

Carbon Supported Mono- and Bi-Metallic Dispersed Thin Film Catalysts for Oxygen Electro-Reduction Reaction in Acid Medium

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The present study reports the use of mono- and binary-metal thin film deposits of Pt, Cu, Ru and Pd dispersed over carbon electrode as electro-catalysts for oxygen reduction. The metals are sequentially electrodeposited on the carbon electrode from their aqueous solutions using the potentiostatic technique. The electrode surface characterization was carried out by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersed X-ray (EDX). The micrographs of SEM analyses showed that the thin films of the various deposits are located at the electrode surface in the nano-scale range. Linear sweep voltammetry was used to investigate the electrode performance towards oxygen reduction in H₂SO₄ solution in the absence and presence of H₂O₂. The results indicated that metal deposits and platinum-metal modified carbon electrodes have shown superior electro-catalytic activity toward oxygen reduction reaction (ORR) as shown by the relative increase in the peak current density values of oxygen reduction.

Keywords: Oxygen reduction, Dispersed electrodes, Pt, Pt-Cu, Pt-Pd.

1. INTRODUCTION

Fuel cells are considered nowadays as very important power sources for electrical devices [1, 2] due to their high energy conversion efficiency, low pollution and low temperature operation [3-7]. However, for a wide application of this technology, the cathodic limitations as the high cost, low catalytic activity and low stability of the cathodes should be reduced [1]. Therefore, the cathode catalyst in these cells is still of a great importance in order to have high efficiency towards the electrochemical oxygen reduction reaction (ORR). The ORR has attracted a great deal of attention due to its importance in electrochemical reactions of many applications [8-10]. Also, it is considered to be

the limiting step in fuel cells due to its slow reaction kinetics at the cathode which hinders the efficiency of energy conversion [1, 10, 11].

The ORR may proceed via two different pathways; either through four electron transfer yielding H_2O or through two electron transfer yielding H_2O_2 [9, 12-14]. The pathway of this reaction was found to depend on the electrode material and the solution composition as well as the solution pH [15]. In addition, the type of electrode material strongly affects the catalytic activity of the cathode catalyst towards the ORR [16]. Therefore, the design of highly active, stable, efficient and cost effective electro-catalysts for ORR is very important in the field of electrochemical energy conversion [17-19].

Platinum is considered as the catalyst of choice for preparation of the fuel cell cathodes because it has high activity and excellent chemical stability towards the ORR [20-23]. However, its high cost and low specific surface area are still obstacles for successful commercialization of fuel cells [10, 11, 21, 24, 25]. Therefore, reducing the amount of loaded platinum by dispersion over a conductive support or replacing platinum by other metal catalysts while maintaining their performance towards the ORR is always the target in fuel cell research [8, 17, 26].

Previous works showed that dispersion of platinum with a secondary metal reduces the platinum utilization and improves the catalytic performance [13, 27, 28]. The enhanced catalytic activity of these dispersed metals might be due to the bi-functional effects in which the unique catalytic properties of each metal combine in a synergetic manner to yield a surface which is more active than each metal alone. Also, an electronic effect can modify the electronic properties of the binary metals to increase the catalytic activity of the surface [29]. In addition, the improved activity and durability for platinum-based catalysts have been achieved by the compositional and morphological control, respectively [30].

Pt-Cu nanoparticles were used as cathodic electrocatalysts and significantly improve the ORR [28, 31, 32]. Liu et al. [31] has developed metallic Pt-Cu multi-nanorods and reported an enhanced electrocatalytic activity and stability for ORR compared to conventional Pt/C catalysts. In the work of Oezaslan et al. [28], it is demonstrated that PtCu_3 , PtCu and Pt_3Cu nanoparticles over carbon can improve ORR activity compared to commercial Pt catalyst.

Palladium-based catalysts are used as alternative catalysts to platinum-based ones for ORR due to their relatively low cost and improvable catalytic activity. Palladium is considered to be a good substitute to platinum as it has similar properties to platinum (same group of the periodic table, similar atomic size and crystalline structure) [33]. Hong et al. [34] prepared Pd-Pt catalysts with hollow nanostructures and found that their electrocatalytic activity is highly dependent on the nanoparticle's morphology. Lim and co-workers [35] also studied oxygen reduction on Pd-Pt bimetallic nanodendrites, which were 2.5 times more active than commercial Pt/C catalyst.

Although many synthetic methods have been used to synthesize active ORR catalysts, it is still necessary to find an economical, simple, and easy methodology to prepare ORR catalysts using minimum amount of expensive Pt metal. The aim of this work is the use of commercial carbon electrode to prepare a catalyst for enhancing the ORR composed of mono-metal deposits as Pt, Cu, Ru, and Pd as well as binary metal deposits as Pt-Cu, Pt-Ru and Pt-Pd using the potentiostatic polarization technique in acid medium. The aim also involves a study of hydrogen peroxide reduction reaction

(HPRR), since hydrogen peroxide might appear either as a product or as an intermediate during the ORR according to the following reactions [13, 15]:



In addition, it can be used as a source of oxygen because H_2O_2 generates O_2 during its decomposition:



and also it can interact with oxidized catalyst surface producing oxygen [9] through reducing the surface.

2. EXPERIMENTAL TECHNIQUES

Electrochemical measurements were performed in 0.5 M H_2SO_4 solution in a conventional three electrode cell, where the carbon electrodes modified with electrodeposition of thin films of mono-deposit (as Pt, Cu, Ru and Pd deposits) and binary deposits (as Pt-Cu, Pt-Ru and Pt-Pd deposits) were used as working electrodes. A platinum wire served as a counter electrode and a silver/silver chloride electrode immersed in 1 M KCl solution was used as a reference electrode for which all potentials reported herein are referred to. The carbon electrode used as a support electrode is a commercial carbon that is pre-activated before metal deposition by heating at 200°C in an electric oven for 1.0 hour. After activation, it was mechanically polished with metallographic papers of various grades to a mirror finished surface. This step was necessary to remove any impurities on its surface. The electrode surface was then degreased with acetone, rinsed with distilled water and dried with a soft tissue paper and finally mounted in a Teflon holder as a disc. The apparent surface area of the disc exposed to the solution had calculated from the geometrical dimensions and recording a value of 0.132 cm^2 , the current density is referred to this area.

In all experiments and before electrodeposition of metal catalysts, the potential of the carbon working electrode was scanned several cycles from the potential of hydrogen gas evolution (-0.6 V) to that of oxygen evolution (+1.8 V) in 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1} until attaining stable voltammogram curve. This step is also necessary to obtain reproducible data. The electrodeposition of Pt, Cu, Ru or Pd on the carbon electrodes (either as mono- or binary-deposits) was performed potentiostatically from the corresponding metal salt solutions at the appropriate deposition potentials for different times. The following represent the solution and the deposition potential for various deposits:

i) Pt was deposited from 0.01 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution in 0.5 M H_2SO_4 at a potential value of -0.200 V.

ii) Cu was deposited from a saturated solution of copper tetramine sulfate complex at a potential value of -0.350 V.

iii) Ru was deposited from 0.01 M $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ solution in 0.5 M H_2SO_4 solution at a potential value of -0.500 V.

iv) Pd was deposited from 0.01 M PdCl₂ solution in 0.5 M H₂SO₄ solution at a potential value of -0.400 V.

Values of the deposition potential mentioned above were chosen based on the values of the reduction peak potential of the corresponding metal ions when the working electrode was polarized in the metal ions solution using the linear sweep voltammetry technique (the corresponding figures are not included). After the electrochemical deposition process, the electrode was rinsed with distilled water and transferred to an electrolytic cell containing the test solution where the oxygen reduction reaction was studied.

All chemicals used in this work were reagent grade products (Sigma–Aldrich) and used as received without further purifications. Triply distilled water was used throughout for the preparation of solutions. Scanning electron microscopy (SEM), (XRD) and (EDX) analysis were used to examine the surface of the carbon modified electrodes prepared by the above mentioned methods and provide information about the morphology of thin films present on the electrode surface. Linear sweep voltammetric measurements were employed for ORR and HPRR measurements in order to record the cathodic polarization curves. The lower potential limits were set at potentials high enough to avoid the absorption or the adsorption of hydrogen, while the upper potential limits were set at potentials low enough in order to avoid the formation of high valence oxides. The electrochemical measurements were performed by using an Autolab potentiostat/galvanostat CHI version 15.03 (Austin, Texas., USA) and the experiments were controlled with (CHI660e) software. Measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

The modified electrodes thus prepared are used as electrocatalysts for the ORR in H₂SO₄ solution. Platinum is known to be an important catalytically active metal for this reaction. At present, carbon supported Pt nanoparticles represent the most popular commercial cathode catalysts for ORR in fuel cell applications [36-39]. In this study, dispersed platinum over carbon electrode was used as a catalyst to investigate the performance of the ORR in H₂SO₄ solution. Platinum particles were electrodeposited on carbon electrode potentiostatically at -0.2 V for 20 minutes. Cyclic voltammograms recorded for this electrode as well as a massive platinum electrode sheet with area of 0.96 cm² (for comparison) in 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹ can be seen in **Fig. (1)**. Regarding the cathodic (II_c) and anodic (II_a) peaks appear in the negative potential range (-0.1 to -0.25 V) for both electrodes in the voltammograms, these peaks were reported by many researchers that they represent the hydrogen adsorption/desorption on platinum [36, 37, 40, 41]. In our set of experiments, cyclic voltammetry was carried out in 0.5 M H₂SO₄ solution starting from a positive potential value of +1.2 V going to -0.32 V in the negative sweep then the scan was reversed in the positive sweep up to +1.2 V. This technique of polarization was carried out in order to start with a hydrogen-free electrode surface if polarization starts from the hydrogen gas evolution potential region at -0.32 V. Upon scanning the potential of the working electrode towards the cathodic direction (from +1.2 to -0.32 V),

the oxygen reduction current starts to increase at +0.335 V (I_c) once the reduction of the surface platinum oxide commences [42].

