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Effect of Potentiostatic Double Pulse Parameters on the Electrodeposition of Silver Nanoparticles for Electrocatalytic Oxidation of Ethanol in Fuel Cells

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Abstract

Silver nanoparticles were electrodeposited on graphite by means of the double-pulse technique from cyanide-free bath to be used as electrocatalyst of ethanol oxidation in fuel cells. The effect of double-pulse parameters on the electrocatalytic performance and the stability of the electrocatalyst during the ethanol electrooxidation in alkaline media was investigated by field emission scanning electron microscope (FESEM), XRD and different electrochemical testing methods.The results derived showed that increasing the nucleation potential cathodically increase the nucleation rate and particle density and decrease the particle size. Meanwhile, increasing nucleation time increase the particle density, decrease particle size and increase disparity. On the other hand, increasing growth time increases the particle size, whereas increasing growth potential cathodically from (OCP) is beneficial. The double pulse electrocatalyst shows superior electrocatalytic performance and poisoning resistance over pulsed current electrodes.

1. Introduction

Direct alkaline ethanol fuel cells (DEAFCs) have received considerable attention nowadays as a cleanrenewable source of energy since the shortage of energy becoming more serious. These fuel cells can be used for portable, backup, transportation, and stationary power applications. The electrochemical oxidation of ethanol in alkaline media, occurs according to the following equations:

$$CH3CH2OH + 12OH^{-} \longrightarrow 2CO2 + 9H2O + 12\,e^{-} \quad \text{anodic reaction} \quad (1)$$

$$3O2 + 6H2O + 12e^{-} \longrightarrow 12OH^{-} \quad \text{cathodic reactionb} \quad (2)$$

$$CH_3CH_2OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad (3)$$

Noble metals and alloys have been recommended as efficient catalysts for fuel cells [1]. The high cost of these materials constitute great drawback for fuel cell commercialization. A lot of scientific research work has been trying to improve the efficiency of fuel cells in aspects of cheap catalytic material such as silver [1-23] to achieve good balance between cost and performance. It is well established that activity of catalysts is attributed to their size and distribution, i.e. dispersed distributions of nanoparticles in order to achieve large surface area to volume ratio [24]. However, the method of fabrication of these catalysts remains a challenge. In a previous repaper, accepted for publication in the Egypt. J Chem., 2019, the authors electrodeposited silver nanoparticles on graphite electrode from non- cyanide bath by pulsed and direct current techniques. They optimized the pulse parameters to exhibit peak current density of 30mA/cm^2 for the oxidation of ethanol in alkaline media which shows a higher activity than both of the direct current technique (10 mA/cm^2) or the commercial E-TEK PtRu/C electrocatalyst (20mA/cm^2 [25]) under the same testing conditions. It is suggested that the double - pulse technique is a convenient electrochemical tool for controlling the preparation of metallic nanoparticles [26-33]. A nucleation pulse with duration of milli-seconds is first applied to nucleate metal particles on the substrate spontaneously, thus preventing progressive nucleation. Then a growth pulse, at a slow rate, i.e. at low overpotential was used to grow the metal particles to the desired final diameter of nm.

The aim of the present paper was to electrodeposit Ag nanoparticles on graphite electrode from non- cyanide bath by potentiostatic double-pulse technique. The influence of pulse parameters on electrocataytic activity of Ag/C electrode for ethanol oxidation in alkaline media has been studied.

2. Materials and methods

Double- pulse plating of silver was performed on graphite electrode from non-cyanide bath containing silver nitrate, sodium hyposulphite, potassium metabisulfite, ammonium acetate and aminothiourea at pH 5.5-6. The anode was silver wire. IVIUMSTAT, Netherlands Potentiostat/Galvanostat was used for plating. The electrodeposition has been realized by double-pulse technique according to the following parameters: nucleation potentials (E_1) of -870 to -1550 mV against (Ag/AgCl) reference electrode for nucleation time (t_1) ranging from 100 to 800 ms and growth potentials (E_2) of 20 to 250 mV with respect to open circuit potential (OCP) after deposition for growth time (t_2) ranging from 90 to 500 s. (OCP) after deposition was -200mV vs (Ag/AgCl).

