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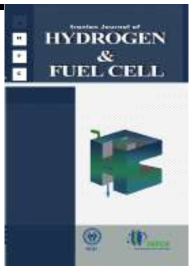

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Platinum nanoparticles/functionalized carbon nanoparticles composites supported on the carbon-ceramic electrode and their electroactivity for ethanol oxidation

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Abstract

The electrocatalytic oxidation of ethanol was studied for the platinum nanoparticles/functionalized carbon nanoparticles composites supported at the carbon-ceramic electrode (PtNPs/tosyl-CNPs/CCE) as an electrocatalyst in acidic medium. The PtNPs/tosyl-CNPs/CCE electrocatalyst was synthesized by electrodeposition of PtNPs on/in casted tosyl-CNPs at the CCE. The characterization of the fabricated nanocomposite was done by X-ray powder diffraction (XRD) spectroscopy, field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray (EDX) spectroscopy. The obtained electrocatalytic oxidation of ethanol was studied by cyclic voltammetry and chronoamperometry techniques. The results showed that the PtNPs/tosyl-CNPs/CCE was electrocatalytically more active than PtNPs/CCE and had high anodic peak current densities, low onset potential, low poisoning and high stability. Hence, the proposed nanocomposite, PtNPs/tosyl-CNPs/CCE, can be extended as an attractive and promising electrocatalyst for the ethanol electrooxidation reaction in fuel cells.

1. Introduction

Direct ethanol fuel cells (DEFCs) have great mass energy density. Compared with other fuels, ethanol can be handled, transmitted and stored easily [1-3] and has features and specifications such as being less permeable through polymeric membranes as well as cost-effective and having a higher boiling point

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and low toxicity [4-6]. So that, in previous decades, the peruse of electrooxidation of ethanol and the fabrication of a direct ethanol fuel cell has attracted a lot of studies [7, 8]. As reported in the literature, the ethanol oxidation reaction mechanism is much more complex due to the fact that the complete oxidation of ethanol evolves into the cleavage of the carbon-carbon bond and transfer of twelve electrons. Therefore, ethanol electrooxidation at a lower temperature requires more active electrocatalysts [9]. Up to now, platinum (Pt) and platinum-based alloys have been the most widely used catalysts for ethanol oxidation reactions (EOR) [10, 11], e.g., Pt [12], Pt/Ni [13], PtPd [14-16], PtSn/C [17-20], PtRu/C [21, 22], PtRh/SnO_2 [23] and so on. However, problems such as CO poisoning on the Pt electrocatalyst becomes an important as well as controversial issue and controversial because it reduces the number of active reaction site available and breaks the carbon-carbon bond in larger alcohol molecules needed for high energy. Therefore, it is necessary to use new types of electrocatalysts to improve the speed of ethanol oxidation, and new supports for electrocatalysts to reduce the amount and the cost. Actually, choosing the right material to support Pt electrocatalysts is an essential component that may affect owing to their interactions and surface [24-26]. A Pt based catalyst supported on carbon is one of the most studied systems [1, 27-30]. Size and distribution of the electrocatalyst nanoparticles can be optimized by using suitable support materials. The prominent features of carbon materials, such as their tuneable form, porosity, chemical stability, corrosion resistance, low-priced, size, good thermal resistance, electrical conductivity and chemical stability, have made them very interesting to researchers. Carbon nanomaterials come in several forms and structures, such as carbon nanotubes (MWCNT and SWCNT) [3, 31-36], nanostructured carbon black [37-40], carbon nanofibers [41-45], mesoporous carbon [46, 47] and graphene oxide[48-52], and have been found to be good supports for metal nanoparticles catalysts.

In this work, the platinum nanoparticles (PtNPs) supported on/in tosyl functionalized carbon nanoparticles (tosyl-CNPs) at the carbon-ceramic electrode (CCE) as a homemade substrate was used as an electrocatalyst for ethanol oxidation. The physicochemical features of the PtNPs/tosyl-CNPs/CCE were characterized employing different techniques including X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and field emission scanning electron microscopy (FE-SEM); its electrocatalytic activity during ethanol electrooxidation was comprehensively studied with cyclic voltammetry and chronoamperometry methods. It was found that PtNPs/tosyl-CNPs/CCE was electrocatalytically more active than a Pt-alone nanoparticles modified carbon-ceramic electrode and had satisfactory stability and acceptable stability and reproducibility during continuous cycling or when stored in ambient conditions.

