

Full Paper

Pulsed Electrodeposition of Platinum Nanoparticles on Fluorine Doped Tin Oxide in Molten Salt and Its High Electrocatalytic Activity Towards Ethanol Oxidation

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Abstract- This paper presents pulse potential electrodeposition of platinum nanoparticles on fluorine doped tin oxide (FTO) from $\text{AlCl}_3\text{-NaCl}$ molten salt containing K_2PtCl_6 at 393K. The results showed that by optimizing the deposition parameters including the on potential, off potential, on time and duty cycle we are able to improved catalytic performance of PtNPs/FTO modified electrode for ethanol electrooxidation. The two- level factorial design was used to screen and optimize the pulse potential electrodeposition variables. The prepared PtNPs/FTO electrodes were characterized by scanning electron microscopy, Energy-dispersive X-ray spectroscopy and cyclic voltammetry. The prepared PtNPs/FTO exhibited high performance in the electrocatalytic oxidation of ethanol in alkaline solution.

Keywords- Platinum nanoparticles, Molten salt, Electrodeposition, Experimental design, Electrocatalytic oxidation

1. INTRODUCTION

In recent years, noble metal nanoparticles have gained interest due to their extraordinary catalytic activities [1-3]. Particularly, platinum nanoparticles have attracted considerable

interests because of its importance in many technical applications such as in direct ethanol fuel cells [4], sensors [5], biosensors [6], dye-sensitized solar cells [7] and other fields.

Several methods have been reported for deposition of platinum nanoparticles on electrode surfaces including: sputter deposition [8], atomic layer deposition [9], dip coating [10], chemical reduction [11] and electrochemical deposition [12-14]. Among them, the electrochemical deposition has simple operation and it is an eminent method for the preparation of nanostructures and control of the size. Pulse electrodeposition has numerous advantages in terms of controlled particle size, stronger adhesion, uniform electrodeposition, and reduction in internal stress [15]. S. K. Buratto et al. [16] reported the pulse potential deposition of platinum nanoparticles from platinic acid $\text{H}_2\text{Pt}(\text{OH})_6$ and they control the size, morphology and loading of platinum nanoparticles from $\text{H}_2\text{Pt}(\text{OH})_6$ by controlling the deposition parameters. Experimental design is a powerful statistical tool for discovering the important factors and optimization of a response by tuning these factors. L. Hallez et al. [17] reported experimental design to estimate the effect of the electroplating parameters on four properties of hard chromium electrodeposits.

Electrodeposition of metals from molten salts offer advantages such as wide electrochemical window, high thermal stability, high deposition rates and high electricity conduction. Molten salts can function as solvents and during electrolysis, the liberation of hydrogen molecule will not occur [18,19]. We [20] reported electrochemical deposition of silver in molten salt eutectic of $\text{Ca}(\text{NO}_3)_2\text{-NH}_4\text{NO}_3$.

Ethanol oxidation has attracted much attention in recent years, since it is an ideal combustible material for direct alcohol/air fuel cells. The advantages of the ethanol are: it is a liquid fuel available at low cost, high energy density, low toxicity, easily handled, transported and stored. The electrooxidation of ethanol has been investigated on many materials, and platinum was considered is one of the most active catalysts for ethanol C-C bond cleavage [21-23].

Although the ethanol oxidation reaction on platinum nanoparticles has been extensively studied in acid solution [24-26], there are few works in alkaline solution [27,28]. The investigations of the electrooxidation of ethanol in alkaline electrolyte have been increased due to the possibility of using less noble metals and overpotentials of oxidation were found to be significantly lower [29]. A. V. Tripkovic et al. reported [30] that the kinetics of the oxygen reduction reaction is more facile in a basic medium, so the alkaline solution may improve direct alcohol fuel cells performance.

