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Evaluation of Ag as an Active Direct Ethanol Fuel Cell Electrode Catalyst Prepared by Pulsed Current Electrodeposition Technique

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PULSED current electrodeposition of Ag (Ag) on graphite from non-cyanide bath has been employed. The influence of pulse parameters on electrocatalytic activity of Ag catalyst for ethanol oxidation in alkaline media have been evaluated by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and cyclic voltammetry (CV). The results reveal that the optimum condition can be obtained at 60 % duty cycle, 50 mA cm^{-2} Peak current density, 10 s. deposition time, and 10 Hz pulse frequency. The electrocatalytic activity and long-term stability of Ag/C electrode prepared, at corresponding optimum condition, by pulsed-current (PC) and direct-current (DC) electrodeposition for ethanol oxidation in alkaline media have been compared. The results illustrate that PC Ag catalyst exhibits higher oxidation peak current density, higher surface coverage, higher poisoning tolerance as well as smaller charge transfer resistance, in alkaline ethanol solution, than that prepared by DC technique and thus can be used as an active anode material for direct ethanol fuel cell at a reduced cost.

Keywords: Pulsed current electrodeposition, Electrocatalytic activity, Nanoparticles, Ag deposition, Fuel cells.

Introduction

Noble metals and alloys have been extensively investigated as the electrocatalysts for oxidation of alcoholic fuel cells. However, their high price constitutes a major barrier to the commercialization of these fuel cells as a renewable source of energy. It is, therefore, desired to develop low-cost non-noble electrocatalysts with comparable efficiency towards ethanol oxidation reaction. This research aims to investigate Ag as an alternative. Of course this type of catalyst will be much more economic than that of platinum or palladium-based alloys. However, some studies [1-23] have been done on Ag-based catalysts, but the mechanism of ethanol oxidation on Ag- based electrocatalyst is not yet known. Ag deposits are required to be in the nano-sized, where the size and the distribution are very

important parameters to be controlled [24]. Highly distributed catalyst nanoparticles with small size and narrow size distribution are essential for higher electrocatalytic performance wherein large surface to volume ratio can be achieved [25]. Therefore, the development of a preparation method to achieve more favorable dispersion and smaller particle sizes is still a challenge. Among these techniques the electrochemical deposition is preferred for their simplicity, rapid, high sensitivity, ease of fabrication, reproducibility as well as cost effectiveness in comparison with the other sophisticated non-electrochemical techniques [26,27]. The traditional DC electrodeposition techniques, galvanostatic or potentiostatic from solution is not so successful, as the homogeneity in particle size and especial particle distribution is disappointing in comparison

to the pulse techniques such as galvanostatic PC and potentiostatic double pulse (DP).

Moreover, in DC electrodeposition there is a concentration difference condition which leads to what is called polarization in concentration difference restrains the nucleation and growth of coating. PC technique holding a relaxation time (off-time)for ions diffusing which can keep the stable concentration of ions between the surface of the cathode and the bulk of solution, and minimize this type of polarization.

Moreover, PC electrodeposition provides better control of microstructure and resulting properties of the coating due to controlling deposition parameters [28]: pulse duty cycle, pulse frequency and peak current density. One of the advantage of PC deposition is that we can apply higher current densities. High current density leads to higher nucleation rate and lower growth rate of grains, which result in finer grain particles [29]. In the case of DC deposition high current densities can result in powdery or burnt deposits.

In this paper, Ag nanoparticles were electrodeposited on graphite electrode by PC technique from non-cyanide electrolyte. The influence of pulse parameters on electrocatalytic activity and long-term stability of Ag catalyst for ethanol oxidation in alkaline media have been studied.

Experimental

Electrodeposition of Ag was carried out on graphite surfaces from cyanide-free thiosulfate baths containing $AgNO_3$ as a source of Ag (Table 1). Graphite substrate of 3 cm^2 surface area was used as a working electrode (cathode). Prior to electrodeposition, the substrate was a mechanically polished using SiC emery paper of different grads up to 1200, then degreased with acetone, rinsed with distilled water and dried. The anode employed was pure Ag wire. Plating was carried out using IVIUMSTAT, Natherlands Potentiostat/Galvanostat. The electrodeposition

has been realized by PC technique. Pulse duty cycle of 20 to 80 %, at frequencies 10, 25, and 50 Hz with peak current densities ranging from 30 to 321 mA cm^{-2} and deposition time from 2 to 30 s. were employed. In a separate series of experiments galvanostatic DC electrode position was carried out at current densities 1-3 mA cm^{-2} and deposition time ranging from 1-5 min. (Table 1). After electrodeposition processes, the cathode was washed with distilled water and dried. The surface morphology and particle size of the Ag deposit prepared by PC and DC plating were investigated by Field Emission Scanning Electron Microscopy (FE-SEM, QUANTA EG), and X-ray diffraction (XRD) respectively. XRD patterns were obtained over the diffraction angle range (2θ) 4–80° using anX'Pert PRO – PANalytical, Netherlands diffractometer with copper target and nickel filter and at room temperature. A monochromatic Cu Kα radiation was selected at wave length 1.54052 A°, at generator voltage 45 kV, and generator current 40 mA, with step size 0.02°and scan speed 0.05 s. Ag loading was determined by EDX (QUANTA EG) attached to FE-SEM. The electrocatalytic activity and long- term stability of catalysts for ethanol oxidation in alkaline media were studied by electrochemical methods such as cyclic voltammetry, chronopotentiometry, and electrochemical impedance spectroscopy. The electrochemical measurements were performed with a conventional three-electrode system. The catalyst was used as the working electrode, a platinum wire as counter electrode and Ag/AgCl as the reference electrode. The electrolyte was 1M KOH with or without 1M CH_3CH_2OH at room temperature. Autolab (PGSTAT 30, Netherlands) Potentiostat/Galvanostat equipped with a frequency response analyzer (FRA) was used.

