pH environment rather than under high pH conditions as commonly employed for Pt/CNT [7].

Fig. 2a shows the TEM image of as-received CNT. Using the modified polyol approach, excellent Pt–Ru/CNT formation was obtained as illustrated in Fig. 2b. On the other hand, using the conventional polyol method without modification, the Pt–Ru/CNT has a poor formation as can be seen from Fig. 2c. Furthermore, from the detailed TEM image of the prepared Pt–Ru/CNT electrocatalyst as shown in Fig. 2d, one can clearly see that the prepared Pt–Ru/CNT using modified EG has uniform particle dispersion and small particle sizes. The average particle size is about 3.5–4.0 nm. This is, in fact, just about the ideal size of Pt–Ru electrocatalyst for methanol electrooxidation [23]. In addition to particle morphology, the composition of the prepared Pt–Ru electrocatalyst is also of vital importance to have excellent electrocatalytic activity and poison-resistance in methanol electrooxidation. It was found from ICP-OES test that the metal deposition efficiency for Pt–Ru/CNT was significantly improved from about 40% to >98% using the modified polyol method. The prepared Pt–Ru/CNT turned out to have a percentage composition of 19.87 wt.%Pt–9.91 wt.%Ru with an atomic ratio of Pt:Ru = 1:0.962 very close to the intended ratio of 1:1. Even with such a weight percentage composition, the Pt–Ru catalyst is estimated to cover only about 12.5–25% of the total CNT surface areas. Therefore, there are in fact still ample rooms

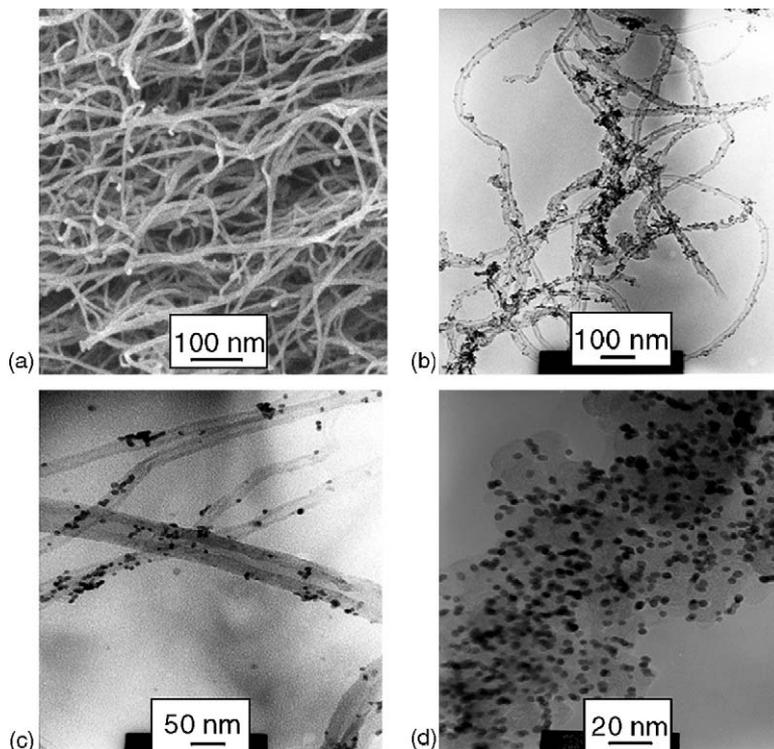


Fig. 2. Transmission electron microscopy (TEM) images of (a) as-received CNT, (b) Pt–Ru/CNT prepared using modified EG approach, (c) Pt–Ru/CNT prepared using unmodified EG approach, and (d) Pt–Ru/CNT prepared using modified EG approach in magnified details.

