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Simulation of Electrorefining Process Using Time-dependent Multi-component Electrochemical Model: REFIN

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Abstract

REFIN model is applied to analyze a series of experiments that had been conducted by Tomczuk, et al. at Argonne National Laboratory (ANL) in the U.S.A.. Predicted results from REFIN model for the electrorefining experiment are compared with the published experimental results. It is demonstrated that REFIN model can predict faradic current of each element and electrochemical potential as a function of time over the entire campaign of the electrorefining experiment. The elemental concentration changes agree with the experimental results well. Elemental concentration changes during an open-circuit equilibration period are revealed to suggest that the electrorefining process could not be adequately described by the equilibrium model often applied for an electrode surface. Surface potential drop is changed according to equilibrium potential of chemical species with high activity in liquid metal.

Introduction

Partitioning and transmutation of long-lived radioisotopes can be one of the ultimate solutions for spent nuclear fuel waste management. Partitioning capability plays a critical role in reducing the toxicity of wastes that will be finally disposed of at a storage site.[1] Pyrochemical partitioning is a high temperature (~500°C) metallurgical and electrochemical

process being developed to separate toxic elements from spent nuclear fuel wastes.[2] In the process, molten salt electrolyte and liquid metal electrodes are used to dissolve spent nuclear fuel and to separate by groups of elements at controlled electrochemical conditions.[2] The process has potential advantage over conventional aqueous processes in overcoming the proliferation issue associated with plutonium diversion.[1] In order to make this processing practical, electrochemical behaviors of nuclear materials in the process need to be well understood for improving its performance and the accuracy of material accounting.

A time-dependent electrorefining model has been developed for the characterization and performance analysis of a multi-component pyro-processing.[3] The new numerical model, designated as REFIN, employs the diffusion layer theory taking into account of diffusion and electromigration in diffusion layers and a generalized Butler-Volmer kinetics model at electrode interfaces. The resulting set of partial differential equations is converted, by the method of lines, into a set of ordinary differential equations that is numerically solved by combining the backward difference scheme and Newton's method. REFIN model is schemed to handle a liquid metal electrode and/or a solid electrode. REFIN model, possesses a unique advantage over other existing models developed for pyroprocessing in its capability of simulating transient phenomena under either electrochemical potential or faradic current control.

In this paper, REFIN is applied to Tomczuk's electrorefining experiment. Tomczuk et al. conducted a series electrorefining experiment at ANL for the study of the electrodeposition of uranium and plutonium to solid cathode as a part of the development of pyroprocessing.[4] They investigated the evolution of concentrations in molten salt and liquid metal phases with the examination of the deposition morphology formed on a solid cathode under the pure uranium deposition condition. They had also compared experimental results with simulation results by a thermodynamic model. Kobayashi et al., who developed a simulation code, TRAIL, has also simulated these experiments.[5] This experiment, hence, provides a good basis for comparison of developed models on their capability of predicting electrorefining process data.

The electrorefiner for the Tomczuk et al.'s experiment is composed of a liquid cadmium anode, LiCl-KCl (58.2-41.8 m/o) molten salt electrolyte, and a solid iron cathode as

schematically shown in Figure 1. The liquid cadmium anode layer was placed at the bottom of electrorefiner with about an 11.3 cm thickness. LiCl-KCl molten salt layer covered the liquid cadmium layer with a 10.3 cm thickness. The solid iron cathode was rotated at 35 rpm for the experiment. U, Pu, Ce, Y, and Nd were initially dissolved in molten salt and liquid cadmium. Liquid cadmium and molten salt were mixed using a mechanical stirrer in order to enhance the mass transport between the liquid phases. Constant current was provided by a regulated power supply for electrotransport of elements in the electrorefiner. Tomczuk, et al. have conducted five tests over the entire campaign. In each test, the electrorefiner was operated for a preset time at a selected constant current. After each test, the solid cathode was removed from the electrorefiner and was carefully analyzed. The crucible contents were also analyzed with sampling after 16 hour mixing. Applied current history of experiment is shown in Figure 2.