The nanosized structure of Ag/C catalysts and its distribution as well as the average particle size were investigated by Field Emission Scanning Electron Microscope (FE-SEM, QUANTA EG). The particle size was then confirmed by X-ray diffraction (XRD -X'Pert PRO – PANalytical, Netherlands) using Scherrer formula. The Ag loading was determined by energy dispersive X-ray spectroscopy (EDX) equipped to FE-SEM. The electrocatalytic activity, surface coverage, electrochemical active surface area (EASA), long-term stability and ethanol oxidation resistance were evaluated by cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy, respectively. Double-Pulse (DP) technique was also compared with pulsed-current (PC). The electropchemical measurements were conducted with a traditional three electrode configuration. The catalyst, Pt – wire, and Ag/AgCl were used as working, auxiliary, and reference electrodes, respectively. 1M KOH with or without 1M ethanol was the solution. Autolab (PGSTAT30) Netherlands potentiostat/galvanostat with a frequency analyser (FRA) was used.All chemicals used in both the electrodeposition and the electrochemical measurments are analar grades.

3. Results and discussion

To optimize the electrode activity, the influence of double-pulse parameters: nucleation potential, nucleation time, growth potential and growth time are examined by cyclic voltammetry. The peak current densities and onset potentials are used for comparison and the data are shown in Figs 1-4. Fig.1 shows the effect of nucleation potential on the electrocatalytic activity of Ag/C electrode; prepared by double-pulse electrodeposition technique: nucleation time 800 ms, growth potential -320 mV, growth time 90 s and at different nucleation potentials: -870, -1070, and -550mV vs (Ag/AgCl) reference electrode; for ethanol oxidation in alkaline media (1M KOH + 1 M CH_3CH_2OH) at 50 mV/S scan rate. It is clear that, double-pulse plating at -1070 mV nucleation potential exhibits the highest electrocatalytic activity for ethanol oxidation. This is indicated by the negatively shifted onset potential as well as significantly high peak current density.

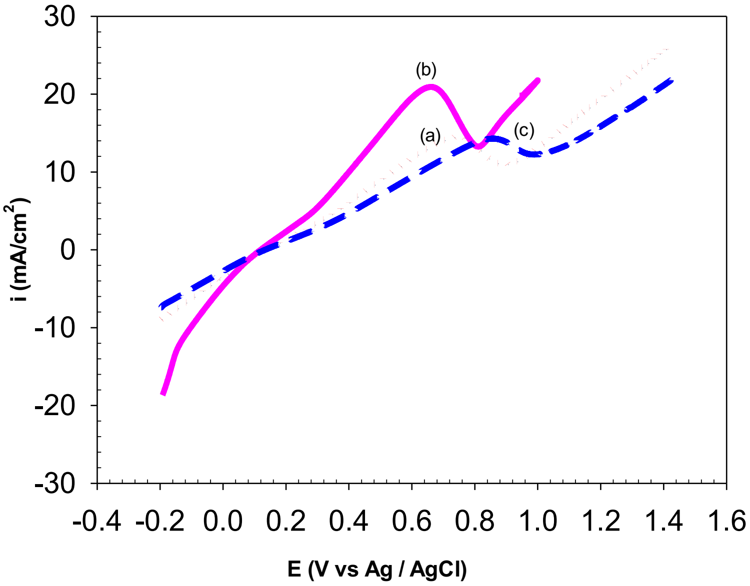

Fig 1 : Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50mV/s on Ag/C electrode prepared by double pulse electrodeposition technique: Nucleation time 800ms , Growthpotential -320mV, Growth time 90s, and different nucleation potential (a) -870,(b) -1070& (c)-1550mV (vs Ag/AgCl)

The results can be interpreted in the light of an increase in nucleation potential, from -870 to -1070 mV, leading to the increase in deposition overpotential, increase in nucleation rate, increase in particle density, decrease in particle size, and increase in electrocatalytic activity. Too much increase in nucleation potential, -1550 mV, is determined due to progressive hydrogen evolution.

Fig. 2: shows the effect of nucleation time on electrocatalytic activity of Ag/C electrode prepared by double-pulse technique at -1070mV nucleation potential, growth potential -320 mV, growth time 90 s and different nucleation time. It is obvious that optimum condition displays with 800 ms nucleation time which can be explained in terms of an increase in nucleation time from 100 to 800 ms increase the particle density, decrease particle size and increase dispersity.

