

# Identification of Time-Varying Mixed Potential Processes

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**Abstract:** - The identification problem of nonlinear model for electroless nickel plating is considered in this paper. The identification method is developed for estimation of the constant electrochemical parameters and time-varying mixed potential parameters. The efficiency of the method proposed is demonstrated in the simulation experiment.

**Keywords:** - time-varying, nonlinear, identification, mixed potential, approximation

## 1 Introduction

Electroless nickel plating is a widely used process in electronic industry. Unlike electric nickel plating it produces a very uniform alloy and has good corrosion protection properties. However, a precise control is required in microchip industry because of increasingly higher packing rate. The goal of the process control is to stabilize the thickness and phosphorus content of an alloy at desired level. In the literature several mathematical models of the process were developed [1]-[8] in the framework of chemical and electrochemical reaction theory. The mixed potential theory is developed in [4]-[6]. In [7] and [8] a complete model for monitoring of the unobservable nickel plating process was proposed and control algorithm was developed. The model proposed is highly nonlinear and to improve control quality several constant parameters and time-varying mixed potential parameters have to be estimated.

In this paper estimation problem of the unknown parameters for the electroless nickel plating model is studied and identification procedure is proposed.

## 2 Process model

The general structure of the process model is depicted in Fig. 1 (for details, see [7]).

The model is composed of the dynamic linear block in series connection with two static nonlinear blocks  $F_1$  and  $F_2$  and controller  $F_3$ . A set of ordinary linear differential equations is used to describe concentration dynamics of the process. Concentration of species affects the equilibrium potentials ( $F_1$  block) and equilibrium potentials in its turn affect to the current densities of the electrode reactions ( $F_2$  block).

State-space representation of the concentration dynamics and nonlinear function  $F_1$  are assumed to be known. State variable  $c$  is also assumed to be observable. According to the Nernst equation [4], equilibrium potentials of the electrode reactions can be evaluated from concentration of substances due to the assumptions above.

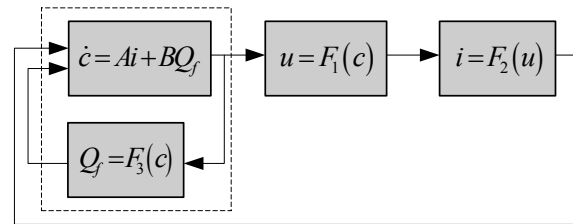


Fig. 1 The process model

The static nonlinear block  $F_2$  can be represented by system of Volmer-Buttler equations, which correspond to four reactions of the process:

$$\begin{cases} \dot{i}_1 = (A/A_{max}) \cdot i_{01} \cdot \left[ e^{k_1 \alpha_{a1} (\Phi - U_1)} - e^{-k_1 (1 - \alpha_{a1}) (\Phi - U_1)} \right] \\ \dot{i}_2 = (A/A_{max}) \cdot i_{02} \cdot \left[ e^{k_2 \alpha_{a2} (\Phi - U_2)} - e^{-k_2 (1 - \alpha_{a2}) (\Phi - U_2)} \right] \\ \dot{i}_3 = (A/A_{max}) \cdot i_{03} \cdot \left[ e^{k_3 \alpha_{a3} (\Phi - U_3)} - e^{-k_3 (1 - \alpha_{a3}) (\Phi - U_3)} \right] \\ \dot{i}_4 = (A/A_{max}) \cdot i_{04} \cdot \left[ e^{k_4 \alpha_{a4} (\Phi - U_4)} - e^{-k_4 (1 - \alpha_{a4}) (\Phi - U_4)} \right] \end{cases}, \quad (1)$$

where

- $i_j$  – current densities, A/cm<sup>2</sup>,
- $i_{0j}$  – exchange current densities, A/cm<sup>2</sup>,
- $\alpha_{aj}$  – anodic apparent transfer coefficients,
- $A$  – loading factor,
- $A_{max}$  – maximum admissible loading factor,
- $k$  – temperature voltage (constant), V<sup>-1</sup>,
- $U_j$  – equilibrium potentials, V,
- $\Phi$  – mixed potential, V.