Table 1

Comparison of compositions of two Pt–Ru/CNT electrocatalysts prepared using modified and unmodified polyol methods

| Preparation method | Initial composition based on catalyst precursors ^a | | Final composition calculated from ICP–OES analysis | |
|--------------------|---|----------------------|--|----------------------|
| | Weight percent (wt.%) | Atomic ratio (Pt:Ru) | Weight percent (wt.%) | Atomic ratio (Pt:Ru) |
| Modified polyol | Pt (20.04), Ru (10.19) | 1:0.981 | Pt (19.87), Ru (9.91) | 1:0.962 |
| Unmodified polyol | Pt (19.99), Ru (10.24) | 1:0.988 | Pt (10.56), Ru (1.69) | 1:0.309 |

^a The weight of CNT was 0.70 g for each.

on CNT surfaces for preparation of Pt–Ru electrocatalyst with higher weight percentages (e.g., >60 wt.%), which makes the fabrication of a high catalyst loading (e.g., >2 mg cm⁻²) DMFC electrode much easier on either carbon cloth or membrane due to a smaller amount of carbon material involved in the process. On the other hand, when using unmodified EG method, the catalyst deposition efficiency was poor and the resultant electrocatalyst composition was low in Ru element with a poor atomic ratio of 1:0.309 as shown in Table 1. Thus, the use of modified polyol approach indeed did improve the Pt–Ru formation on CNT supports with desired electrocatalyst composition. In fact, our investigations also indicated that a variety of CNT-supported, precious metal-based multi-component catalysts, e.g., Pt–Ru–Ir, Pt–Ru–Os, Pt–Ru–Ir–Rh, etc., can be prepared using this modified polyol approach as well with good catalyst morphologies and controlled compositions.

The successful preparation of Pt–Ru/CNT with excellent catalyst morphology and controllable compositions can be attributed to several factors:

- The preparation process properly controlled the reaction solution pH at a specific range of 3 < pH < 4 to regulate the ζ potential on CNT surface so as to obtain a suitable metal deposition environment. By carefully adjusted the metal deposition solution with a suitable amount of NaOH aqueous solution to a pH value close to where the IEP takes place on the CNT surface and precipitation of undesired Ru salts can be avoided, a suitable Pt–Ru deposition environment on the CNT surfaces was created. Since there is no net surface charge at the IEP, the adsorption of different ligand-complexed ions on the CNT surfaces will occur at almost the same specific rates. Thus, the composition of the final electrocatalyst product will depend mainly on the composition of the starting reactant solution, which can be readily controlled as desired. This is, in fact, the key to obtain controlled compositions for Pt–Ru/CNT.
- The preparation process used sodium hydrogen sulfite (NaHSO₃) aqueous solution as an additive to modify the main reducing agent, i.e., EG. This was due to the fact that sulfite species is commonly used in the reductive formation of Pt–Ru electrocatalyst [24,25] with a stronger reducing capability than EG. It is able to form more stable complex ions of platinum and ruthenium in a low pH environment leading to better dispersion and, in turn, narrower nanoparticle formation. In particular, the use of NaHSO₃ substantially promotes the conversion efficiency of complexed ruthenium ion to metal about two to three times higher than before at a lower pH range of 3–4. This is indeed a significant improve-

ment in reductive preparation of Pt–Ru/CNT electrocatalyst using sulfite species as a modification agent to EG. It should be mentioned that at low pH values the capability of EG in the complexation of metal ions becomes relatively weak. The introduction of NaHSO₃ as a modification agent into the reaction solution provides the needed assistance in this respect. Thus, the dual role of NaHSO₃ as a second chelating agent and as an enhancing reduction agent is also of special importance in the successful preparation of Pt–Ru/CNT.

- The preparation process employed a microwave heating approach to shorten reaction time and promote uniform formation of Pt–Ru/CNT. This heating method has advantages over conventional conductive heating in that it is more uniform and effective. Therefore, suitable reaction temperatures can be reached within a much shorter time interval. In general, microwave irradiation heating can increase the reaction kinetics by 1–2 orders of magnitude over conventional heating methods within a short reaction time improving electrocatalyst nanoparticle uniform formation and dispersion. The best reaction temperature was found to be around 110–150 °C and the reaction time was dramatically reduced from 6 to 8 h to about 30–60 min using the modified EG with microwave irradiation heating.
- The preparation process limited the addition of water content to control the particle sizes of the catalyst. It was found [7] that the amount of water added to EG significantly affect the particle sizes of CNT-supported electrocatalysts. In general, the higher water content in EG, the larger Pt particle size on CNT. Therefore, the water content in the modified reducing agent was properly controlled so as to obtain the best performance and prevent the catalyst particles from aggregation. A water-content of 2–5 vol.% generally gave quite satisfactory results in particle formations.