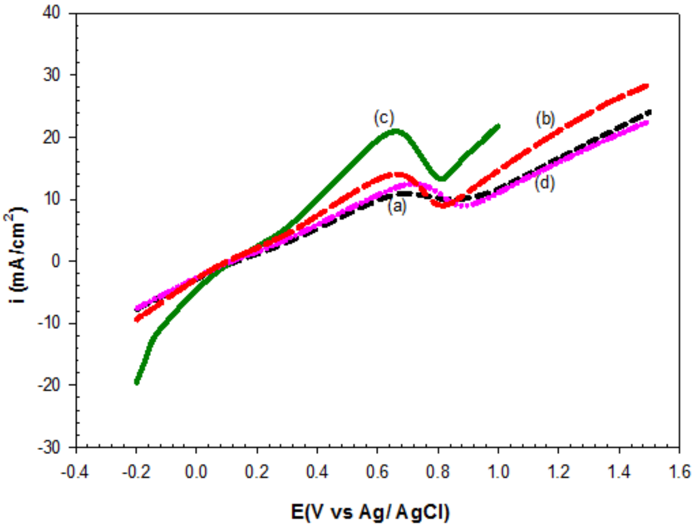

Fig 2: Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50mV/s on Ag/C electrode prepared by double – pulse electrodeposition technique: Nucleation potential -1070 mV, Growth potential-320 mV, Growth time 90s, and different Nucleation time (a) 100, (b) 400,(c) 800 & (d)1000ms)

Fig.3 shows the effect of growth time on Ag/C electrode prepared by double-pulse technique: nucleation potential -1070 mV, nucleation time 800 ms, growth potential -320 mV and different growth time. It can be seen that increasing time of growth leads to lowering the electrode activity due to the increase of particle size.

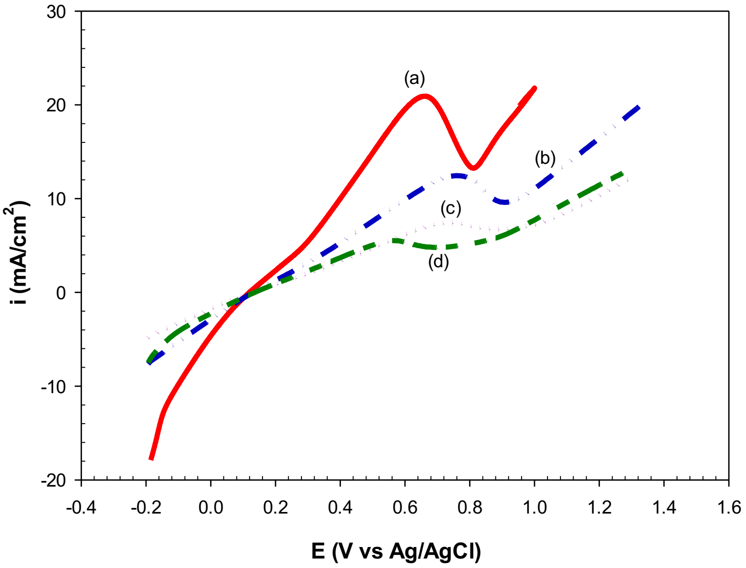

Fig 3: Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50mV/s on Ag/C electrode prepared by double – pulse electrodeposition technique: Nucleation potential -1070 mV, Nucleation time 800ms, Growth potential -320 mV, and different Growth time (a) 90, (b) 180, (c) 360 & (d) 500s

Fig.4 illustrates the effect of growth potential which reveals that increasing growth potential -250 mV cathodically from OCP (-200 mV) to become -450 mV is beneficial. It seems that, this cathodicoverpotential is high enough to control particle growth but low enough to suppress the formation of new nuclei. An overpotential of -20 to -250 mV was reported [34] to grow the metal particles to the desired diameter. Therefore, the optimum condition for fabricating Ag/C electrode catalyst by double-pulse electrodeposition technique is -1070 mV nucleation potential,800ms nucleation time, -250mV vs OCP growth potential and 90s growth time. This optimum condition depicts 40 mA/cm^2 electrodeposition peak current density which is higher than that of the commercial E-TEK Pt-Ru/C electrode (20 mA/cm^2) [25].