Results and Discussions

Figure 1 illustrates the anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media, 1M KOH + 1M CH_3CH_2OH, on Ag/C electrodes prepared by PC technique at 10 Hz

TABLE 1. Silver electrodeposition bath composition.

Component	Content, gL^{-1}	DC Operating condition
Silver nitrate	50	
Sodium hyposulphite	225	1- Current density: 1-3 mA cm^{-2}
Potassium metabisulphite	40	2- Deposition time: 1-5 min
Ammonium acetate	25	3- pH: 5.5 – 6
Aminothiourea	0.6	4- At room temperature

pulse frequency, 30 mA cm^{-2} peak current density, 2 s. deposition time and various pulse duty cycles of 20, 40, 60, and 80 %. The results not only show that the peak current density of ethanol oxidation increases with increasing in duty cycle parameter from 20 to 60 %, then decreases for higher duty cycle value of 80 %, but also show that the starting potentials for ethanol oxidation, i.e. onset potential, shift to more negative direction, indicating ethanol electrooxidation is more efficient in the following manner:

60% > 80%, 40 % > 20 % duty cycle

A lower onset potential indicates that the overpotential for ethanol oxidation is lower and that electrocatalytic ethanol oxidation occurs more easily on the electrode [30]. It is well known that the onset potential is related to the breaking of C-H bonds and subsequent removal of intermediates by oxidation with $(OH)_{ads}$ [31,32].

As the duty cycle increases, off-time (t_{off}) decreases and grain size of deposited Ag also decreases. This may be related to the relaxation

time of the pulse (t_{off}) which is beneficial for the growth of grains because it allows the diffusion of ions from bulk solution to the surface of the electrode and thus lowers the concentration polarization in the next pulse on-time. The subsequent changes in charge and mass transfer process could modify the morphology, chemical composition, and the properties of coatings. As the duty cycle exceeds 60 to 80 %, a decrease in electrocatalytic performance is shown indicating that there is a threshold for particle size to show the best performance.

Figure 2 illustrates the effect of peak current density on electrocatalytic activity of Ag/C electrodes prepared by PC technique at 60 % pulse duty cycle, 10 Hz pulse frequency, and 2 s. deposition time. It is clear that as peak current density increases, activity of Ag electrocatalyst also increases from 30 to 50 mA cm^{-2}, after which, it decreases at higher current density values. This behavior may be interpreted in terms of high current density causes higher nucleation rate and lower growth rate of crystallites, thus resulting
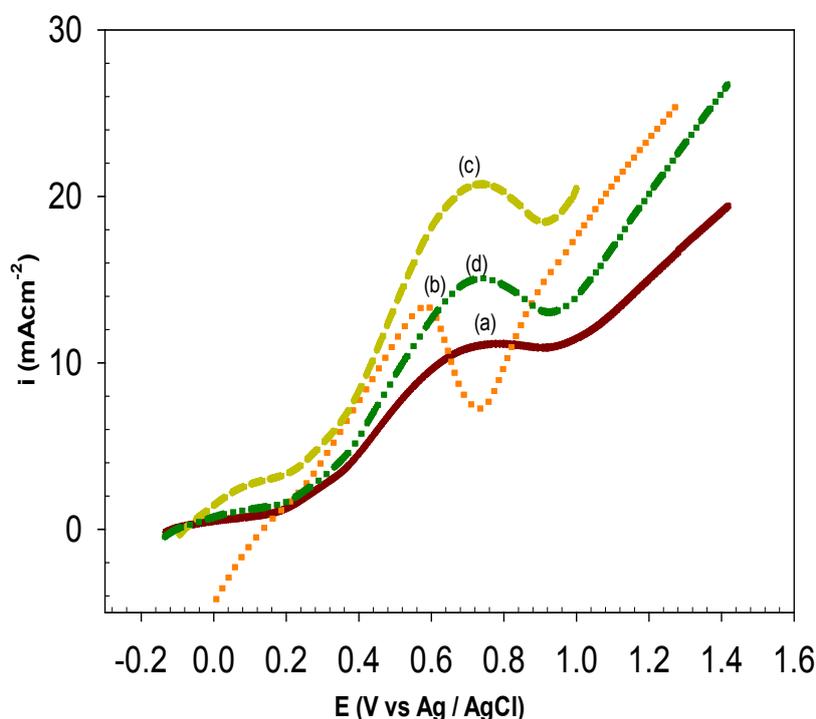

Fig. 1. Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50 mVs^{-1} on Ag/C electrode prepared by PC electrodeposition technique: pulse frequency 10Hz, peak current density 30 mA cm^{-2}, deposition time 2 s, at different pulse duty cycles of (a) 20, (b) 40, (c) 60, (d) 80%.

in finer grain structure [29]. At higher current densities, the crystallite size reduction reached its limiting value due to saturation of nucleation rate. These nano grains exhibited a higher activity and could react with O_2 to form dark, burning deposits which impair the electrocatalytic performance.

