Catalyst Behavior Analyzed via General Regression Model with the Parameters Depending on a Covariate

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ABSTRACT: In this work, the catalytic activity of modified glassy carbon electrodes with xPd−yLaNi0.5Fe0.5O3−chitosan as an anodic catalyst for the polymeric fuel cell was investigated with cyclic voltammetry and controlled potential coulometry techniques; x and y are the mass loading of noble metal and mixed oxide, respectively. For the first time, the statistical regression mixed models were used to compare the electrocatalytic ability of nanocomposites in a fuel cell. The nonlinear regression model of \( y_j = f(x_i, s_j) + \epsilon_i \) was considered and simulated, where \( X_i \) is a random variable, \( s_j \) is a covariate value, \( \epsilon_i \) is a normal random error variable, and \( \theta \) is a P-dimensional vector of parameters of the mentioned model. A strategy to make a mixed model was proposed by using the maximum likelihood or mean square error methods. Then, the appropriate linear and nonlinear models were applied to the electrochemical results. The equations of current density vs time were obtained via the coulometry techniques; and the mass loadings of noble metal and mixed oxide, respectively. In the following discussion, for the first time, use of the nonlinear regression model to analyze the behavior of prepared catalysts is described as

\[
y_{ij} = f(x_{ij}, \theta(s_j)) + \epsilon_i
\]

for \( i = 1, 2, ..., n \) and \( j = 1, 2, ..., J_i \); where \( X_i \) is a random variable, \( s_j \) is a covariate value, \( \epsilon_i \) is a normal random error variable with

\[
E(\epsilon) = \mathbf{0}, \quad V(\epsilon) = E(\epsilon\epsilon^T) = \sigma^2 I
\]
and $\theta$ is a P-dimensional vector of parameters of the mentioned model and it can be modeled as

$$\theta_l = g(s_j; \gamma) + \epsilon_l$$  \hspace{1cm} (3)

for $l = 1, 2, \ldots, P$ and $j = 1, 2, \ldots, J$ as another regression model, where $\gamma$ is the L-dimensional vector of the parameters and $\epsilon$ is a normal random error variable with

$$E(\epsilon) = 0, \quad V(\epsilon) = E(\epsilon^2) = \delta^2 I$$  \hspace{1cm} (4)

We proposed a strategy to make a mixed model by using the maximum likelihood or mean square error (MSE) methods.\(^{19,20}\)

For this, first, a regression model of $\theta_l$ on $s_j$ where $j = 1, 2, \ldots, J$ was estimated. Then, the new models were taken instead of each related parameter. To illustrate the idea, studies were conducted by using the simulation method\(^{21}\) and this strategy was applied to the electrochemical results. To do this, assume according to the $l$th parameter of the main regression model, a model of $\theta_l$ on $s_j$ in the form

$$\hat{\theta}_l s_j = g(s_j; \hat{\gamma}) + \hat{\epsilon}_l$$  \hspace{1cm} (5)

for $j = 1, 2, \ldots, J$ and $l = 1, 2, \ldots, P$ is possible to estimate. Therefore, one can estimate the latter mentioned model as follows

$$\hat{\theta}_l s_j = \hat{g}(s_j; \hat{\gamma}) + \hat{\epsilon}_l$$  \hspace{1cm} (6)

for $l = 1, 2, \ldots, P$ or

$$\hat{\theta}_l s_j = b_0 + b_1 s_j + b_2 s_j^2 + \cdots + b_k s_j^k$$  \hspace{1cm} (7)

for $l = 1, 2, \ldots, P$ and $k \geq 1$.

### EXPERIMENTAL SECTION

All chemicals were purchased from Merck and employed without further purification. Chitosan with medium molecular weight (400,000 Da) was purchased from Fluka. All solutions were prepared in distilled water.