3.2. Physical characteristics of prepared Pt–Ru/CNT electrocatalyst and DMFC anode

Fig. 3A shows XRD patterns of (a) acid-treated CNT and (b) Pt–Ru/CNT electrocatalysts. The acid-treated CNT exhibited characteristic diffraction peaks at $2\theta = 26.8^\circ, 43.1^\circ, 53^\circ$ and 79° . These peaks can be attributed to the hexagonal graphite structures (002), (100), (004) and (110) of the multi-walled CNT [9]. The first peak at 26.8° is particularly pronounced. After the reductive deposition process, the 26.8° diffraction peak has substantially diminished and the others have disappeared indicating the formation of Pt–Ru electrocatalyst on the CNT surfaces. The generated new diffraction peaks corresponded to Pt(111), Pt(200), Pt(220), and Pt(311) of Pt-rich f.c.c. phases. How-

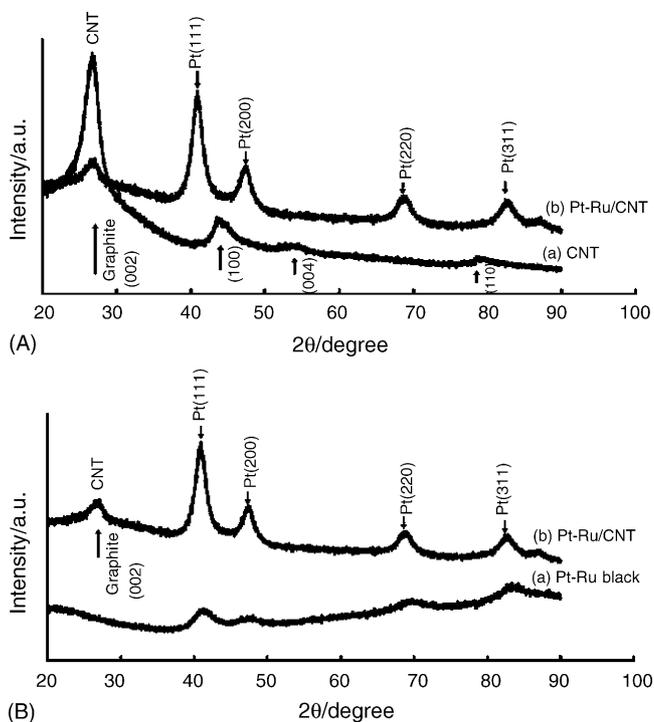


Fig. 3. Comparison of XRD patterns: in (A) shows that of (a) acid-treated CNT, and (b) Pt–Ru/CNT; in (B) shows that of (a) Pt–Ru black and (b) Pt–Ru/CNT.

ever, the resultant characteristic peaks are not sharp and, in fact, no obvious peaks corresponding to hcp particles of the Ru element can be seen. This phenomenon is commonly found for carbon-supported Pt–Ru electrocatalysts [26–29] except those of highly Ru-rich particles.

Further comparison with the XRD pattern of a Pt–Ru black standard as shown in Fig. 3B, it can be seen that both do reveal similar characteristic peaks at the same positions except the remaining CNT signal at $2\theta = 26.8^\circ$. Once again, this proves that the formation of electrocatalyst on the CNT surface by reductive deposition do indeed correspond to that of Pt–Ru. The absence of peaks for the Ru element in Pt–Ru/CNT can be attributed to the relative small size of the Ru atom that is embedded in the Pt–Ru crystalline structure. Nevertheless, it is interesting to note that by oxidizing carbon-supported Pt–Ru electrocatalysts in an oxygen environment at an elevated temperature, e.g., 400°C , the characteristic diffraction peaks corresponding to those of RuO_2 , in particular $\text{RuO}_2(1\ 1\ 0)$, $\text{RuO}_2(1\ 0\ 1)$ and $\text{RuO}_2(2\ 1\ 1)$, will appear due to formation of different crystalline structures. This phenomenon may be employed to qualitatively examine the composition of bi- or multi-component Pt alloy electrocatalysts.

