

Electrodeposition of Iridium Oxide by Cyclic Voltammetry: Application of Response Surface Methodology

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Abstract. The effects of scan rate, temperature, and number of cycles on the coating thickness of IrO_x electrodeposited on a stainless steel substrate by cyclic voltammetry were investigated in a statistical system. The central composite design, combined with response surface methodology, was used to study condition of electrodeposition. All fabricated electrodes were characterized using electrochemical methods. Field emission scanning electron microscopy and energy-dispersive X-ray spectroscopy were performed for IrO_x film characterization. Results showed that scan rate significantly affects the thickness of the electrodeposited layer. Also, the number of cycles has a greater effect than temperature on the IrO_x thickness.

1 Introduction

Measurement of solution pH is important and critical in various industries. Classic glass electrode pH probes exhibit several disadvantages, including instability at high temperatures and mechanical fragility [1]. Alternatively, solid-state pH sensors can be used as glass pH sensors. IrO_x is one of the best pH-sensitive materials given its robust shape, fast response, and high stability over a wide range of pressure and temperature [2,3]. Techniques in fabricating IrO_x pH sensors include (i) sputtering, (ii) the sol-gel process, (iii) thermal oxidation of iridium, and (iv) electrodeposition. Among these methods, electrodeposition is considered the most advantageous because it can be performed using a low-cost fabrication process, requires low temperature, uses an affordable substrate, and allows versatility in the use of sensor shapes [4,5].

Optimization techniques such as response surface methodology (RSM) has recently been applied to optimize electrodeposition involving various alloys. However, no statistical studies have been reported on the fabrication of an IrO_x pH sensor by electrodeposition. The use of RSM in statistical analysis elucidates the aforementioned process. RSM also decreases the number of required experimental runs to create statistically valid results and saves time and resources. The first step in RSM involves the design of experiments (DOE), which determines the number of experiments that provide reliable and acceptable measurements of the chosen response. Central composite design (CCD) can be employed by RSM as an experimental design to fit a model by the least-squares technique. CCD requires a minimum number of experiments as the standard 2ⁿ factorial with its origin at the centre and 2ⁿ axial points fixed axially at a distance, say α , from the centre and replicate

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experiments at the centre. RSM helps investigate the effects of interactions among independent variables on a selected response.

2 Materials and methods

Iridium (IV) chloride hydrate, oxalic acid, potassium carbonate (anhydrous), 30% hydrogen peroxide, and universal pH buffers (4, 7, and 9) were purchased from Sigma–Aldrich (USA). All chemicals were used without further purification. A type-316 stainless steel was used as a substrate, and an Ag/AgCl reference electrode was used with the pH sensor for potential recording.

Table 1. Codified and normal values of the experimental design levels

Parameters	Levels				
	-1	-0.5	0	0.5	1
Scan Rate (mV/s) :A	50	87.5	125	162.5	200
Temperature (°C) :B	25	35	45	55	65
Cycles (cycle) :C	100	200	300	400	500

Stainless steel electrodes were fabricated as described in our previous work [10]. A high-performance potentiostat/galvanostat (Autolab/PGSTAT128N, the Netherlands) was used for electrodeposition and electrochemical experiments. CV was applied for electrodeposition in a potential range of -0.5 V to 0.65 V versus Ag/AgCl at various scan rates, temperatures, and cycles, as indicated in Table 1.

An electrodeposition solution was prepared as mentioned by Yamanaka [6]. Electrochemical impedance spectroscopy (EIS) measurements were conducted using an Autolab/PGSTAT128N potentiostat. The frequency used for the impedance measurements ranged from 0.01 Hz to 10 kHz. NOVA-1.8 was used for the EIS measurements and curve fitting analysis. A field-emission scanning electron microscope (HITACHI) and an EDX quantitative energy dispersive X-ray analyser were used to examine the characteristics of the electrode surface.

3 Design of experiments, analysis, and model fitting

This study aims to define the functional relationship among scan rate, temperature, number of cycles, pH sensitivity, and IrOx coating thickness by RSM with CCD. Design-Expert version 6.0.6 (Stat-Ease, Inc., USA) was used to generate the regression model as well as perform statistical and data analyses. The variables in this study included three numerical factors: scan rate (X1), temperature (X2), and number of cycles (X3). The three independent variables and experimental design levels are shown in Table 1. Twenty experimental runs were determined from CCD, including eight factorial points, six axial points, and six centre points. The axial distance (α) from the centre point was set at 0.5 in coded units. The two-factor interaction model (2FI) to predict the optimal point can be written as follows:

$$Y = \gamma_0 + \sum_{i=1}^k \gamma_i X_i + \sum_{i < j} \gamma_{ij} X_i X_j + \epsilon_\alpha \quad (1)$$

where Y represents the response (pH sensitivity and IrOx coating thickness), and γ_0 , γ_i , denote the constant coefficient and the first linear coefficient, respectively. γ_{ij} is the linear model coefficient, X_i and X_j are the coded independent variables, and ϵ is the standard error. Statistical “p” values less than 0.0500 were used to indicate the significant factors of the model.