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**Table 1. List of All Modified Electrodes Employed in the Present Study**

| modified electrode | Pd (mg cm$^{-2}$) A component | $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (mg cm$^{-2}$) B component |
|--------------------|-------------------------------|---------------------------------------------------------------|
| GC/A−4B−CH         | 0                             | 4                                                             |
| GC/0.8A−3.2B−CH    | 0.8                           | 3.2                                                           |
| GC/1.6A−2.4B−CH    | 1.6                           | 2.4                                                           |
| GC/2.4A−1.6B−CH    | 2.4                           | 1.6                                                           |
| GC/3.2A−0.8B−CH    | 3.2                           | 0.8                                                           |
| GC/4A−0B−CH        | 4                             | 0                                                             |

**Figure 1.** Cyclic voltammograms of methanol oxidation at (a) +0.5 to +1.5 V, (b) −1.0 to +0.7 V, and (c) −1.0 to +1.5 V vs Hg/HgO on modified electrodes in 0.80 M methanol and 1.00 M KOH.
On the basis of our previous work, the glassy carbon (GC) electrode was modified with palladium nanoparticles (A component) and LaNi$_{0.5}$Fe$_{0.5}$O$_3$ (B component) nanoparticles dispersed into chitosan (CH) polymer. These modified electrodes have been denoted as GC/$x$A−$y$B−CH ($x$ and $y$ can be 0, 0.8, 1.6, 2.4, 3.2, and 4 mg cm$^{-2}$). Table 1 offers the list of all modified electrodes. The electrochemical behavior of modified electrodes was investigated by SAMA Electroanalyser (Isfahan, Iran) by using cyclic voltammetry and controlled potential coulometry techniques in a three-electrode cell at room temperature ($T = 301$ K), for 500 s and different potentials. In this way, the working, counter, and reference

| S   | A       | B       | C       | A       | B       | C       |
|-----|---------|---------|---------|---------|---------|---------|
| 2   | 78.624 82 | −26.237 80 | 2.922 020 | 80.93023 | −27.123 25 | 3.069 766 |
| 25  | 113.523 39 | −31.337 22 | 3.429 315 | 112.900 95 | −31.000 21 | 3.397 758 |
| 50  | 152.139 06 | −37.089 04 | 4.008 089 | 149.966 83 | −36.578 75 | 3.905 945 |
| 75  | 192.271 20 | −43.443 97 | 4.674 282 | 190.976 54 | −42.737 10 | 4.572 127 |
| 100 | 235.479 65 | −51.744 36 | 5.471 440 | 234.830 06 | −50.975 26 | 5.396 304 |
| 125 | 282.504 34 | −60.825 51 | 6.382 312 | 282.427 39 | −60.793 23 | 6.378 474 |
| 150 | 332.452 32 | −71.685 63 | 7.468 529 | 333.268 55 | −72.191 02 | 7.518 639 |
| 175 | 385.991 24 | −83.990 52 | 8.697 364 | 387.453 52 | −85.168 62 | 8.816 798 |
| 200 | 444.877 12 | −98.589 45 | 10.161 934 | 446.322 31 | −99.126 03 | 10.272 952 |
| 225 | 507.882 04 | −115.488 37 | 11.847 271 | 508.654 92 | −115.863 26 | 11.887 099 |
| 250 | 576.417 46 | −135.105 15 | 13.812 550 | 574.771 34 | −134.580 30 | 13.659 241 |

Figure 2. Estimated parameter curves of (a) A, (b) B, and (c) C vs a covariate value ($s$).
electrodes were the modified GC, platinum, and Hg/HgO electrodes, respectively. A mixture of potassium hydroxide solution with a known methanol concentration (1 M KOH + 1.54 M methanol) was considered as the electrolyte.