Figure 3 illustrates the effect of deposition time on electrocatalytic activity of Ag/C electrodes prepared by PC technique. It can be shown that as the deposition time increases, the electrocatalytic property increases from 2 to 10 s., after which it decreases. Long time is necessary
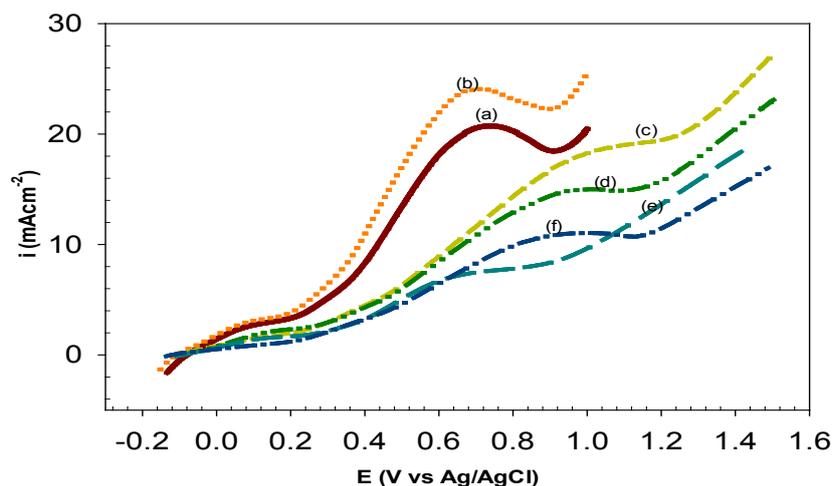

Fig. 2. Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50 mVs⁻¹ on Ag/C electrode prepared by PC electrodeposition technique: duty cycle 60%, pulse frequency 10 Hz, deposition time 2 s and different peak current density: (a) 30, (b) 50, (c) 100, (d)143, (e) 321 mA cm⁻² .

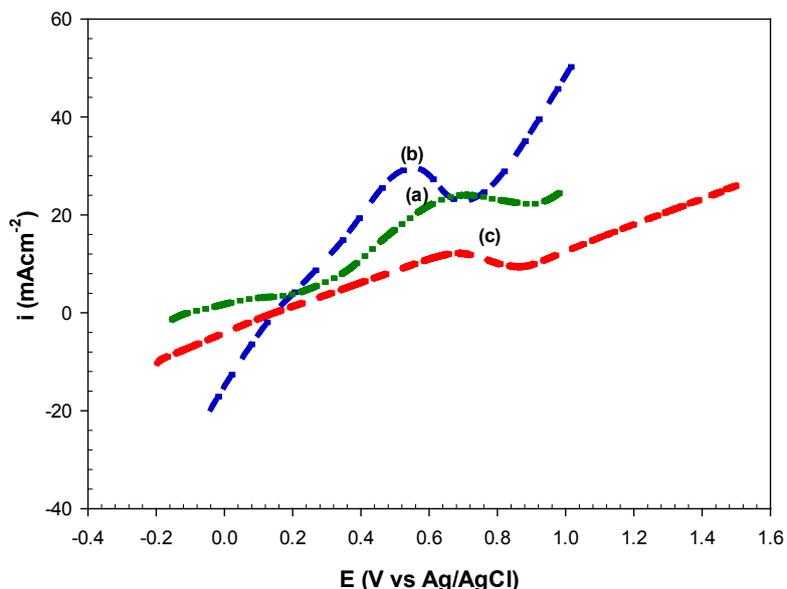
Fig. 3. Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50 mVs⁻¹ on Ag/C electrode prepared by PC electrodeposition technique: duty cycle 60%, peak current density 50 mA cm⁻², pulse frequency 10 Hz, and different deposition time: (a) 2, (b) 10& (c) 30 s.
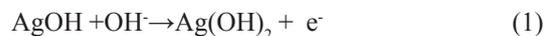
in order to deposit a sufficient amount of metal at certain peak current density. Excess time can be related to the hypothesis that the properties are dependent on the deposition time especially in the nano range where time enhances the probability of precipitation of particles on each other which may disturb the finer grained structure.

Figure 4 illustrates the effect of pulse frequency on electrocatalytic activity of Ag/C electrodes prepared by PC technique. It is obvious to note the detrimental effect of increasing frequency above 10 Hz. This is because t_{on} and t_{off} values are too small that deposition may be regarded as continuous plating. From Fig. 1-4 one can easily deduce the optimum condition for electrode preparation by PC technique as follows: 60 % duty cycle, 50 mAm^{-2} peak current density, 10 Hz pulse frequency and 10 s. deposition time. This optimum condition exhibits peak current density of 30 mA cm^{-2} for the oxidation of ethanol in alkaline media on Ag/C electrode prepared by PC technique which shows a higher activity than that of the commercial E-TEK PtRu/C electrocatalyst (20mA cm^{-2}) [33] under the same testing condition.