4 Results and discussion

4.1 Fabrication of pH electrodes

The FESEM images in Figure 1 reveal that the electrodeposited layer becomes more prone to cracking as the number of cycles increases, leading to enhanced IrO_x thickness. All fabricated electrodes became crack-free after fabrication. Cracks result from layer dehydration in high-vacuum FESEM. This phenomenon clearly indicates that dehydration occurs more slowly in thicker layers than in thinner layers. Thus, more cracks are observed under fast-drying high-vacuum FESEM conditions.

4.2 Response surface methodology model equations

In this study, RSM was used to design an experiment and investigate the effect of independent variables such as scan rate, temperature, and cycles on three responses: IrO_x coating thickness, pH electrode sensitivity, and Cathodic Storage Charge Capacity (CSC_C). The RSM result showed no significant relationship between the independent variables and pH electrode sensitivity, which is consistent with previous findings. CSC_C is directly related to IrO_x thickness; thus, the DOE software was solely used to examine coded experimental models equations of IrO_x thickness and the interaction of the significant terms in the proposed model.

4.2.1 Coded experimental model equations for oxide thickness

The DOE software suggested a 2FI model considering the adjusted R-squared and the predicted R-squared rather than other models. The regression model for IrO_x thickness, in coded factors, is shown by the following 2FI model equation:

$$H=931.20-(511.59A) + (386.71B) + (403.76C) - (98.63AB) - (433.63AC) + (35.37BC) \quad (2)$$

where H is the IrO_x thickness (nm). A, B, and C represent the scan rate, temperature, and number of cycles, respectively. According to equation 5, the predicted R² of 0.2651 is not as close to the adjusted R² of 0.8911 as normally expected. This discrepancy suggests a large block effect or a problem with this model.

To address this problem, insignificant terms (AB and BC) should be removed from the proposed model to obtain an improved equation. The improved equation in terms of coded factors after removing the insignificant terms is shown as follows:

$$H=+931.20-(511.59A)+(386.71B)+(403.76C)-(433.62AC) \quad (3)$$

According to equation 3, the predicted R² of 0.7444 is in agreement with the adjusted R² of 0.8897. Adequate precision measures the signal-to-noise ratio. A ratio greater than 4 is acceptable. The adequate precision ratio of 26.438 indicates an adequate signal. Therefore, this model can be used to navigate the design space. As indicated in Eq. (3), the main effects of temperature and number of cycles correlate positively with the IrO_x thickness. The coefficients for scan rate (A) and number of cycles (C) are larger than the coefficients for temperature, indicating that parameters (A) and (B) have a more significant effect on the IrO_x thickness than parameter (B).

Figure 2 shows the predicted result obtained from Eq. (3), which is in agreement with the experimental data, thereby indicating the reliability of the improved model for predicting IrO_x coating thicknesses under various electrodeposition conditions. An acceptable correlation-to- linear regression fit was also obtained, with an R² of 0.9255 for IrO_x thickness.

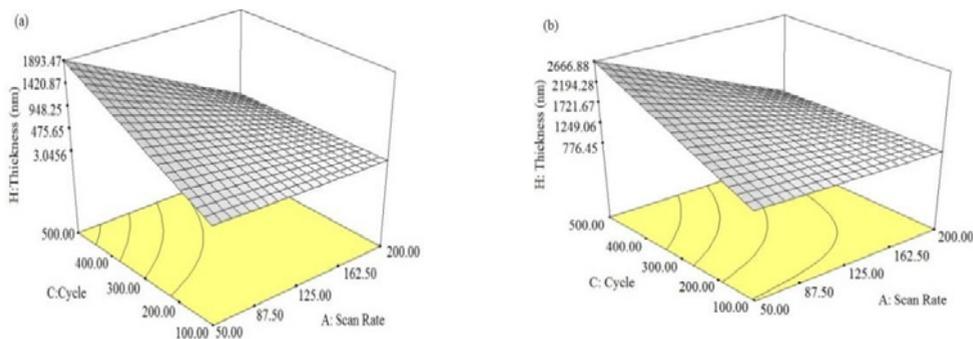


Figure 3. Response surface and contour plot of IrO_x coating thickness (nm) as a function of the number of cycles and scan rate at minimum and maximum temperatures: (a) 25 °C (b) 65 °C.

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