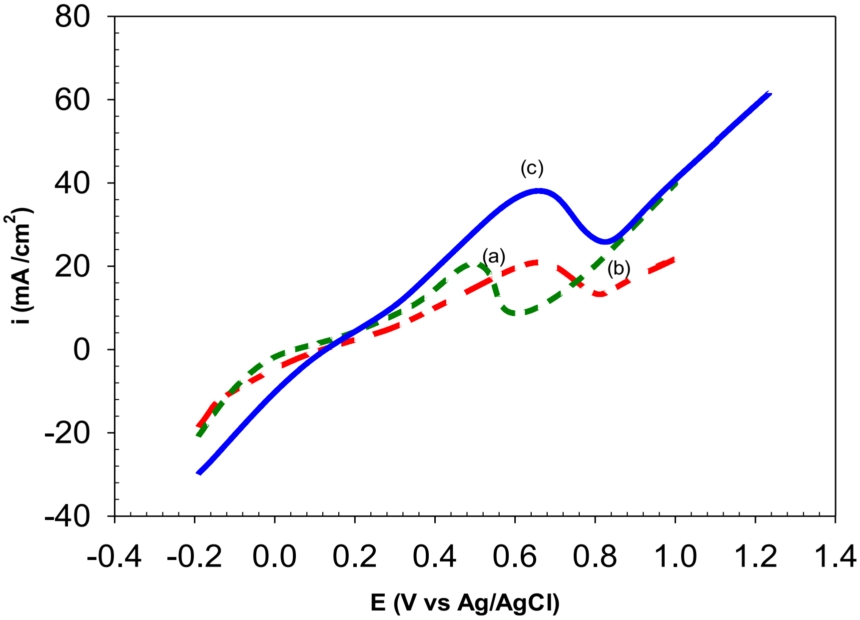

Fig 4: Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50mV/s on Ag/C electrode prepared by double – pulse electrodeposition technique: Nucleation potential -1070 mV, Nucleationtime 800ms, Growth time 90 sand different Growth potential (a)-220,(b)-320&(c)-450 mV(vs Ag/AgCl).

The mechanism of electrooxidation of ethanol can be summarized by the following equations:

$$12AgOH + 12OH^- \longrightarrow 12Ag(OH)_2 + 12\ e- \quad (4)$$

$$12Ag(OH)_2 + CH_3CH_2OH \longrightarrow 12\ Ag(OH) + 2CO_2 + 9H_2O \quad (5)$$

$$CH_3CH_2OH + 12OH^- \longrightarrow 2CO_2 + 9H_2O \quad (6)$$

It is interesting to note that cyclic voltammograms of calysts, Ag/C, show hydrogen adsorption/desorption reactions. The hydrogen desorption peaks imply electrochemically active surface area indicating that order of metal species deposition on Ag/C support has a different stoichiometry for the reactions. However, incorporation of Ag/C matrix may be able to alternate the current intensities for the different catalytic reactions.

Fig. 5 shows the anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50 mV/s on Ag/C electrode prepared by double-pulse & pulsed current electrodeposition techniques at their corresponding optimum conditions. In their paper accepted for publication in the Egypt. J Chem., 2019, the autors determined the optimum conditions of pulsed current electrodeposition techniques as follows: 60% duty cycle, 50 mAcm^2 peak current density, 10 s deposition time and 10 Hz pulse frequency. It is worthy to note that double-pulse electrodeposition technique excels the other. That is to say, it shows preferential electrocatalytic performance for ethanol oxidation in alkaline media. The behavior of double-pulse electrocatalysts are then compared with the pulsed current electrode catalysts by the following different electrochemical methods.

Fig. 6 presents the relationship between oxidation peak current densities and scanning rates for ethanol oxidation on Ag/C electrocatalyst prepared by (a) double-pulse and (b) pulsed current techniques at their corresponding optimum conditions. The slope of the straight line is proportional to the surface coverage of the coating, according to the following equation [35]:

$$i_P=(n^2\ F^2\ /\ 4RT)\ \upsilon\ A\ \zeta \qquad (7)$$

where ζ is the surface coverage (mole /cm^2), υ is the potential scan (mV/s), A is the surface area of the electrode (cm^2), R is the gas constant (JK^{-1} mole^{-1}), n is the number of electrons transferred for Ag$^+$/Ag^{++} system, and F is Faraday constant (C/mole). Again double-pulse technique excels pulsed-current. That is to say, double-pulse electrode shows higher surface coverage of Ag nanoparticles and hence higher electrocatalytic performance than that of pulsed-current technique for the oxidation of ethanol in alkaline media.