In this study, we report the electrochemical deposition of platinum nanoparticles on Fluorine Doped Tin Oxide (FTO) from $\text{AlCl}_3\text{-NaCl}$ molten salt containing K_2PtCl_6 at 393K. In order to characterize the surface of the modified electrode, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and cyclic voltammetry (CV) were employed. The pulsed electrodeposition parameters included: on potential, off potential, on

time and duty cycle. Fractional factorial design (FFD) was employed to optimize the effective pulsed electrodeposition factors on the voltammetric response of ethanol.

2. EXPERIMENTAL

2.1. Materials

The mixture of $\text{AlCl}_3\text{-NaCl}$ (99.99% purity) with the eutectic composition (66:34 mol%) was purchased from Merck. Platinum element were introduced into the bath in the form of solid K_2PtCl_6 (were prepared by platinum nugget in laboratory [31]). All other chemicals were of analytical reagent grade from Merck, and all aqueous solutions were prepared with distilled water.

2.2. Apparatus and software's

All electrochemical experiments were performed in a three-electrode electrochemical cell. A working electrode was a FTO glass (Solaronix, $8\Omega/\text{square}$), a Ag/AgCl electrode was employed as the quasi-reference electrode, and a Pt wire was employed as the counter electrode. The FTO glass was sonicated in acetone and, then in distilled water to clean the surface. The potential of the working electrode is computer-controlled by a $\mu\text{AUTOLAB}$ Type III potentiostat/galvanostat (EcoChemie, The Netherlands) using GPES software. Minitab 16 software was employed for design, and optimization. The composition of PtNPs/FTO was investigated by Energy-dispersive X-ray spectroscopy (EDX)(RONTEC,QUANTAX). Scanning electron microscopy (SEM) (VEGA\\TESCAN), was utilized to determine the size and morphology of Pt nanoparticles on the electrode surface and operated at an accelerating voltage of 15 kV.

2.3. Preparation of PtNPs/FTO

Pt was electrochemically deposited on a FTO glass from $\text{AlCl}_3\text{-NaCl}$ molten salt containing 1 mM K_2PtCl_6 at 393 K using pulsed potential electrodeposition. Fig.1 shows the pulse potential electrodeposition profile consisted of process parameters. Moreover, the percent duty cycle (DC %) can be defined as:

$$\text{DC}(\%) = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \times 100 \quad (1)$$

In order to optimize electrodeposition parameters, each of them were investigated in a proper range then an optimized value was determined for each, using design of experiment method.

2.4. Electrochemical characterization

To characterize the catalytic activity of PtNPs/FTO electrodes, cyclic voltammetry (CV) was performed in basic solutions (NaOH, 0.1 M) containing ethanol (0.05 M). For the CV characterization of the ethanol oxidation the conditions 20 cycles, 100 mVs⁻¹ and -1 V to +0.6 V vs. Ag/AgCl were used as potential limits.

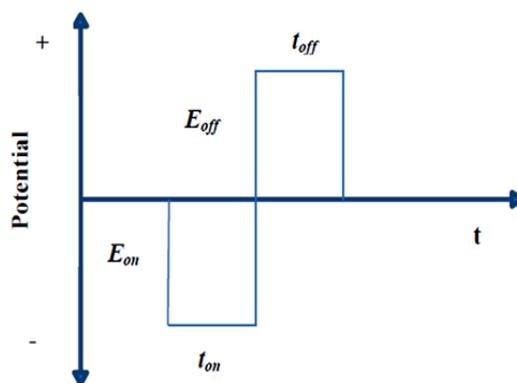


Fig. 1. Principle of the pulsed electrodeposition process

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry in AlCl₃-NaCl molten salt

Fig. 2 shows the cyclic voltammograms (CV) obtained on a FTO electrode in the AlCl₃-NaCl melts before and after the addition of K₂PtCl₆ at 393 K. Here the potential was scanned from 0.6 V to -0.2 V vs. Ag/AgCl. Curve (a) corresponds to a CV without K₂PtCl₆, in this range of potentials, there is no obvious cathodic or anodic signal. CV of the melt containing K₂PtCl₆ (curve(b)) shows two cathodic reduction peaks, peak (I) and peak (II) was attributed to reduction of Pt(IV) to Pt(II) and Pt(II) to Pt(0), respectively [32].