It is generally believed that it is very difficult to ignore the hydrogen adsorption/desorption and double layer regions. But, as reported above, we start the polarization from a positive potential value going to a more negative potential in the negative sweep. At the final potential (-0.32 V), hydrogen evolution process starts. Reversing the scan towards the anodic direction and after the anodic peaks (II_a), the oxidation of platinum is observed as a broad peak (I_a) appears in the potential range from +0.55 to +1.10 V. It is found from Fig. (1) that, the cyclic voltammetric behaviour of the two electrodes is the same except that the current density values in case of the dispersed electrode are much higher than that obtained in case of the massive one. This could possibly due to the high specific surface area available on the dispersed electrode [1, 23, 39].

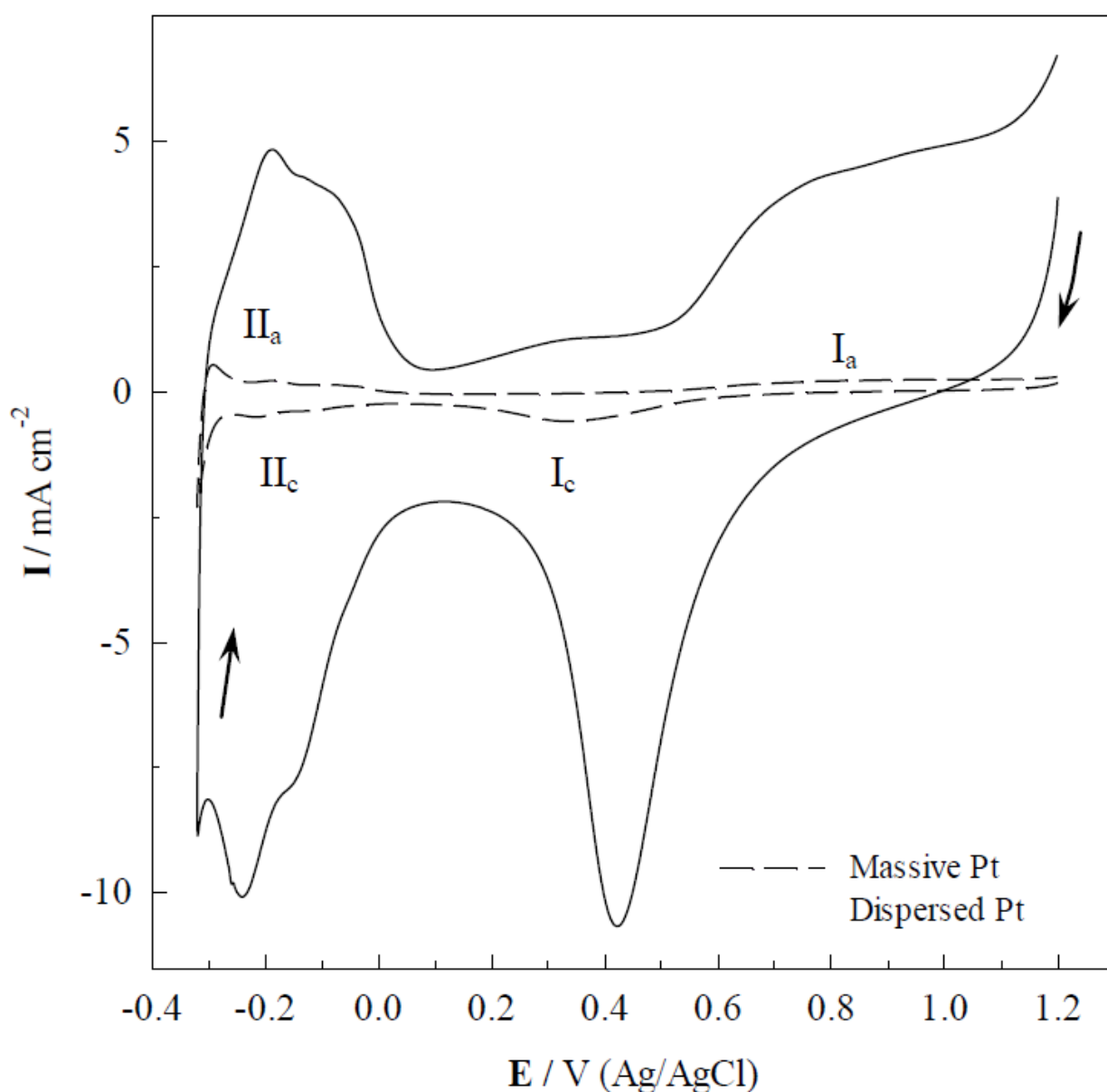


Figure 1. Cyclic voltammograms of massive Pt and dispersed Pt(20 min)/C electrodes in 0.5 M H_2SO_4 solution at 50 mV s^{-1} .

The behaviour of massive platinum electrode in hydrogen peroxide solution was studied. The linear sweep voltammetric experiments were carried out on massive platinum electrode in different concentrations of hydrogen peroxide solutions prepared in 0.5 M H_2SO_4 .

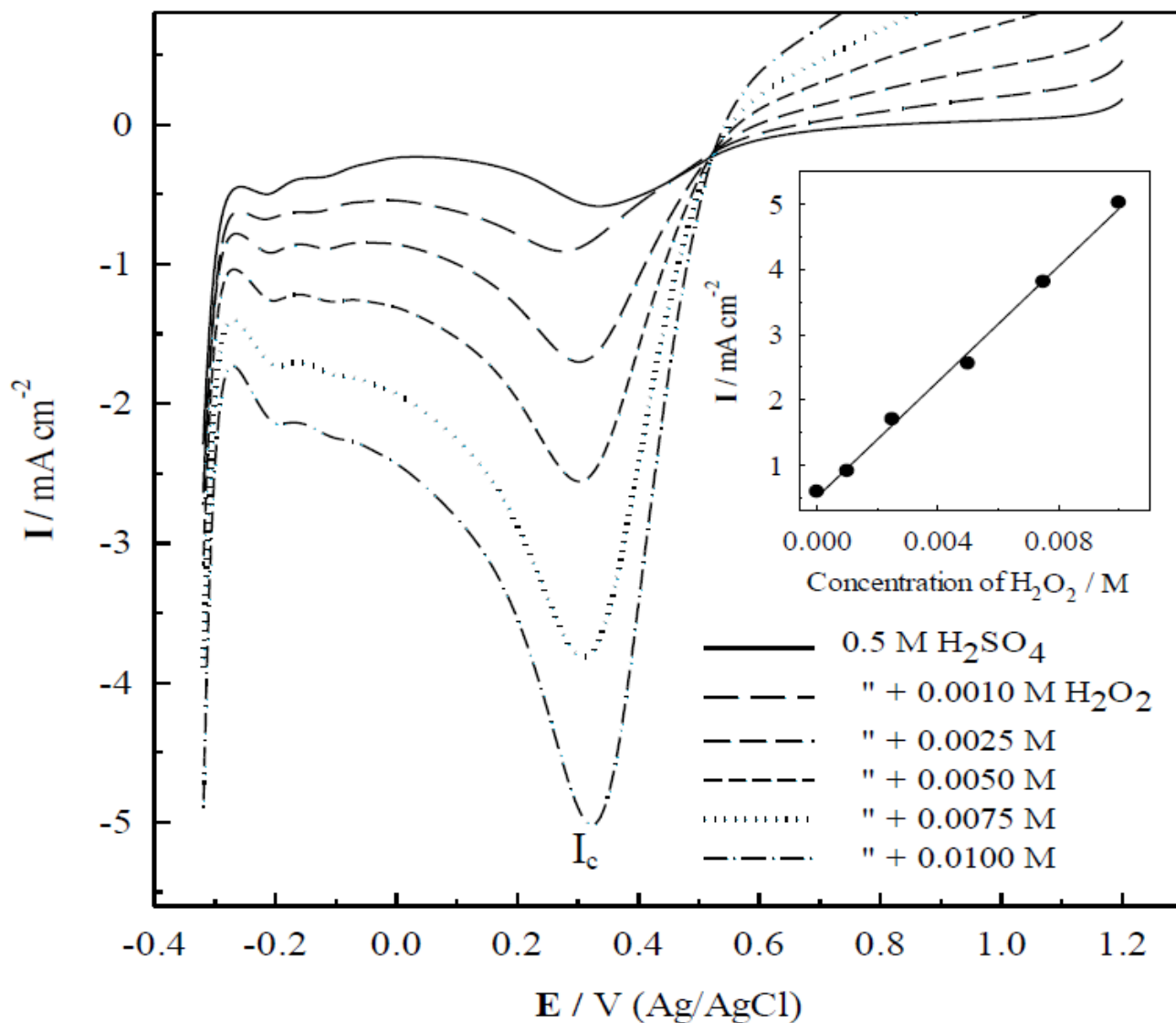


Figure 2. Linear sweep voltammetry of massive Pt electrode in different concentrations of H_2O_2 solutions at 50 mV s^{-1} . Variation of oxygen reduction peak current density (I_c) with H_2O_2 concentrations is represented in the inset figure.

In these experiments, polarization started from +1.2 to -0.32 V and the results are represented in Fig. (2). The reduction peak at +0.333 V is possibly represents the reduction of oxygen, the current density values of which increases with increasing the peroxide concentration. It is reported that, H_2O_2 decomposes producing adsorbed OH species when interacts with reduced surface sites [9]. These adsorbed OH species are thereafter reduced and the resulting current is the sum of both processes, the reduction of O_2 and the reduction of adsorbed OH species. In addition, the peak potential of this peak is slightly shifted to less negative values with increasing the hydrogen peroxide concentration. A previous study of quartz crystal microbalance showed that, in H_2SO_4 solution, H_2O_2 is considered to

contribute to the formation of Pt-oxide [43]. This also could explain the increase of the peak current density values of the reduction peak at +0.333 V with the H_2O_2 concentration. The inset figure in Fig. (2) represents the variation of the reduction peak current density of O_2 (I_c) with the peroxide concentration. A straight line relation was obtained along the concentration range studied.