Electrorefining Process Model

Electrorefining process is modeled with the diffusion layer theory and the Butler-Volmer reaction kinetics as done in REFIN. Tomczuk et al.'s electrorefiner is well stirred with the rotating cathode and the mechanical stirrer. Therefore, it is assumed that a well-defined diffusion layer is developed in the electrorefiner. The geometry of electrorefiner is transformed to a one-dimensional multi-region structure, considering diffusion layers and a solid cathode.

Electrochemical reactions take place at the interface between electrodes and electrolyte during the electrorefining process. One-step transfer of electrons is assumed in all reactions. At liquid cadmium anode, U, Pu, and Nd are electrodissoved according to the following reaction formulas;



where subscript (*Cd*) indicates that elements are dissolved to liquid cadmium, (*Salt*) indicates that elements are dissolved at LiCl-KCl molten salt, and (*S*) indicates that elements are solid deposits. At the solid cathode, cations are electrodeposited according to the following reactions.



Other elements in the electrorefiner such as Li, K, and Cl can also react electrochemically at the surface. In the present model, these reactions are also taken into account.

Current densities are expressed by the modified Butler-Volmer relation. Current density of each chemical species is a function of activities of the chemical species in liquid metal and in molten salt. At liquid cadmium anode, current density of elements is expressed as function of overpotential, η_i , as follows;

$$i_i^a = i_{0,i}^0 (a_{i,r})^{(1-\alpha_i)} (b_{i,r})^{\alpha_i} \left[\left(\frac{a_i}{a_{i,r}} \right) \exp\left(\frac{n_i \alpha_i F}{RT} \eta_i^a \right) - \left(\frac{b_i}{b_{i,r}} \right) \exp\left(-\frac{n_i (1-\alpha_i) F}{RT} \eta_i^a \right) \right] \quad (7)$$

where subscript, r , indicates a reference state that is the bulk liquid metal or molten salt conditions in the model. The anode overpotential η_i^a is expressed for each of the i -th element, as follows;

$$\eta_i^a = E_a - E_{i,r} = E_a - E_{0,i}^0 + \frac{RT}{n_i F} \ln \frac{a_{i,r}}{b_{i,r}} \quad (8)$$

where E_a is the surface potential drop at anode, $E_{i,r}$ is the equilibrium potential of i -th element in referenced to bulk, $E_{0,i}^0$ is the standard electrode potential, a_i is the activity of i -th element in liquid cadmium anode, b_i is the activity of i -th element in molten salt. In the experiment, a solid cathode is utilized and the activity in solid cathode is assumed unity neglecting the effect on a solid solution. Then current density of the i -th element is expressed, as follows;

$$i_i^c = i_{0,i}^0 (b_{i,r})^{(1-\beta_i)} \left[\left(\frac{b_i}{b_{i,r}} \right) \exp\left(-\frac{n_i \alpha_i F}{RT} \eta_i^c \right) - \exp\left(\frac{n_i (1-\alpha_i) F}{RT} \eta_i^c \right) \right] \quad (9)$$

where the cathodic overpotential is expressed as followings

$$\eta_i^c = E_c - E_{i,r} = E_c - E_{0,i}^0 - \frac{RT}{n_i F} \ln b_{i,r} \quad (10)$$

Standard exchange current density in Eq. (7) and Eq. (9) is a function of rate constant and is expressed as follows;

$$i_{0,i}^0 = n_i F k_{f,i}^{1-\alpha_i} k_{b,i}^{\alpha_i} \quad (11)$$

where $k_{f,i}$ and $k_{b,i}$ are the forward and backward rate constant, respectively. It is difficult to measure the forward and backward rate constant separately. In the model, standard rate constant of reaction, k_i , is defined to overcome the difficulty, as shown in Eq. (12).

$$k_i = k_{f,i}^{1-\alpha_i} k_{b,i}^{\alpha_i} \quad (12)$$

Inserting Eq. (12) to Eq. (11), the standard rate constant can be determined from standard exchange current density, as follows;

$$i_{0,i}^0 = n_i F k_i \quad (13)$$

The basic parameters involved in the model include diffusion layer thickness, standard electrode potential, activity coefficient of chemical species, and electrochemical kinetic parameters such as standard exchange current density and transfer coefficient. These parameters have to be evaluated to the accuracy that is required for the prediction of electrorefining process accurately. Available experimental data are, however, inadequate and not fully qualified.