Mixed potential in (1) is unobservable function in time. With respect to the mixed potential it is known that it satisfies to the charge conservation equation:

$$i_1 + i_2 + i_3 + i_4 = 0. \quad (2)$$

The model (1) is known as two-directional electrode model, because it is represented as difference between anodic and cathodic current densities.

The loading factor, defined as the total metal area of plates immersed in the solution per bath volume, is strongly jumping and observable process.

The objective is to identify the exchange current densities and anodic apparent transfer coefficients of the electrode reactions as well as mixed potential function using available measurements of concentration  $c$ , current density  $i$  and loading factor  $A$ .

### 3 Identification method

We start from excluding loading factor from the further analysis. Take into consideration scaled current densities:

$$\{i_{A,j}(t) = i_j(t) \cdot (A_{\max}/A(t)), j = \overline{1,4}. \quad (3)$$

According to (3) the system of equations (1) reduces to the next form:

$$\begin{cases} i_{A,1} = i_{01} \cdot [e^{k_1 \alpha_{a1}(\Phi - U_1)} - e^{-k_1(1-\alpha_{a1})(\Phi - U_1)}] \\ i_{A,2} = i_{02} \cdot [e^{k_2 \alpha_{a2}(\Phi - U_2)} - e^{-k_2(1-\alpha_{a2})(\Phi - U_2)}] \\ i_{A,3} = i_{03} \cdot [e^{k_3 \alpha_{a3}(\Phi - U_3)} - e^{-k_3(1-\alpha_{a3})(\Phi - U_3)}] \\ i_{A,4} = i_{04} \cdot [e^{k_4 \alpha_{a4}(\Phi - U_4)} - e^{-k_4(1-\alpha_{a4})(\Phi - U_4)}] \end{cases} \quad (4)$$

It should be emphasized that since the loading factor  $A$  enters to every equation of (1) with the same factor charge equation (2) still holds for scaled current densities.

Though the model (4) is nonlinear, we, nevertheless, can use linearization technique to estimate unknown parameters. This is because the control objective in electroless nickel plating is stabilization for thickness of the alloy. In terms of the model this means stabilization of mixed potential and equilibrium potentials of the reactions. So the variation of overpotentials is small enough to use equivalent to (4) linear model.

To turn to linear model for (4) we create the 1<sup>st</sup> order Taylor series expansion of the current densities at  $\Phi - U_j$ :

$$i_{A,j}(\Phi, U_j) = i_{A,j}(\Phi_0, U_{j,0}) + i'_{A,j}(\Phi_0, U_{j,0}) \cdot (\eta_j - \eta_{j,0}) + o(|\eta_j|), j = \overline{1,4}, \quad (5)$$

with overpotential  $\eta_j$  being defined as

$$\eta_j = \Phi - U_j. \quad (6)$$

Now the system (4) can be represented in linear form as

$$\begin{cases} i_{A,1} = a_1 + b_1((\Phi - \Phi_0) - (U_1 - U_{01})) + o(|\eta_1|) \\ i_{A,2} = a_2 + b_2((\Phi - \Phi_0) - (U_2 - U_{02})) + o(|\eta_2|) \\ i_{A,3} = a_3 + b_3((\Phi - \Phi_0) - (U_3 - U_{03})) + o(|\eta_3|) \\ i_{A,4} = a_4 + b_4((\Phi - \Phi_0) - (U_4 - U_{04})) + o(|\eta_4|) \end{cases}, \quad (7)$$

where

$$a_j = i_{A,j}(\Phi_0, U_{0j}), \quad b_j = i'_{A,j}(\Phi_0, U_{0j}), \quad j = \overline{1,4}. \quad (8)$$