2. Experimental

2.1.Chemicals

Carbon nanoparticles with surface tosyl groups (tosyl-CNPs) were purchased from Cabot (ca. 9 to 18 nm diameters) Emperor 2000™, Cabot Corporation. Methyltrimethoxysilane (MTOS), ethanol, methanol, H_2SO_4, HCl, $H_2PtC_{16}.5H_2O$ and graphite powder of high purity were purchased from Merck or Fluka. Doubly distilled water was used throughout the experiments.

2.2.Preparation of PtNPs/CCE and PtNPs-CNPs/CCE

A carbon-ceramic electrode, as a substrate for the electrocatalyst, was prepared by the sol-gel method. The proposed electrocatalysts were prepared in three steps: in the first step, a portion of 0.9 ml MTMOS was mixed with 0.6 ml methanol. Then, 0.6 ml HCl 0.1 M was added as a catalyst and the mixture was stirred with a magnetic stirrer for 45 minutes until the solution became clear. Next, 0.3 g graphite powder was added to the contents and the resulting mixture was shaken manually for 20 minutes. The obtained uniform and homogeneous mixture was packed into a Teflon tube with an internal diameter of 3 mm and a length of 10 mm and dried for 24 hours at ambient temperature. A copper wire was used to make connections and the surface of this electrode was prepared before each use with 1500 emery paper, mechanical polishing occurred. In the second step, to obtain a stable suspension 1 mg of tosyl-CNP was added to 1 ml of deionized water and homogenized by sonication for 15 minutes. Then, 20 µl of this suspension was cast on the surface of the electrode prepared in the first step and dried in the air to remove solvent for 20 min at room temperature [53, 54]. Finally, in the third step, the PtNPs were electrodeposited with -0.3 V potential in an aqueous solution of 0.1 M H_2SO_4 containing $H_2PtC_{16}.5H_2O$ at 25 ºC in/on the surface of the tosyl-CNPs/CCE. The PtNPs were prepared in a similar manner for electrodeposited on the surface of bare CCE [55].

2.3.Instrumentation

An AUTOLAB PGSTAT-100 (potentiostat/galvanostat) equipped with a USB electrochemical interface and a driven GEPS software were used for the electrochemical experiments in a conventional three-electrode electrochemical cell at room temperature. The modified electrode (PtNPs/CCE, PtNPs/tosyl-CNPs/CCE) was used as the working electrode. A platinum wire and a saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively. Energy-Dispersive X ray spectroscopy (EDX) and Field Emission Scanning Electron Microscopy (FE-SEM) were performed on a LEO 440i Oxford instrument. XRD measurements of the PtNPs/ tosyl-CNPs was investigated using a Brucker AXF (D8 Advance) X-ray power diffractometer with a Cu-Ka radiation source (l = 0.154056 nm) generated at 40 kV and 35 mA.

3. Results and discussion

3.1.Physical characterization

The surface morphology and chemical structural characterizations of the tosyl-CNPs/CCE and PtNPs/tosyl-CNPs/CCE were done by FE-SEM and EDX. FE-SEM images of the surface of the tosyl-CNPs/CCE and PtNPs/tosyl-CNPs/CCE are presented in Fig. 1.A and 1.C, respectively. Highly magnified FE-SEM images of the same materials are presented in Fig.1.B and 1.D, respectively. As can be seen in image A, the casting of tosyl-CNPs suspension on the surface of CCE resulted in a completely rough surface which increases the area of the substrate surface and provides a high surface for metal NPs electrodepositions. Fig. 1.B of the carbon nanoparticle material confirms a particle size in the range of 10-50 nm radiuses. Image C shows the electrodeposited of PtNPs on/in tosyl-CNPs/CCE. Fig. 1.C and 1.D display PtNPs in the form of clusters anchored on the film of tosyl-CNPs. Due the electrodeposition of the PtNPs, an increase in the area of the electrocatalyst surface and consequently in its electrocatalytic activity occurred. This shows the deposition of PtNPs on/in the tosyl-CNP particles at the surface of carbon-ceramic electrode was achieved. Fig. 1.F shows the corresponding EDX spectrum of the PtNPs/tosyl-CNPs/CCE. The presence of Pt peaks in the spectra confirms the presence of PtNPs in the nano-composite [56, 58].