Figure 5 shows (a): the cyclic voltammogram for Ag/C electrode prepared at the optimum condition in 1 M KOH at scan rate of 50 mVs^{-1} vs. Ag/AgCl. It is shown that two redox peaks of Ag species appear in the voltammogram, one in the anodic direction at about 0.6 V due to the formation of Ag(OH)$_2$ and the other in cathodic direction at 0.15 V due to the reduction of Ag(OH)$_2$ to AgOH according to the following reaction:

$$AgOH + OH^- \rightarrow Ag(OH)_2 + e^- \qquad (1)$$

(b): shows the cyclic voltammogram for Ag/C electrode prepared at the optimum conditions in 1 M KOH and 1M ethanol at 50 mVs^{-1}. It has been characterized by two well defined anodic current peaks: one in the forward corresponding to the oxidation of chemisorbed species coming from ethanol adsorption. The other one is associated with the removal of carbonaceous species not completely oxidized in the forward scan [34-36]. It is well known that the electrooxidation of organic compounds in alkaline media requires the presence of oxide, hydroxide and /or oxyhydroxide groups [37]. On Ag/C electrode, the oxidation process of ethanol starts at a potential value corresponding to the formation of Ag(OH)$_2$ species, as can be seen from Fig. 5a and 5b and the oxidation process starts as Ag II species is formed. So it is suggested that, ethanol is oxidized on Ag-based electrodes through the reaction with
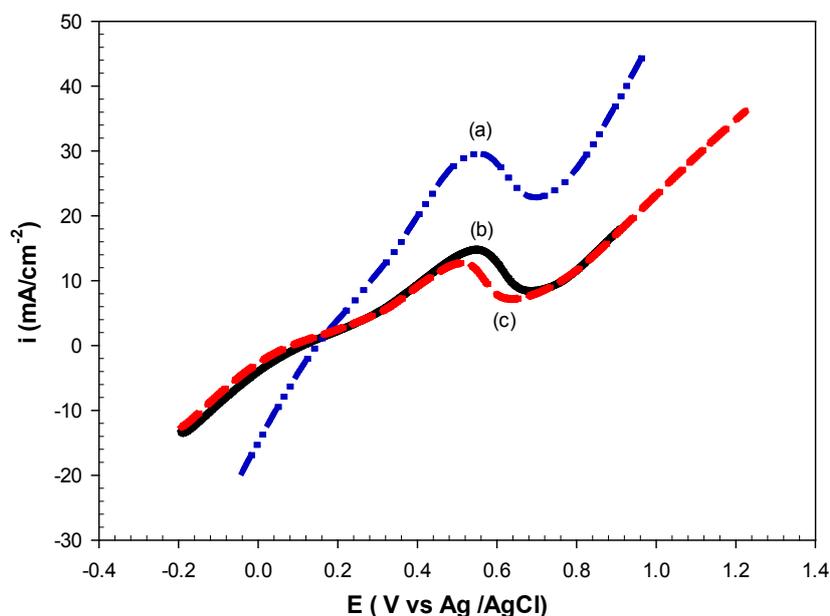

Fig. 4. Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50 mVs^{-1} on Ag/C electrode prepared by PC electrodeposition technique: pulse duty cycle 60%, 50 mA cm^{-2} peak current density, 10 s deposition time and different pulse frequency (a) 10, (b) 25 & (c) 50 Hz.

Ag(OH)$_2$ to form AgOH, i.e. Ag(OH)$_2$ acts as an oxidizing agent for ethanol [38] according to the following equation:

12Ag(OH)$_2$ + CH$_3$CH$_2$OH → 12AgOH + 2CO$_2$ +

9H$_2$O   (2)

Figure 6 represents the anodic cyclic voltammogram of Ag/C electrode prepared by PC electrodeposition technique at optimum condition
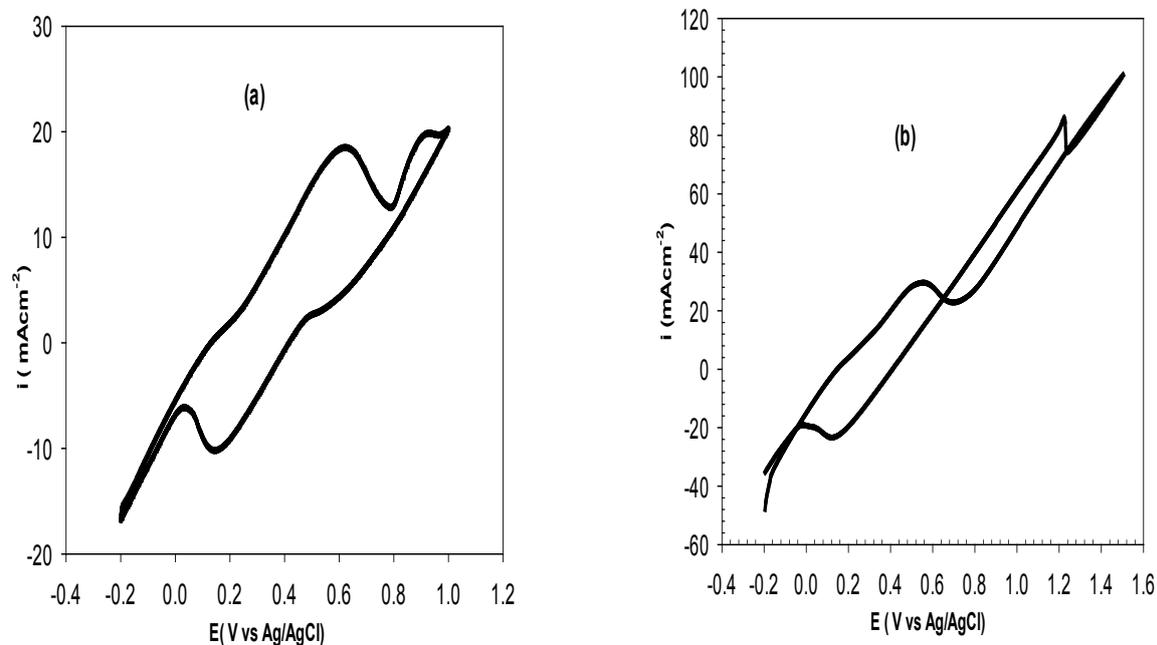