It can be seen that the XRD pattern of the prepared Pt–Ru/CNT matches perfectly well with that of the Pt–Ru black alloy reference, which directly proves the obtained Pt–Ru/CNT was an alloy catalyst. In addition, if the prepared catalyst was independent Pt/Ru nanoparticles or a combination of the two, the distinctive peaks of the Ru element should appear in the XRD pattern. However, they did not. It is, therefore, concluded that the prepared Pt–Ru/CNT was indeed an alloy catalyst. The XRD information was commonly employed by researchers to calculate the mean size of carbon-supported electrocatalyst nanopar-

ticles using Scherrer's formula [27,28], but the accuracy could be poor. More recent work on the use of microwave synthesis and XRD characterizations of alloyed Pt–Ru nanoparticles can be found from the report of Liu et al. [30]. They used a thiol compound to stabilize the polyol-generated catalyst nanoparticles in a toluene solution, and then mixed and attached them to carbon black powders. However, this work is quite different from the present study and care should be taken in making any comparison.

The SEM image of the prepared anode is shown in Fig. 4a and that of a commercial anode with Pt–Ru/C coating obtained from E-TEK is shown in Fig. 4b. It can be seen that the prepared anode using Pt–Ru/CNT has a compact structure while that of the commercial anode is quite loose and porous. The relatively more compact structure is expected to provide more active surface area for methanol electrooxidation. In fact, the Pt–Ru/CNT was much bulkier than the commercial Pt–Ru/C and required some delicate efforts to prepare into a good electrode structure. Different from the E-TEK electrode, the electrode surface of the prepared Pt–Ru/CNT electrode was basically a mixture of Pt–Ru/CNT and Nafion[®] ionomer without the use of any Teflon[®] binder. In addition, Fig. 4c illustrates the SEM backscattering electron image (BEI) of the prepared anode using Pt–Ru/CNT. The light color of the image corresponds to the presence of catalyst metal. Thus, it can be seen that the distribution of electrocatalyst on the anode is very even. With such a compact structure and even distribution of anode electrocatalyst, it is naturally expected to have good performance for the fabricated DMFC.

3.3. Performance of Pt–Ru/CNT on electrooxidation of methanol

Fig. 5 compares the electrocatalytic activity on methanol electrooxidation of (a) a commercial Pt–Ru/C, and (b) prepared Pt–Ru/CNT in $0.5\ \text{M}\ \text{H}_2\text{SO}_4 + 1\ \text{M}\ \text{CH}_3\text{OH}$ solution using an electrochemical test cell. The graph illustrates the methanol electrooxidation currents obtained from linear-sweep voltammograms. It clearly shows better performance for Pt–Ru/CNT than that of a commercial Pt–Ru/C electrocatalyst (20 wt.%Pt–10 wt.%Ru on carbon black) obtained from Johnson–Matthey. This can be attributed to several factors, including (i) the prepared Pt–Ru/CNT electrocatalyst possesses perfect nanoparticle sizes and ideal compositions that enhance its electrocatalytic activity, (ii) the functional groups formed on the CNT surfaces result in high hydrophilicity that creates better electrochemical reaction environments on the electrode, and (iii) the high electronic conductivity of the CNT lowers the resistance in methanol electrooxidation. More importantly, this result proves that the use of modified polyol approach is effective in preparation of Pt–Ru/CNT anode electrocatalyst with high catalytic activity for methanol electrooxidation.

3.4. Performance of a single-cell DMFC using Pt–Ru/CNT anode electrocatalyst

The performances of the fabricated single-cell DMFC at various temperatures are illustrated in Fig. 6. It can be seen that