**RESULTS AND DISCUSSION**

**Cyclic Voltammetry Investigations.** The cyclic voltammmograms of methanol oxidation on different modified electrodes were recorded at three potential ranges (Figure 1). On the basis of Figure 1a, for the GC/0A−4B−CH electrode, the peak of methanol oxidation appeared at 1.28 V. By increasing the contribution of A to B component in the catalyst, the current density was increased so the peak at 1.28 V was detected with difficulty. As seen from Figure 1b, the peak comparison for GC/4A−0B−CH and GC/3.2A−0.8B−CH electrodes proved that the presence of B components shifted the potential and current to more negative and higher values, respectively. By decreasing the contribution of A to B component in the catalyst, the peak methanol oxidation disappeared. Figure 1c shows the cyclic voltammograms of methanol oxidation on different modified electrodes at a wider potential range. According to this, there are two peak methanol oxidations (1.28 V for B component and 0.43 V for A component, individually) at forward sweep for modified electrodes. To include both peaks of methanol oxidation on such electrodes with different contributions of A and B components, the potential 1.2 V was selected for the controlled potential coulometry technique.

**Simulation Study.** To study this approach, the model is defined as

$$Y|\varepsilon = f(A, B, C, D, x) + \varepsilon$$  

where

$$f(A, B, C, D, x) = A + Bx + Cx^2 - \text{IID}$$  

$$\varepsilon \sim N(s, 10)$$ is a random variable, the sample size $n = 100$, the iteration number $N = 1000$, the main random variable $x = \text{seq}(0, 10, \text{length} = 10)$, the fixed values of $D = \text{seq}(1.8, 2.8, \text{length} = 11)$, and the covariate values $s = (2, 2.5, 50, 75, 100, 125, 150, 175, 200, 225, \text{and} 250)$. We assume that there is a relation between the parameters and the covariate given by the equation

$$Y|s = A(s) + B(s)x + C(s)x^2 + \varepsilon$$  

The mixed model is extracted as

$$\hat{Y}|s = \hat{A}(s) + \hat{B}(s)x + \hat{C}(s)x^2$$

Not only is this a generalized model but it can also estimate the response variable according to optional values of the covariate.

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**Table 3. Individual and General Regression Models for Estimating the Current Density**

| A percent | B percent | model = $f(t, P_A)$ | sig value |
|-----------|-----------|---------------------|-----------|
| 0         | 100       | $\log(J/t) = 1.40 - [0.718 \times \log(t)] + [0.153 \times \log(t)^2]$ | $2 \times 10^{-10}$ |
| 40        | 60        | $\log(J/t) = 1.58 - [0.692 \times \log(t)] + [0.144 \times \log(t)^2]$ | $2 \times 10^{-10}$ |
| 60        | 40        | $\log(J/t) = 1.74 - [0.775 \times \log(t)] + [0.154 \times \log(t)^2]$ | $2 \times 10^{-10}$ |
| 100       | 0         | $\log(J/t) = 1.97 - [0.708 \times \log(t)] + [0.200 \times \log(t)^2]$ | $2 \times 10^{-10}$ |

$$P_A = 1 - P_B$$

where $P_A$ is the individual and general estimations of variables.
i.e., $s = 10, 40, \text{ and } 230$. We hope the estimated model, with all mentioned models being significant, can help us to forecast the response variable even in impossible situations. We used the maximum likelihood estimator and mean square error (MSE) methods to estimate the regression (linear and/or nonlinear) of the involved models by usage R (SPSS) software. The results of

![Figure 4. Current density vs time curves on the basis of the experimental and estimated data for (a) GC/0A−4B−CH, (b) GC/0.8A−3.2B−CH, (c) GC/1.6A−2.4B−CH, (d) GC/2.4A−1.6B−CH, (e) GC/3.2A−0.8B−CH, and (f) GC/4A−0B−CH electrodes.](image-url)
the simulation are subsequently stated. The estimated parameters are displayed in Table 2 where
\[
\hat{A}_s = 78.44 + 1.27s + 0.00287s^2
\]  
(12)
and
\[
\hat{B}_s = -26.17 - 1.109s - 0.00127s^2
\]  
(13)

The curves of estimated parameters are shown in Figures 2 and 3.

