Characterization and performance evaluation of Pt–Ru/C–TiO$_2$ anode electrocatalyst for DMFC applications

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ARTICLE INFO

ABSTRACT

In this study, the effect of introduction of titania (TiO$_2$) material into Pt–Ru/C anode electrocatalyst on the performance of direct methanol fuel cells (DMFCs) was investigated. TiO$_2$ materials were first synthesized applying a sol–gel method and then incorporated directly into commercial Pt–Ru/C anode electrocatalyst with different TiO$_2$ weight ratios (5, 15, and 25 wt.%) to improve the performance of the DMFC. For comparison, the anode electrocatalysts with the same TiO$_2$ weight ratios were also prepared using commercial TiO$_2$ materials. The performance tests of the DMFCs based on these composite anode electrocatalysts were conducted and their performances were also compared to that of a DMFC based on a traditional anode electrocatalyst (Pt–Ru/C) under various operating conditions. In addition, 4 h short-term stability tests were conducted for all the manufactured DMFCs. The highest power densities were found as 705.12 W/m^2 and 709.32 W/m^2 at 80 °C and 1 M for the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts containing 5 wt.% of commercial and in-house TiO$_2$, respectively. The results of the short-term stability tests showed that introduction of 5 wt.% of commercial TiO$_2$ into commercial Pt–Ru/C anode electrocatalyst improved its stability characteristics significantly.

Introduction

Over the last years, fuel cells have been considered as one of the state-of-the-art alternative energy technologies primarily due to their high energy conversion efficiency and low emissions. Among the different fuel cell types, direct methanol fuel cells (DMFCs), which generate electricity by direct oxidation of methanol and reduction of oxygen, have started to come into prominence. DMFCs have started to be used in a large number of applications ranging from portable power to vehicle applications [1–3]. Despite the many advantages of

DMFCs (e.g., simplicity of handling and storage of liquid methanol, quick refuelling capability, and being able to operate without reformer [4–6]), there are still some constraints to be overcome, including high cost of platinum electrocatalyst, low durability and stability, relatively low electrical efficiency due to the sluggish reaction kinetics at the anode and cathode, methanol crossover problem, and poisoning of precious platinum electrocatalyst via carbon monoxide (CO) [7–10].

A various number of experimental and numerical studies, including re-designing the architecture of the Membrane Electrode Assembly (MEA) and its components and developing alternative materials and manufacturing techniques, have been carried out to mitigate the negative effects of the above-mentioned problems as well as to achieve an improved DMFC performance [11–14]. As one of the most important components of a DMFC, significant research efforts have focused on the synthesis of robust anode electrocatalyst with higher electrocatalytic activity so as to improve the methanol oxidation reaction (MOR) kinetics as well as to achieve an enhanced DMFC performance [15–17]. Conventionally, carbon supported or unsupported Pt–Ru has been used as the anode electrocatalyst for DMFCs instead of bare platinum since incorporation of second substrate (e.g., Ru) aids in removing the intermediates from the surface which thus hampers poisoning of precious metal [18]. Otherwise, the absorbed intermediates (e.g., CO) bring about a kinetic obstacle by transforming electrochemically active areas into inactive areas through occupying the available spaces. In other words, alloying Pt and Ru as an anode electrocatalyst promotes the oxidation of CO to carbon dioxide (CO_2) and mitigates the problem of Pt poisoning [19]. However, using this anode electrocatalyst still does not yield the desired performance, electrocatalytic activity, and durability goals, especially when the lifetime of DMFC is considered. To achieve improved MOR kinetics, Pt–Ru anode electrocatalyst has been modified by dispersing them on highly conductive nanoparticles with high surface area or by incorporating non-noble metals into the anode electrocatalyst [19–23].

Suitability of an anode electrocatalyst support is highly dependent on several performance-enhancing properties: an acceptable stability and durability in acidic porous media, a sufficient surface area for well-proportioned dispersion of fine particles of anode electrocatalyst, and a proper electrical conductivity [14]. However, the electrocatalytic activity of Pt–Ru anode electrocatalyst markedly depends on the structure, particle size, and Pt or Ru content in it. Many research studies have been conducted to optimize the Pt–Ru anode electrocatalyst towards previously-mentioned properties (e.g., [24,25]). These studies showed that either a high anode electrocatalyst loading (~2.0–8.0 mg cm^{-2}) or highly-pure methanol based diluted solution is required when Pt–Ru is used as the anode electrocatalyst. However, higher electrocatalyst loading or usage of highly-pure methanol based diluted solution results in relatively high material costs, creating constraints towards the widely-usage of DMFCs in the commercial market [26]. Seeing that reduction of the electrocatalyst loading from the present 2.0–8.0 mg cm^{-2} to <1.0 mg cm^{-2} without performance compromise and optimization of catalytic activity via appropriate supporting materials are matters of vital importance [18].

As previously emphasized, there have been significant research efforts on re-designing the architecture of the anode electrocatalyst to address Pt poisoning problem and to achieve a higher activity for the MOR by making further modifications. Another widely-accepted approach is to incorporate non-noble metals or metal oxides into the anode electrocatalyst to make it more capable of absorbing oxygenated species, to improve its CO tolerance, and ultimately to enhance the MOR [27]. The main aim for incorporating non-noble metals or metal oxides into anode electrocatalyst is to oxidize the intermediates thoroughly to CO_2 and to facilitate the breaking of carbon–carbon bonds in methanol [28]. Recent studies showed that several metal oxides, including IrO_2, V_2O_5, CeO_2, WO_3, MO_3, and TiO_2, have been extensively used as a support for Pt-based electrocatalysts to improve their catalytic activity for the MOR [26,29–34].

