

Nanostructured PtRu alloys as electrocatalyst for direct methanol fuel cells applications

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Carbon supported PtRu alloys (atomic ratio 1:1) as nano-electrocatalysts were prepared by chemical impregnation reduction method by using H_2PtCl_6 and $RuCl_3$ as metal precursors and $NaBH_4$ as reducing agent at room temperature. The prepared nanoparticles were characterized by X-Ray Diffraction (XRD), Energy-Dispersive X-Ray Analysis (EDAX) and Field Emission Scanning Electron Microscope (FESEM). The results showed that the PtRu nanoparticles are present in Face-Centered Cubic structure (fcc) with high degree of alloying. The nanoparticles were highly dispersed on the carbon support. The electrochemical performance of the prepared nanocatalysts towards methanol electro-oxidation was evaluated using electrochemical half cell measurements. The results showed that, the prepared nanocatalysts exhibited higher electrocatalytic activity in terms of onset potential and current density in comparison with the commercial PtRu/C catalysts (E-TEK). These results suggest that the prepared nanocatalyst have a potential as promising electrocatalyst for methanol electro-oxidation in direct methanol fuel cells applications.

في هذا البحث تم تحضير سبائك نانوية من (البلاتين - الروثينيوم) على سطح من حبيبات الكربون بطريقة تخفيض الإشباع الكيميائية باستخدام حمض الهيدروكلوريك وروثينيوم سداسي و ثالث كلوريد الروثينيوم كمواد أولية للتفاعل و استخدام (هيدروبورو الصوديوم) $NaBH_4$ كمعامل اختزال عند درجة حرارة الغرفة. تستخدم تلك السبائك كمحفزات كهربية لخلايا الوقود. وتم تحليل العناصر باستخدام الأشعة السينية ذات الطاقة (EDAX) والميكروسكوب الإلكتروني الماسح ذو المجال المشع (FESEM) والميكروسكوب الإلكتروني الماسح (SEM) لتحديد مورفولوجيا السطح و قياس التركيب البلوري باستخدام حيود الأشعة السينية (XRD). ومن النتائج التي تم استخلاصها ان التركيب البلوري من النوع المكعبي ممرکز الوجه و ذو درجة عالية من السبك (Alloying) و ان هذه الحبيبات النانوية تنتشت بشكل عالي على سطح حبيبات الكربون الحاملة لها. تم فحص معدل الاداء الكهروكيميائي للحبيبات النانوية و مقارنتها باحد المنتجات للمحفزات الموجودة في الأسواق E-TEK حيث تظهر معدل أداء عالي مما يعطى انطباعا بقدرتها على الاستخدام كمحفزات لخلايا الوقود ذات الأكسدة المباشرة للميثانول.

Keywords: Fuel cells, Nanocatalysts, PtRu alloys, direct methanol fuel cells

1. Introduction

Direct Methanol Fuel cells (DMFCs) have attracted more attention in the last decades as power sources for portables electronic devices (laptop, cell phone), electric vehicle and for transportation applications due to the simplicity of the system, high electronic density of methanol as fuel at lower operation temperature, and ease of handling of methanol liquid fuel [1-3]. The commercialization of DMFCs is hindered by some challenges such as the poor kinetics of methanol oxidation at the anode catalysts and methanol crossover from anode side to cathode side through the proton exchange membranes [4-6].

Pt is well known as active electrocatalyst for methanol oxidation but poisoning of its surface by CO, formed as intermediate in the dehydrogenation of methanol, inhibiting the oxidation reaction. In this regard, many research work was devoted to enhance the catalytic activity of Pt catalyst through the alloying of Pt with other elements such as Ru, Sn and Mo [7-11]. The role of the second metal is discussed by bifunctional mechanism according to which the CO formed on Pt surface can be oxidized into CO_2 by action of surface oxygenated groups formed on the second metals. The second metal may also modify the electronic structure of Pt, which leads to weakening of Pt-CO bond and therefore enhancing the catalytic activity of the Pt alloys [12-14].

Carbon supported PtRu alloy nanoparticles with nominal atomic ratio (Pt:Ru, 1:1) are still considered to be the best anode catalyst for methanol electrooxidation due to their tolerance toward CO, and they are widely used in DMFCs [15, 16].