The XRD pattern of the obtained nano-composite is presented in Fig. 1.E. In the XRD pattern, the peak appearing at 2θ value of ca. 26.6° is related to the hexagonal graphite plane (002) of carbon originating from the carbon nanoparticles support [56, 57]. In addition, peaks of face center cubic (fcc) crystalline platinum particle crystals in the XRD patterns were observed at ca. 39.9°, 46.4° and 67.6° with the planes (111), (200) and (220), respectively.

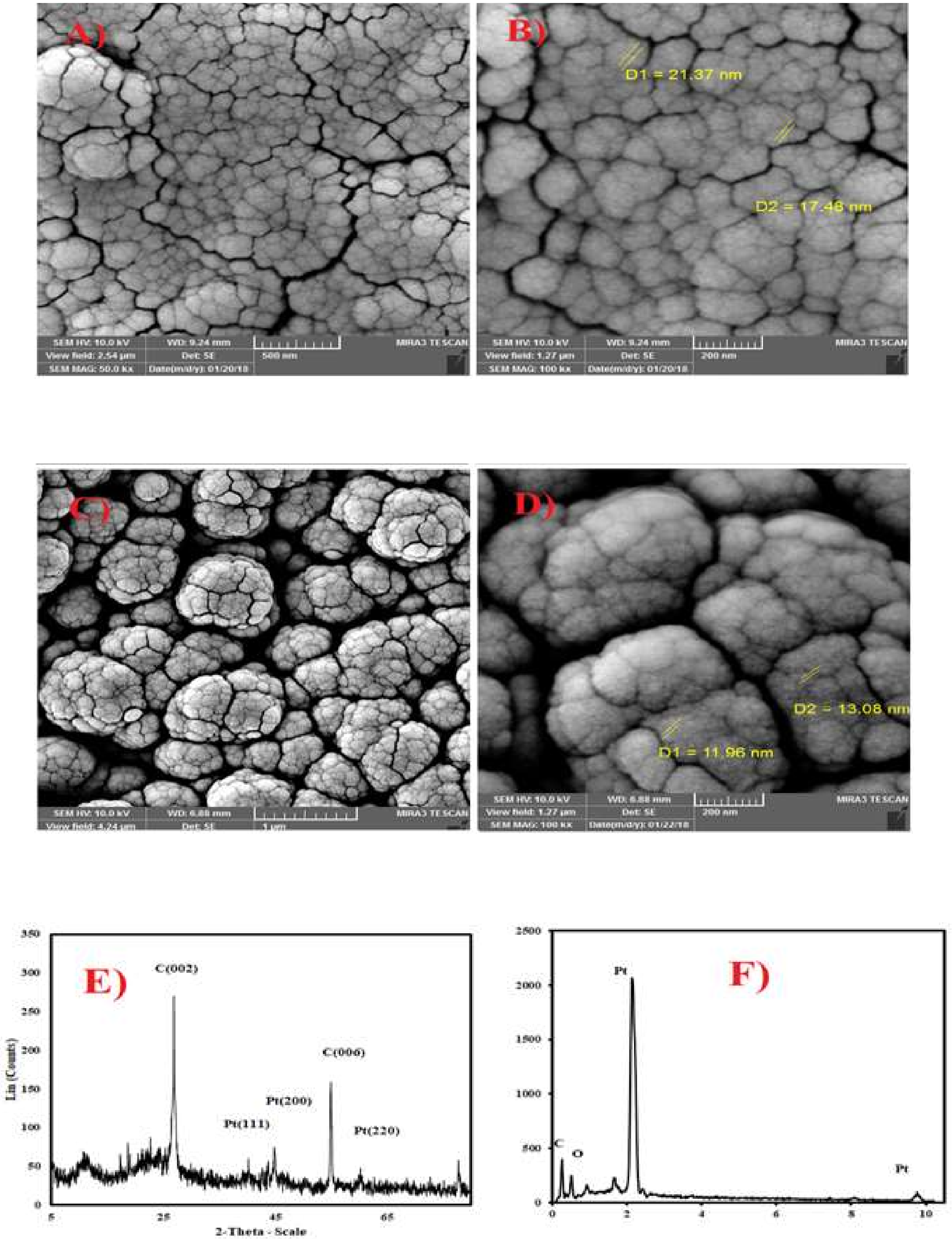

Fig. 1. SEM images of A) tosyl-CNPs/CCE, B) HRSEM image of of tosyl-CNPs/CCE, C) PtNPs/tosyl-CNPs/CCE, D) PtNPs/tosyl-CNPs/CCE, E) XRD spectra of PtNPs/tosyl-CNPs, and F) EDX analysis of PtNPs/tosyl-CNPs.

3.2.Electrochemical characterization

The cyclic voltammetry technique was used to examine the electrochemical behavior of the PtNPs/tosyl-CNPs and PtNPs modified CCE in 0.1 M H_2SO_4 aqueous solution within the potential range between -0.3 and 1.3 V. Firstly, cyclic voltammograms (CVs) of the bare CCE (curve a), PtNPs/CCE (curve b) and PtNPs/tosyl-CNPs/CCE (curve c) are shown in Fig. 2. In the figure (curves b and c), two pairs of peaks (I/I' and II/II') in negative potential regions and a pair of peaks (III/III') in a positive potential region are observed. The oxidation and reduction peak pairs (I/I' and II/II') correspond to