Among all the metal oxides, titania (TiO_2) is one of the most promising promoters due mainly to its ability to remain stable under acidic environments and reduce the adsorption energy of CO. Hence, when Pt–Ru/C anode electrocatalyst is supported on TiO_2, Pt becomes more effective in terms of activity for the same oxidation reactions and thus leads to a decrease in the adsorption energy of CO. With the existence of TiO_2, the reduction of Ti^{3+} takes place and thus brings about an increase in the electronic density on Pt. The bonds between the Pt and CO become weaker, leading to an increase in the mobility of CO groups on Pt [35]. In addition, during the MOR, TiO_2 facilitates the adsorption of hydroxide (OH) species, leading to an increase in the rate of conversion of the catalytically poisonous intermediates (e.g., CO) into CO_2. Several studies were conducted to investigate the performance of Pt–Ru/C–TiO_2 as anode electrocatalyst used to promote the MOR. The results of the conducted studies revealed that mixing TiO_2 materials with Pt–Ru/C could improve the electrocatalytic properties of Pt–Ru/C, especially for methanol electrooxidation. For instance, Wang et al. [36] prepared TiO_2– promoted Pt–Ru/C anode electrocatalysts adding TiO_2 nanoparticles directly to Pt–Ru/C and investigated electrocatalytic activity and stability properties of the anode electrocatalyst in the MOR through cyclic voltammetry. Their study results clearly demonstrated that the introduction of TiO_2 materials into Pt–Ru/C anode electrocatalyst provides an improved electrocatalytic performance during the MOR.

The literature survey discussed above indicates that introduction of TiO_2 materials into Pt–Ru/C anode electrocatalyst could be useful for achieving an improved DMFC performance. As was already discussed, although some studies have been conducted to investigate the electrochemical, catalytic, stability, and methanol tolerance characteristics of Pt–Ru/C–TiO_2 as a potential anode electrocatalyst, there is no work in the literature related to the performance comparison of DMFCs based on Pt–Ru/C–TiO_2 anode electrocatalyst containing commercial and in-house synthesized TiO_2. In this study, a simple preparation procedure of a composite anode electrocatalyst was carried out, and the performances of the DMFCs based on Pt–Ru/C–TiO_2 anode electrocatalysts were investigated. Towards this direction, TiO_2 nanoparticles were synthesized by a sol–gel method and Pt–Ru/C–TiO_2 anode electrocatalysts containing 5, 15, and 25 wt.% of in-house synthesized TiO_2 with respect to

the amount of commercial Pt—Ru/C anode electrocatalyst were prepared. Then, Pt—Ru/C—TiO$_2$ anode electrocatalysts with the same weight ratios were also prepared using commercial TiO$_2$ materials. The DMFCs based on these anode electrocatalysts were manufactured and a series of experiments were conducted to evaluate the performances of the DMFCs under various operating temperatures (45 °C, 60 °C, and 80 °C) and methanol concentrations (0.5 M, 0.75 M, 1 M, and 1.5 M). In addition, 4 h short-term stability tests were carried out for all the DMFCs to assess their short-term stability characteristics.

Experimental

Materials

The commercially available Nafion® 115 membrane was obtained from DuPont Corp. (Delaware, USA). The cathode electrocatalyst (Platinum, nominally 60% on high surface area advanced carbon support, HiSPEC® 9100) and the anode electrocatalyst (Platinum, nominally 50%, Ruthenium nominally 25% on high surface area advanced carbon support, HiSPEC® 12100) were purchased from Alfa Aesar® (Karlsruhe, Germany). The PTFE treated carbon cloth (ELAT LT1400W) was used as the anode backing layer and obtained from Nuvant Systems Inc. (Crown Point, IN, USA) and used as received. Hydrogen peroxide (Emsure®, chemical purity 30 wt.%) and sulphuric acid (Emsure®, chemical purity 95—97 wt.%) were purchased from Merck (Darmstadt, Germany) and used without further purification. 15 wt.% Nafion solution (equivalent weight = 1100 g mol^{-1} SO$_3$H) was obtained from Ion Power Inc. (Delaware, USA). All chemicals, including isopropyl alcohol (Aldrich) and methanol (Aldrich), were reagent grade and used without further purification. The commercially available TiO$_2$ (P25) nanoparticles were obtained from Degussa-Huls (Frankfurt-Main, Germany). For the sol—gel synthesis, TiO$_2$, tetrabutyl-orthotitanate (TBOT) (99% purity, from Aldrich Inc.), nitric acid (65% purity, from Aldrich Inc.), and ethanol (99% purity, from Aldrich Inc.) were used without further purification.

Preparation of in-house TiO$_2$ nanoparticles

In this study, a sol—gel method given in Ref. [37] was modified to synthesize TiO$_2$ material having small crystallite sizes. The molar ratio of [HNO$_3$]/[Ti] = 0.087, [H$_2$O]/[Ti] = 4, and [Ethanol]/[Ti] = 27 were used in the preparation. First, the required amount of TBOT and ethanol were mixed at room temperature and then water mixed with HNO$_3$ was added to this ethanol-TBOT mixture. After adding the water-acid mixture, hard transparent TiO$_2$ gel was obtained in 5 min. The gel was heated from room temperature to 400 °C at 10 °C/min and calcined at 400 °C for 6 h. Finally, calcined TiO$_2$ gel was ground and sieved to less than 200 μm to use in the preparation of anode electrocatalyst composites.

Membrane activation and MEA manufacturing process

In order to clean and activate the membranes, the Nafion® 115 membranes (10 cm × 10 cm) were boiled for 1 h at 90 °C in each of the following solutions consecutively; 3 wt.% hydrogen peroxide (H$_2$O$_2$), deionized (DI) water, 5 wt.% sulphuric acid (H$_2$SO$_4$), and deionized (DI) water. After the membranes were cleaned and activated, the following steps were carried out in the MEA manufacturing process. As the first step, the electrocatalyst inks were prepared for both the anode and cathode sides. The electrocatalyst loadings at the anode and cathode sides were taken as 4 mg$_{PtRu}$/cm^2 and 2 mg$_{Pt}$/cm^2, respectively. Appropriate amounts of deionized water, Nafion® solution, and isopropyl alcohol were added to the electrocatalyst powder to form the ink. Then, the ink was first mixed by magnetic stirrer for 45 min and then ultrasonic bath for 2 h to make the ink more homogeneous. These steps were applied in the preparation of both the cathode and anode electrocatalysts. After the electrocatalyst ink preparation process, electrocatalyst coating process was applied as the second step in the MEA manufacturing process. In this step, the prepared electrocatalyst inks were put into the container of the air spray and then the backing layers with an area of 25 cm^2 were coated by air-spraying technique. During the electrocatalyst coating process, backing layers (carbon cloth for the anode side and the carbon paper for the cathode side) were placed to the vacuum table at 55 °C. As the last step, the hot-press process was carried out. In this process, the membrane was placed between the coated cathode and anode backing layers and pressed at 120 °C and 6.89 MPa for 4 min [38,39].