Combining all free terms in every equation of (7) into one

$$d_j = a_j - b_j(\Phi_0 - U_{0j}) \quad (9)$$

and ignoring approximation error we obtain the next equivalent form of (3):

$$\begin{cases} i_{A,1} = d_1 + b_1\Phi - b_1U_1 \\ i_{A,2} = d_2 + b_2\Phi - b_2U_2 \\ i_{A,3} = d_3 + b_3\Phi - b_3U_3 \\ i_{A,4} = d_4 + b_4\Phi - b_4U_4 \end{cases} \quad (10)$$

By summing all four equations in (10) and using charge conservation identity (2) we derive the next expression for mixed potential  $\Phi$ :

$$\Phi = \frac{-\sum_{i=1}^4 d_i + \sum_{i=1}^4 b_i U_i}{\sum_{i=1}^4 b_i}. \quad (11)$$

Emphasize that equation (11) gives the straightforward way to estimate time-varying mixed potential provided that we know estimates of unknown coefficients  $b_j$  and  $d_j$ .

The substitution of the (11) to (10) allows us to eliminate the mixed potential and to represent the system (10) as:

$$\begin{cases} i_{A,1} = \gamma_1 + \beta_{21}\Delta U_{21} + \beta_{31}\Delta U_{31} + \beta_{41}\Delta U_{41} \\ i_{A,2} = \gamma_2 + \beta_{12}\Delta U_{12} + \beta_{32}\Delta U_{32} + \beta_{42}\Delta U_{42} \\ i_{A,3} = \gamma_3 + \beta_{13}\Delta U_{13} + \beta_{23}\Delta U_{23} + \beta_{43}\Delta U_{43} \\ i_{A,4} = \gamma_4 + \beta_{14}\Delta U_{14} + \beta_{24}\Delta U_{24} + \beta_{34}\Delta U_{34} \end{cases} \quad (12)$$

with  $\Delta U_{ij}(t) = U_i(t) - U_j(t)$  and  $\gamma_i, \beta_{ij}$  being defined as

$$\gamma_i = \frac{d_i \sum_{j \neq i} b_j - b_i \sum_{j \neq i} d_j}{\sum_{j=1}^4 b_j}, \quad (13)$$

$$\beta_{ij} = \frac{b_i b_j}{\sum_{k=1}^4 b_k}. \quad (14)$$

Note, that the next identities are hold:

$$\sum_{i=1}^4 \gamma_i = 0, \quad (15)$$

$$\beta_{ij} = \beta_{ji}, \quad (16)$$

$$\beta_{ij} = \frac{\beta_{ik}\beta_{jl}}{\beta_{kl}}. \quad (17)$$

The regression vector for (12) is given by:

$$\theta = [\gamma_1 \ \gamma_2 \ \gamma_3 \ \beta_{12} \ \beta_{13} \ \beta_{14} \ \beta_{23} \ \beta_{24} \ \beta_{34}]^T. \quad (18)$$

And regression matrix is:

$$X = [\Delta U_{21} \ \Delta U_{31} \ \Delta U_{41} \ \Delta U_{32} \ \Delta U_{42} \ \Delta U_{43}].$$

Take into attention that we deal with multi-objective optimization problem, because coefficients (18) have to be chosen to satisfy to four different equations of the system (12). One way to operate with multi-objective problem is to transform it to single-objective problem. For example, sum of four objectives with weights  $\omega_k$  leads to the next function to be minimized:

$$J = \frac{1}{2} \sum_{k=1}^4 \omega_k \sum_{l=1}^N (i_{A,k}(t_l) - \hat{i}_{A,k}(t_l))^2. \quad (19)$$

Now the optimization problem is to find coefficients  $\beta_{ij}$  and  $\gamma_i$  which minimize objective function (19) subject to constraints (15)-(17). This problem can be solved by nonlinear least squares method or, in well-

posed case, subject to only linear constraints (15), (16) by conventional least squares method.