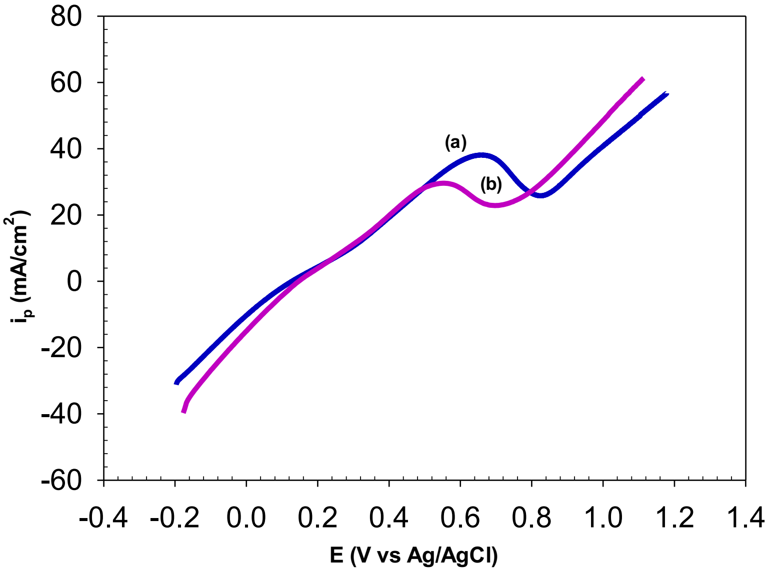

Fig 5: Anodic branch of cyclic voltammogram for ethanol oxidation in alkaline media at scan rate 50mV/s on Ag/C electrode prepared by (a) double – pulse, (b) pulsed current, electrodeposition techniques at corresponding optimum conditions.

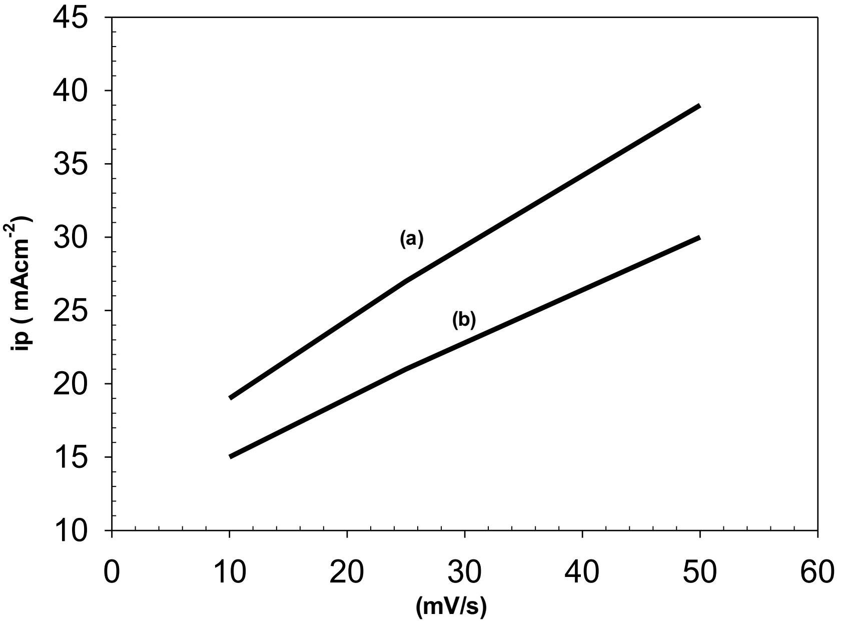

Fig. 6: The relation between anodic peak current densities and scan rates forAg/C electrode prepared by (a) double-pulse, (b) pulsed currenttechniques at corresponding optimum condition for ethanol oxidation in alkaline media.