Performance testing

The performance tests of the fabricated DMFCs were conducted using the methodology discussed in this section. Firstly, two gaskets with the thickness of 0.1 mm were placed on the cathode and anode flow field plates. The MEA was placed between these gaskets and the assembled cell was tightened. The torque applied for tightening the cell was increased gradually until the compression ratio of the MEA reached to the range of 20 ± 5% [40]. Keeping the compression ratio in this range is crucial for preventing the possible leakage during the operation of the cell and obtaining higher performance values. This ratio was found by dividing the difference between the non-compressed and compressed MEA thicknesses to the non-compressed thickness of a given MEA as discussed in our previous study [41].

After the single cell was assembled as discussed above, the pretreatment procedure was carried out to make the MEA fully-hydrated. In this regard, deionized water and humidified oxygen with very high volumetric flow rates (5 ml/min for the flow rate of deionized water and 1000 ml/min for the flow rate of oxygen) were passed through the anode and cathode flow channels of the single cell, respectively. The operation conditions, such as cell temperature and cathode inlet pressure, were chosen as 80 °C and 1.35 bar absolute, respectively. This pretreatment period took almost 28 h for each MEA.

After the pretreatment procedure was completed, a performance testing procedure was followed to generate the polarization curve. In-house tests were performed using a custom-built computer aided DMFC test station. During the tests, oxygen gas was passed through a mass flow controller and a humidifier just before entering the cathode side of the fuel cell. At this stage, the line that humidified oxygen passes

is heated to keep the temperature of the cell more uniform. On the other hand, methanol solution passes through a magnetic drive gear pump before entering the anode side of the cell. The line that methanol solution passes is also heated. More detailed information about this test station and its components can be found in Ref. [41]. During the experiments, the flow rates of the methanol solution and oxygen were set to 1.94 ml/min and 400 ml/min, respectively. The outlet pressure of the oxygen tank and the cathode inlet pressure were set to 1.5 and 1.35 bar absolute, respectively. The methanol concentration was varied from 0.5 M to 1.5 M. The operating temperature of the cell was altered from 45 °C to 80 °C. The voltage was changed between open circuit voltage (OCV) and 0.2 V and the corresponding current values at the steady state conditions were recorded. This procedure was repeated until the difference between the two consecutive polarization curves became negligible.

Results and discussion

Physical characterization of electrocatalysts

Wide-angle X-Ray Diffraction (XRD) (Philips X'pert Pro XRD, operated at 40 kV and 45 mA) was used to determine the crystalline phases present in the anode composite, sol—gel made TiO_2 and commercial TiO_2 (P25) and also average crystallite sizes were calculated from the peak broadening of the highest intensity diffraction peaks using Scherrer equation. As seen from Fig. 1(a) and (b), the diffraction peaks observed at ~25.3° of 2Θ corresponds to carbon (002) crystalline plane and also to (101) crystalline plane of anatase TiO_2. Unfortunately, it is difficult to distinguish TiO_2 from carbon since the amount of carbon is much larger than TiO_2; thus, not being possible to observe the other diffraction peaks of TiO_2 at higher 2Θ. However, as seen in Fig. 1(c) and (d), XRD patterns of sol—gel made TiO_2 and commercial TiO_2 (P25) show that the sol—gel made TiO_2 consists of solely anatase crystalline phase of TiO_2, whereas commercial TiO_2 (P25) is a mixture of anatase and rutile crystalline phases. The locations of the diffraction peaks are found using Powder Diffraction File of International Centre for Diffraction Data [42]. The average crystallite size for the anatase phase in sol—gel made TiO_2 calculated using Scherrer equation is 11.98 nm (±1 nm), while the average crystallite sizes for anatase and rutile phases in the commercial TiO_2 are 19.51 nm (±1 nm) and 33.89 nm (±1 nm), respectively. Sol—gel made TiO_2 has smaller crystallite size than commercial TiO_2. Besides, the 2Θ peaks observed at ~40, 47 and 68° 2Θ as seen in Fig. 1(a) and (b) are due to the presence of metallic Pt, whereas no diffraction peaks corresponding to metallic Ru is observed; thus, the crystallite size of Ru is less than 5 nm. In fact, it is known that the crystallite sizes less than 3—5 nm cannot be observed with wide-angle X-Ray Diffraction (XRD) [43]. Our XRD results for PtRu/C are in parallel with the literature [44,45]. Moreover, it was found that the addition of TiO_2 made with modified sol—gel method did not change the crystalline phases of PtRu/C anode electrocatalyst.

The element mapping obtained using Energy Dispersive X-Ray (EDX) seen in Fig. 2(a) and (b) shows that Ti, Ru, Pt, and O elements are fairly well dispersed on the anode which are in parallel with the XRD results seen in Fig. 1(a—d).

Performance testing of the DMFCs

As discussed in Section Membrane activation and MEA manufacturing process, the MEAs with 25 cm^2 active areas were manufactured using air-spraying technique to investigate the effect of introduction of TiO_2 nanoparticles directly to commercial Pt—Ru/C anode electrocatalyst and to compare the performances of DMFCs based on Pt—Ru/C—TiO_2 and Pt—Ru/C anode electrocatalysts. In this section, the effects of operating temperature, methanol concentration, the weight ratio of TiO_2 on the performance of the manufactured DMFCs are discussed. In addition, the results of the short-term stability tests of these DMFCs are presented.

Effect of operating temperature

Operating temperature is one of the main parameters that has an influence on both the electrode activation [46,47] and methanol crossover [48]. Basically, increasing operating temperature leads to following effects: an improvement in the reaction rate of electro-oxidation of methanol at the anode, an increase in the rate of undesired methanol crossover from the anode to cathode mainly due to swelling of the membrane, a deterioration in the dimensional stability of the membrane, and finally an improvement in the rate of oxygen reduction reaction (ORR) at the cathode [49,50]. The simultaneous effects of the above-mentioned phenomena generally bring an increase in the overall performance of the DMFCs made of conventional materials up to 80 °C. Taking the operating temperature higher than 80 °C is known to cause membrane dehydration [51], a higher rate of methanol crossover [52], and catalyst degradation [53]. As the introduction of TiO_2 to the anode electrocatalyst may cause a different combined effect, a series of experiments were carried out at the operating temperatures of 45 °C, 60 °C, and 80 °C, the constant methanol concentration of 1 M, the methanol flow rate of 1.94 ml/min, and the oxygen flow rate of 400 ml/min.