Fig. 5. (a) Cyclic voltammogram for Ag/C electrode prepared at the optimum conditions by pulse-current technique in 1 M KOH at 50 mVs^{-1} and deaeration. (b) by PC technique in alkaline ethanol solution at 50 mVs^{-1}.
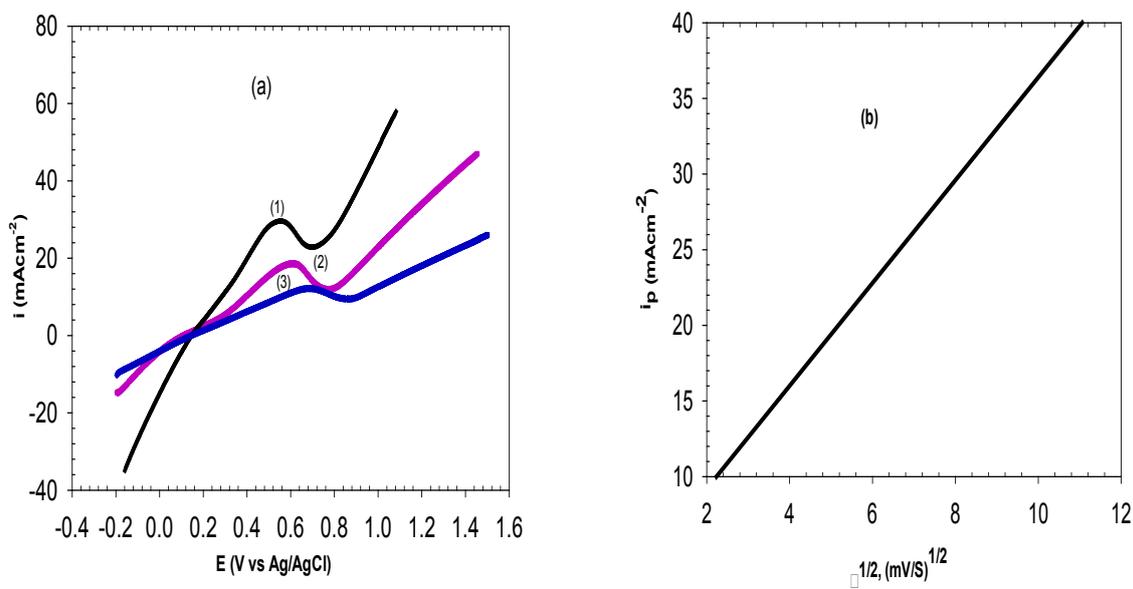

Fig. 6. (a) Anodic cyclic voltammograms of Ag/C electrode prepared by PC electrodeposition technique at optimum conditions in alkaline ethanol solution and at various scan rates (1) 10, (2) 25 and (2) 50 mVs^{-1}. (b) The relation between anodic peak current densities and square root of the scan rate of Ag/C electrodes.

in 1 M KOH and 1M ethanol and at various scan rates. It can be seen that, the peak current densities (i_p) of ethanol oxidation increase with rising of scan rate. When i_p values are plotted against the square root of scan rate ($v^{1/2}$), Fig. 6b, straight line is obtained. This behavior suggests that the oxidation process is controlled by mass transfer.

The electrocatalytic activity and stability of Ag/C electrode prepared by PC and DC electrodeposition techniques at corresponding optimum conditions, for ethanol oxidation in alkaline media have been compared in Fig. 7 - 10. The optimum conditions of DC technique was: 2 mA cm^{-2} current density and 3 min deposition

time. However, it is not necessary to declare detailed DC data in this text. Figure 7 represents the anodic branch of cyclic voltammogram which shows higher activity (i_p) for PC over than that of DC technique. Figure 8 represents the i_p values plotted against scan rate (v) for the two techniques. The surface coverage (ζ) of Ag^{++}/Ag$^+$ redox species was determined from the slope of the straight line according to the following equation [39]:

$$i_p = (n^2F^2/4RT)\, vA\zeta \tag{3}$$

where v is the potential scan rate, A the surface area of the electrode, R the gas constant, n the number of transferred electrons, F the Faraday constant
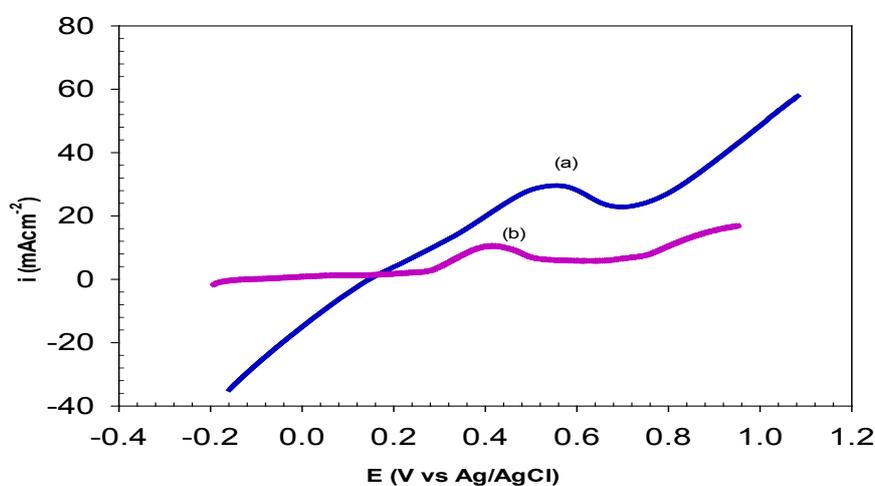