the adsorption/desorption of hydrogen and the third pair of peaks (III/III') is related to the formation of platinum oxides and their reduction on the electrocatalysts surface. This is analogous to the behavioral patterns reported by Breiter et al. [59].

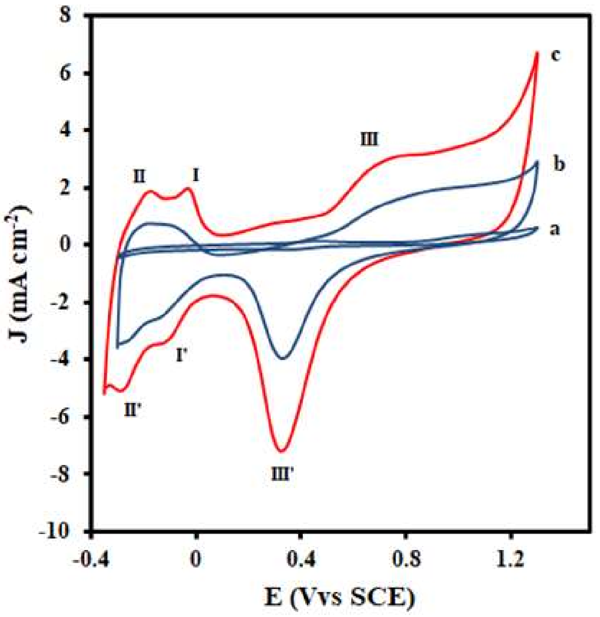

Fig. 2. Cyclic voltammograms of CCE (curve a), PtNPs/CCE (curve b), and PtNPs/tosyl-CNPs/CCE (curve c) in 0.1 M H_2SO_4 at a scan rate of 50 mV/ s^{-1}.

The most important physical property of this type of electrocatalyst is the number of active sites available or actual active surface area (Ar). The actual active surface area of the PtNPs/tosyl-CNPs is equivalent to the number of Pt sites available for hydrogen adsorption/desorption [52]. Hence, the calculation of actual active surface area (A_r) of the modified electrode with PtNPs/tosyl-CNPs is obtained from the charge for hydrogen adsorption. A_r can be determined from the following equation:

$A_r = Q_H / Q_o$

Where Q_o is the charge for a monolayer adsorption of hydrogen on the surface of Pt (210μC/ real cm^2) and Q_H is the coulombic integrated charge associated with the hydrogen adsorption region (μC). The A_r value was 5.428 cm^2 mg^{-1} for PtNPs/tosyl-CNPs.

As can be seen in Fig. 2 curve a, these phenomena do not appeared on the bare CCE due to the absence of PtNPs.