The power and polarization curves obtained from the experiments conducted with the DMFCs based on Pt—Ru/C—TiO_2 (in-house synthesized and commercial) and Pt—Ru/C anode electrocatalysts are presented in Fig. 3(a—d). Fig. 3(a—c) exhibit the effect of operating temperature on the performance of the DMFCs based on Pt—Ru/C—TiO_2 anode electrocatalysts containing 5, 15, and 25 wt.% of TiO_2, whereas Fig. 3(d) exhibits the performance of the DMFC based on Pt—Ru/C anode electrocatalyst. These figures elucidate that with an increase in the operating temperature in the range of 45 °C and 80 °C, the performance of the DMFCs containing Pt—Ru/C—TiO_2 anode electrocatalysts improves in a similar manner with the DMFC containing conventional Pt—Ru/C anode electrocatalyst. It was also seen that the DMFCs based on Pt—Ru/C—TiO_2 anode electrocatalysts containing 15 and 25 wt.% of both in-house and commercial TiO_2 yield better performance in comparison to the TiO_2-free DMFC at any given temperature. As the temperature increases from 45 °C to 80 °C, the peak power densities for the DMFC without TiO_2 and with 5, 15, and 25 wt.% of in-house TiO_2, increase from 317.16 W/m^2 to
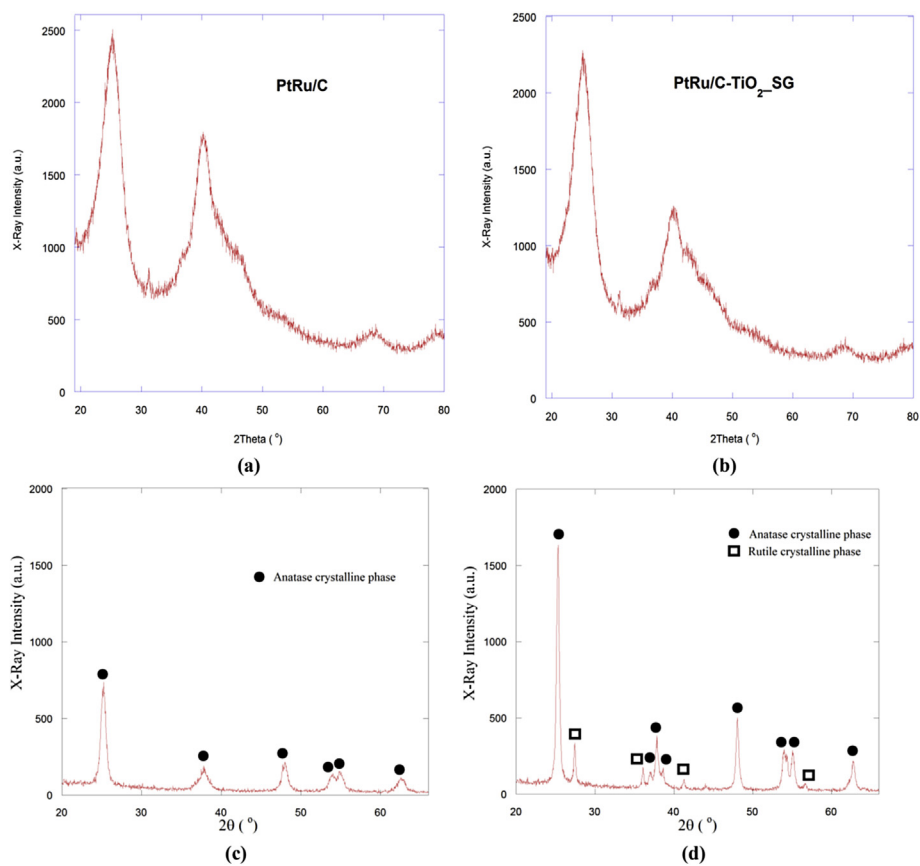
Fig. 1 − XRD diffraction patterns for (a) PtRu/C anode, (b) PtRu/C sol−gel made TiO₂ anode composite, (c) sol−gel made TiO₂, and (d) commercial TiO₂ (P25).
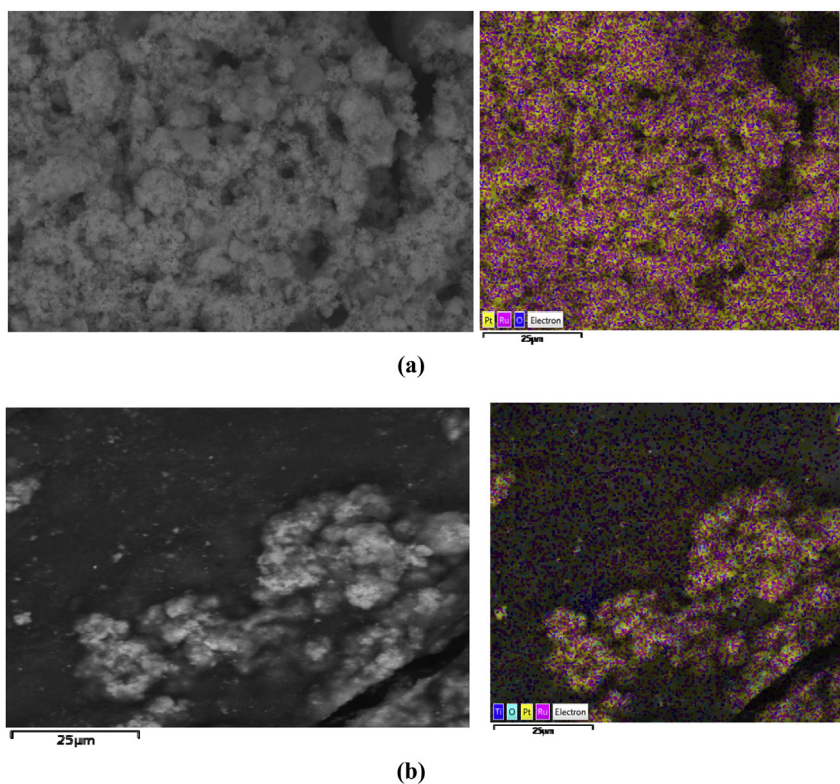