The optimality conditions require first derivatives of (19) with respect to regression vector (18) to be zero in optimum point:

$$\frac{\partial J}{\partial \theta_1} = -\omega_1 \sum_{k=1}^N (i_{A,1}(t_k) - \theta_1 - \theta_4 X_1 - \theta_5 X_2 - \theta_6 X_3) + \omega_4 \sum_{k=1}^N (i_{A,4}(t_k) + \theta_1 + \theta_2 + \theta_3 + \theta_6 X_3 + \theta_8 X_5 + \theta_9 X_6), \quad (20)$$

$$\frac{\partial J}{\partial \theta_2} = -\omega_2 \sum_{k=1}^N (i_{A,2}(t_k) - \theta_2 + \theta_4 X_1 - \theta_7 X_4 - \theta_8 X_5) + \omega_4 \sum_{k=1}^N (i_{A,4}(t_k) + \theta_1 + \theta_2 + \theta_3 + \theta_6 X_3 + \theta_8 X_5 + \theta_9 X_6), \quad (21)$$

$$\frac{\partial J}{\partial \theta_3} = -\omega_3 \sum_{k=1}^N (i_{A,3}(t_k) - \theta_3 + \theta_5 X_2 + \theta_6 X_4 - \theta_9 X_6) + \omega_4 \sum_{k=1}^N (i_{A,4}(t_k) + \theta_1 + \theta_2 + \theta_3 + \theta_6 X_3 + \theta_8 X_5 + \theta_9 X_6), \quad (22)$$

$$\frac{\partial J}{\partial \theta_4} = -\omega_1 \sum_{k=1}^N X_1 \cdot (i_{A,1}(t_k) - \theta_1 - \theta_4 X_1 - \theta_5 X_2 - \theta_6 X_3) + \omega_2 \sum_{k=1}^N X_1 \cdot (i_{A,2}(t_k) - \theta_2 + \theta_4 X_1 - \theta_7 X_4 - \theta_8 X_5), \quad (23)$$

$$\frac{\partial J}{\partial \theta_5} = -\omega_1 \sum_{k=1}^N X_2 \cdot (i_{A,1}(t_k) - \theta_1 - \theta_4 X_1 - \theta_5 X_2 - \theta_6 X_3) + \omega_3 \sum_{k=1}^N X_2 \cdot (i_{A,3}(t_k) - \theta_3 + \theta_5 X_2 + \theta_7 X_4 - \theta_9 X_6), \quad (24)$$

$$\frac{\partial J}{\partial \theta_6} = -\omega_1 \sum_{k=1}^N X_3 \cdot (i_{A,1}(t_k) - \theta_1 - \theta_4 X_1 - \theta_5 X_2 - \theta_6 X_3) + \omega_4 \sum_{k=1}^N X_3 \cdot (i_{A,4}(t_k) + \theta_1 + \theta_2 + \theta_3 - \theta_6 X_3 - \theta_8 X_5 - \theta_9 X_6), \quad (25)$$

$$\frac{\partial J}{\partial \theta_7} = -\omega_2 \sum_{k=1}^N X_4 \cdot (i_{A,2}(t_k) - \theta_2 + \theta_4 X_1 - \theta_7 X_4 - \theta_8 X_5) + \omega_3 \sum_{k=1}^N X_4 \cdot (i_{A,3}(t_k) - \theta_3 + \theta_5 X_2 + \theta_7 X_4 - \theta_9 X_6), \quad (26)$$

$$\frac{\partial J}{\partial \theta_8} = -\omega_2 \sum_{k=1}^N X_5 \cdot (i_{A,2}(t_k) - \theta_2 + \theta_4 X_1 - \theta_7 X_4 - \theta_8 X_5) + \omega_4 \sum_{k=1}^N X_5 \cdot (i_{A,4}(t_k) + \theta_1 + \theta_2 + \theta_3 - \theta_6 X_3 - \theta_8 X_5 - \theta_9 X_6), \quad (27)$$

$$\begin{aligned} \frac{\partial J}{\partial \theta_3} = & -\omega_3 \sum_{k=1}^N X_6 \cdot (i_{A,3}(t_k) - \theta_3 + \theta_5 X_2 + \theta_7 X_4 - \theta_9 X_6) + \\ & + \omega_4 \sum_{k=1}^N X_3 \cdot (i_{A,4}(t_k) + \theta_1 + \theta_2 + \theta_3 - \theta_6 X_3 - \theta_8 X_5 - \theta_9 X_6) \end{aligned} \quad (28)$$