Many methods have been developed to prepare supported PtRu nanoparticles [17-19], among these methods is the impregnation reduction method in which the metal precursors impregnated with the support in a solvent followed by reduction with reducing agent. This method has been advantageous that it is a simple method, low cost, suitable for large-scale production and highly dispersed PtRu nanoparticles could be obtained [19].

Recently many groups of research reported on the preparation of PtRu/C by impregnation reduction method using NaBH₄ as reducing agent. It was found that the addition of some stabilizers such as Citric Acid (CA) [20], TetrOctylAmmonium Bromide (TOAB) can produce well-dispersed PtRu nanoparticles [6, 21].

In this work, 60 wt. % PtRu nanoparticles (atomic ratio 1:1) supported on carbon black were prepared from H₂PtCl₆ and RuCl₃ as metal precursors and NaBH₄ as reducing agent at room temperature without using of a stabilizer agent. The PtRu/C nanocatalysts were characterized using X-ray diffraction (XRD), and Field Emission Scanning Electron Microscopy (FESEM). The morphology of the catalysts layers fabricated from the prepared catalysts was investigated by Scanning Electron Microscopy (SEM). The electrocatalytic activity of carbon-supported PtRu nanoparticles for the electrochemical methanol oxidation reaction was investigated using Cyclic Voltammetry (CV) measurements and compared with that of commercial 60 wt. % PtRu/C (E-TEK) (atomic ratio 1:1)

2. Experimental work

2.1. Methods

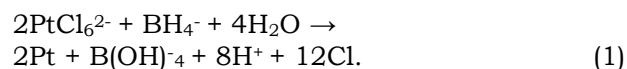
2.1.1. Preparation of carbon supported PtRu nanocatalyst

An amount of carbon black powder (Grade n-234, Iodine number (ID) 136 ±6 g/100g,

Dibutyl Phthalate (DBP) = 142 ±6 g/100g) was obtained from Carbon Black Alexandria Company, Alexandria, Egypt, and was dispersed in 20 ml of distilled water and ultrasonicated for 30 min. An appropriate amount of H₂PtCl₆ (ACROS) and RuCl₃ (Aldrich) to give 60 wt. % PtRu on the carbon support (with nominal atomic ratio of Pt:Ru, 1:1) dissolved in distilled water was added to the carbon black suspension. The solution mixture was kept under stirring for 30 min and then ultrasonicated for 30 min. Subsequently, the solution was reduced by addition of 50 ml of NaBH₄ solution (0.5, 1 and 2M). The reaction mixture was kept under stirring for two different reaction times of 2 and 3 hrs at room temperature to ensure the complete reduction.

The solution was then centrifuged and the carbon supported PtRu catalysts powder was washed many times with distilled water to ensure the removal of undesirable ions in the prepared catalysts. Finally, the prepared catalyst was dried at 100 °C overnight under vacuum.

The reductive reactions can be summarized by the following equations:



PtRu/C 60 wt. % (1:1) obtained from (E-TEK) was used to compare the prepared PtRu/C nanocatalysts in terms of electrochemical characteristics and structure.

2.2. Characteristics of PtRu/C nanocatalysts

2.2.1. Physical characteristics

2.2.1.1. X-Ray Diffraction (XRD) X-ray diffraction patterns of the nanocatalysts were obtained using (Schimadzu 7000, Japan) diffractometer, operating with Cu K α radiation ($\lambda=0.154060$ nm) generated at 30 kV and 30 mA with scanning rate of 2° min⁻¹ for 2 θ values between 20 and 80 degrees.

2.2.1.2. Energy Dispersive Analysis of X-ray (EDAX) Chemical composition analysis of the prepared PtRu nanocatalysts and the

commercial catalyst by EDAX was performed with an EDAX analyzer combined with scanning electron microscope (JEOL JSM 6360LA, Japan).

2.2.1.3. Field Emission Scanning Electron Microscopy (FESEM) The nanomorphology of PtRu/C catalysts was investigated using FESEM (JEOL 7600, Japan). The samples for analysis were prepared by dispersion of PtRu/C powder in ethanol with ultrasonic bath for 30 minutes. Then a Carbon rod (5 mm in diameter) is polished and its surface tension is released using Hydrophilic Treatment device (JEOL HDI 400) for 2 minutes. The suspended solution is spread on the Carbon surface and a thin layer of Pt is DC sputtered for 2 minutes with a current of 20 μ A to increase the surface conductivity.