Fig. 2 − EDX element analyses for (a) PtRu/C anode and (b) PtRu/C sol−gel made TiO₂ anode composite.
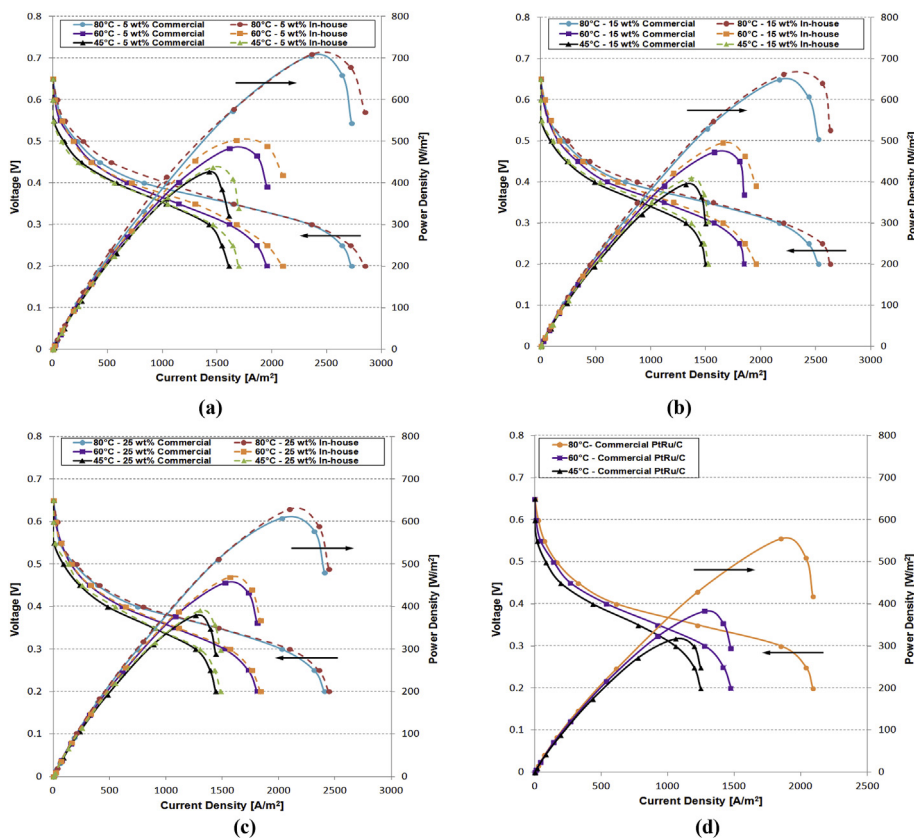
Fig. 3 — Power and polarization curves at 45 °C, 60 °C, and 80 °C and 1 M methanol concentration for the DMFCs based on Pt—Ru/C—TiO$_2$ anode electrocatalyst (a) with 5 wt.% of commercial and in-house TiO$_2$, (b) with 15 wt.% of commercial and in-house TiO$_2$, (c) with 25 wt.% of commercial and in-house TiO$_2$, and (d) without TiO$_2$.

554.64 W/m^2, 437.52 W/m^2 to 709.32 W/m^2, 409.44 W/m^2 to 662.16 W/m^2, 390.48 W/m^2 to 628.68 W/m^2, respectively. At 80 °C, it was found that the maximum power densities of the DMFCs based on Pt—Ru/C—TiO$_2$ anode electrocatalyst containing 5 wt.% of commercial and in-house TiO$_2$ are 27.1% and 27.9% higher than that of the DMFC based on commercial Pt—Ru/C anode electrocatalyst. The better performance gained by the addition of TiO$_2$ to the anode electrocatalyst could be explained as follows [54]. The robust electronic interactions between the introduced TiO$_2$ nanoparticles and Pt—Ru/C may deteriorate adsorption ability of the intermediates and thus facilitates the conversion of the intermediates into CO. In addition, TiO$_2$ nanoparticles play a significant role in the enhancement of the electrocatalytic properties of the Pt—Ru/C anode electrocatalyst by increasing the interface and utilizing Pt. TiO$_2$ nanoparticles could also be beneficial in increasing the rate of water displacement process, which is basically intermediary process in the MOR. Ordinarily, this intermediary process is conducted by Ru in conventional DMFCs based on commercial Pt—Ru/C anode electrocatalyst. Therefore, the main contribution of TiO$_2$ nanoparticles to the DMFC performance could also be related to this acceleration in the water discharging.

Effect of methanol concentration
The methanol concentration is another key parameter that possesses a significant effect on the performances of DMFCs