Koyama et al. evaluated the standard electrode potential of elements contained in the spent fuel at temperature 673K, 723K, and 773K.[6] At 773K, they are evaluated the standard electrode potentials of U, Pu, and Nd but those of Li, K, and Cl. In the present model, the chemical reactions between solvent components such as Li, K, and Cl are allowed for the generality in the model even though absolute magnitude of reaction rate is not meaningful. In order to maintain consistency, Hammer's method is employed.[7] Standard electrode potential is recalculated using a recent data of Gibbs free energies of formation of chlorides, ΔG_f^0 as follows;

$$E_i^0 = -\frac{\Delta G_{f,i}^0}{F} \quad (14)$$

As shown in Table 1, standard electrode potential is directly obtained using Eq. (14) and then can be transformed to standard electrode potential referenced to Ag/AgCl reaction. The result shows difference from Koyama et al.'s data by about 0.23~0.27V. Koyama et al. evaluated the reported data with reference to Ag/AgCl electrode. In the model, the standard electrode potential with reference to Ag/AgCl electrode is calculated, assuming the unit activity of Ag^+

ion. This potential difference, hence, may have been induced by the activity of Ag^+ ion in molten salt.

Table 2 summarizes other kinetic parameters such as transfer coefficient, rate constant, and diffusion coefficient used in the model. These values are not known for all elements contained in spent nuclear fuel. Most of parameters in Table 2 are determined by author's judgment in order to facilitate predictions by the model. Especially, transfer coefficient and rate constant are not measured except for several elements. Transfer coefficient is a measure of the symmetry of the energy barrier that can vary current density exponentially. Transfer coefficient can be experimentally measured with exchange current density by Tafel's method. Transfer coefficient of Cd is measured to 0.13 in LiCl-KCl molten salt.[10] Transfer coefficient of most elements, however, is not available. It is assumed in model that the energy barrier is symmetric in both directions and hence a transfer coefficient of 0.5 is chosen. Standard exchange current density is given as Eq. (13). In reference [10], standard rate constant of Cd is measured as a 0.4 [cm/sec]. Standard rate constant of most elements, however, is not available in molten salt. For this reason, the rate constant in molten salt is fixed to 0.1 for all the elements.

Nawada et al. have evaluated the activity coefficient of U and Pu as a function of their concentrations, respectively.[12] They evaluated the activity coefficient from the excess Gibbs energy data and fitted activity coefficient as a linear function of the mole fraction. Activity coefficient of U varies from 81.5 to 88.7 as the concentration of U in liquid Cd varies from zero to the solubility limit (1.128 at%). Activity coefficient of Pu varies from 1.39×10^{-4} to 2.37×10^{-4} as the Pu concentration in liquid Cd varies zero to the solubility limit (1.805 at%). Activity coefficient of Nd in liquid Cd is reported to 1.3×10^{-8} .[6] In the molten salt, Koyma's data is utilized as the activity coefficients of elements.[6]

Diffusion layer thickness is dependent on the hydrodynamic conditions of the electrorefiner. Kobayshi et al. evaluated diffusion layer thickness on the basis of polarization data measured for uranium in a 10 g scale electrorefiner using Ag/0.1mol%AgCl reference electrode using simulation code, TRAIL.[5] At interface between solid cathode and molten salt, evaluated diffusion layer thickness is 0.002 cm. At interface between molten salt and liquid cadmium, diffusion layers are evaluated as 0.002 cm, respectively. In this paper, the evaluation

of diffusion layer thickness is postponed due to lack of data. Instead, Kobayashi's evaluation as diffusion layer thickness is used to simulate Tomczuk et al.'s experiment.

Results and discussion

Operation history of Tomczuk, et al.'s experiment is simulated using the REFIN model. Simulation is started from the second test using the end condition of the first test because initial condition of the first test is not available from the reference [4].