3.3.Electrocatalytic activity of the PtNPs/tosyl-CNPs/CCE toward ethanol oxidation

The electrocatalytic activity of the ethanol oxidation of PtNPs/tosyl-CNPs/CCE toward the ethanol oxidation was evaluated by cyclic voltammetry in 0.3 M ethanol and 0.1 M H_2SO_4 electrolyte at 50 mV s^{-1}. Fig. 3 shows the CVs of ethanol on the bare CCE (curve a), PtNPs/CCE (curve b), and PtNPs/tosyl-CNPs/CCE (curve c) electrocatalysts, respectively.

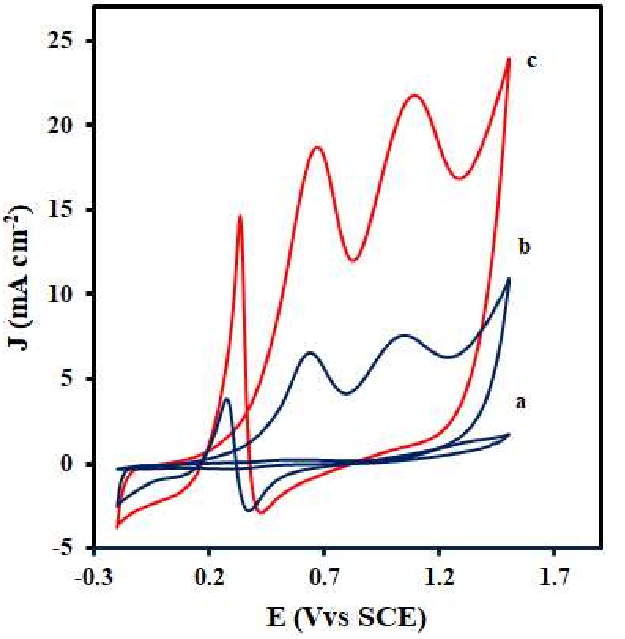

Fig. 3. CVs of the 0.3 M ethanol on the CCE (curve a), PtNPs/CCE (curve b), and PtNPs/tosyl-CNPs/CCE (curve c) in 0.1 M H_2SO_4 at a scan rate of 50 mV s^{-1}.

As shown in Fig. 3, CVs of ethanol oxidation in the acidic media have two peaks in the forward scan and one in the backward scan. The first anodic peak is related to the oxidation of chemical absorption ethanol molecules on the electrocatalystsurface. The second peak is related to the complete oxidation of a number of intermediates formed during the oxidation of ethanol [60]. Also, the cathodic peak is related to the ethanol adsorbates re-oxidation.

Fig. 3 displays that the onset potentials of ethanol electrooxidation on the PtNPs/tosyl-CNPs /CCE and PtNPs/CCE electrocatalysts are about 0.19 V and 0.37 V versus SCE. From the comparison of the CVs of curve b and c in Fig. 3, it is evident that the two electrocatalysts exhibit the same properties, except that the peak currents density in the anodic going potential scan on the PtNPs/tosyl-CNPs electrocatalyst are much higher than the peak currents density on the PtNPs electrocatalyst. In addition, the onset potential for ethanol electrooxidation is an important index for the determination of electrocatalytic activity It should be noted that the onset potential for PtNPs/tosyl-CNPs/CCE has shifted toward negative potentials. This result illustrates that the prepared nanocomposite could present a favorable activity toward the oxidation of ethanol. Additionally, these results demonstrate that the tosyl-CNPs, a three-dimensional structure, used as a support of PtNPs facilitates the electron transfer kinetics for the electrode reactions. The high electronic and ionic transport capacity of the tosyl-CNPs film on the electrode surface highly favors the electron transfer for the electrooxidation of ethanol [3]. Also, the enhanced performance of PtNPs is attributed to better mass transport inside the tosyl-CNPs, a highly conducting network, good dispersion of ultrafine PtNPs on/in the tosyl-CNPs, higher utilization of PtNPs, and finally higher electrochemical activity of the PdNPs, suggesting that PtNPs/tosyl-CNPs/CCE is a good electrocatalyst for ethanol electrooxidation in acidic media. Conversely, according to curve a, no obvious peak for ethanol oxidation was observed on the bare CCE.