Table 5. Integrated Charge Exchanged over Time Intervals for $P_{A=0.00}$

| $P_{A=0.00}$ | $\int_{t_1}^{t_2} f(t) \, dt$ |
|---------------|-------------------------------|
| $t_1$ | $t_2$ |
| 0.00 | 90.16  |
| 0.00 | 135.26 |
| 0.00 | 171.49 |
| 0.00 | 202.93 |
| 0.00 | 231.24 |
| 0.00 | 257.27 |
| 0.00 | 281.56 |
| 0.00 | 304.45 |
| 0.00 | 326.17 |
| 0.00 | 346.91 |
| 0.00 | 366.81 |
| 0.00 | 385.97 |
| 0.00 | 404.48 |

Table 6. Integrated Charge Exchanged over Time Intervals for $P_{A=0.40}$

| $P_{A=0.40}$ | $\int_{t_1}^{t_2} f(t) \, dt$ |
|---------------|-------------------------------|
| $t_1$ | $t_2$ |
| 0.00 | 190.18  |
| 0.00 | 272.63 |
| 0.00 | 336.56 |
| 0.00 | 390.82 |
| 0.00 | 438.82 |
| 0.00 | 482.47 |
| 0.00 | 522.70 |
| 0.00 | 560.25 |
| 0.00 | 595.60 |
| 0.00 | 629.12 |
| 0.00 | 661.05 |
| 0.00 | 691.62 |
| 0.00 | 720.99 |

Table 7. Integrated Charge Exchanged over Time Intervals for $P_{A=0.60}$

| $P_{A=0.60}$ | $\int_{t_1}^{t_2} f(t) \, dt$ |
|---------------|-------------------------------|
| $t_1$ | $t_2$ |
| 0.00 | 1277.21  |
| 0.00 | 389.33 |
| 0.00 | 474.90 |
| 0.00 | 546.79 |
| 0.00 | 609.97 |
| 0.00 | 666.97 |
| 0.00 | 719.31 |
| 0.00 | 767.94 |
| 0.00 | 813.57 |
| 0.00 | 856.68 |
| 0.00 | 897.63 |
| 0.00 | 936.73 |
| 0.00 | 974.20 |

The curves of estimated parameters are shown in Figures 2 and 3.
### Table 8. Integrated Charge Exchanged over Time Intervals for $P_A = 1.00$

| $P_A$ | $t_2$ | $t_1$ | $f(t)$ | $t_f$ |
|-------|-------|-------|--------|-------|
| 1.00  | 1418.10 | 1515.29 | 0.00   | 1680.16 |
| 0.60  | 1402.20 | 1503.30 | 0.00   | 1679.30 |
| 0.40  | 1401.40 | 1502.50 | 0.00   | 1678.50 |
| 0.20  | 1400.60 | 1501.70 | 0.00   | 1677.70 |

**Real Data.** For real data, we consider the following two conditions. First case: For constant potential at $+1.2$ V, the proposed model was considered for experimental data of different percentages of A and B to find a general model. The general model can predict the value of the response variable (output) for each percentage of A and B. Second case: For constant percentage of A and B, the proposed model was considered for experimental data of different values of the potential to find a general model. The general model can predict the value of the response variable (output) for each applied potential. According to the percentages of A and B components, several nonlinear regressions of current density were chosen in $J/(\text{mA cm}^{-2})$ for these data. The exchanged charge over this time based on the A-level percentage was $P_A \times A \times (1 - P_A) \times B$. Let $P_A = \{0.00, 0.20, 0.40, 0.60, 0.80, 1.00\}$ and $t = \{0.2, ..., 300\}$ per second. The results are as follows and show that all models are significant. The summary of the model equivalent to $P_A = 0.00, P_B = 1.00$ follows.

**Formula:**

$$J/(\text{mA cm}^{-2}) \sim a + bT + cT^2$$

| parameters estimate | std. error | $t$-value | $P$-value |
|---------------------|-------------|-----------|------------|
| $a$                 | 1.400190    | 0.002894  | 483.8      |
| $b$                 | -0.718050   | 0.003431  | -209.3     |
| $c$                 | 0.153938    | 0.001019  | 151.1      |

Residual standard error: 0.01307 on 1497 degrees of freedom; achieved convergence tolerance: $2.257 \times 10^{-16}$.