[4]. Thus, in order to investigate the effect of methanol concentration on the performance of the DMFC containing Pt—Ru/C—TiO$_2$ anode electrocatalyst, the experiments were carried out at the methanol concentrations of 0.5 M, 0.75 M, 1 M, and 1.5 M, the operating temperature of 80 °C, the methanol flow rate of 1.94 ml/min, and the oxygen flow rate of 400 ml/min. The results of the performed experiments demonstrated that as the methanol concentration was increased from 0.5 M to 1 M, the peak power densities also increased, whereas the peak power densities decreased at the methanol concentrations more than 1 M for all the DMFCs based on both Pt—Ru/C—TiO$_2$ and commercial Pt—Ru/C anode electrocatalysts (Fig. 4(a—d)). When the DMFCs were fed with 1 M methanol solution, the maximum power densities were achieved as 705.12 W/m^2, 649.44 W/m^2, 608.16 W/m^2, 709.32 W/m^2, 662.16 W/m^2, and 628.68 W/m^2 for the DMFCs based on Pt—Ru/C—TiO$_2$ anode electrocatalysts with 5, 15, and 25 wt.% of commercial and in-house TiO$_2$, respectively. For the DMFC based on commercial Pt—Ru/C anode electrocatalyst, the value of the maximum power density was found as 554.64 W/m^2 when the DMFC was operated at 1 M solution. For all studied methanol concentrations (0.5 M, 0.75 M, 1 M, and 1.5 M), the maximum power densities were provided by the DMFC based on Pt—Ru/C—TiO$_2$ anode electrocatalyst with 5 wt.% of in-house TiO$_2$, whereas the lowest power densities were achieved for the DMFC based on Pt—Ru/C anode electrocatalyst.
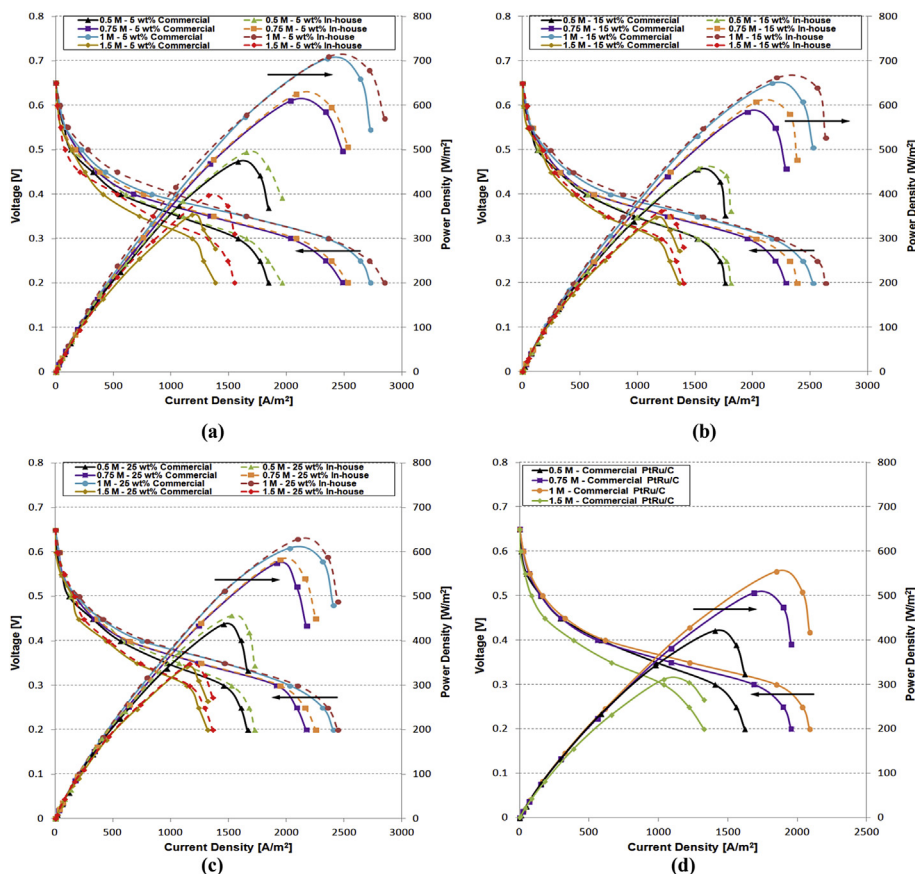
Fig. 4 − Power and polarization curves at 0.5 M, 0.75 M, 1 M, and 1.5 M and 80 °C for the DMFCs based on Pt−Ru/C−TiO$_2$ anode electrocatalyst (a) with 5 wt.% of commercial and in-house TiO$_2$, (b) with 15 wt.% of commercial and in-house TiO$_2$, (c) with 25 wt.% of commercial and in-house TiO$_2$, and (d) without TiO$_2$.

The results of the above-mentioned experiments can be explained by the fact that the concentration of the methanol supplied to the DMFC has a remarkable impact on both the mass transport rate of the methanol from flow channels to the electrocatalyst coated surface of the backing layer and the rate of methanol crossover from the anode to cathode. When methanol is supplied at low concentrations, such as 0.5 M, the limiting current density becomes low and thus results in a poor DMFC performance [52]. As the methanol concentration increases, the negative effects of methanol crossover phenomenon become more prominent. As can be seen from Fig. 4(a−d), as the methanol concentration was increased, the voltage at especially low current densities started to decrease due to adverse effects of the previously-mentioned methanol crossover phenomenon. In addition, the permeated methanol initiates an exothermic reaction with oxygen [55], resulting in an increase in the consumption rate of oxygen within the Pt/C cathode electrocatalyst. The escalating rate of the generated water also increases the mass transfer resistance within the cathode electrocatalyst. As a result, the ratio of the usable oxygen at the cathode decreases, leading to a significant increase in the cathode activation and concentration polarizations. Therefore, there should be an optimal methanol concentration that yields the best performance, which corresponds to ~1 M at 80 °C for each DMFC manufactured in this study.

Effect of weight ratio of TiO$_2$

The results of the conducted experiments for investigating the effect of operating temperature indicated that the highest power density was achieved as 709.32 W/m^2 at 80 °C and 1 M methanol concentration and provided by the DMFC based on Pt−Ru/C−TiO$_2$ anode electrocatalyst containing of 5 wt.% of in-house TiO$_2$. This performance is about 27.9% higher than that of the DMFC based on commercial Pt−Ru/C anode electrocatalyst. This could be explained by the fact that the introduction of TiO$_2$ nanoparticles into Pt−Ru/C anode electrocatalyst enhances the MOR activity by facilitating the conversion of CO into CO$_2$. Introduced TiO$_2$ nanoparticles provide additional OH species and these OH species facilitate the conversion of CO derivative intermediates into CO$_2$ [56].