3.2. Design of experiment

In pulse potential electrodeposition four parameters, including on potential (E_{on}), off potential (E_{off}), on time (t_{on}) and duty cycle (DC%) can be adjusted independently. By varying these parameters for electrodeposition of Pt on FTO, response of PtNP/FTO modified electrode to ethanol electrooxidation was changed. The two-level factorial design was used to screen and optimize the pulse potential electrodeposition variables affecting the catalyst activity. The oxidation peak current density of ethanol at a concentration of 0.05 M in 0.1 M NaOH was selected as the response. The fixed levels of these four variables are listed in Table 1.

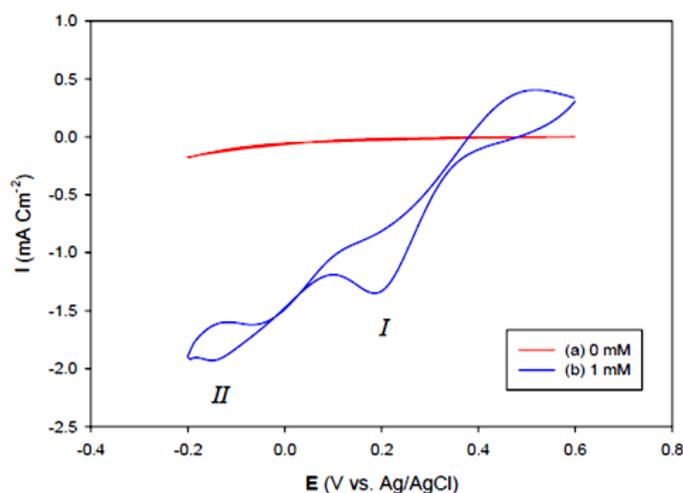


Fig. 2. Cyclic voltammograms at FTO electrode in the (a) molten salt ($\text{AlCl}_3\text{-NaCl}$) and (b) molten salt containing 1 mM K_2PtCl_6 at a scan rate of 50 mVs^{-1}

Table 1. Factors and levels for 2^{4-1} fractional factorial design

Factor		Level	
		-	+
A	on potential (V)	-0.15	0
B	off potential (V)	+0.4	+0.6
C	on time (s)	0.05	0.1
D	duty cycle (%)	1	40

Therefore, the 2^{4-1} factorial design is obtained by Minitab software. A total of 11 experiments were employed in this work, including three center points per block. Run time of pulsed electrodeposition was 500 s. Table 2 shows the results of FFD experimental design matrix together with the analytical response for each run. The oxidation peak current density of 0.05 M ethanol is ranged from 0.84 to 5.59 mA cm^{-2} .

The importance of these four factors can be understood using Pareto chart. The statistical evaluation of results (Table 2) produced the standardized main effect Pareto chart as illustrated in Fig. 3. The chart displays the absolute value of the effects and draws a reference line on the chart. Any effect that extends past this reference line is potentially important. The reference line corresponds to the 95% confidence level. According to the Pareto chart, factors B, D, C, A and the two-factor interactions of AD are the significant factors. Factor B (E_{off}) has the largest effect, indicating the fact that anodic dissolution of platinum deposits was occurred appreciably at more positive off potential. Interactions between factors (A and D) E_{on} and DC% had a significant effect on the optimization process. If one at a time method was used for optimization, this main factor was not considered. It can be seen that low off

potential, on time and duty cycle resulted in higher increase in the current. Based on response optimizer function, the optimum values of the factors were -0.15 V, +0.4 V, 0.05 s, 1% for E_{on} , E_{off} , t_{on} and DC, respectively. When low positive off potential was applied, dissolution of platinum during the anodic pulse is occurred less frequently. At low level of on time, nucleation was more efficient than growth. During the off time (t_{off}) was applied, any weak concentration gradient created during the short t_{on} was allowed to dissipate and the electrolyte solution refreshed near the electrode surface [16].