2.2.1.4. Morphological Characterization (SEM) The surface of the catalysts layers electrode was scanned with scanning electron microscope (JEOL JSM 6360LA, Japan) to investigate the homogeneity of the electrocatalyst onto the carbon paper and identify the structure of the electrode surface after the electrochemical characterization. Also the surface of the carbon paper was examined

2.2.2. Electrochemical characterization

2.2.2.1. Preparation of the working electrode For preparation of the working electrode, the catalyst powder was dispersed in 2-propanol (Aldrich) and 5 % Nafion solution (Aldrich). The dispersion was then ultrasonicated for 15 min to form the catalyst ink, which was coated onto the carbon paper (E-TEK) and then was dried for 1h at 80 °C. The metal loading in the working electrode (cell area 2 cm²) was controlled to be 2 mg of PtRu/cm² for all samples.

2.2.2.2. Electrochemical half-cell measurements The electrochemical set-up consists of a Voltalab PGP 201 potentiostat controlled by computer and conventional three-electrode cell in which the Saturated Calomel Electrode (SCE) and platinum gauze were used as reference and counter electrodes, respectively. A Pt electrode (2×2cm²) was used as counter

electrode. Carbon paper containing the catalysts layer was used as the working electrode. The CV's were recorded in the range 0-1 V versus (SCE) at a scan rate of 10 mVs⁻¹. All potentials in this work are given in the Reversible Hydrogen Electrode (RHE) scale. A 200 ml electrolyte solution was used and the distance between counter electrode and working electrode was 5 cm. The cyclic voltammetry measurements were performed with 1M methanol (Fluka) in 1M H₂SO₄ (Aldrich). All the solutions were prepared from high purity sulfuric acid, methanol and distilled water and deaerated by passing of N₂ gas for 30 minute prior to any measurement. The measurements were carried out at room temperature using unstirred solution and the cyclic voltammograms were recorded after 20 activation cycles.

3. Results and discussions

3.1. XRD analysis

Fig. 1 and fig. 2 show the XRD patterns for the prepared PtRu/C nanocatalyst at different concentration of reducing agent, NaBH₄ and the prepared PtRu/C prepared at two different times in comparison with commercial PtRu/C (E-TEK) catalyst, respectively. The XRD patterns of all prepared catalysts exhibited diffraction peaks of (111), (200) and (220); the peaks characteristic of face centered cubic (fcc) structure of pure Pt crystalline (JCPDS-ICDD, Card No. 04-802).

From fig. 1, it is observed that the diffraction peaks for the prepared catalysts are shifted to slightly higher 2 θ values than the corresponding of pure Pt as the NaBH₄ concentration increases from 0.5 to 1 then to 2 M. The increase of NaBH₄ concentration may be enhancing the reduction of Ru ions into ruthenium metals which can be incorporated into the lattice structure of Pt [21]. The replacement of some Pt atoms in the Pt fcc crystal structure by the smaller Ru atoms ($r_{Ru} = 0.133$ nm and $r_{Pt} = 0.138$ nm) is combined with decrease in the lattice constant and can be taken as an indication for the formation of PtRu alloy in the catalyst [22-24].

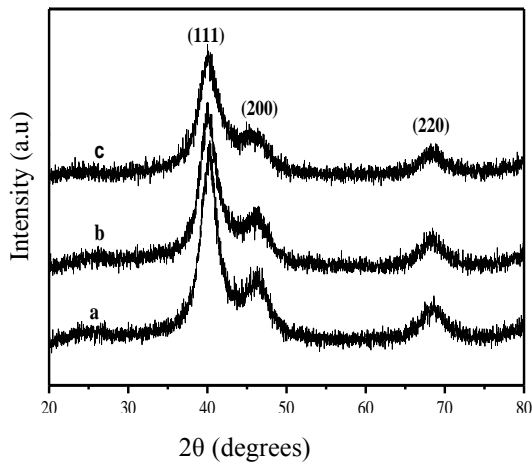


Fig.1. XRD Patterns of PtRu/C Prepared with Different Concentrations of NaBH₄ (a) 0.5,(b) 1, and (c) 2 M. (Reaction Time: 2 hrs).