The behaviour of the Pt/C electrodes, prepared by deposition of Pt on carbon for different times, is studied in 0.5 M H_2SO_4 at a scan rate value of 50 mV s^{-1} and represented in Fig. (3 a). Different time of deposition is required to obtain different platinum loading on the carbon surface. In these experiments also and for each modified electrode, polarization was started from +1.2 to -0.32 V. It is observed from this figure that the catalytic activity of the modified Pt/C electrode is increased with increasing the deposition time of Pt. The reduction of oxygen commences with the start of platinum oxide reduction which appears as a sharp peak (I_c) at +0.40 V. The increased values of current density of all of these peaks with increasing the Pt deposition time could be attributed to the increase of the number of surface active sites as the time of Pt deposition increase. Moreover, a series of redox peaks appeared in the anodic and cathodic sweeps in the potential range from -0.3 to +0.01 V (II_a and II_c) due to the hydrogen adsorption/desorption. Another broad anodic peak (I_a) appeared in the potential range from +0.52 to +1.1 V which may be attributed to the formation of the platinum oxide species as PtO or PtOH. This peak also increased with increasing the deposition time. Variation of the reduction peak current density of oxygen [peak (I_c) at +0.40 V] with the Pt deposition time is represented inset. This result shows that the peak current density values of the reduction of oxygen is increased with increasing the deposition time of platinum. The same observation was reported by Ke et al. [12] for the increase of oxygen reduction peak with platinum loading in Pt/C electrodes. Thus, high deposition time of Pt is preferred to obtain high catalytic activity for oxygen reduction. Comparing the current density values of the oxygen reduction peak obtained in case of massive platinum electrode with that obtained in case of dispersed electrodes, it can be seen that the difference in the active surface area lead to the conclusion that the latter case represents the best method, with respect to platinum, for catalysing the oxygen reduction process.

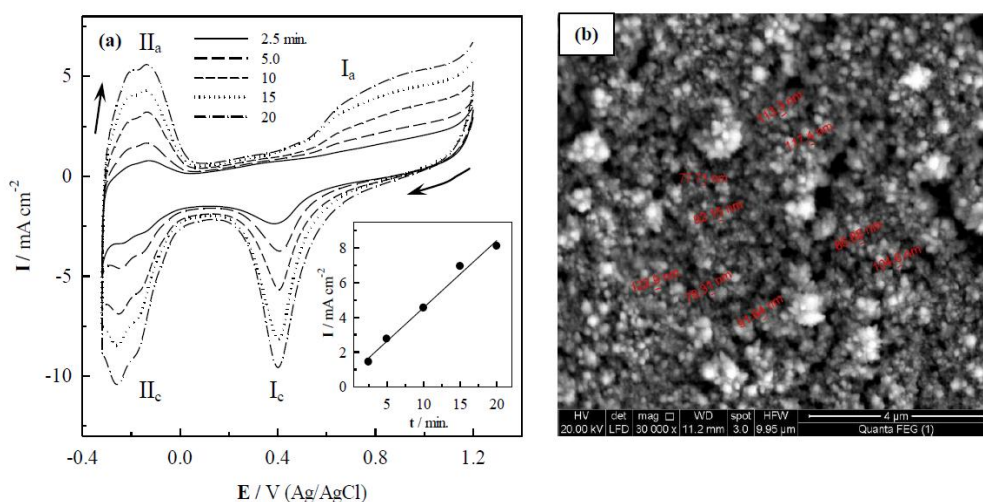


Figure 3. (a) Linear sweep voltammetry of Pt/C electrodes in 0.5 M H_2SO_4 solution at 50 mV s^{-1} . Variation of oxygen reduction peak current density (I_c) with deposition time is represented in the inset figure. (b) Scanning electron micrograph of Pt(20 min)/C electrode.

SEM analysis was recorded for Pt/C modified electrode deposited for 20 minutes, and represented in Fig. (3 b). It is observed that, a homogeneous distribution of platinum particles over the electrode surface appeared as a nearly spongy-like structure with about 60 μm average thickness (as reported from special SEM analysis) that led to a high specific surface area. Particle size was found to be in the range of 70 to 120 nm. This could explain the high activity of this Pt/C modified electrode compared to massive platinum one.

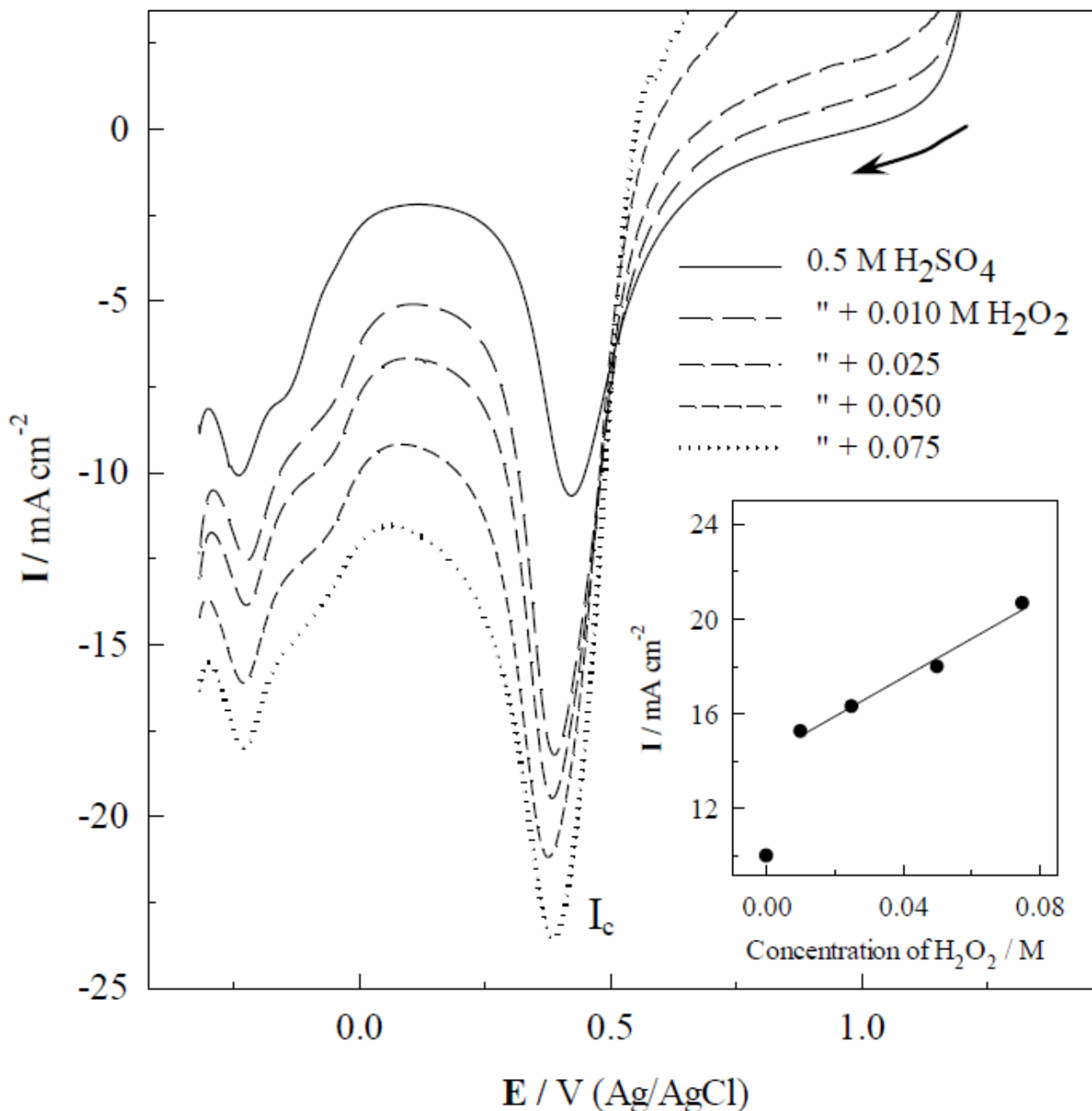


Figure 4. Linear sweep voltammetry of Pt(20 min)/C electrode in different concentrations of H₂O₂ solutions at 50 mV s⁻¹. Variation of oxygen reduction peak current density (I_c) with H₂O₂ concentrations is represented in the inset figure.

The behaviour of Pt/C modified electrode was studied in H₂SO₄ solution in presence of different concentrations of hydrogen peroxide using the linear sweep voltammetry in the potential

range started from +1.2 to -0.32 V. Results are represented in Fig. (4) which showed that the peak current density values of the reduction of oxygen (I_c) that appears at about +0.4 V increased with increasing the hydrogen peroxide concentration. The peak current density values of this peak are linearly related to the peroxide concentration as represented in the inset figure. Comparing the results obtained in Fig. (2) with that in Fig. (4), it is noticed that the peak current density values of oxygen reduction obtained at dispersed platinum electrode are much higher than the corresponding values obtained at the massive platinum electrode for one and the same H_2O_2 concentration. This is possibly due to the higher electrode surface area inherent with the dispersed electrodes.