Fig.7 presents the Nyquest plot of the electrochemical impedance spectroscopy for the two electrocatalyst. It is obvious that double-pulse electrocatalyst displays smaller charge transfer resistance than pulsed-current which means smaller ethanol oxidation reaction resistance has been occurred. This is in good agreement with the excellent catalytic performance of double-pulse electrode catalyst for ethanol oxidation in alkaline media.

Fig.8 presents the chronopotentiometric curves of the two electrocatalysts, double pulse &pulsed current, for ethanol oxidation at a constant current density of 3 mA/cm^2 in 1 M KoH + 1M CH_3CH_2OH solution. It is worth to note that the double-pulse electrode is difficult to poison by reaction intermediates than pulsed current one all over the tested time.. Since after 4000s double pulse and pulsed- current electrodes depict a potential of 400&800 mV, respectively. So, it shows better steady – state performance than the pulsed current electrode for ethanol electrooxidation in alkaline media which is well consistent with the above electrochemical measurements.

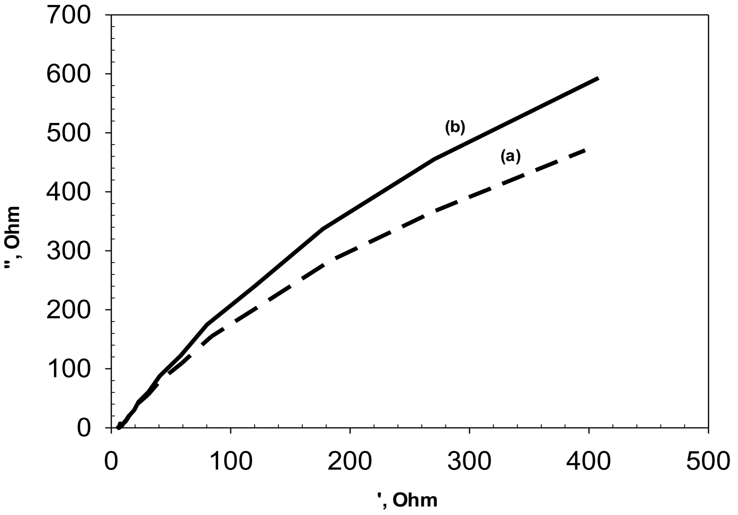

Fig.7: Nyquist plot on Ag/C electrode prepared by (a) double-pulse and (b) pulsed techniques at corresponding optimum conditions for ethanol oxidation in alkaline media (frequancy:10kHz - 0.1 Hz, potential 500 mVAg/AgCl, amplitude :0.01 V)

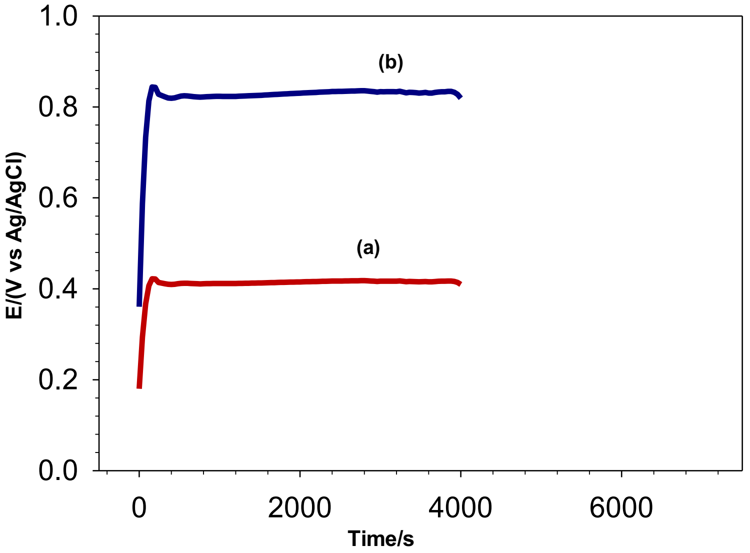

Fig. 8: Chronopotentiometric curves of ethanol oxidation on the two electrocatalysts prepared by (a) double pulse and (b) pulsed current techniques at 3 mA/cm^2 in MKOH + 1M ethanol solution