4. Parameters affecting the ethanol electrooxidation

4.1. Effect of ethanol concentration

The amount of fuel concentration used can have a direct effect on the electrocatalyst performance. Therefore, the concentration of fuel was inspected by the cyclic voltammetric method and the optimum concentration for highest activity was determined. Fig.4.a shows the anodic peak current density versus the fuel concentration. It is obvious; the ethanol concentration increases as the anodic peak current density increases until the ethanol concentration reaches 1.8 M, then the anodic peak current density remains constant. This is due to saturation of the active sites of the electrocatalyst surface by ethanol molecules at higher concentrations. A plot of the logarithm of anodic peak current density versus the logarithm of ethanol concentration is demonstrated in Fig. 4B. There is a linear relationship between them. From the slope of the obtained line, the reaction order is calculated according to the equation below:

Rate α $J = kC^n$

$\log J = \log k + n \log C$

Where J is the anodic peak current density, k is the reaction rate constant, n is the reaction order, and C is the bulk concentration of ethanol. The slope of the acquired line is equal to 0.415 and indicates the reaction order for ethanol electrooxidation.

4.2.Influence of upper limit potentials (EU) (anodic reversal potential)

The effect of upper limit potentials (EU) on ethanol electrooxidation was studied to inspect the relationship between fuel electrooxidation and the formation of Pt oxide species. CVs of ethanol oxidation on the PtNPs/tosyl-CNPs/CCE for EU of +0.8 to +1.5 V were shown in Fig. 5. As can be seen in Fig. 5, increasing the final positive potential limit causes both the anodic peak potential (E_{pa}) and anodic peaks current density (J_{pas}) from the oxidation of ethanol on the PtNPs/tosyl-CNPs/CCE to remain

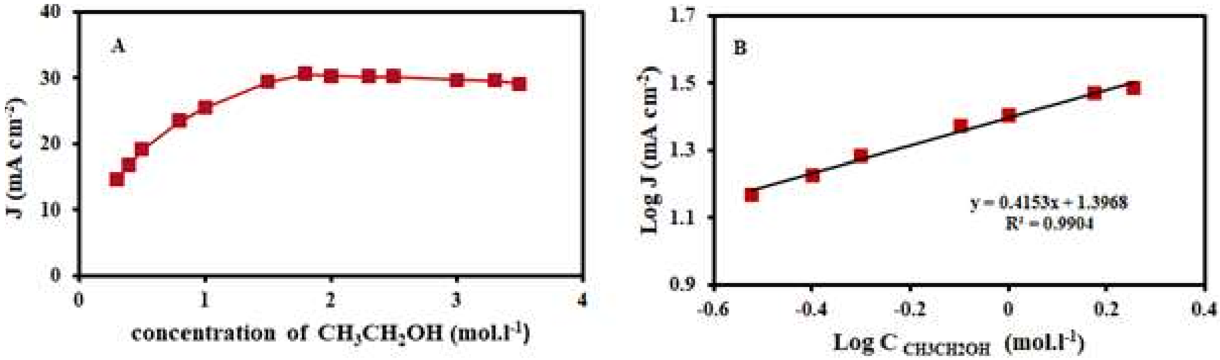

Fig. 4. A) Plot of anodic peak current density vs concentration of ethanol in 0.1 M H_2SO_4 at room temperature, B) The logarithm of anodic peak current density (logJ) versus the logarithm of ethanol concentration (logC).