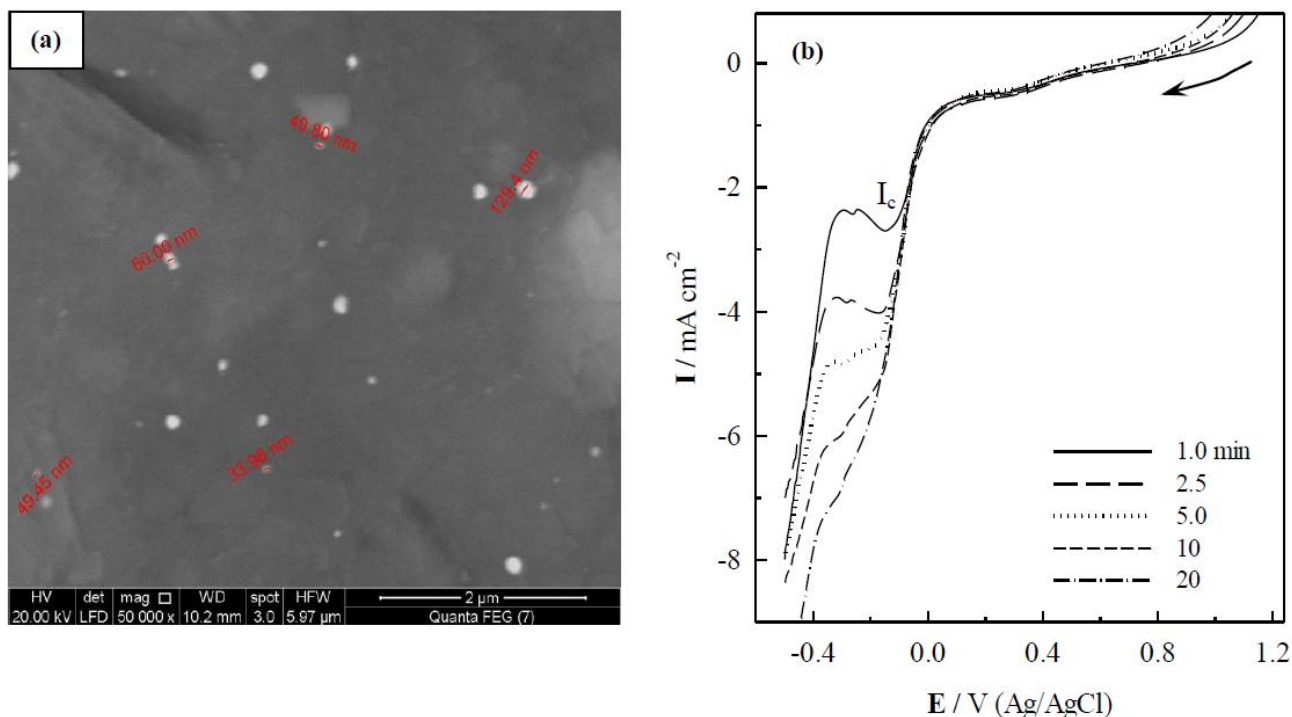


Figure 5. (a) Scanning electron micrograph of Cu(20 min)/C electrode. (b) Linear sweep voltammetry of Cu/C electrodes in 0.5 M H_2SO_4 solution at 50 mV s^{-1} .

ORR was also studied at a modified Cu/C dispersed electrode. Copper was deposited potentiostatically on carbon electrode at -0.35 V. Various amounts of Cu deposits were achieved by using different time of deposition. SEM analysis was carried out for Cu/C modified electrode, which is electrodeposited for 20 minutes, and represented in Fig. (5 a). It is observed that, particles of copper metal in the range of 30 to 120 nm are randomly distributed on the carbon. The linear sweep voltammetric curves of Cu/C electrodes, which are deposited at -0.35 V for different times, in the potential range starting from +1.2 to -0.5 V are represented in Fig. (5 b). Upon starting the polarization from a relatively positive potential (+1.2 V), partial dissolution of copper in the studied electrolyte could occur with the formation of copper ions [44]. The formation of copper oxide at such relatively positive potential is possible in addition to the attack of the formed ions by dissolved oxygen [45]. In Fig. (5 b), oxygen reduction starts once the reduction of Cu-oxide commences at the cathodic peak that appears at about -0.13 V (I_c). This explanation was also proposed by Moreir et al. [46] for the cathodic peak current associated with the reduction of the anodically formed oxide film in concentrated H_2SO_4

solution. The current density value of Cu-oxide reduction peak was found to increase with increasing the deposition time of copper. However, the peak potential value is slightly shifted towards more negative potentials and became broad with increasing the amount of copper deposits. This shift could be due to the IR drop at relatively high current density values. At a relatively high deposition time, this peak is merged with hydrogen evolution.

Previous studies reported that, alloying of Pt with 3d transition metals including Cu can further improve the ORR activity of Pt [28, 47]. This improvement was interpreted in terms of the addition of non-noble metal core can change the geometric as well as the electronic structure of Pt, which ultimately enhances its activity [29]. Therefore, thin film deposition of a bi-metallic catalyst was prepared by the electrodeposition of both Cu and Pt over the commercial carbon electrode. Two types of binary catalyst were prepared; either Cu/Pt/C or Pt/Cu/C. For the former one, platinum was first electrodeposited potentiostatically at -0.2 V for 20 minutes. Then, copper was electrodeposited at -0.35 V for different times. The cyclic voltammetric behaviour of these modified electrodes was studied in 0.5 M H₂SO₄ solution and represented in Fig. (6 a). It is found that, upon deposition of copper over the Pt/C electrode, the cyclic voltammetric characteristics of copper clearly appear specially in the positive sweep represented by the formation of the oxidation peak of copper (I_a) at about +0.17 V. On the other hand, the hydrogen adsorption/desorption peaks characteristic for the existence of platinum at the electrode surface are gradually disappear upon Cu deposition indicating the partial covering of Pt-active sites by Cu particles. In the negative sweep, oxygen reduction starts to occur at platinum (that still exist) at the cathodic peak of +0.45 V (I_c). The peak current density value of this peak was found to increase upon the deposition of copper and almost unaffected by increasing the amount of copper deposited. The increase of current density value of oxygen reduction at platinum upon the presence of copper reflect the improved ORR activity of the catalyst. A similar observation was drawn when Sarkar et al. [48] and Gupta et al. [49] made a comparison between the commercial pure Pt and Pt-Cu core-shell nanoparticles that showed an improved ORR activity upon alloying with Cu. Moreover, in the potential range from about 0.0 V up to -0.32 V (in the cathodic scan) the current density values are relatively high compared to that obtained in case of platinum alone. This is because at this potential region, the reduction of copper oxide is possible to take place at -0.24 V (II_c). The current density value of this reduction peak was found to be affected by the amount of deposited copper up to 15 minutes deposition.

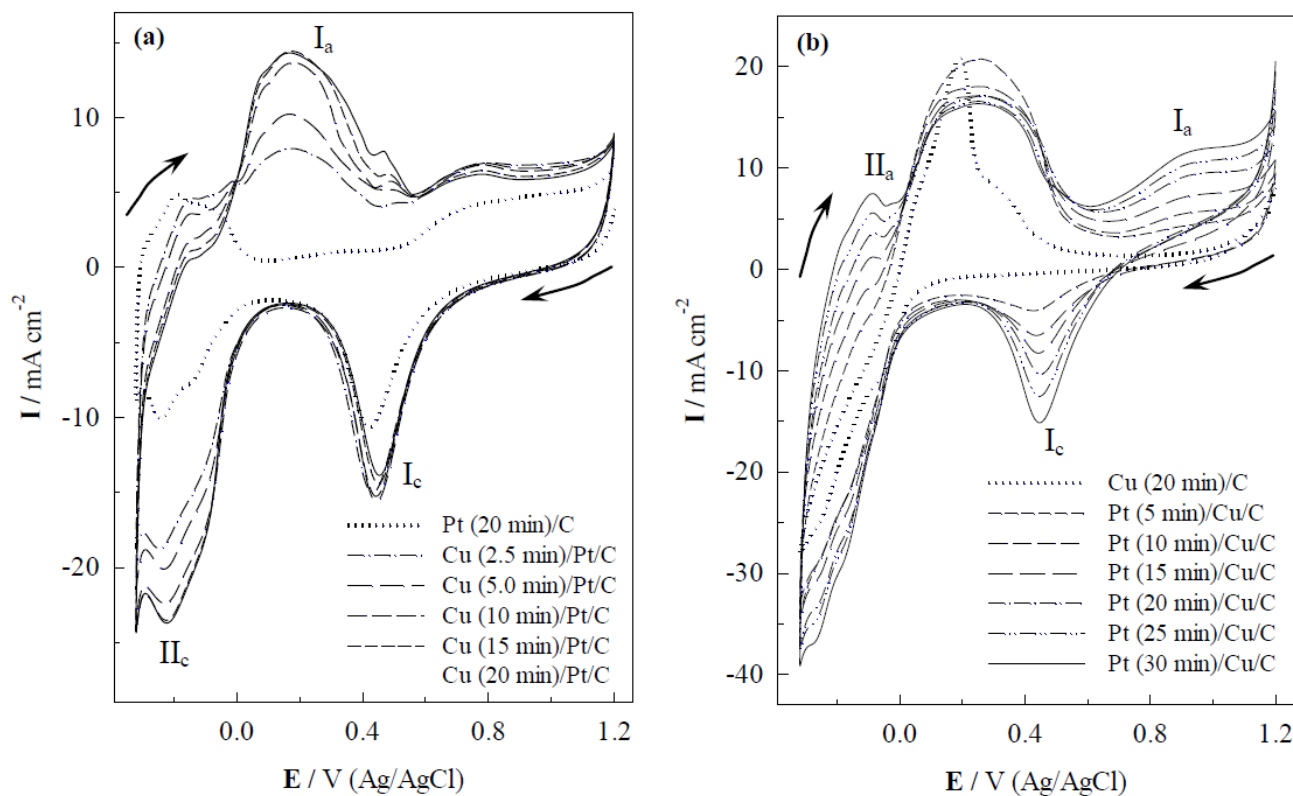
SEM analysis was recorded for the Cu(15 min)/Pt(20 min)/C modified electrode and represented in Fig. (6c). It is observed that, a homogeneous distribution of platinum and copper nanoparticles, in the range of 20 to 40 nm, appeared on the carbon with about 80 μm average thickness.