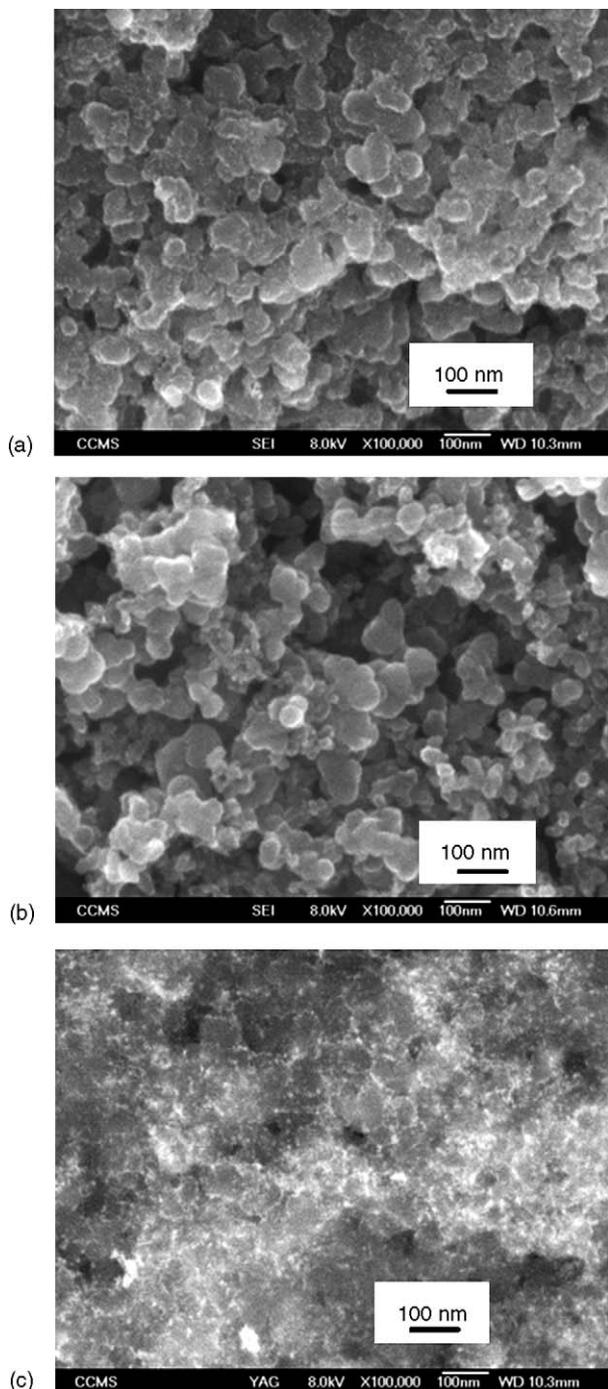


Fig. 4. SEM images of (a) the prepared anode using Pt–Ru/CNT, (b) a commercial anode with Pt–Ru/C coating obtained from E-TEK, and (c) backscattering electron image (BEI) of the prepared anode using Pt–Ru/CNT.

in general the cell exhibits excellent performance. In addition, Furthermore, Fig. 7 compares the performances of single-cell DMFCs at 60 °C using Pt–Ru/CNT electrocatalyst-based anode and a commercial Pt–Ru/C anode (E-TEK), respectively. The diagram illustrates the plots of I – V and I – P (power density) curves. Clearly, the fabricated cell using prepared Pt–Ru/CNT electrocatalyst significantly outperformed the comparison cell using commercial Pt–Ru/C anode. A maximum power density

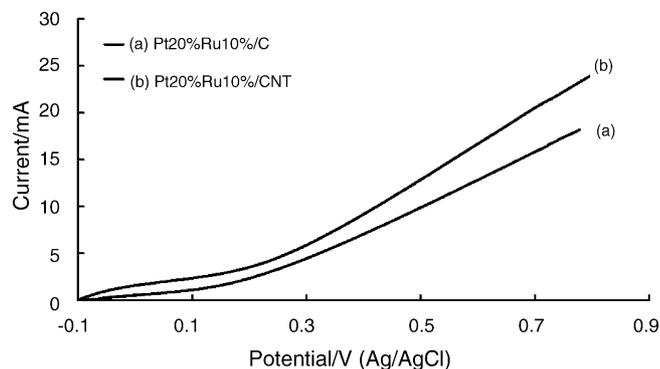


Fig. 5. Tests on electrocatalytic oxidation activity of (a) a commercial Pt–Ru/C, and (b) prepared Pt–Ru/CNT in 0.5 M H₂SO₄ + 1 M CH₃OH solution using an electrochemical test cell at room temperature and with a sweep rate of 10 mV s⁻¹.

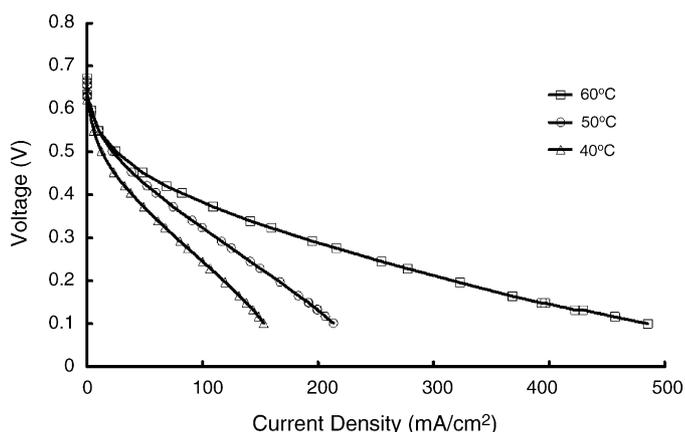


Fig. 6. Performances of the fabricated single-cell DMFC at various operating temperatures using Pt–Ru/CNT anode electrocatalysts coupled with a commercial Pt black cathode (E-TEK).

of 62 mW cm⁻² was obtained around 0.21 V with a current density of 300 mA cm⁻².