Table 2. Design matrix and experimental data of the oxidation peak current density of 0.05 M ethanol for 2^{4-1} fractional factorial design

Run order	E_{on} (V)	E_{off} (V)	t_{on} (s)	Duty cycle (%)	Response (mAcm^{-2})
1	0	0.4	0.05	40	4.63
2	-0.075	0.5	0.075	20.5	2.14
3	-0.075	0.5	0.075	20.5	2.06
4	-0.15	0.4	0.05	1	5.59
5	0	0.4	0.1	1	3.51
6	-0.075	0.5	0.075	20.5	2.08
7	-0.15	0.6	0.05	40	0.84
8	0	0.6	0.1	40	1.52
9	0	0.6	0.05	1	3.13
10	-0.15	0.4	0.1	40	1.08
11	-0.15	0.6	0.1	1	2.44

Therefore, low duty cycle resulted in a higher density of particles on the electrode surface. By applying more negative on potential, the density of nanoparticles increased with a decrease in the nanoparticle size.

3.3. Electrocatalytic performance of the PtNP/FTO electrode

The optimum condition of pulsed electrodeposition was utilized to prepare PtNP/FTO modified electrode. The successful modification of the FTO electrode surface with PtNP was evidenced by the cyclic voltammogram in 0.05 M ethanol and 0.1 M NaOH, as shown in Fig. 4. No oxidation peak of ethanol was observed on the bare electrode surface, but the modified electrode showed two main oxidation steps. The onset of the first step of the ethanol electrooxidation was found to start at a potential of about -0.6 V vs. Ag/AgCl. First anodic peak current density appearing at -0.137 V vs. Ag/AgCl. Desorption of the resulting by

products is illustrated through anodic peak current densities appearing in the reverse scan [27] (at -0.44 V vs. Ag/AgCl for example).

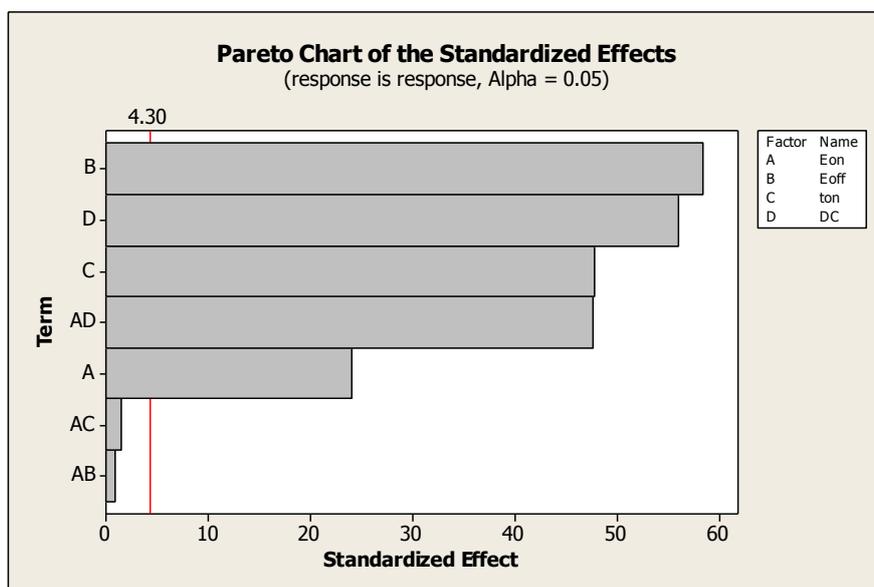


Fig. 3. The standardized main effect Pareto chart for 2^{4-1} fractional factorial design