For the Pt/Cu/C electrode, copper was electrodeposited on carbon electrode from the desired bath for 20 minutes at -0.35 V. Platinum was then electrodeposited at -0.2 V from the previously mentioned bath for different times to get different platinum loading. The cyclic voltammetric behaviour of the prepared modified electrodes was studied in 0.5 M H₂SO₄ solution and represented in Fig. (6 b). Upon deposition of platinum on the Cu/C electrode, Pt oxidation and reduction peaks (I_a and I_c) start to appear in the voltammogram in addition to the anodic peak characteristic for hydrogen desorption (II_a) at about -0.116 V. Moreover, the current density values of the oxygen reduction peak

are increased with the increase of platinum deposition time. SEM analysis recorded for Pt(20 min)/Cu(20 min)/C modified electrode [Fig. (6 d)] showed the existence of both platinum and copper nanoparticles, in the range of 30 to 150 nm, as spherical agglomerates on the carbon surface with a thickness of about 80 μm . EDX and XRD analyses were performed for this electrode as represented in Figs. (6 e and f) respectively. Both analyses confirmed the presence of both Pt and Cu metals on the carbon surface and their chemical composition is represented inset these figures. Regarding these atomic values, the amount of platinum is relatively higher than that of copper. This can explain the increase of the reduction peak current density values of oxygen with increasing the deposition time of platinum.

The enhanced activity of these dispersed surfaces is attributed to the bi-functional effects in which the unique catalytic properties of each of the elements in the alloy combine in a synergetic manner to yield a surface which is more active than each of the elements alone [29, 50]. Junga et al. [51] reported that, the activities of the PtCu_x@Pt/C catalysts towards the ORR significantly changed as a function of the composition of Cu and Pt.

Another study was performed by the simultaneous deposition of platinum and copper from a solution containing the two metal ions species. The electrodes prepared by this method did not show good catalytic behavior towards the ORR compared to both Cu/Pt/C and Pt/Cu/C. Accordingly, the best method for preparing either Pt/Cu/C or Cu/Pt/C catalytic electrodes is by the successive deposition of one over the other not by their simultaneous deposition.



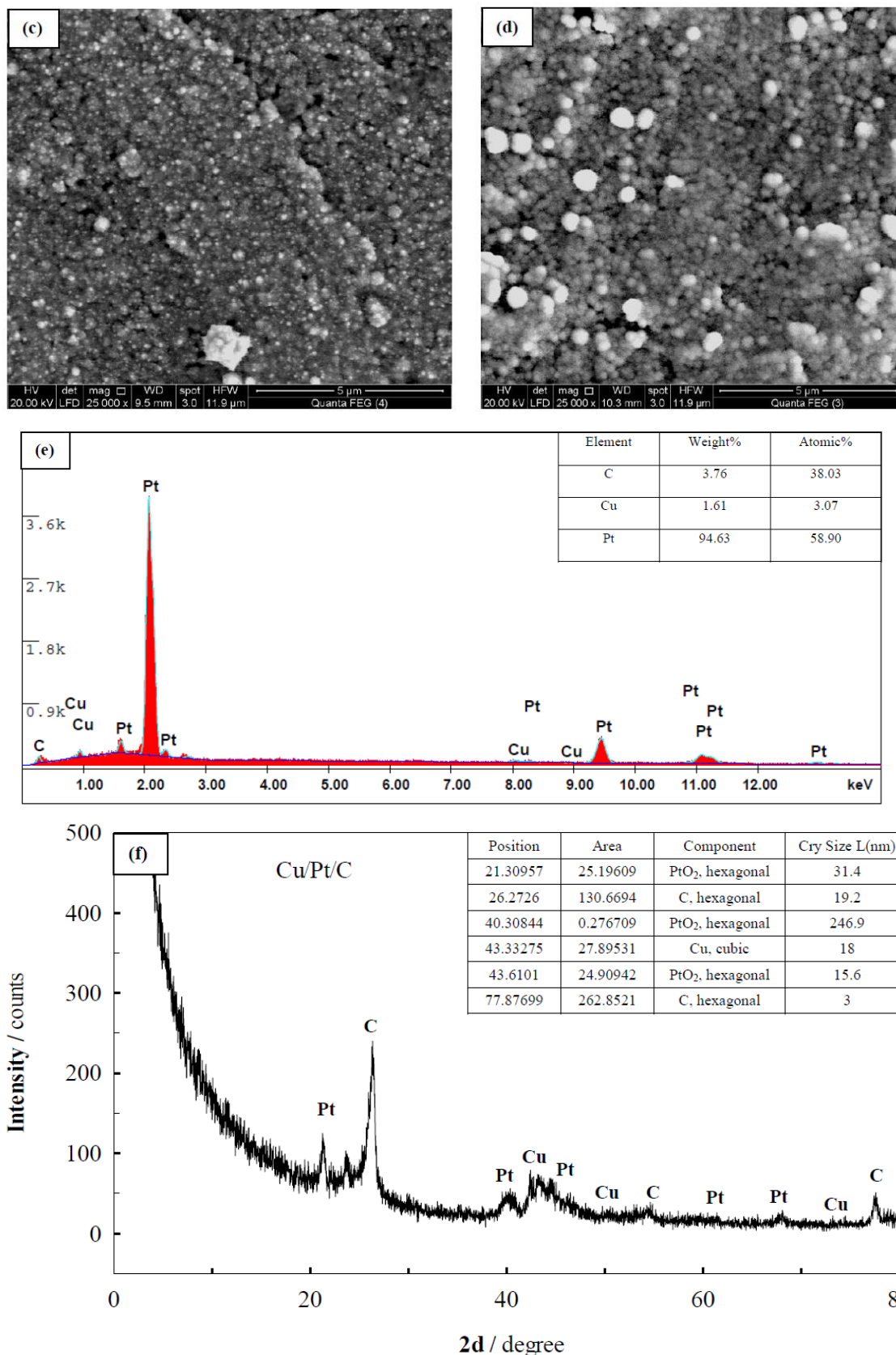


Figure 6. Cyclic voltammograms of (a) Cu/Pt/C and (b) Pt/Cu/C electrodes in 0.5 M H₂SO₄ solution at 50 mV s⁻¹. SEM analyses of (c) Cu(15 min)/Pt(20 min)/C and (d) Pt(20 min)/Cu(20 min)/C electrodes. (e) EDX analysis of Pt(20 min)/Cu(20 min)/C electrode. (f) XRD analysis of Pt(20 min)/Cu(20 min)/C electrode.

The catalytic activity of Ru/C electrode was investigated towards the ORR. Ru was electrodeposited for different times at -0.5 V and the electrochemical behaviour was studied in 0.5 M H₂SO₄ by linear sweep voltammetric technique at a scan rate value of 50 mV s⁻¹ [see Fig. (7 a)]. It is observed that the characteristics of ruthenium appeared after 20 minutes deposition time where peak (I_c) [at +0.870 V] represents the reduction of the higher oxide of ruthenium to the lower oxide. However, another weak cathodic peak (II_c) appears at about +0.260 V could possibly represents the reduction of oxygen that starts with the reduction of ruthenium oxide. The current density value of this peak reflects the low activity of Ru under these experimental conditions. Some researchers also reported the poor activity of Ru [52, 53]. Fig. (7 b) represents the SEM analysis recorded for Ru(20 min)/C and showed that Ru particles in the range of 120-150 nm are distributed randomly over the carbon surface.