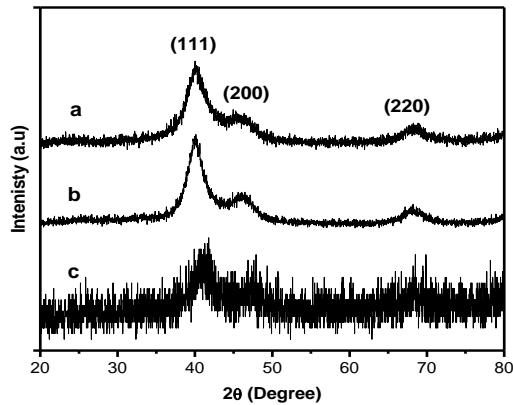


Fig. 2. XRD patterns of PtRu/C Catalysts Prepared at (a) 2hrs, (b) 3h with 2M NaBH₄ and PtRu/C (E-TEK).

In fig. 2 also the increase of the reaction time from 2hrs to 3 hrs is combined with slightly shift to higher 2θ values. Also, the (111) peak intensity increase with increasing the reaction time from 2hrs (fig. 2-a) to 3hrs (fig. 2-b).

The XRD patterns of the prepared catalyst don't display any peaks characteristic for hexagonal closed packed structure of Ru. This results agree with that reported by other groups and this is attributed either to Pt particles decorated by Ru particles [24] or Ru may be present in its hydrous oxide form [25, 26].

The average particle size for the prepared PtRu/C nanocatalysts was calculated from the broadening of (220) peak using Debye-Scherrer equation [287, 28]:

$$d = \frac{0.9\lambda}{B_{2\theta} \cos \theta_{max}} \quad (3)$$

Where λ is the wavelength of the X-ray (1.5406 Å), θ is the angle at the maximum of the peak and $B_{2\theta}$ is the width of the peak at half maxima.

It is observed for the PtRu/C (E-TEK) that the XRD pattern doesn't exhibit well-defined peaks. This could be attributed to the presence of an amount of oxygen in the commercial E-TEK catalysts, which can distort the crystalline structure [24, 29]. So, it was difficult to determine the particle size of the commercial (E-TEK) catalyst.

The structural parameter that indicates the alloy formation in PtRu catalysts is the lattice parameter (a_{fcc}). It was calculated from the angular position of the (220) reflection peak maxima by the following eqs. [30, 31]:

$$a_{fcc} = \frac{\sqrt{2}\lambda_{k\alpha 1}}{\sin \theta_{max}} \quad (4)$$

Where a_{fcc} is the lattice parameter (nm), $\lambda_{k\alpha 1}$ is the wavelength of X-rays used (0.15406 nm) and θ_{max} is the Bragg angle at the peak maximum.

From the value of lattice parameter, we calculated Ru atomic fraction in PtRu alloy by using the following equation proposed by Antolini et al. [20, 32]:

$$a_{fcc} = l_{oc} - kX_{Ru} \quad (5)$$

Where $l_{os} = 3.9155 \text{ \AA}$ is the lattice parameter of pure carbon supported platinum and $k = 0.124 \text{ \AA}$ is a constant.

All structural parameters for the prepared catalysts are shown in table 1.

It is clear from table 1 that the lattice parameters of the prepared catalysts decrease by increasing the concentration of the reducing agent and reaction time which enhance the incorporation of Ru atoms into the lattice structure of Pt and therefore the

decrease in the lattice parameter is attributed to the formation of PtRu alloys in the prepared catalysts.

The lattice parameter reported in this work is smaller than that reported by Yang et al. [19] for the catalysts prepared by the thermal decomposition and for the catalysts prepared by Gonzalez et al. [23] prepared by formic acid method. Also, it is worth to mention that in our work the Ru atomic fraction for PtRu/C prepared at higher concentration of the reducing agent (2M) and reaction time of 3hrs, was calculated to be 0.5 implying that with prolonged reaction time, all Ru are alloyed with Pt and fully alloy of PtRu can be obtained. These results contrast with the result reported by Antonili et al. [32] who stated that it is difficult to obtain PtRu alloy with nominal atomic ratio of 1:1 even at heat treatment up to 700 °C, and with study of Yang et al. [19] in which the fully alloyed PtRu can be obtained only at heat treatment of 500 °C.