Fig. 7. Anodic cyclic voltammogram of Ag/C electrode prepared at corresponding Optimum conditions by (a) PC and (b) DC technique for the ethanol oxidation in alkaline media at 50 mVs^{-1}.
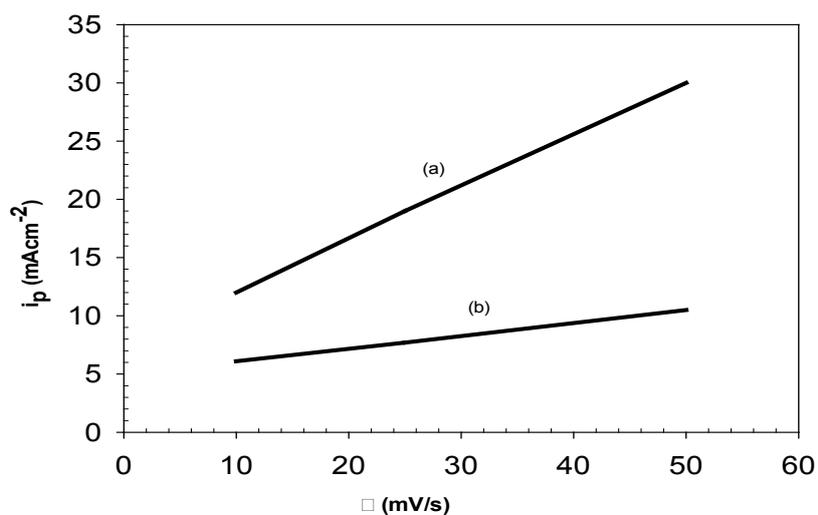

Fig. 8. The relation between anodic peak current densities and scan rates for Ag/C electrode prepared by: (a) PC and (b) DC electrodeposition techniques at corresponding optimum condition for ethanol oxidation in alkaline media.

and T the absolute temperature. It is clear that the slope of the straight line (i_p/v) is proportional to ζ which means as the slope is increased ζ value is also increased. This means that PC electrode displays a higher surface coverage of Ag^{++}/Ag^+ and accordingly higher catalytic activity towards electrooxidation process than that of DC electrode technique.

The long-term stabilities of the two electrocatalysts, PC & DC, for ethanol oxidation have been investigated with chronopotentiometric curves at a constant current density of 3 mA cm^{-2} and the results are shown in Fig. 9. It is clear that the PC electrode demonstrates its catalytic superiority over the entire time scale. Values of the potential for the oxidation of ethanol measured after 4000 S are 0.8 and 1.85V, vs Ag/AgCl reference electrode, on PC and DC electrode catalysts, respectively. This indicates that the PC catalyst is more efficient and poisoning tolerant compared to the other DC catalyst in alkaline media, which is in good agreement with the above cyclic voltammetric analyses.

Electrochemical impedance spectroscopy (EIS) was then applied to compare the impedance characteristics of the two techniques; (Fig. 10). It is obvious that, PC electrode has a lower charge transferresistance (R_{ct}) value with respect to DC, indicating a weaker reaction resistance, i.e. easier oxidation to proceed. Figure 11 shows atypical field emission scanning electron microscope (FE-SEM) images of Ag/C catalyst prepared by (a) PC and (b) DC electrodeposition techniques, respectively. It can be observed that the deposited Ag particles are fine spheres and highly dispersed on graphite with a narrow particle size distribution. However, PC technique is more pronounced. Figure 12 shows the XRD patterns of Ag/C catalysts prepared by the two techniques (a & b), respectively as well as of graphite (C). The peak at 25° corresponds to the (002) reflections of graphite. The Ag nanoparticles reveal the peaks characterized to the (111), (200), and (220) phase of the face- centered cubic (fcc) crystal structure. The peak particle size of Ag nanoparticles calculated using Scherrer formula is 41.4 and110 nm for PC and DC techniques, respectively.

The electrochemically active surface area (EASA) of the two electrodes was evaluated by determining the Coulombic charge (Q) for the reduction of Ag oxide on the corresponding cyclic voltammograms in deaerated 1M KOH solution. coulombic charge was calculated by integrating the oxide reduction peak[40].

$$EASA = Q / [Ag] \, Q_0 \qquad (4)$$

where [Ag] is the Ag loading and Q_0 is the coulombic charge required to reduce monolayer of Ag oxide which is considered here as a constant, so EASA is linearly proportional to $Q / [Ag]$.