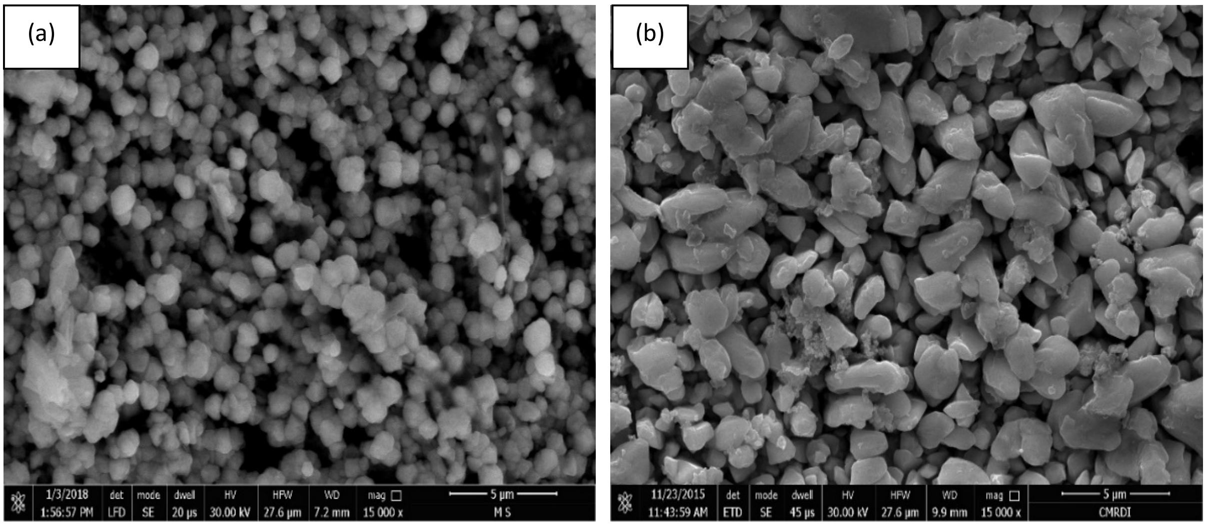

Fig. 9: FESEM images of Ag/C catalyst prepared by (a) double pulse and (b) pulsed current techniques

The FE-SEM images (Fig. 9) of the two electrocatalysts prepared by (a) double pulse and (b) pulsed current techniques indicates that the silver electrodeposited is nanosized particles with narrow size distribution. However, double pulse specimen is more prevalent.

The X- ray diffraction (Fig.10) measurement further confirmed that the Ag prepared by both techniques is nanocrystals. The 2θ of 37^0, 45^0, 65^0 are correspond to the (111), (200), (220) facets of silver. The 2θ of 25 corresponds to (002) reflections of graphite. However, the average particle size of Ag nanoparticles calculated using Scherrer formula equation (1) is 19.8 nm, 41.4 nm for double pulse and pulsed current techniques, respectively.

$$d = k\,\lambda / \beta_{½}\cos.\theta \qquad (8)$$

where: d is the average particle size (nm), λ the wave – length of X-ray radiation, k the coefficient taken here as 1, $\beta_{½}$ the width (in radians) 0f the diffraction peak at half height, θ the angle at the position of the peak maximum.