3.2. EDAX analysis

The chemical compositions for the prepared PtRu/C nanocatalysts and PtRu/C (E-TEK) were determined by EDAX analysis. The results showed that the atomic composition of the prepared catalysts were close to the nominal composition (Pt: Ru, 50:50), while the commercial catalysts showed a deviation from the nominal composition (Pt:Ru, 41.61:58.39). These results showed the high homogeneity of the prepared catalysts. Also EDAX analysis doesn't include any traces of Na, Cl and B ions, which indicates that these ions were successfully removed during the washing process in the preparation step and the prepared catalyst doesn't contaminated with these undesirable ions.

3.3. FESEM analysis

Fig. 3 shows the FESEM images of the PtRu/C prepared with two different concentrations of NaBH₄ at reaction time of 2 hrs. It is observed that, the PtRu/C prepared at low concentration of NaBH₄ fig. 3-a showed some aggregation of nanoparticles. On the other hand in the PtRu/C nanocatalysts

prepared at higher concentration of NaBH₄ fig. 3-b, the image showed highly dispersed PtRu nanoparticles (bright particles) with particle size of 4-6 nm were deposited onto the surface of semispherical carbon support and the nanoparticles are in good contact with the support without any aggregations.

3.4. Morphological characterization

Fig. 4 shows the scanning electron micrographs of the initial carbon paper fig. 4-a and the PtRu/C catalyst layers fig. 4-b before methanol oxidation.

The carbon paper substrate fig. 4-a shows tubular rods interconnected with filling materials of smaller grain size. Fig. 4-b shows the catalyst layer of PtRu/C, which covers completely the carbon paper resulting in a homogeneous layer with porous structure. This morphological properties is favoring the adsorption of the reactants onto the catalyst layer surface

Fig. 4-c shows the SEM micrograph of PtRu/C catalysts layer after methanol oxidation. The micrograph shows that the catalysts layer still keep its porous structure which indicates that the electrodes fabricated from these catalysts layer are stable under these conditions.

3.5. Electrochemical half-cell measurements

In this section the electrochemical characterization was carried out only for the PtRu/C catalysts prepared at 2 M of NaBH₄ with reaction times of 2 and 3 hrs in comparison with the commercial catalysts PtRu/C (E-TEK). The prepared catalysts are donated as PtRu/C (2hrs) and PtRu/C (3 hrs), respectively.

The cyclic voltammograms for the prepared catalysts PtRu/C (2 hrs) and PtRu/C (3 hrs) in 1M CH₃OH/1M H₂SO₄ is shown in fig. 5. fig. 6 shows the cyclic voltammograms for PtRu/C (3 hrs) and E- TEK catalysts. The electrocatalytic activities of the catalysts are evaluated in terms of onset potential and current density for methanol electro-oxidation [33, 34]. The results are tabulated in table 2. The PtRu/C (3 hrs) catalysts exhibited higher

Table 1
The structural parameters of PtRu/C obtained from XRD analysis

NaBH ₄ (M)	Reaction time (hrs)	Particle size (nm)	(220) peak 2θ	lattice parameters a _{fcc} (nm)	X _{Ru}
0.5	2	8.8	67.04	0.349	0
1	2	4.5	68.26	0.3880	0.28
2	2	4.3	68.34	0.3879	0.29
2	3	6.3	68.88	0.3852	0.50