Conventionally, electrocatalyst with high percentage composition (e.g., total catalyst percentage >60 wt.%) are desirable for DMFC applications. Even with such a low weight percentage composition of prepared Pt–Ru/CNT, the tested DMFC using

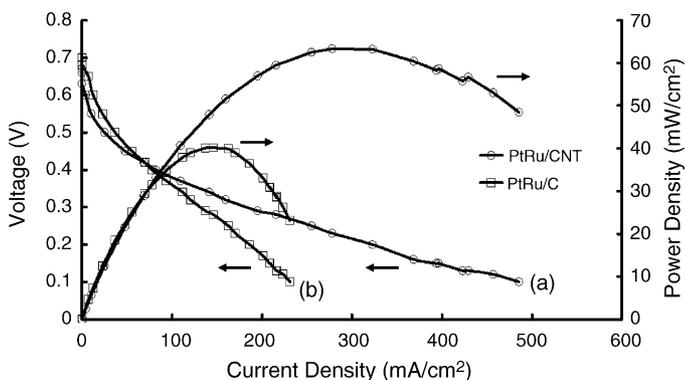


Fig. 7. Comparison of the performance of single-cell DMFC at 60 °C using (a) Pt–Ru/CNT electrocatalyst-based anode and (b) a commercial Pt–Ru/C anode (E-TEK) coupled with a commercial Pt black cathode.

prepared anode electrocatalyst still exhibited excellent performance comparable to any other reported results. Obviously, the distinctive characteristics of prepared Pt–Ru/CNT have reflected in the fabrication of anode and MEA giving rise to enhanced cell performance. Thus, the prepared Pt–Ru/CNT is indeed very suitable for uses in DMFCs as an advanced anode electrocatalyst. However, it has been demonstrated by Yano et al. [31] that carbon-supported Pt–Ru catalyst may not be a panacea for solving CO-poisoning problems. Most commercial Pt–Ru/C catalysts became useless with high concentrations (>50 ppm) of CO in the hydrogen fuel. This indicated that conventional Pt–Ru/C is also difficult to use with high concentrations of methanol fuel in DMFCs. It is anticipated that through the use of our new modified polyol approach, CNT-supported multi-component catalysts with greatly improved electrocatalytic activities for both methanol oxidation and oxygen reduction will be successfully developed. In the meantime, the catalyst loading of DMFC can be significantly reduced in the near future through the use of such high performance CNT-supported catalysts.

4. Conclusions

Carbon nanotube-supported Pt–Ru (Pt–Ru/CNT) with a desired electrocatalyst composition has been successfully prepared using a modified polyol method. Its application as a methanol oxidation electrocatalyst was demonstrated and the performance of a direct methanol fuel cell (DMFC) using the prepared Pt–Ru/CNT as an anode electrocatalyst was investigated. The prepared Pt–Ru/CNT electrocatalyst has a composition close to the intended 20 wt.%Pt–10 wt.%Ru (Pt:Ru = 1:1) and exhibited high electrocatalytic activity on methanol electrooxidation better than that of a commercial 20 wt.%Pt–10 wt.%Ru/C obtained from Johnson–Matthey. In addition, excellent single-cell DMFC performance was observed with both anode and cathode electrocatalyst loadings at 4 mg cm⁻². At 60 °C, a power density of >60 mW cm⁻² at about 0.21 V was obtained. The fabricated cells significantly outperformed a comparison cell using a commercial anode coated with Pt–Ru/C electrocatalyst (E-TEK) of the similar composition and loading. Overall, the prepared Pt–Ru/CNT is very suitable for uses in DMFCs as an anode electrocatalyst due to distinguished characteristics of CNT and the excellent electrocatalyst morphology with the right composition.

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