Setting the first derivatives (20)-(28) to zero produces a linear system of 9 equations in 9 variables. Such system is solvable and its solution is unique if the matrix of coefficients has full rank. Although, due to charge conservation identity and small approximation error this problem is ill-posed for identification purposes we always can add input noise to improve posedness of the problem.

Solution of (20)-(28) subject to constraints (15)-(16) is the least squares solution of the optimization problem with respect to parameter vector (18).

Some transformation from found parameters to primary parameters of interest is required, because parameter vector (18) is not one we are interested in. We call this transformation as inverse transformation. According to the structure of expressions (13), (14) it consists of two steps. The first step is to find  $b_i$  provided that  $\beta_{ij}$  are given. Due to the constraints (16), (17) any four of the coefficients  $\beta_{ij}$  are independent. Hence the system to find linear part of Taylor series expansion  $b_i$  looks, for instance, as follows:

$$\begin{cases} \beta_{12} = b_1 b_2 / \sum_{j=1}^4 b_j \\ \beta_{13} = b_1 b_3 / \sum_{j=1}^4 b_j \\ \beta_{14} = b_1 b_4 / \sum_{j=1}^4 b_j \\ \beta_{23} = b_2 b_3 / \sum_{j=1}^4 b_j \end{cases} \quad (29)$$

The straightforward way to solve the system (29) is to find partial ratios between, for instance,  $b_1$  and  $b_2$ ,  $b_3$ ,  $b_4$ . They are:

$$b_2 = b_1 \frac{\beta_{23}}{\beta_{13}}, b_3 = b_1 \frac{\beta_{23}}{\beta_{12}}, b_4 = b_1 \frac{\beta_{14}\beta_{23}}{\beta_{12}\beta_{13}} \quad (30)$$

Now the sum of the coefficients is given by:

$$\sum_{i=1}^4 b_i = b_1 \left( 1 + \frac{\beta_{23}}{\beta_{13}} + \frac{\beta_{23}}{\beta_{12}} + \frac{\beta_{14}\beta_{23}}{\beta_{12}\beta_{13}} \right) \quad (31)$$

Finally we will have the next solution of (29):

$$\begin{cases} b_1 = \beta_{12} + \beta_{13} + \beta_{14} + \frac{\beta_{12}\beta_{13}}{\beta_{23}} \\ b_2 = \beta_{12} + \beta_{23} + \frac{\beta_{12}\beta_{23}}{\beta_{13}} + \frac{\beta_{14}\beta_{23}}{\beta_{13}} \\ b_3 = \beta_{13} + \beta_{23} + \frac{\beta_{13}\beta_{23}}{\beta_{12}} + \frac{\beta_{14}\beta_{23}}{\beta_{12}} \\ b_4 = \beta_{14} + \beta_{14} \frac{\beta_{14}\beta_{23}}{\beta_{12}\beta_{13}} + \frac{\beta_{14}\beta_{23}}{\beta_{13}} + \frac{\beta_{14}\beta_{23}}{\beta_{12}} \end{cases}$$

According to equation (13) the second step is to find  $d_i$  provided that  $\gamma_i$  and  $b_i$  are given. Unfortunately, 4 unknown coefficients have to be identified and only 3 of them are linearly independent due to constraint (15). To overcome this problem and make inverse transformation we will use mean value of mixed potential. The idea is to assume, that we know one of  $d_i$ , for instance  $d_4$ . Then the system to identify others  $d_i$  is given by:

$$\begin{bmatrix} \gamma_1 \sum_{i=1}^4 b_i + d_4 b_1 \\ \gamma_2 \sum_{i=1}^4 b_i + d_4 b_2 \\ \gamma_3 \sum_{i=1}^4 b_i + d_4 b_3 \end{bmatrix} = \begin{bmatrix} b_2 + b_3 + b_4 & -b_1 & -b_1 \\ -b_2 & b_1 + b_3 + b_4 & -b_2 \\ -b_3 & -b_3 & b_1 + b_2 + b_4 \end{bmatrix} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \end{bmatrix} \quad (32)$$