The summary of the model equivalent to $P_A = 0.20, P_B = 0.80$ follows.

**Formula:**

$$J/(\text{mA cm}^{-2}) \sim a + bT + cT^2$$

| parameters estimate | std. error | $t$-value | $P$-value |
|---------------------|-------------|-----------|------------|
| $a$                 | 1.654462    | 0.004048  | 408.7      |
| $b$                 | -0.753021   | 0.003493  | -156.9     |
| $c$                 | 0.143733    | 0.001425  | 100.9      |

Residual standard error: 0.01829 on 1497 degrees of freedom; achieved convergence tolerance: $1.377 \times 10^{-16}$.

The summary of the model equivalent to $P_A = 0.40, P_B = 0.60$ follows.

**Formula:**

$$J/(\text{mA cm}^{-2}) \sim a + bT + cT^2$$

| parameters estimate | std. error | $t$-value | $P$-value |
|---------------------|-------------|-----------|------------|
| $a$                 | 1.582293    | 0.006851  | 230.97     |
| $b$                 | -0.692841   | 0.008122  | -85.31     |
| $c$                 | 0.144265    | 0.002411  | 59.84      |

Residual standard error: 0.03095 on 1497 degrees of freedom; achieved convergence tolerance: $7.564 \times 10^{-16}$.

The summary of the model equivalent to $P_A = 0.60, P_B = 0.40$ follows.

**Formula:**

$$J/(\text{mA cm}^{-2}) \sim a + bT + cT^2$$

| parameters estimate | std. error | $t$-value | $P$-value |
|---------------------|-------------|-----------|------------|
| $a$                 | 1.741539    | 0.004149  | 419.8      |
| $b$                 | -0.775603   | 0.004919  | -157.7     |
| $c$                 | 0.154073    | 0.001460  | 105.5      |

Residual standard error: 0.01874 on 1497 degrees of freedom; achieved convergence tolerance: $2.055 \times 10^{-16}$.

The summary of the model equivalent to $P_A = 0.80, P_B = 0.20$ follows.

**Formula:**

$$J/(\text{mA cm}^{-2}) \sim a + bT + cT^2$$

| parameters estimate | std. error | $t$-value | $P$-value |
|---------------------|-------------|-----------|------------|
| $a$                 | 2.139579    | 0.009003  | 237.64     |
| $b$                 | -1.019560   | 0.010674  | -95.52     |
| $c$                 | 0.181744    | 0.003169  | 57.36      |

Residual standard error: 0.04067 on 1497 degrees of freedom; achieved convergence tolerance: $8.595 \times 10^{-16}$.
follows.

To have an estimation of exchanged charge over time intervals (Figure 4) can be possible. These values are shown in the following Tables 5.

Then, the fitting of the related graphs and calculation of the exchanged charge over time intervals (Figure 4) can be possible. These values are shown in the following Tables 5–8. It is noteworthy that we considered the logarithm of the response variable with a base of 10, as \( \log_{10}(J/(\text{mA cm}^{-2}))/t(s) \); hence, it is easy to calculate the original response variable, \( J/(\text{mA cm}^{-2}) \), to use the last mixed robust model by putting a new \( p_A \) value and the time values to estimate the related response variable.

Figure 5. Graphs of the current density vs time for methanol oxidation at 1.2 V potential by (a) the individual and general models and forecasting for the new 90% of the A component and (b) the experiment vs its statistical general estimation for \( p_A = 0.9 \) and \( p_B = 0.10 \).