Table 2 presents the particle size, Ag loading, coulombic charge and Q/[Ag] parameters for PC & DC techniques at corresponding optimum conditions. It is worth nothing that PC Ag is highly dispersed on graphite with a narrow particle size distribution and peak particle size smaller than that of DC electrode. Moreover,
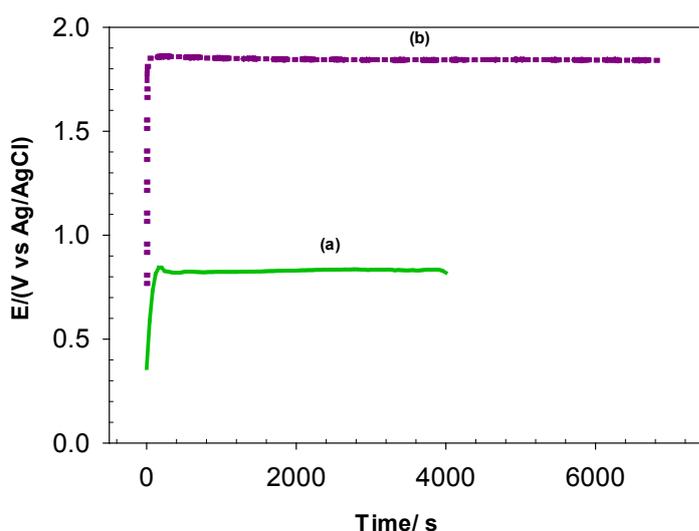
Fig. 9. Chronopotentiometric curves of ethanol oxidation on the two electrocatalysts prepared by (a) PC and (b) DC electrodeposition techniques at 3 mA cm^{-2} and 1M KOH +1M ethanol solution.
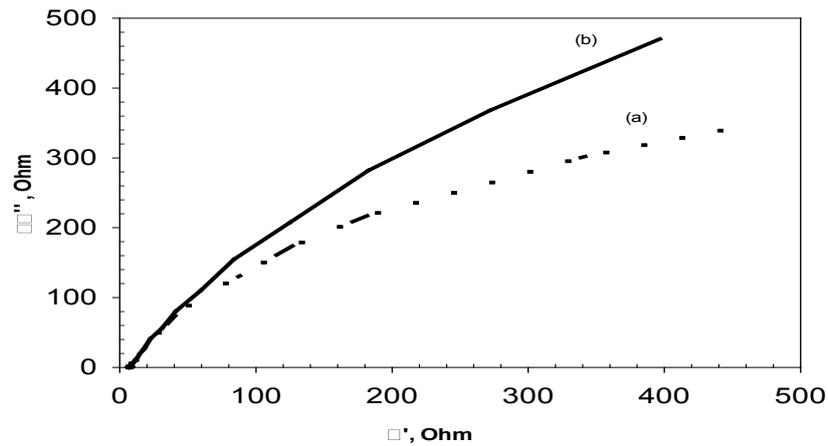
Fig. 10. Nyquist plot on Ag/C electrode prepared by (a) PC and (b) DC techniques at corresponding optimum conditions for ethanol oxidation in alkaline media (Frequency: 10kHz - 0.1 Hz, potential 500 mV vs Ag/AgCl, Amplitude: 0.01 V).
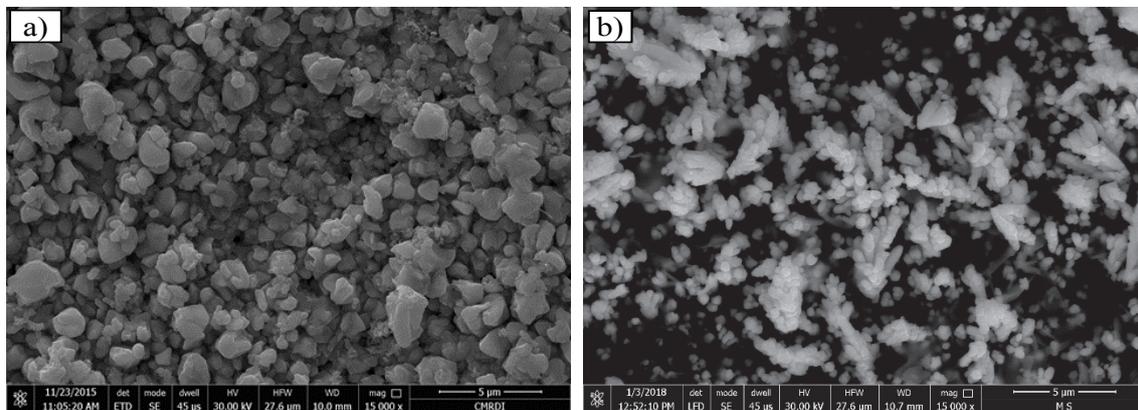