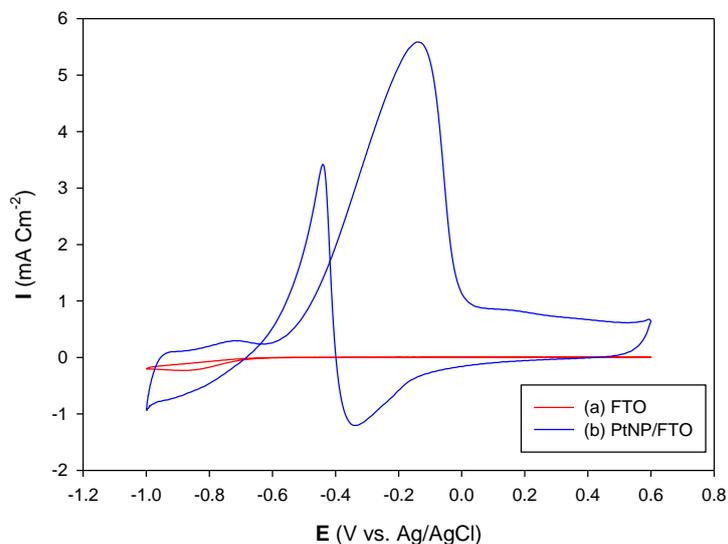


Fig. 4. Cyclic voltammograms recorded at (a) FTO electrode (b) PtNPs/FTO electrode was prepared by optimum conditions in 0.05 M ethanol and 0.1 M NaOH. Scan rate was 100 mVs^{-1}

3.4. Characterization of PtNPs/FTO

SEM was employed to explore the surface morphology and distribution of platinum nanoparticles on the FTO electrode and the images are shown in Fig. 3. The pulse potential

electrodeposition parameters used to deposit Pt onto FTO were as follows: E_{on} was -0.15 V, E_{off} was $+0.4$ V t_{on} was 0.05 s, duty cycle was 1% and run time was 500 s. It was observed that the spherical-like PtNPs had been successfully deposited on the FTO surface with a relative uniform distribution. The Pt nanoparticles have size distribution from ~ 15 nm to ~ 30 nm. Fig. 8 shows a typical energy dispersive spectrum (EDX) for determination of the catalyst composition. The EDX spectrum displays the presence of Sn, O and Pt. The tin and oxygen signals result from the FTO electrode.