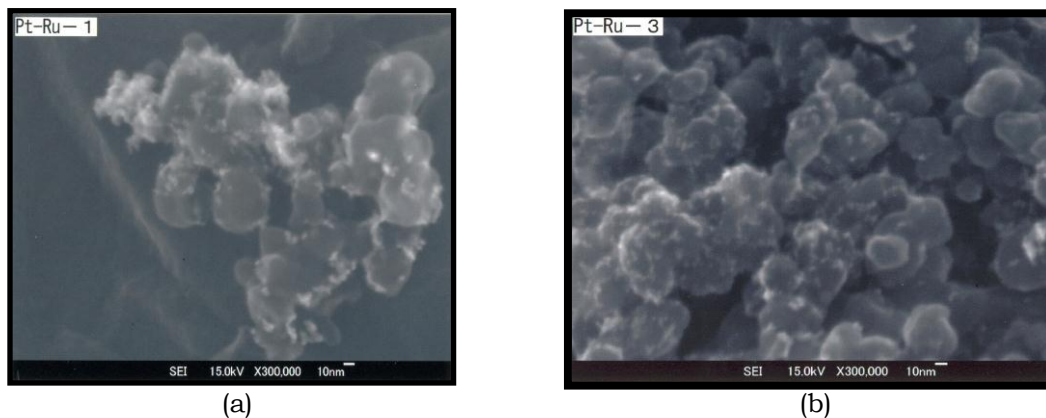


Fig. 3. FESEM images of PtRu/C nanocatalyst prepared at 1M of NaBH₄ (a) 2 M of NaBH₄ (b) with reaction time of 2hrs.

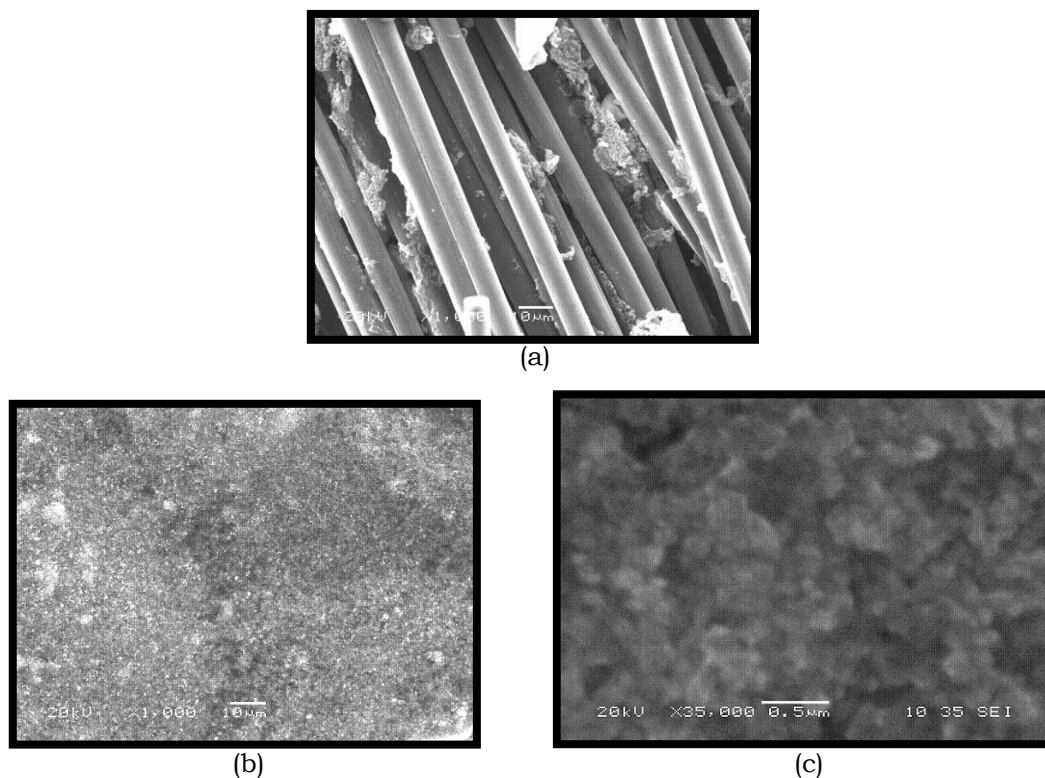


Fig. 4. SEM Micrographs of a- Initial carbon paper, coated catalysts Layer before methanol oxidation b- and after methanol oxidation c.

current density for methanol oxidation (32.4 mA/cm² at 550 mV) than those for PtRu/C (2 hrs) (17 mA/cm² at 550 mV) and for the commercial catalysts (17 mA/cm² at 550 mV), which indicates the highest catalytic activity of PtRu/C (3 hrs) catalysts. Also, the onset potential for the methanol oxidation on the prepared PtRu/C (3 hrs) catalysts shifted to lower potential than that of PtRu/C (2 hrs) and of the commercial (E-TEK) catalysts, which indicates that PtRu/C (3 hrs) was able to reduce the overpotential caused by CO poisoning.

The results showed that the PtRu/C (3 hrs) catalysts with high degree of alloying have higher electrocatalytic activity among all catalysts under investigation.