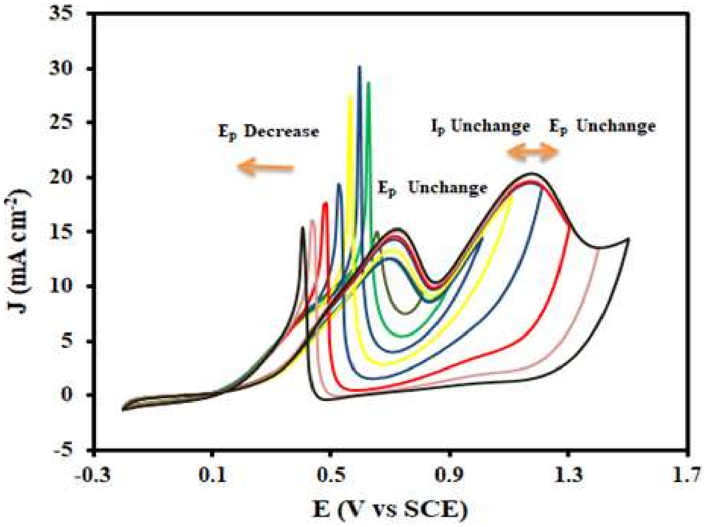

Fig. 5. Effect of upper limit of potential scanning region on the electrooxidation of 0.3 M ethanol on the Pt/ tosyl-CNPs /CCE in 0.1 M H_2SO_4–0.2 →0.8V, –0.2→0.9V, –0.2→1.0V, –0.2→1.1V, –0.2→1.2V, –0.2→1.3V ,–0.2→1.4V ,and –0.2→1.5V at a scan rate 50 mV s^{-1}.

nearly constant, while the anodic peak current density in the backward scan is reduced. The reason for the reduction in the peaks current density in the backward scan is that the accumulation of species produced in the forward scan on the catalyst surface decrease with shifts of final potentials toward more positive values. As a result, the lower interfaces are absorbed on the surface of the electrocatalyst in the backward scan [61, 62].

4.3. Effect of scan rate

The effect of the scan rate on the electrochemical response of 0.3 M ethanol in 0.1 M H_2SO_4 solution at the PtNPs/tosyl-CNPs/CCE utilizing cyclic voltammatric method was studied. The CVs of the ethanol electrooxidation at various scan rates (10-500 mV s^{-1}) are exhibited in Fig. 6. As seen in Fig. 6, the oxidation peaks current density increase as the scan rate increases. In Fig. 6.b, the anodic peak current density (J_{Pa}) in the forward scan vs the square root of the scan rate ($v^{1/2}$) indicates that there is a linear relationship between them and the electrocatalytic reaction on the surface of the PtNPs/tosyl-CNPs/CCE electrocatalyst is controlled by the diffusion process [63].

4.4. Long-term stability of the PtNPs/tosyl-CNP/CCE electrocatalyst

The electrocatalytic activity and stability of the PtNPs/tosyl-CNPs/CCE electrocatalyst was further confirmed via chronoamperometry experiments. To draw the curves of the cronoamorometry, the applied

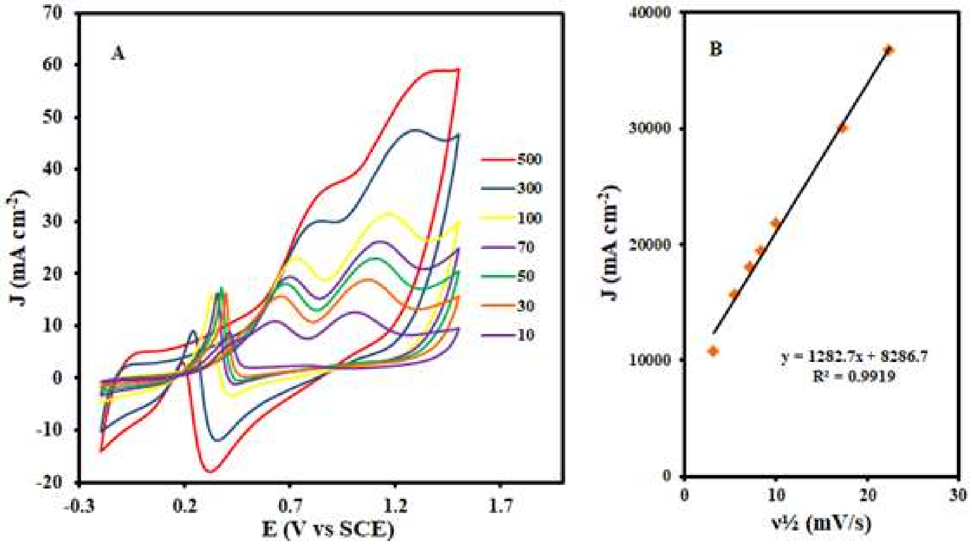

Fig. 6. A) CVs of the PtNPs/tosyl-CNPs/CCE in 0.1M H_2SO_4 containing 0.3 M ethanol at various scan rates, B) Relationship between the forward anodic peak current and square root of the scan rates.