Table 9. Individual and General Regression Models for Estimating the Current Density for \( p_A = 0.40 \) and \( p_B = 0.60 \)

| V level | model = \( f(t) \) | sig value |
|---------|------------------|-----------|
| 0.2     | \( \log_{10}(J \times t) = 0.962 - \{0.997 \times \log_{10}(t)\} + \{0.1895 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-11} \) |
| 0.4     | \( \log_{10}(J \times t) = 1.1498 - \{0.797 \times \log_{10}(t)\} + \{0.084 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-11} \) |
| 0.6     | \( \log_{10}(J \times t) = 1.085 - \{0.378 \times \log_{10}(t)\} + \{0.0041 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-11} \) |
| 0.8     | \( \log_{10}(J \times t) = 1.28 - \{0.355 \times \log_{10}(t)\} + \{0.0073 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-11} \) |
| 1       | \( \log_{10}(J \times t) = 1.296 - \{0.323 \times \log_{10}(t)\} + \{0.0199 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-11} \) |
| 1.2     | \( \log_{10}(J \times t) = 1.4954 - \{0.494 \times \log_{10}(t)\} + \{0.089 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-10} \) |
| \( \nu \) | \( \log_{10}(J \times t) = (0.8690 + 0.473v) - \{[1.484 + 2.6289v - 1.47t^2] \times \log_{10}(t)\} + \{[0.344 - 0.88v + 0.55t^2] \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-10} \) |

Table 10. Individual and General Regression Models for Estimating the Current Density for \( p_A = 0.80 \) and \( p_B = 0.20 \)

| V level | model = \( f(t) \) | sig value |
|---------|------------------|-----------|
| 0.2     | \( \log_{10}(J \times t) = 0.838 - \{0.794 \times \log_{10}(t)\} + \{0.17 \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-11} \) |
| 0.4     | \( \log_{10}(J \times t) = 0.804330 454.85 <2 \times 10^{-16} \) | \( 2 \times 10^{-11} \) |
| 0.6     | \( \log_{10}(J \times t) = -0.708535 0.005133 -138.03 <2 \times 10^{-16} \) | \( 2 \times 10^{-11} \) |
| 0.8     | \( \log_{10}(J \times t) = 0.129911 0.001524 85.25 <2 \times 10^{-16} \) | \( 2 \times 10^{-11} \) |
| 1       | \( \log_{10}(J \times t) = 1.370 + 0.780 \times \log_{10}(t) \) | \( 2 \times 10^{-11} \) |
| 1.2     | \( \log_{10}(J \times t) = 1.370 + 0.780 \times \log_{10}(t) \) | \( 2 \times 10^{-11} \) |
| \( \nu \) | \( \log_{10}(J \times t) = (0.8690 + 0.473v) - \{[1.484 + 2.6289v - 1.47t^2] \times \log_{10}(t)\} + \{[0.344 - 0.88v + 0.55t^2] \times \log_{10}(t^2)\} \) | \( 2 \times 10^{-10} \) |

The summary of the model equivalent to \( p_A = 1.00, p_B = 0.00 \) follows.

Formula: \( J/(\text{mA cm}^{-2}) \sim a + bT + cT^2 \)

| parameters estimate | \( P_a > \beta \) |
|---------------------|------------------|
| \( a \)             | 1.969494 0.004330 454.85 <2 \times 10^{-16} \) |
| \( b \)             | 0.708535 0.005133 -138.03 <2 \times 10^{-16} \) |
| \( c \)             | 0.129911 0.001524 85.25 <2 \times 10^{-16} \) |

Residual standard error: 0.01956 on 1497 degrees of freedom; achieved convergence tolerance: \( 1.165 \times 10^{-8} \).

By combining the parameter estimators from these models

\[
\hat{\beta}_0 = 1.370 + 0.780 \times P_A
\]

\[
\hat{\beta}_1 = -(0.718 + 0.135P_A)
\]

\[
\hat{\beta}_2 = (0.152 - 0.020 \times P_A + 0.014 \times P_A^2)
\]

and putting them in the main model, the mixed regression model was obtained. Finally, this nonlinear regression model can easily estimate the response value, the current density, \( J/(\text{mA cm}^{-2}) \), on the basis of the collaborated participation of A percentage level (B percentage level) and time.

Examples of regression models estimating the current density are reported in Table 3. By combining the A and B levels such as \( P_A \times A \) and \( (1 - P_A) \times B \), the resulting robust model is

\[\log_{10}(J \times tP_A) = \hat{\beta}_0(P_A) + \hat{\beta}_1(P_A) \times \log_{10}(t) + \hat{\beta}_2(P_A) \times \log_{10}(t^2)\] (18)

To have an estimation of exchanged charge over time, we consider the values for \( t_1 \) and \( t_2 \) as displayed in Table 4.