On the other hand, it should be emphasized that the performances of the DMFCs based on Pt−Ru/C−TiO$_2$ anode electrocatalysts containing commercial or in-house TiO$_2$ deteriorate as the weight ratio of TiO$_2$ is increased from 5 wt.% to 25 wt.%. More specifically, as the TiO$_2$ weight ratio was increased from 5 wt.% to 15 wt.%, the peak power densities at 80 °C and 1 M as presented in Fig. 5(a) and (b) decreased from 705.12 W/m^2 to 649.44 W/m^2, 709.32 W/m^2 to 662.16 W/m^2 for the DMFCs based on on Pt−Ru/C−TiO$_2$ anode electrocatalysts containing of commercial and in-house TiO$_2$, respectively. Furthermore, as the TiO$_2$ weight ratio was increased from 15 wt.% to 25 wt.%, the performance deterioration trend
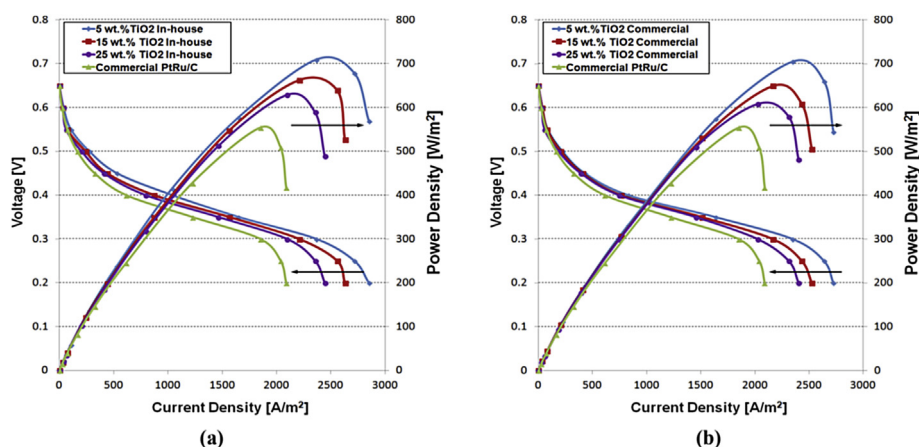
Fig. 5 — **Power and polarization curves for the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalyst (a) with 0, 5, 15, and 25 wt.% of in-house synthesized TiO$_2$ and (b) with 0, 5, 15, and 25 wt.% of commercial TiO$_2$ at 80 °C and 1 M.**

continued. The decrease in the performances could be associated with the fact that excessive amount of TiO$_2$ may prevent the transportation of the electrons to the Pt–Ru anode electrocatalyst by creating an additional barrier between the electrons and Pt–Ru. As previously mentioned, the additional OH species, which are originated from the presence of TiO$_2$, may also obstruct the adsorption of CH$_3$OH by occupying the active areas [36].

Stability tests
The stability characteristic demonstrates a DMFC's ability to provide constant power or current density at a fixed voltage during continuing operation [57]; therefore, it possesses a considerable importance as a criterion in the performance evaluation of DMFCs. It is desired that a DMFC provides a constant power density value at a given voltage for a certain period of time during its operation. Therefore, the short-term stability tests were conducted to evaluate the stability performances of all the DMFCs manufactured.

In the stability tests, the operating temperature and cathode inlet pressure were kept at 80 °C and 1.35 bar absolute, respectively. The flow rates of the 1 M methanol solution and oxygen were set to 1.94 ml/min and 400 ml/min, respectively. In order to record the power density values, the voltage was set to 0.3 V and kept at this value for 4 h. As can be seen from Fig. 6, the stability characteristics of all the DMFCs were determined using the recorded power density values. Apparently, the majority of the power density loss occurred in the first 20 min of the stability tests. This drop in the power density could be both related to instabilities, such as insufficient diffusion of methanol to the anode reaction area and oxygen to the cathode reaction area [58]. Therefore, the power density values after the first 20 min were considered in the determination of stability characteristics of the DMFCs.

On the one hand, as seen from Fig. 6, a slow decline in the power density during the short-term stability tests, and this decrease in the power density could be related to decrease in the rate of MOR due mainly to the platinum electrocatalyst poisoning, increasing rate of methanol crossover because of the swelling of the membrane, decrease in the ORR because of the crossed-over methanol at the cathode, and increasing

amount of water at the cathode. In addition, during the tests sudden power density drops and increases were observed. These fluctuations in the power densities could be related to heterogeneity of the methanol concentration and unforeseen events during the short-term stability tests. Here it is also worthwhile to note that similar to proton exchange membrane fuel cells (PEMFCs), DMFCs suffer from the negative effect of so-called water flooding phenomenon that occurs at the cathode. Hence, the time-dependent power density fluctuations could also be attributed to the water flooding phenomenon. That is, possible adequacies in the water removal process could block the oxygen flow paths temporarily, leading to an instantaneous drop in the power density. However, as can be seen from Fig. 6, the fluctuations especially in the power density value of the DMFC based on Pt–Ru/C–TiO$_2$ anode electrocatalyst containing 5 wt.% of commercial TiO$_2$ were much lesser than those of other DMFCs. This can be an indicator for the improved stability of the DMFC based on Pt–Ru/C–TiO$_2$ anode electrocatalyst with the 5 wt.% of commercial TiO$_2$. The improved stability characteristic of this DMFC is explained by the enhanced electrocatalytic properties of Pt–Ru/C–TiO$_2$ anode electrocatalyst and utilizing of Pt.