potential of the electrocatalyst is fixed at a constant amount and current density variations are recorded with time. Fig. 7.a shows the chronoamperograms of 0.3 M ethanol in 0.1 M H_2SO_4 on the PtNPs/tosyl-CNPs/CCE and the PtNPs/CCE at 0.6 V for 2000 s. The results illustrate that the current density indicate less decay at the surface of PtNPs/tosyl-CNPs/CCE for a long duration in ethanol electrooxidation.

To study the effect of continuous cycling in the repeated scans, continuous CVs of 150 cycles in a solution containing 0.1 M H_2SO_4 and 0.3M ethanol were investigated. Anodic peak current density (% Jpa) vs cycles numbers are shown in Fig.7.b. Fig.7.b. indicates that when increasing the number of scan cycles the anodic peak current density of PtNPs/tosyl-CNP/CCE for ethanol oxidation is first enhanced by continuous cycling and then remains constant. It is concluded that due to the presence of tosyl-CNP, PtNPs/tosyl-CNPs/CCE electrocatalyst exhibits high long-term stability.

5. Conclusion

In summary, in this work a new electrocatalyst has been developed for the electrocatalytic oxidation of ethanol in acidic media by electrodeposition of PtNPs on/in carbon nanoparticles with surface tosyl groups (tosyl-CNPs) as a support. The effect of the tosyl-CNPs as a support on the electrocatalytic activity of the PtNPs was investigated. Topography and the features of the PtNPs/tosyl-CNPs were scrutinized utilizing techniques such as FE-SEM, EDX, XRD and electrochemical methods. Then it was used as electrocatalyst for ethanol oxidation in acidic media. The results illustrated that the usage of PtNPs/tosyl-CNPs has a greater effect on the electrocatalytic activity of PtNPs than PtNPs alone for the oxidation of ethanol, i.e., very high anodic peaks current density in the forward scan, low onset potential, low poisoning and high stability. Thus, the use of PtNPs supported on tosyl-CNPs results in a very promising electrocatalytic composite for further application in fuel cells.

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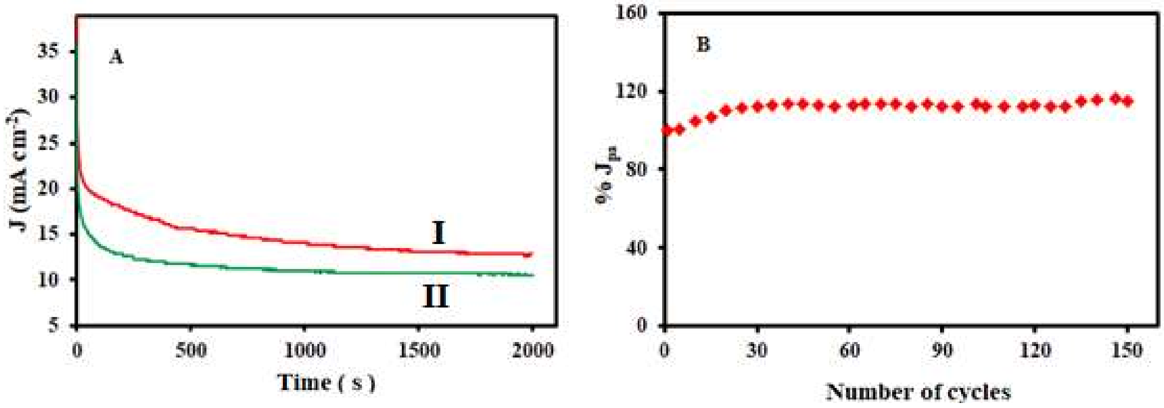

Fig.7. A) Chronoamperometry curves of PtNPs/tosyl-CNPs/CCE (I) and PtNPs/CCE (II) in 0.1 M H_2SO_4 solution containing 0.3 M ethanol at 0.6V and B) the anodic peak current density in forward scan for different cycles relative to the first cycle.

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