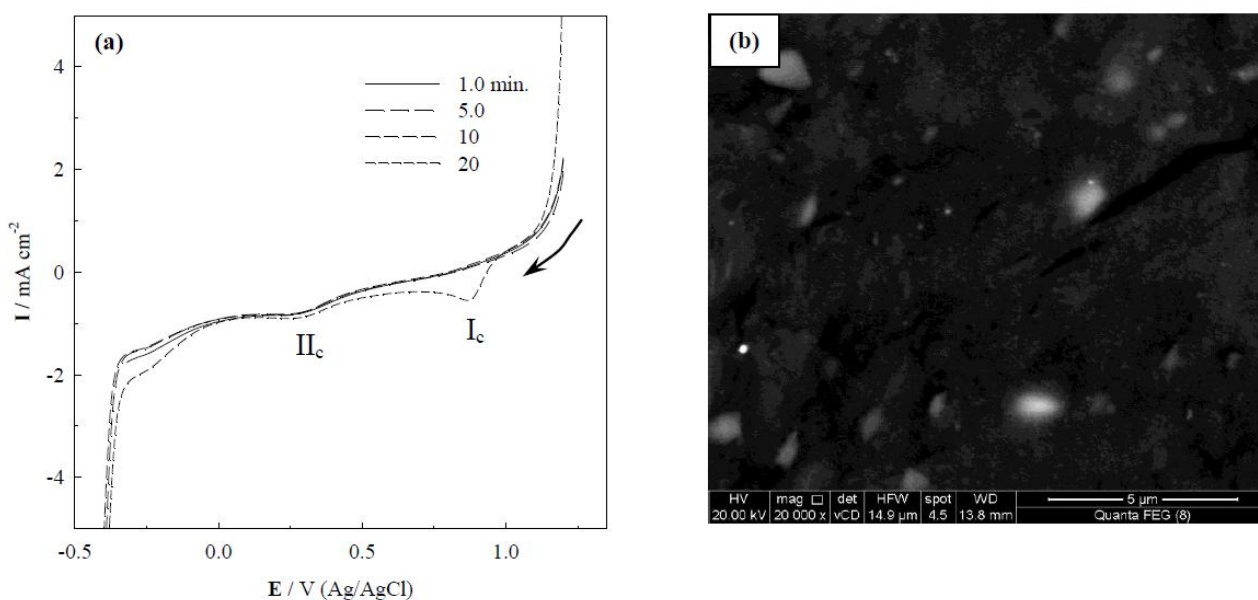
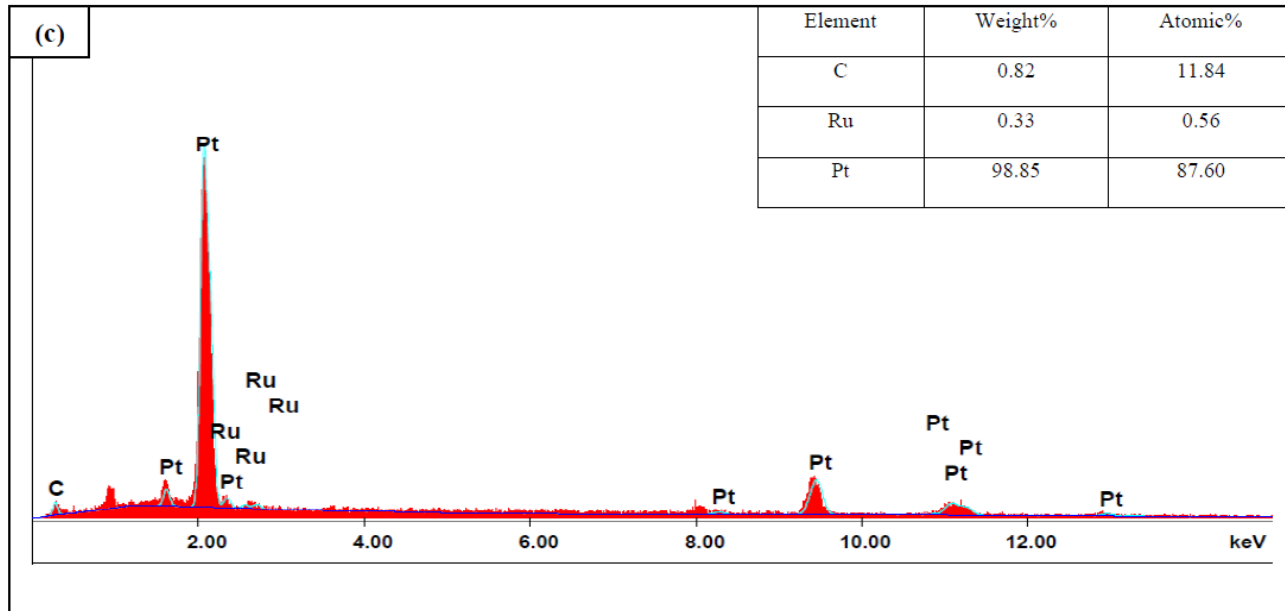
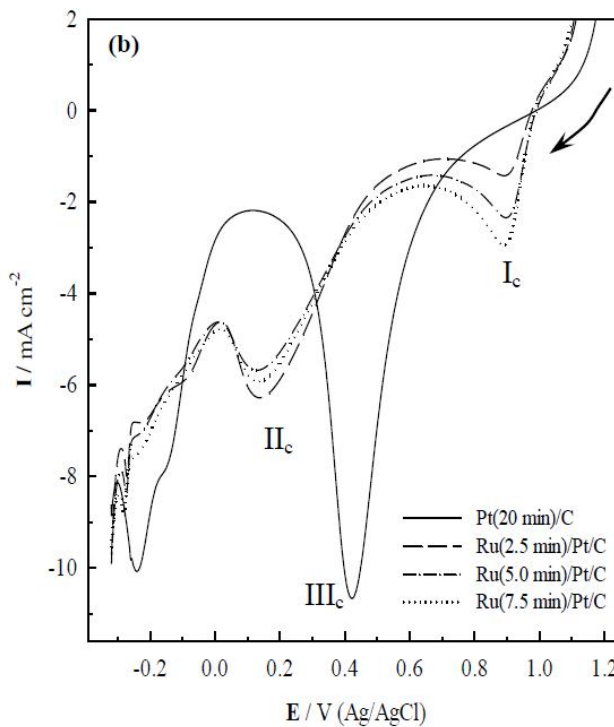
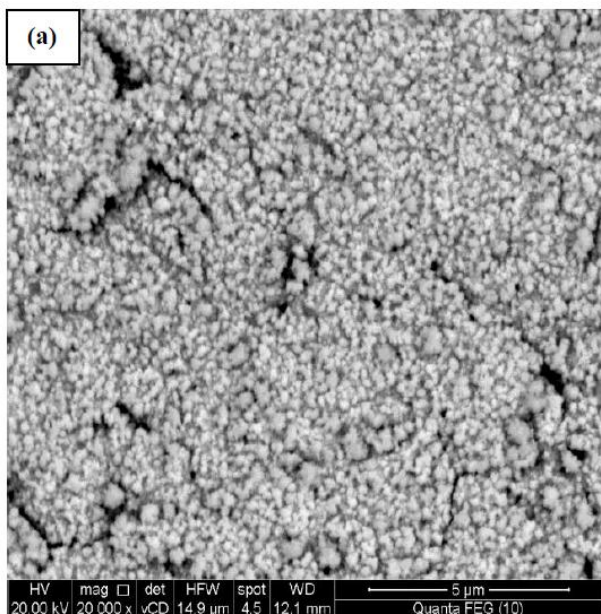


Figure 7. (a) Linear sweep voltammetry of Ru/C electrodes in 0.5 M H₂SO₄ solution at 50 mV s⁻¹. (b) Scanning electron micrograph of Ru(20 min)/C electrode.

The bi-metallic catalyst was prepared by the electrodeposition of both Ru and Pt over the commercial carbon electrode giving Ru/Pt/C. For this electrode, platinum was first electrodeposited potentiostatically at -0.2 V for 20 minutes after which ruthenium was electrodeposited at -0.50 V for different times. SEM, EDX and XRD analyses were recorded for the Ru(5 min)/Pt(20 min)/C modified electrode and represented in Figs. (8) a, c and d, respectively. It is observed from SEM analysis that, a nearly complete coverage of platinum particles surrounded by ruthenium particles in the range of 70-150 nm on the carbon surface with a thickness of about 100 μm. EDX and XRD analyses confirmed the presence of both platinum and ruthenium metals over carbon and their chemical composition is represented inset. The linear sweep voltammetric behaviour of these modified electrodes was studied in 0.5 M H₂SO₄ solution and represented in Fig. (8 b). It is found that, upon deposition of ruthenium over the Pt/C electrode, the reduction peaks of ruthenium appeared at the potential values of about +0.90 V (I_c) and +0.145 V (II_c). The peak current density value of the reduction peak (I_c) is increased with increasing the deposition time of ruthenium. Two important

observations were noticed when comparing the results of oxygen reduction in Fig. (7 a) and Fig. (8 b). The first one is the negative shift in peak potential of oxygen reduction upon the deposition of ruthenium over platinum.



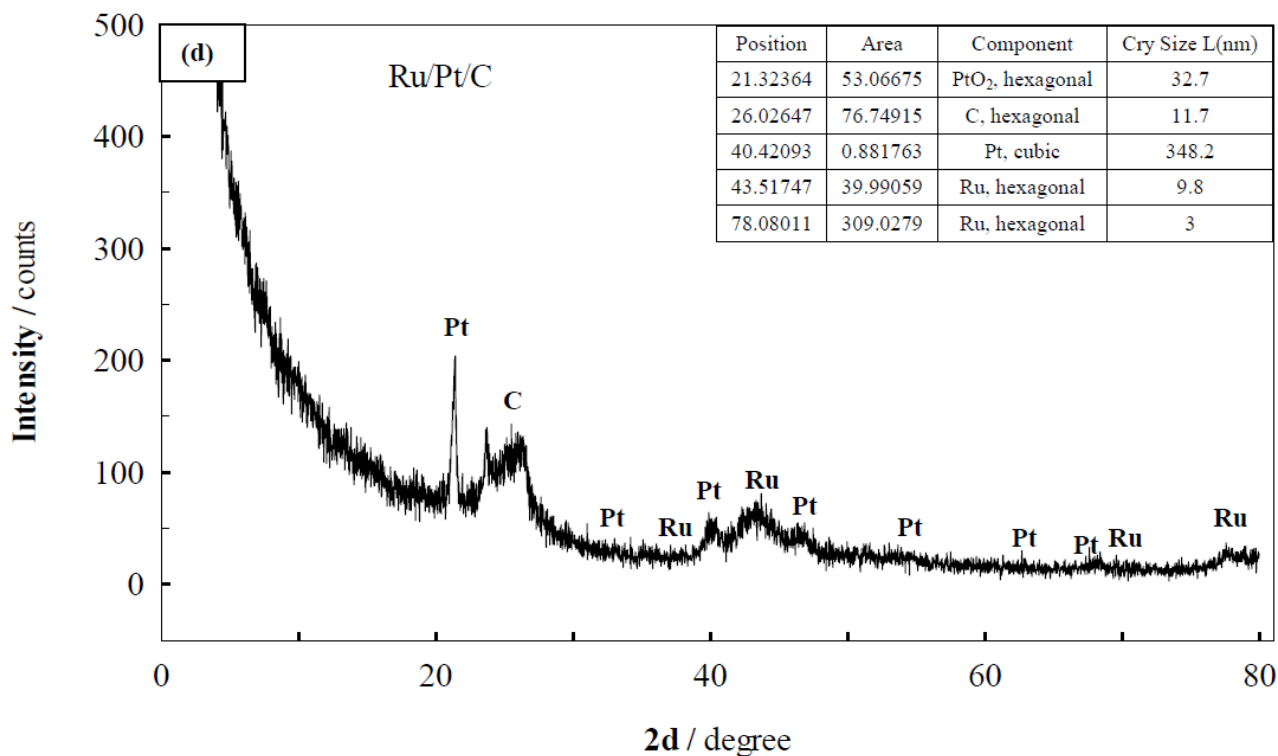


Figure 8. (a) Scanning electron micrograph of Ru(5 min)/Pt(20 min)/C electrode. (b) Linear sweep voltammetry of Ru/Pt/C electrode in 0.5 M H₂SO₄ solution at 50 mV s⁻¹. (c) Energy dispersive X-ray spectrum of Ru(5 min)/Pt(20 min)/C electrode. (d) X-ray diffraction of Ru(5 min)/Pt(20 min)/C electrode.