Furthermore, after 3 h operation at previously-mentioned operating conditions, the recorded power densities started to decrease; however, the decline in the power density of the DMFC based on Pt–Ru/C–TiO$_2$ electrocatalyst containing 5 wt.% of commercial TiO$_2$ was almost negligible. This can be associated with the improved electrocatalytic properties of Pt–Ru/C–TiO$_2$ anode electrocatalyst containing 5 wt.% of commercial TiO$_2$; hence, TiO$_2$ nanoparticles facilitates the conversion of CO into CO$_2$. As previously mentioned in Section Effect of weight ratio of TiO$_2$, this facilitation in the conversion of CO into CO$_2$ mitigates the electrocatalyst poisoning phenomenon and improves the stability of the anode electrocatalyst towards the MOR [36]. The stability characteristics of the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts with relatively higher TiO$_2$ weight ratios (15 and 25 wt.%) are consistent with their performances. These relatively worse stability characteristics of the DMFCs based on Pt–Ru/C–TiO$_2$ with 15 and 25 wt.% of TiO$_2$ may be related to occupied active sites because of the excessive amount of TiO$_2$. Namely,
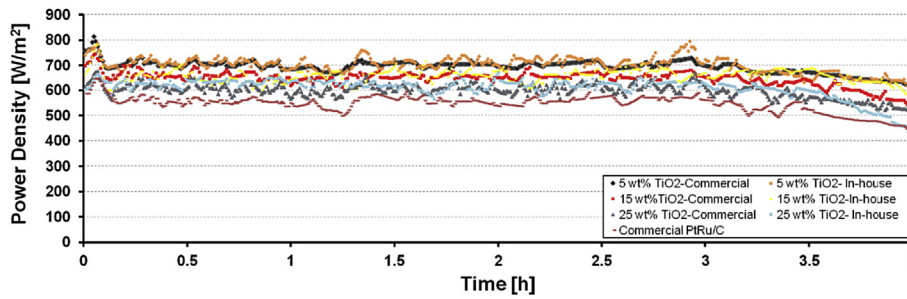
Fig. 6 – Short-term stability tests of the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts with 0, 5, 15, 25 wt.% of commercial and in-house TiO$_2$ at the cell voltage of 0.3 V, the operating temperature of 80 °C, and the methanol concentration of 1 M.
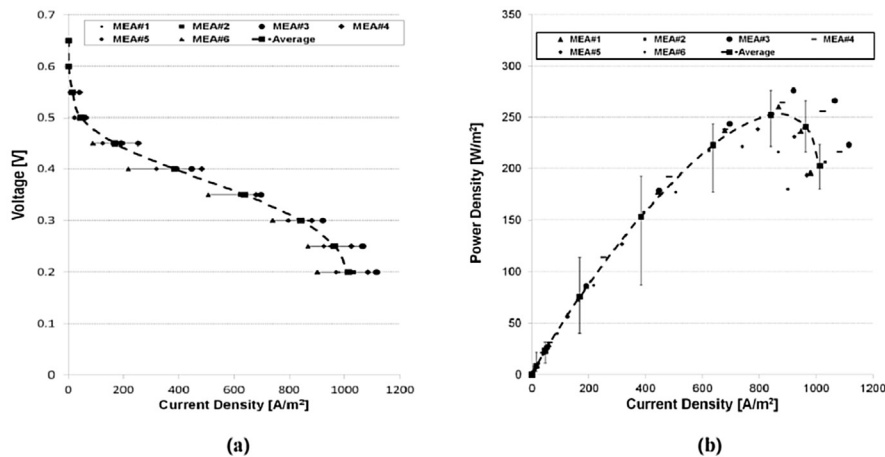

Fig. 7 – (a) Polarization curves generated from six different DMFCs based on commercial Pt–Ru/C anode electrocatalyst at 80 °C and methanol concentrations of 1 M and (b) Power curves obtained from six different DMFCs based on commercial Pt–Ru/C anode electrocatalyst at 80 °C and 1 M.

excessive amount of TiO$_2$ might also obstruct the adsorption of CH$_3$OH, leading to a significant drop in the power density.

Repeatability tests

In the experimental studies, it is not always possible to achieve the same results or values when the experiments are repeated in the same conditions due to the error in measurement and precision in the manufacturing and instrumentation. In order to assess the repeatability of the experimental studies, six DMFCs with 2 mg$_{PtRu}$/cm^2 anode and 1 mg$_{Pt}$/cm^2 cathode electrocatalyst loadings were fabricated applying the same manufacturing process discussed in Section Membrane activation and MEA manufacturing process. The performances of these DMFCs were investigated at the operating temperature of 80 °C, the methanol concentration of 1 M, the methanol flow rate of 1.94 ml/min, and the oxygen flow rate of 400 ml/min. The results of these conducted experiments for six different DMFCs are presented in Fig. 7. In order to calculate the deviation from the average peak power density value, firstly, the average peak power densities of these DMFCs were calculated. Then, the differences between the lowest peak power density and average peak power density and the highest peak power density and average peak power density were calculated. All these calculations revealed that the error in the value

of the peak power density for the conducted experiments is estimated to be +10.94% and −12.34%.

Conclusions

In this study, the performances of the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts containing of 5, 15, and 25 wt.% of either in-house synthesized or commercial TiO$_2$ were investigated experimentally. The performances of these DMFCs were also compared to that of the DMFC based on commercial Pt–Ru/C anode electrocatalyst. In this regard, the performance tests were conducted at different temperatures (45 °C, 60 °C, and 80 °C) and 1 M methanol concentration to assess how the temperature affects the performance of these DMFCs. Then, the effect of different methanol concentrations (0.5 M, 0.75 M, 1 M, and 1.5 M) on the performances of these DMFCs were investigated keeping the operating temperature constant at 80 °C. The main conclusions derived from the experiments are listed as follows.

- As the operating temperature is increased from 45 °C to 80 °C, the performances of all the DMFCs based on both Pt–Ru/C–TiO$_2$ and commercial Pt–Ru/C anode electrocatalysts improve significantly.

- For all the studied methanol concentrations (0.5 M, 0.75 M, 1 M, and 1.5 M), all the DMFCs based on Pt–Ru/C–TiO$_2$ and commercial Pt–Ru/C anode electrocatalysts provide their maximum power densities at 1 M methanol concentration.
- The DMFC based on Pt–Ru/C–TiO$_2$ anode electrocatalyst containing of 5 wt.% of commercial TiO$_2$ provided the best performance with the power density value of 705.12 W/m^2 at 80 °C and 1 M methanol concentration among all the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts containing of commercial TiO$_2$.
- Of all the DMFCs based on Pt–Ru/C–TiO$_2$ anode electro-catalysts containing in-house synthesized TiO$_2$, the maximum power density was found as 709.32 W/m^2 at 80 °C and 1 M methanol concentration and provided by the DMFC based on Pt–Ru/C–TiO$_2$ anode electrocatalyst containing of 5 wt.% of in-house synthesized TiO$_2$.
- The DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts containing 5 wt.% of commercial TiO$_2$ and in-house synthesized TiO$_2$ yielded 27.1% and 27.9% more power density in comparison to the DMFC based on commercial Pt–Ru/C anode electrocatalyst.
- The DMFC based on Pt–Ru/C–TiO$_2$ anode electrocatalyst containing of 5 wt.% of commercial TiO$_2$ has more prom-ising characteristic with regard to stability as compared to all other DMFCs tested in this study.

The results of this study indicated that the DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts containing 5 wt.% of in-house synthesized TiO$_2$ or commercial TiO$_2$ provide distin-guishably better performance as compared to the DMFC based on commercial Pt–Ru/C anode electrocatalyst. Pt–Ru/C–TiO$_2$ anode electrocatalysts seem to be very promising in terms of achieving an improved performance and better stability for DMFC applications. As a future study, it is intended to make a long-term stability tests for DMFCs based on Pt–Ru/C–TiO$_2$ anode electrocatalysts.

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