Clearly, the system (32) is linear and can be solved by classical gaussian elimination method. The solution is then expressed as linear function of  $d_4$ . Denote

$$d_{i,0} = \frac{b_i(\gamma_1 + \gamma_2 + \gamma_3) + b_4 \gamma_i}{b_4} \quad (33)$$

$$d_{i,1} = \frac{b_i}{b_4} \quad (34)$$

Now the next solution can be obtained:

$$\begin{bmatrix} d_1 \\ d_2 \\ d_3 \end{bmatrix} = \begin{bmatrix} d_{1,0} \\ d_{2,0} \\ d_{3,0} \end{bmatrix} + \begin{bmatrix} d_{1,1} \\ d_{2,1} \\ d_{3,1} \end{bmatrix} d_4 \quad (35)$$

Based on identities (33)-(35) we rewrite expression for mixed potential (11) as follows:

$$\Phi = \frac{-\sum_{i=1}^3 d_{i,0} - d_4 \left( 1 + \sum_{i=1}^3 d_{i,1} \right) + \sum_{i=1}^4 b_i U_i}{\sum_{i=1}^4 b_i} \quad (36)$$

Since the coefficients  $b_j$  were identified before, equation (36) contains only one unknown variable  $d_4$ . Assumption about known mean value of mixed potential helps to find it. Necessitate mean value of the identified mixed potential function to be equal to its value in linearization point:

$$\frac{1}{N} \sum_{i=1}^N \Phi_i = \Phi_0, \quad (37)$$

where N is number of available samples. By taking into account (36) we rewrite equation (37) as:

$$\frac{1}{N} \sum_{i=1}^N \left[ \frac{-\sum_{j=1}^3 d_{j,0} - d_4 \left( 1 + \sum_{j=1}^3 d_{j,1} \right) + \sum_{j=1}^4 b_j U_i}{\sum_{j=1}^4 b_j} \right] = \Phi_0. \quad (38)$$

The next solution of equation (38) for  $d_4$  can be found:

$$d_4 = \frac{-N \sum_{j=1}^3 d_{j,0} - N \Phi_0 \sum_{j=1}^4 b_j + \sum_{i=1}^N \sum_{j=1}^4 b_j U_i}{N \left( 1 + \sum_{j=1}^3 d_{j,1} \right)}.$$

Now based on the system (32) we are able to evaluate others  $d_i$  and then starting from the identity (9)

$$d_j = a_j - b_j(\Phi_0 - U_{0j}),$$

we can evaluate coefficients of Taylor series expansion (5) for all reactions. Then the separate nonlinear systems to identify parameters of two-directional model due to (2) are given by:

$$\begin{cases} i_{0j} \left[ e^{k_j \alpha_{aj} \eta_{0j}} - e^{-k_j (1-\alpha_{aj}) \eta_{0j}} \right] = a_j \\ i_{0j} k_j \left[ \alpha_{aj} e^{k_j \alpha_{aj} \eta_{0j}} + (1-\alpha_{aj}) e^{-k_j (1-\alpha_{aj}) \eta_{0j}} \right] = b_j \end{cases}, j = \overline{1, 4}. \quad (39)$$

Finally after calculating exchange current densities from the first equation of (39) and substituting these to the second equation we obtain the solution of (39) which is given by:

$$\begin{cases} \alpha_{aj}^{opt} = \frac{b_j}{a_j k_j} - \frac{e^{-k_j \eta_{0j}}}{1 - e^{-k_j \eta_{0j}}} \\ i_j^{opt} = \frac{a_j}{e^{k_j \left( \frac{b_j}{a_j k_j} - \frac{e^{-k_j \eta_{0j}}}{1 - e^{-k_j \eta_{0j}}} \right) \eta_{0j}} (1 - e^{-k_j \eta_{0j}})} \end{cases}, j = \overline{1, 4}. \quad (40)$$

Resulted expressions (40) give a way to estimate parameters of the two-directional electrode model (1) on condition that Taylor series expansion coefficients are known.