It can be concluded that this enhancement in the electrocatalytic activity and CO-tolerance for the prepared catalyst could be attributed to its good structural properties which makes the dissociation of water on Ru faster at low potentials and, thereby, the surface oxygenated groups (Ru-OH) oxidize the CO species that are adsorbed on neighboring Pt sites in accordance with the bifunctional mechanism [35]. Also, time of reaction was limited to 3 hrs because it is already all metal ions (Pt and Ru) have been reduced to their metal states. These features make the prepared nanocatalysts have a potential use as electrocatalyst for methanol electro-oxidation in direct methanol fuel cells.

Table 2
The electrocatalytic activity of the PtRu/C catalysts and E-TEK catalyst

Catalysts	Onset potential (mV) vs. (RHE)	Current density (mA/cm ²) At 550 mV
PtRu/C (2 hrs)	75	17
PtRu/C (3hrs)	60	32.4
PtRu/C (E-TEK)	65	17

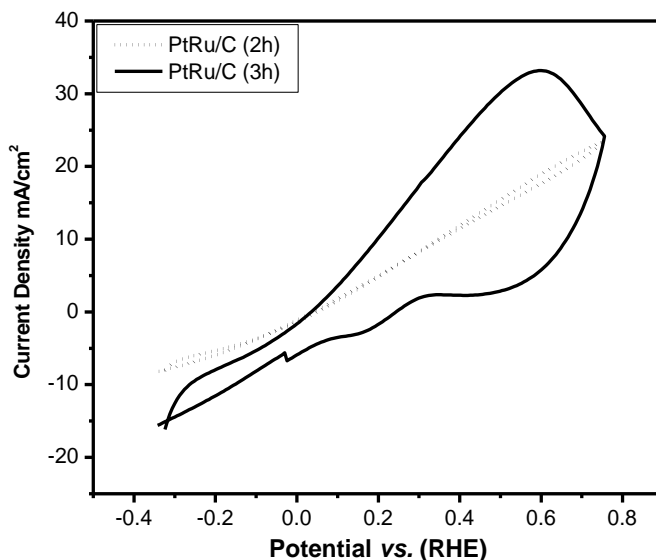


Fig. 5. Cyclic Voltammograms of PtRu/C (2 hrs) and PtRu/C (3 hrs) Catalysts in 1 M CH₃OH/1 M H₂SO₄.

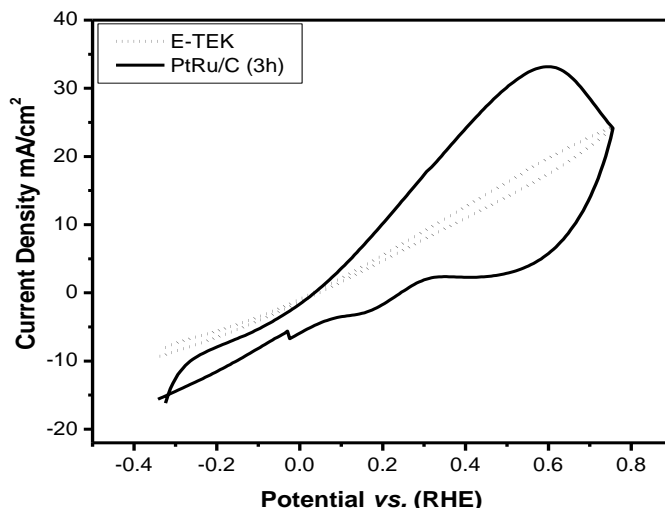


Fig. 6. Cyclic Voltammograms for the prepared PtRu/C (3 hrs) Catalysts and Commercial PtRu/C (E-TEK) in 1 M CH₃OH/1 M H₂SO₄.

4. Conclusions

PtRu/C nanocatalyst was prepared by impregnation reduction method using NaBH₄ at room temperature. XRD analysis showed that the PtRu nanocatalyst has fcc structure of Pt and fully alloyed PtRu nanoparticles can be obtained with high concentration of the reducing agent and at prolonged reaction time.

The prepared nanocatalyst with high degree of alloying exhibited higher electrocatalytic activity in terms of onset potential and current density for methanol electro-oxidation in comparison with the commercial catalysts (E-TEK), which makes this preparation method have a potential use in preparation of highly catalytic electrocatalysts for DMFC. The single cell measurements are under investigation.

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