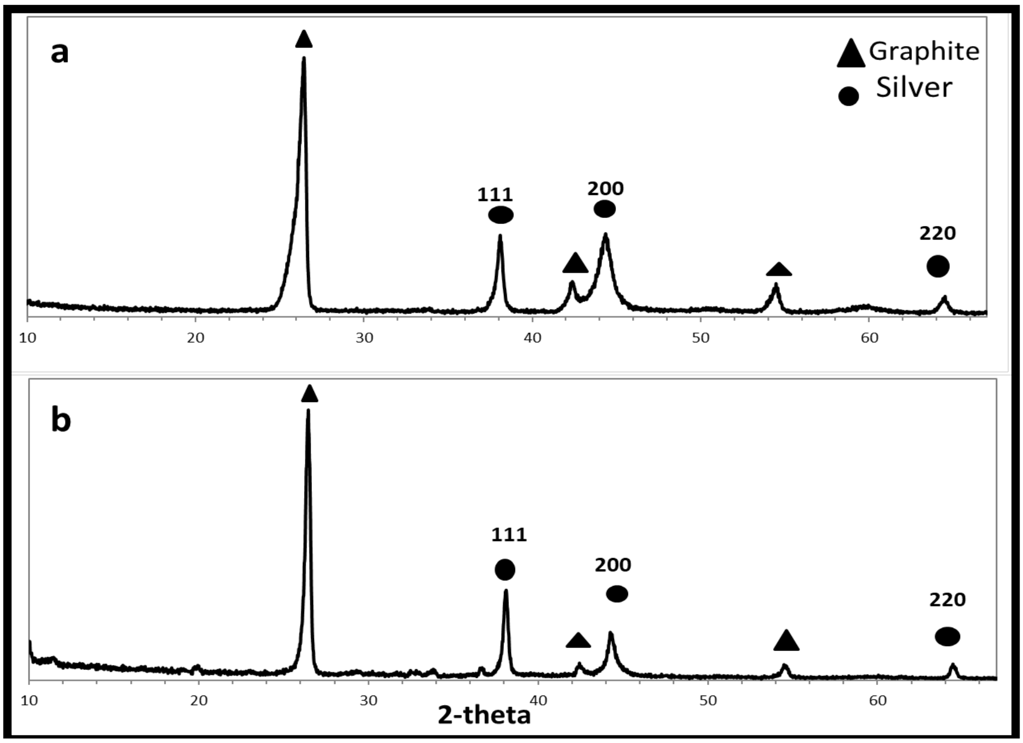

Fig. 10 :XRD pattern of Ag/C catalyst prepared by (a) double-pulse,(b) Pulsed current electrodeposition techniques

The electrochemical active surface area (EASA, cm^2/mg) was determined for the double-pulse electrode technique at optimum conditions and compared with that for pulsed-current and direct current. Integration of oxide reduction peak of the cyclic voltammograms in deaerated 1M KoH solution was used [36] to estimate the Coulombic charge :

$$Q \text{ in } (mc/cm^2).\ EASA = Q / [Ag]\, Q_0 \qquad (9)$$

Where Q is the coulombic charge for Ag oxide reduction, [Ag] the Ag loading and Q_0 the coulombic charge required for reduction of monolayer of Ag oxide which can be considered here as a constant. Therefore, EASA is linearly proportional to Q /[Ag].

It is obvious from the results in Table 1 that the double pulse technique exhibits larger EASA over the pulsed current technique due to the better dispersion of Ag and smaller particle size. EASA, in turn is the key role of the high electrocatalytic activity &stability of such electrode. The results also demonstrate that the electrode preparation method have a significant influence on the performance of the electrode and so, double-pulse electrodeposition technique has great potential to be used in alkaline direct ethanol fuel cell technologies.

Table 1: particle size (d), silver loading [Ag], coulombic charge (Q) and Q / [Ag],

of double pulse (DP), and pulsed current (PC) techniques

Technique	Particle size (nm)	Silver loading [Ag] (mg/cm^2)	Coulombic charge Q (mc/cm^2)	Q / [Ag] (mc/mg)
DP	19.8	0.137	255.7	1872
PC	41.4	0.271	180.4	665

Conclusion

1- The double-pulse parameters in electrodeposition of silver on graphite (Ag/C) have been optimized at: -1070mV (vs Ag/AgCl reference electrode) nucleation potential, 800ms nucleation time, -450mV growth potential and 90s growth time for ethanol oxidation in alkaline media.
2- Increasing the nucleation overpotentialcathodically increases nucleation rate and particle density and decrease particle size.
3- Increasing nucleation time increases the particle density, decrease particle size and increases dispersity.
4- Increasing growth overpotentialcathodically to 250mV with respect to (OCP) is beneficial since it is high enough to control particle growth and in the same time is low enough to suppress new nuclei formation.
5- Increasing growth time is detrimental since it increases the particle size above the desired diameter.
6- Double-pulse Ag/C electrocatalyst shows superior electrocatalytic performance and poisoning resistance than that of pulsed-current and direct current Ag/C electrodes.
7- Double-pulse electrodeposition technique, therefore, looks promised to be used for the fabrication of efficient silver electrocatalysts for ethanol oxidation in alkaline media.
8- Double-pulse silver electrocatalyst has been proved to be an alternative active cheap electrode for direct alkaline ethanol fuel cells (DAEFCs).

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