The overall identification procedure consists of the following steps:

1. Specify mixed potential linearization point.
2. Calculate equilibrium linearization points based on available measurements.
3. Find least-squares solution of linear problem (12).
4. Calculate Taylor series expansion coefficients.
5. Calculate estimates of the parameters according to equation (40).
6. Evaluate mixed potential curve.

The best estimate we can achieve without knowledge of the noise structure is bounded by the approximation error. In other words we can't achieve the true values of estimated parameters due to unaccounted approximation errors. But, if overpotential (6) varies a lot, a way to reduce approximation error is data clustering, identification of parameters on every cluster independently and then combining the results.

## 4 Results and discussion

### Example 1.

Here we show the best possible estimate of the unknown parameters. The true values for parameters to be identified are listed in table 1. Current densities, equilibrium potentials and mixed potential are known.

Table 1. The true values of the unknown parameters

Reaction	$i_0^{\text{true}}$ , mA	$\alpha_a^{\text{true}}$
1	17.68	0.53
2	0.498	0.38
3	2.509	0.413
4	1.611	0.535

Then coefficients (8) of the linear system (10) can be obtained and the parameters of interest can be estimated according to (41). Parameters estimated in that way are listed in table 2.

Table 2. The best possible estimate

Reaction	$i_0^{\text{est}}$ , mA	$\alpha_a^{\text{est}}$
1	17.65	0.532
2	0.494	0.370
3	2.526	0.412
4	1.561	0.525

We observe that the true and identified parameters are different; however, it seems that this accuracy is quite enough for identification (the maximum error is about 3%)

**Example 2.**

Here based on known equilibrium potentials and current densities we estimate time-varying mixed potential and unknown electrochemical parameters. We will use the same values for parameters to be identified as in the example 1. Estimated parameters are listed in table 3.

Table 3. Estimates of electrochemical parameters

Reaction	$i_0^{est}$ , mA	$\alpha_a^{est}$
1	16.19	0.561
2	0.52	0.404
3	2.56	0.417
4	1.64	0.533

The mixed potential evolution in time and its estimate are depicted on figure 2.

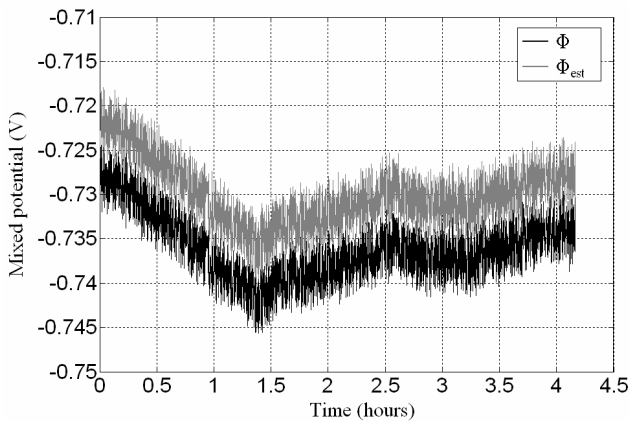


Fig. 2. Mixed potential evolution in time.

Knowledge of good average values of mixed potential is significant in the proposed identification algorithm. Otherwise though estimate of mixed potential still will track its true dynamics, the estimates of exchange current density and anodic apparent transfer coefficients will be biased.

**5 Conclusion**

In this work a novel identification procedure of nonlinear electroless nickel plating model was presented. The algorithm produces accurate and informative estimates results and can be used for synthesis of model-based control law, thickness alloy and phosphorous content estimation.

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