Fig. 11. FE-SEM images of Ag/C catalyst prepared by (a) PC and (b) DC electrodeposition techniques at corresponding optimum conditions.
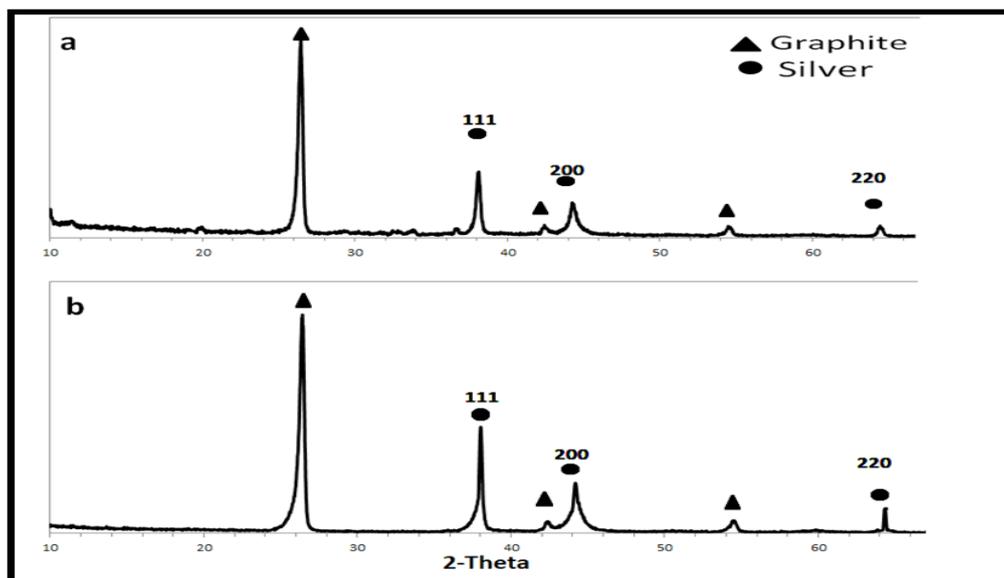

Fig. 12. XRD pattern of Ag/C catalyst prepared by (a) PC, (b) DC electrodeposition techniques at corresponding optimum conditions.

TABLE 2. Particle size, silver loading, coulombic charge Q, (mc/cm²) and Q /[Ag], for PC & DC techniques.

Technique	Particle size/ d (nm)	silver loading / [Ag] (mg/cm²)	Columbic charge / Q (mc/cm²)	Q / [Ag] (mc/mg)
PC	41.40	0.2711	180.40	665.4
DC	110	0.3379	67.20	198.9

its electrochemical active surface area (EASA) is larger. This confirms our speculation that the differences in electrocatalytic activities and long-term stability are primarily a result of achievement of these parameters. Accordingly, Ag/C electrode, prepared by PC technique, looks promised in direct ethanol fuel cell (DEFC) applications.

Conclusions

The following remarks can be outlined:

1. The optimum condition for preparing Ag/C electrode catalyst by pulsed current (PC) technique is 60% duty cycle, 50 mA cm⁻² peak current density, 10 s deposition time and 10Hz pulse frequency. This is indicated by the significantly high ethanol oxidation peak current density(i_p) and negatively shifted onset potential.
2. Ag/C electrocatalyst prepared by PC electrodeposition technique at optimum condition shows higher activity for ethanol oxidation than a commercial E-TEK Pt Ru/C electrocatalyst.
3. The mechanism of ethanol electrooxidation in alkaline media on Ag/C electrode catalyst is accomplished through catalytic role of Ag^+/Ag^{++} redox species, and the oxidation reaction is diffusional controlled.
4. Ag/C electrocatalyst prepared by PC technique shows better electrocatalyst performance and long-term stability for ethanol oxidation than that prepared by DC technique. This is indicated not only by higher i_p value but also higher surface coverage of Ag+/Ag++ redox species on Ag/C electrode prepared by PC technique. Moreover, PC electrode is more resistant to poisoning by the reaction intermediates since the polarization potential on it increases very slowly with time at constant current density compared to that on DC electrode. In addition smaller charge transfer resistance (R_{ct}) of PC electrode is obtained which is a sign for easier ethanol oxidation.
5. There is a correlation between particle size and its distribution and electrocatalytic behavior of the catalyst. The highest activity for ethanol oxidation on Ag/C electrode displayed with 41.4 nm particle size.
6. PC may be regarded as a promising synthesis procedure of electrode catalysts for its simplicity, rapid, high sensitivity, reproducibility and low cost.
7. Ag catalysts are promising anode material with fair balance between cost and performance.

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تقييم القدرة الحفزية للفضة المترسبة بطريقة التيار المتقطع كالكترود خلية الوقود التي تعمل بالأكسدة المباشرة للكحول الايثيلي

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تم في هذا البحث دراسة الترسيب الكهربي للفضة علي الجرافيت باستخدام التيار المتقطع من محاليل لا تحتوي علي السيانيد. كما تم دراسة تأثير العوامل المختلفة علي ترسيب الفضة علي الجرافيت وعلي كفاءتها فى الأكسدة الحفزية للكحول الأيثيلي فى وسط قلوي باستخدام طرق الفحص تحت المجهر الألكتروني، حيود الأشعة السينية والفولتاميتري الدائري. وقد أظهرت النتائج أن أفضل ترسيب يمكن الحصول عليه عند تيار 50 مللي أمبير/سم2، 10 ثوان وقت للترسيب و 10 هيرتز تردد النبضة. هذا وقد تم دراسة الخواص الحفزية الكهروكيميائية للفضة المترسبة عند الظروف السابق ذكرها وذلك علي الأكسدة الحفزية للكحول الإيثيلي فى الوسط القلوي ومقارنتها بالفضة المترسبة بطريقة التيار المستمر. وقد أظهرت النتائج أن الفضة المترسبة بطريقة التيار المتقطع تعطي نتائج أفضل من تلك المترسبة بطريقة التيار المتقطع، وذلك من حيث أعلي قيمة لتيار التأكسد، مقدار تغطية السطح، الاحتفاظ بالقدرة الحفزية لسطح الالكترود والمقاومة القليلة لإنتقال الشحنات. وعلي هذا الأساس يمكن الاستخدام الاقتصادي للفضة المترسبة بطريقة التيار المتقطع فى الأكسدة المباشرة للكحول الايثيلي.