The second observation is the relative increase of the peak current density values obtained in case of Ru/Pt/C electrode than those obtained in case of Ru/C. This leads to the conclusion that, the activity of ruthenium towards the ORR depends on the substrate. In addition, upon deposition of ruthenium over platinum, the oxygen reduction peak due to the presence of platinum (III_c) is disappeared [see Fig. (8 b)]. Results in this study show that, Ru/Pt/C electrode has a relatively poor activity towards the ORR compared to Pt(20 min)/C. This may be due to the partial coverage of ruthenium particles over platinum deposits, as indicated from the SEM analysis of Fig. (8 a), which could reduce the active surface area of platinum and hence decrease the activity towards the ORR. On the other hand, in alkaline medium, Hosseini et al. [54] reported that the addition of Ru has influenced the catalytic activity of electrocatalyst towards ORR which can be related to synergistic effect.

Palladium is another metal that was investigated to be used to enhance the ORR in H₂SO₄. Pd/C electrode was prepared by the potentiostatic deposition of palladium on carbon electrode at -0.4 V. The behaviour of the Pd/C electrodes, prepared by deposition of Pd on carbon for different times, is studied by linear sweep voltammetric technique in 0.5 M H₂SO₄ at a scan rate value of 50 mV s⁻¹ and represented in Fig. (9 a). It is observed that, the behaviour of this electrode is resembling to that of platinum but with relatively higher current density values for the reduction peaks either at +0.410 V (I_c) that corresponds to the reduction of oxygen or that for the adsorption of hydrogen at -0.05 V (II_c). Hydrogen evolution reaction commences negative to -0.2 V. Liu et al. [55] noticed the same

observations for the polarization of palladium in acid medium. Variation of the reduction peak current density of oxygen (I_c) with the Pd deposition time is represented inset. This result shows that the peak current density value of the reduction of oxygen is increased with increasing the deposition time of palladium. SEM analysis was recorded for Pd(20 min)/C and represented in Fig. (9 b). It shows that noodles shaped particles in the form of trees are located over the carbon surface leading to a high specific surface area.

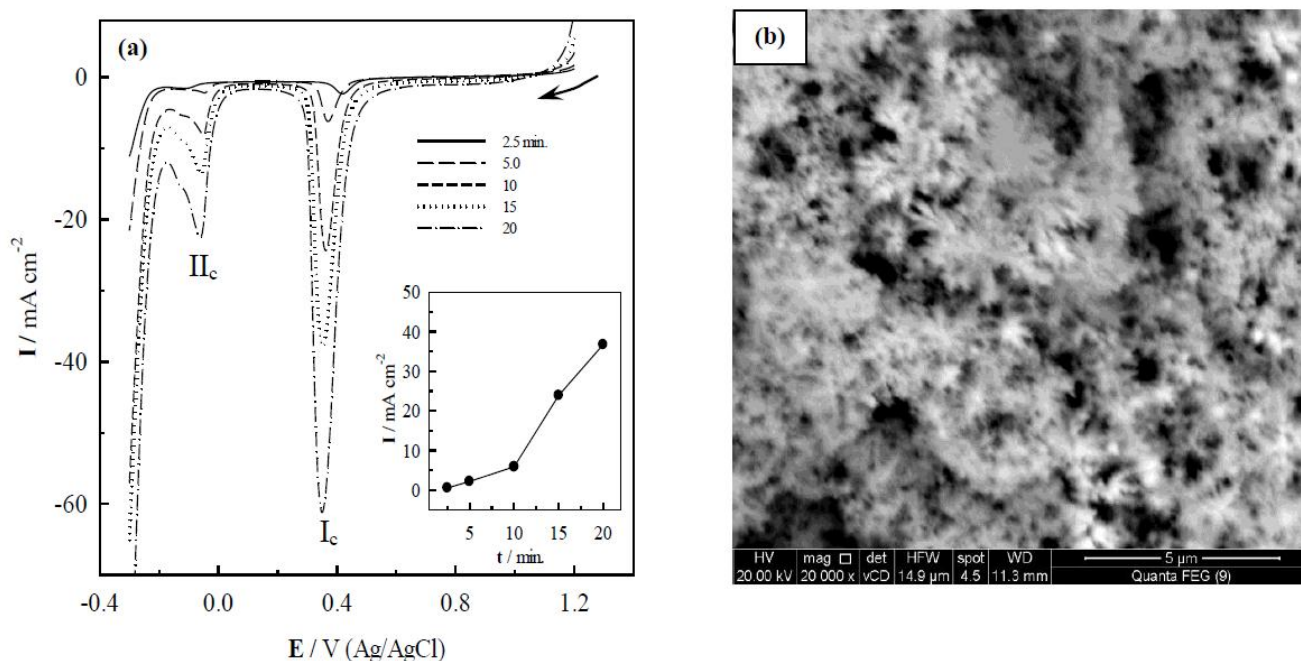
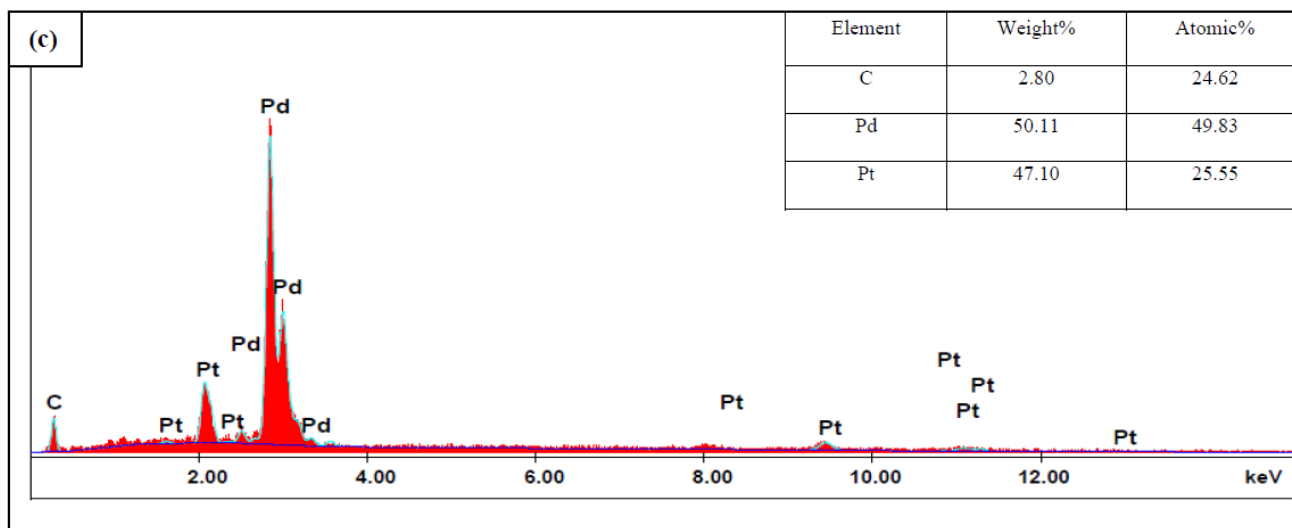
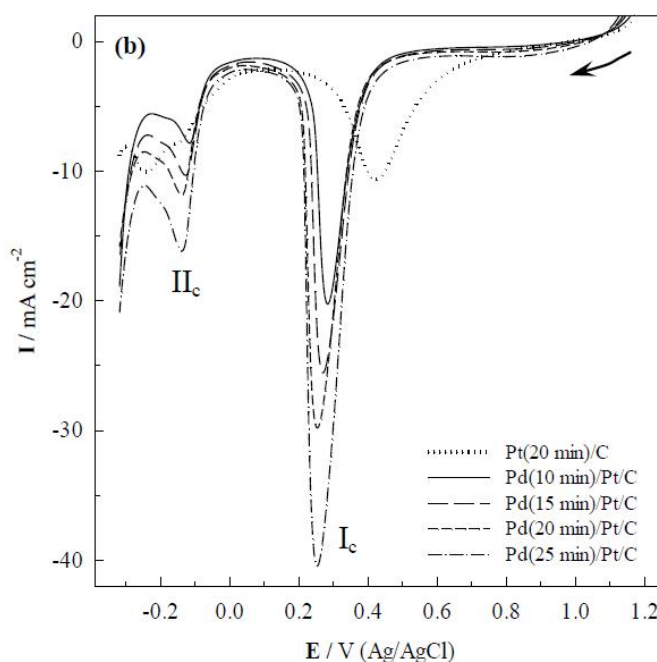
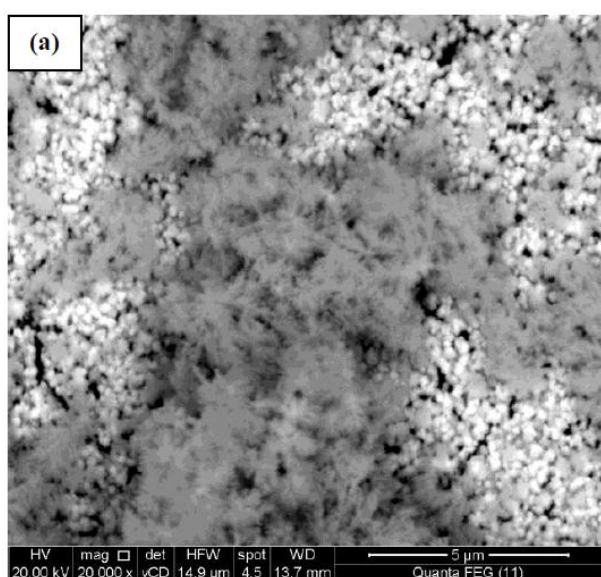


Figure 9. (a) Linear sweep voltammetry of Pd/C electrodes in 0.5 M H_2SO_4 solution at 50 mV s^{-1} . Variation of oxygen reduction peak (I_c) with deposition time is represented in the inset figure. (b) Scanning electron micrograph of Pd(20 min)/C electrode.