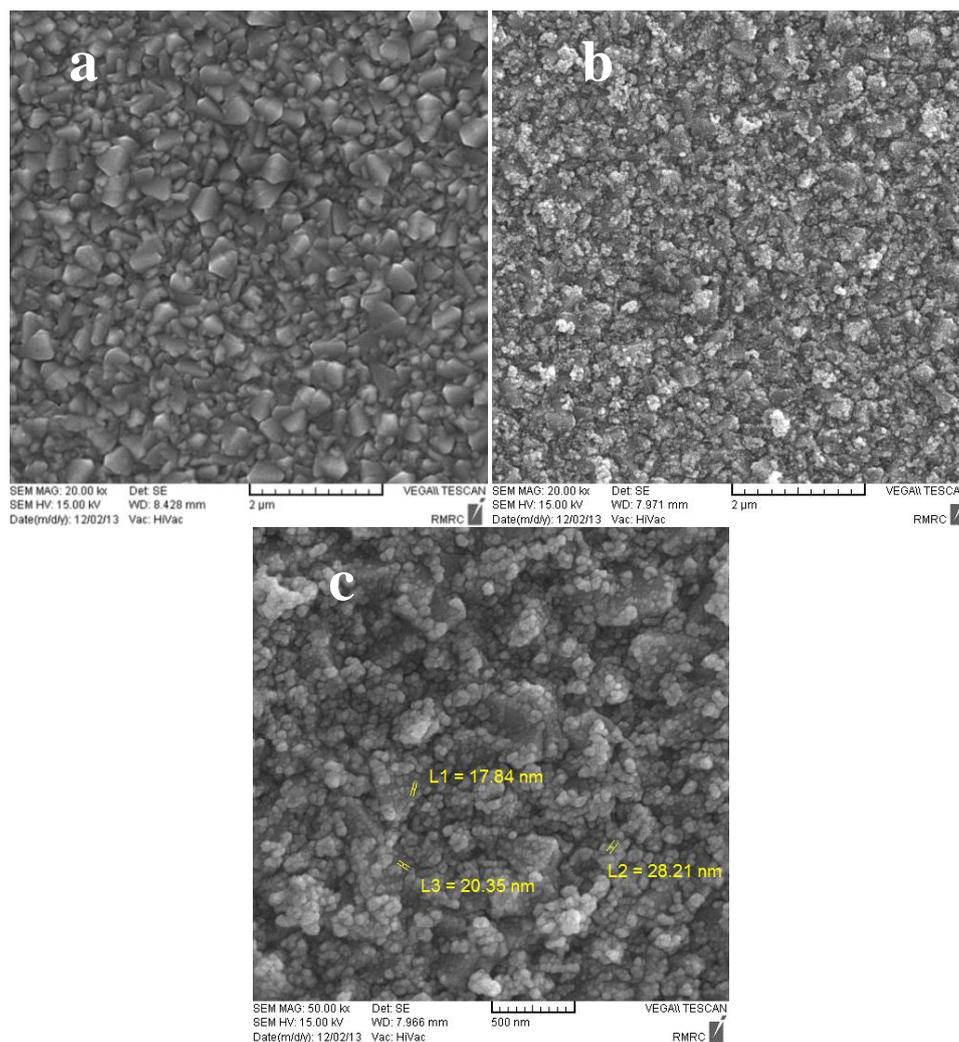


Fig. 7. SEM images of (a) FTO, (b) and (c) PtNPs/FTO with different magnification

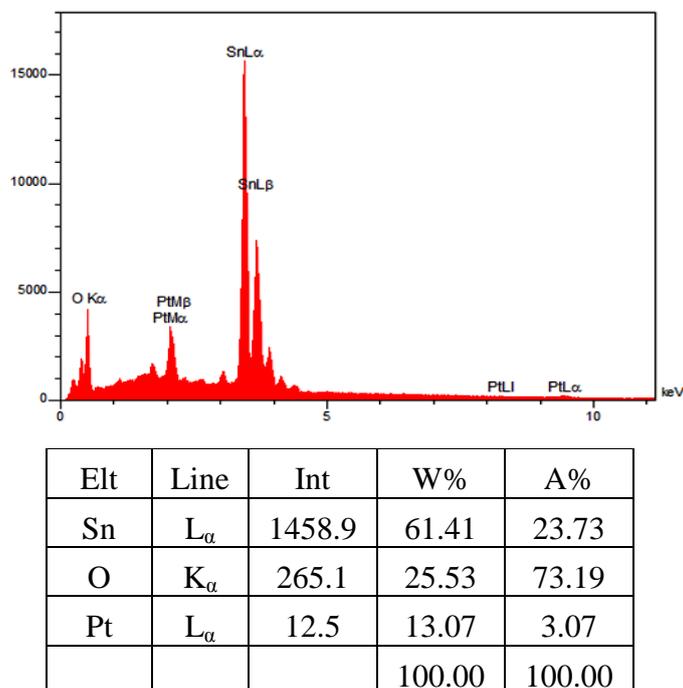


Fig. 8. The EDX pattern of PtNPs/FTO

4. CONCLUSIONS

We have shown that electrochemical deposition of platinum nanoparticles is possible from $\text{AlCl}_3\text{-NaCl}$ molten salt containing K_2PtCl_6 at 393K. In order to optimize pulsed potential electrodeposition parameters, each of them were investigated in a proper range then an optimized value was determined for each, using fractional factorial design. The optimum values of the factors were -0.15 V, +0.4 V, 0.05 s, 1% for E_{on} , E_{off} , t_{on} and DC, respectively. The surface morphology of the modified electrode was investigated by SEM, EDX and CV. The PtNPs/FTO showed highly improved electrocatalytic activity towards ethanol electrooxidation. The value of 5.59 mA cm^{-2} was obtained for optimum response in 0.05 M ethanol, 0.1 M NaOH and scan rate 100 mVs^{-1} . Pulsed potential electrodeposition is a favorable technique for producing small particles at high density.

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