Then, the fitting of the related graphs and calculation of the exchanged charge over time intervals (Figure 4) can be possible. These values are shown in the following Tables 5–8.
5 shows that the estimation for $P_A=0.90$ is reasonably located between the two levels $P_A=0.80$ and $P_A=0.10$.

At first, we consider the fixed percentages $p_A = 0.40$ ($p_B = 0.60$) and $p_B = 0.80$ ($p_B = 0.20$) of A and B, respectively. Let the applied potential be considered as $E = \{0.2, 0.4, 0.6, 0.8, 1.0, 1.2\}$. It was chosen by several nonlinear regressions of current density, $J/(mA\ cm^{-2})$, for these data. The exchanged charge over this time was measured on the basis of the measures mentioned above at $t = \{0.2,..., 300\}$ per second. The results are as follows and show that all models are significant.

For example, following is the summary of the model equivalent to $P_A = 0.40$, $P_B = 0.60$, and $E = 0.2$ V.

$$\text{Formula: } J/(mA\ cm^{-2}) \sim a + bT + cT^2$$

| Parameter | Estimate | Std Error | $t$-value | $P_t$ (>|t|) |
|-----------|----------|-----------|-----------|-------------|
| $a$       | 0.961945 | 0.001445  | 665.5     | <2 x 10^{-16} |
| $b$       | -0.997022| 0.001530  | -651.4    | <2 x 10^{-16} |
| $c$       | 0.189549 | 0.000404  | 469.2     | <2 x 10^{-16} |

Residual standard error: 0.006902 on 2494 degrees of freedom.

A convergence tolerance of $1.754 \times 10^{-8}$ was achieved. By combining the parameters’ estimators from these models

$$\hat{\alpha}_0(v) = 0.8690 + 0.473v$$

(19)

$$\hat{\alpha}_1(v) = 1.484 + 2.6289v - 1.47v^2$$

(20)

$$\hat{\alpha}_2(v) = 0.344 - 0.88v + 0.55v^2$$

(21)

and putting them in the main model, the mixed regression model was obtained. Finally, this nonlinear regression model can easily estimate the response value, the current density, $J/(mA\ cm^{-2})$, on the basis of the participation potential level and the time.

Examples of regression models to estimate the current density are reported in Tables 9 and 10. By combining the fixed mentioned levels of A and B and potential levels, the resulting robust model is

$$\log_{10}(J \times t^v) = \hat{\alpha}_0(v) + \hat{\alpha}_1(v) \times \log_{10}(t) + \hat{\alpha}_2(v) \times \log_{10}(t^2)$$

(22)

Hence, the fitting of the related graphs and calculation of the exchanged charge over time intervals (Figure 6 and 7) can be possible.
CONCLUSIONS

In this work, the catalytic activity of modified glassy carbon electrodes with α-Pd−γ-LaNi5–Fe3−χO4−ϕ−chitosan as an anodic catalyst toward methanol oxidation was investigated with cyclic voltammetry and controlled potential coulometry techniques; x and ϕ are the mass loading of noble metal and mixed oxide, respectively. The results of the simulation method to extract a suitable mixed model and robust model show that on the basis of the skill of the statistician, this strategy usually works well. It would be better, before starting the related trials, to consult a statistician, and the points of the covariate values should be more. For example, it is impossible to repeat the trials for all arbitrary percentages of the A and B components without spending time and chemicals. But with the use of this method, the same results can be obtained with less expense and time. Although we can estimate the regression model for each value of the percentage, it is possible to estimate the regression model for another new value of percentage; meaning, not only by use of the mixed model can we estimate the response variable for all possible percentage values but we can also forecast it for each arbitrary value of the covariate \( P_x 0 \leq P_x \leq 1 \).

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Notes
The authors declare no competing financial interest.

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