The study also was extended to investigate the effect of dispersing palladium on Pt/C electrode on enhancing the catalytic activity towards oxygen reduction. For this purpose, palladium was deposited over Pt/C electrode [platinum is deposited at -0.2 V for 20 minutes] for different times. SEM, EDX and XRD analyses were recorded for Pd(25 min)/Pt(20 min)/C modified electrode and represented in Figs. (10) a, c and d, respectively. It is observed from the SEM analysis that, a nearly complete coverage of platinum particles on the carbon surface and palladium noodles appeared over the dispersed platinum. Both platinum and palladium appeared on the surface which means that it is expected to have the effect of the two metals on the activity of this electrode towards the ORR. EDX and XRD analyses confirmed the presence of both platinum and palladium metals over carbon and their chemical composition is represented inset. The particles of both are found to be in the range of 50-130 nm with about $150 \mu\text{m}$ thickness. The thickness of Pd-Pt layer is demonstrated from SEM analysis by recording the image from the side of the electrode as represented in Figs. (10 e). The linear sweep voltammetric behaviour of these modified electrodes was studied in 0.5 M H_2SO_4 solution and represented in Fig. (10 b). It was also found that, the current density values of Pd-oxide

reduction peak (I_c) [that is equivalent to the reduction of oxygen] are increased with increasing the deposition time of palladium. A similar observation was also made for the increase of the oxygen reduction peak current density with the increase of Pt/Pd deposition cycles [56]. Obviously, the Pd/Pt/C electrodes showed an enhanced catalytic performance than Pd/C. This can be concluded based on two important observations that are seen in Fig. (10 b). The first one is shift of the onset and the half wave potential of ORR at the Pd/Pt/C electrodes. The second one is the increase of the peak current density of oxygen reduction at the Pd/Pt/C electrodes relative to that at the Pt/C electrode. From the result of Fig. (10 b), Pd(25 min)/Pt(20 min)/C modified electrode showed higher current density value for oxygen reduction than that obtained at platinum alone (the Pt/C modified electrode). This indicates that the presence of palladium over platinum/carbon enhances the catalytic activity of platinum towards the oxygen reduction reaction.



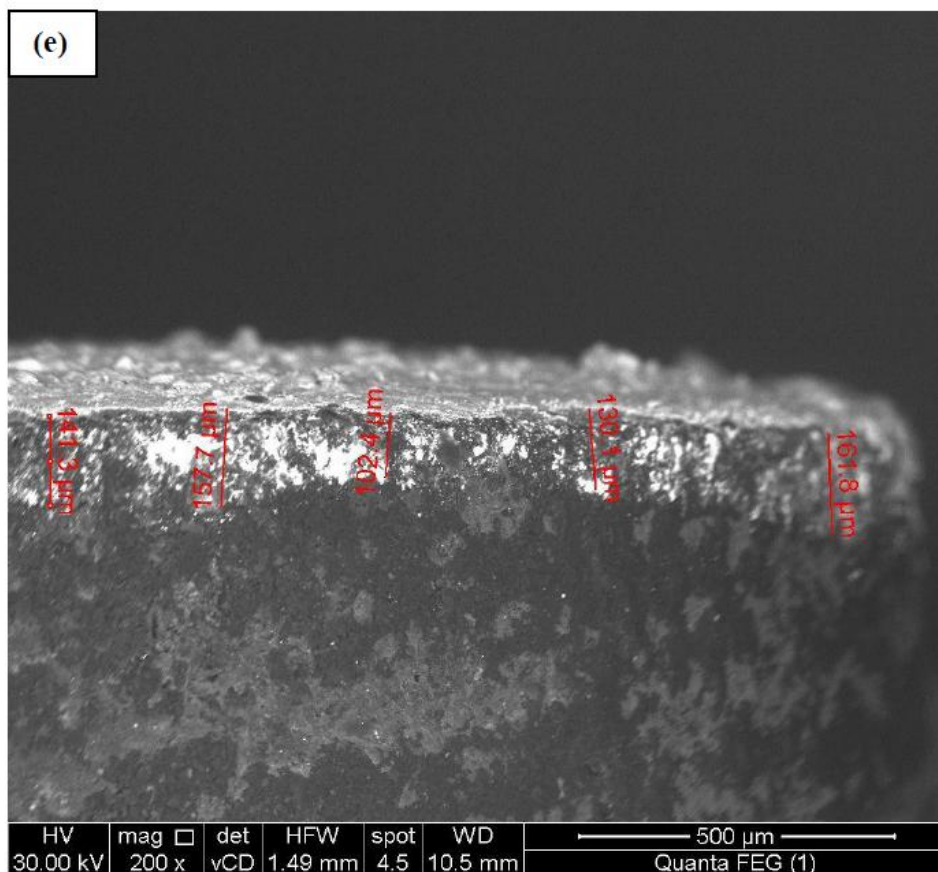
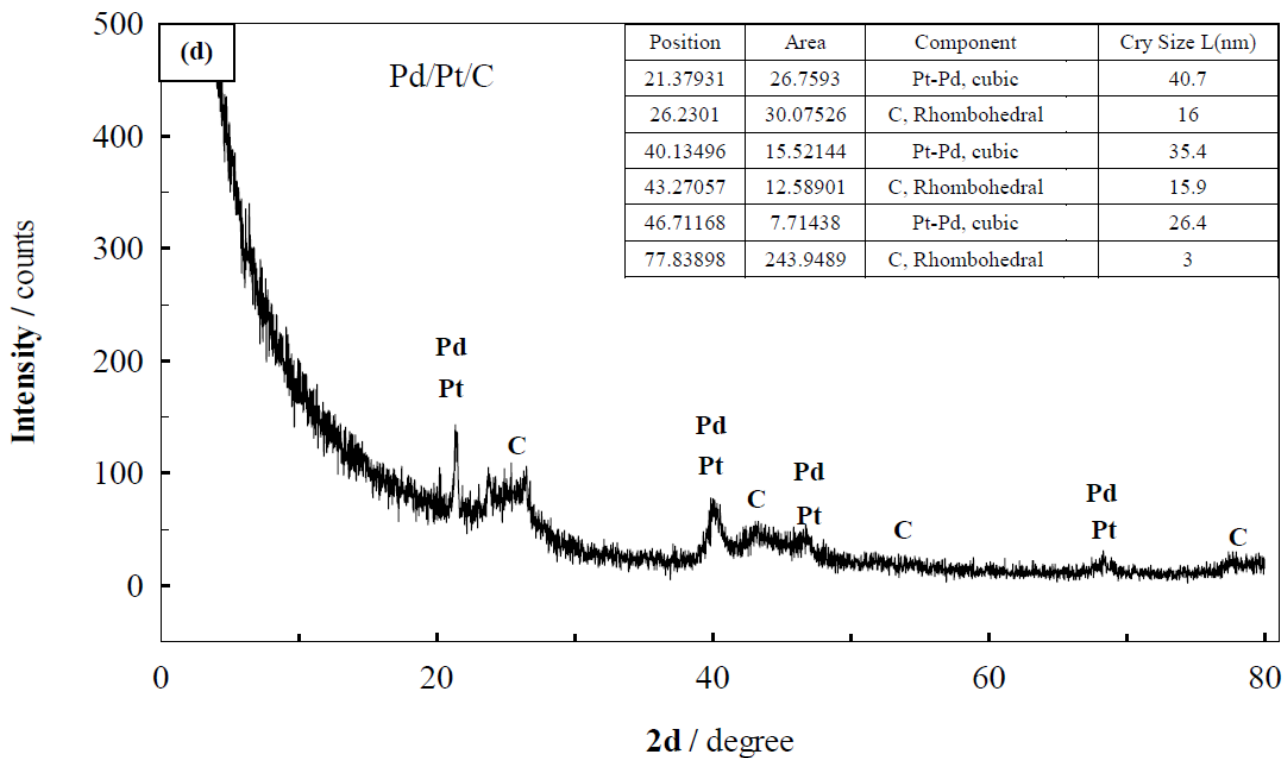


Figure 10. (a) Scanning electron micrograph of Pd(25 min)/Pt(20 min)/C. (b) Linear sweep voltammetry of Pd/Pt/C electrode in 0.5 M H₂SO₄ solution at 50 mV s⁻¹. (c) Energy dispersive X-ray spectrum of Pd(25 min)/Pt(20 min)/C electrode. (d) X-ray diffraction of Pd(25 min)/Pt(20 min)/C electrode. (e) Scanning electron micrograph of Pd(25 min)/Pt(20 min)/C from the electrode side.

The catalytic performances of all prepared types of electrodes towards ORR, in the form of oxygen reduction peak current density values, in 0.5 M H₂SO₄ are represented in the following table (1) for comparison.

Table 1. The peak current density values of oxygen reduction at different prepared electrodes.

Electrode type	Values of the peak current density of oxygen reduction (mA cm ⁻²)
Massive platinum	0.445
Pt(20 min)/C	9.247
Cu(15 min)/Pt(20 min)/C	13.854
Pt(25 min)/Cu(20 min)/C	9.953
Ru(2.5 min)/Pt(20 min)/C	2.473
Pd(20 min)/C	44.049
Pd(25 min)/Pt(20 min)/C	38.807

It is shown from this table that the best catalytic performance towards ORR is achieved using the electrode prepared by the electrodeposition of palladium either over carbon (Pd/C) or over platinum electrodeposited on the carbon electrode (Pd/Pt/C). Comparing the data recorded for the modified electrodes prepared by Pt and Cu, it is concluded that deposition of copper over platinum is more preferred for the performance of the catalytic activity towards the ORR than deposition of platinum over copper.

4. CONCLUSION

Potentiostatic deposition of various metals as platinum, copper, ruthenium and palladium over commercial carbon electrode proves to be an acceptable method for preparing various mono- and bi-metallic catalysts for the electro-reduction of oxygen in acid medium. Deposition of platinum over carbon showed good catalytic enhancement towards the ORR compared to massive platinum. Palladium as well as consecutive dispersing of palladium and platinum showed the best performance as mono- and bi-metal catalyst towards ORR compared to other modified electrodes. Electrode prepared by the electrodeposition of copper over Pt/C comes in the second place. Dispersion of platinum with ruthenium deposition doesn't show good catalytic performance towards the ORR compared to other modified electrodes.

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