Concentration changes of uranium and plutonium in liquid cadmium and molten salt are predicted by REFIN model as shown in Figure 3 and Figure 4, respectively. Concentration changes of uranium and plutonium in liquid cadmium anode are also shown in Figure 5. The Tomczuk, et al.'s experimental results and TRAIL calculation results are compared with the present results. The calculated results of each element in each region agree well with experimental results and TRAIL calculation results. REFIN model predictions in Figure 3 show that concentration of uranium is increased while that of plutonium is decreased during the equilibration period at the end of each experiment in liquid cadmium. As shown in Figure 4, concentration of uranium is decreased and concentration of plutonium is increased during equilibration in molten salt. Uranium and plutonium are exchanged with each other between molten salt and liquid cadmium during the period. As plutonium is more active than uranium, as shown in Table 1, plutonium, therefore, tend to be oxidized from liquid cadmium and uranium tend to be reduced into liquid cadmium. This situation illustrates that uranium is electrotransported beyond the equilibrium condition between liquid cadmium and molten salt during test 2 and test 3 by the externally applied current after test 4. Exchange reaction during equilibration is decreased. It can be explained by lower current density and uranium depletion from electrorefiner. Current density is half times than test 2 and test 3, as shown in Figure 2. Equilibration behaviors are well illustrated with concentration changes according to transferred metal fraction from anode to cathode, as shown in Figure 6. During each equilibration period, concentration in molten salt is changed rapidly.

Calculation results of ANL thermodynamic code are also compared with the present results in Figure 6. It is evident that the transient during the equilibration process cannot be

predicted by the thermodynamic model. Detailed understandings of the transients make possible, for the first time, by REFIN model may help understand the underlying process and in process material accounts after each experiment.

Current is one of the main control parameters of electrorefining process. Current density at interface between electrode and electrolyte determines reaction kinetics of multi-component system. At low current density, the reaction rate is governed by electrochemical activation step. At high current density, the reaction rate is governed by mass transfer limit. At medium current density, some element is activation-controlled while another element is mass transfer controlled. The selection of proper current density, hence, can enhance the performance of electrorefining process. In the present model, the current density of each element is calculated by the modified Butler-Volmer relation that is fully general encompassing both activation-control and diffusion-control conditions. The calculation results are shown in Figure 7 and Figure 9.

As shown in Figure 7, plutonium is not deposited to cathode until test 5. Uranium is electrodissoved from the liquid cadmium anode as shown in Figure 9 and electrodeposited to the solid cathode as shown in Figure 7. No plutonium deposition to cathode is caused due to low surface potential drop that is the potential difference between electrode and the outer Helmholtz plane of electrolyte. Plutonium equilibrium potential at cathode is not higher than surface potential drop as shown in Figure 8 and plutonium electrodeposition is not started at the solid cathode. Plutonium and uranium, however, are electrodissoved from anode, together as shown in Figure 9. Even if plutonium is more active metal than uranium, current density of uranium is higher than that of plutonium. As shown in Figure 10, plutonium has a higher difference between surface potential drop and equilibrium potential than uranium. Uranium activity in liquid metal is however, five orders higher than plutonium. Current density is determined from the modified Butler-Volmer kinetics using overpotential and activity. Neodymium is expected to be electrodissoved from anode and electrodeposited to cathode. Very low concentration of neodymium, however, made its effect negligible on the whole electrorefining process.

Cell potential of electrorefiner is the sum of potential drops in each region including diffusion layer, interfaces, and bulk. As shown in Figure 11, the potential drop in diffusion layer is found to be very small. Hence, only surface potential drop is considered in the calculation of the cell potential neglecting others. Then cell potential is calculated as shown in Figure 12. The measured cell potential is close to the calculated value.

Conclusions

In this paper, a new mathematical model, REFIN is applied to simulate electrorefining process. REFIN predicted current densities of each chemical species participating in electrochemical reactions at interface between an electrode and an electrolyte, concentration changes during electrochemical processing, potential profile of external constant current source, and current density profiles of all chemical species. REFIN has successfully simulated the transient phenomena of the electrorefining process. Hence, this model can be applied to study detailed transient of the material redistribution process.

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Table 1. Standard electrode potential.

	ΔG_f° [4] [kcal/g-atom of Cl]	E^0 vs. Cl_2/Cl^- [V]	E^0 vs. Ag/AgCl [V]	Koyma's Data[9][V]	*Difference [V]
K/K+	-86.7	3.760	2.865	-	-
Li/Li+	-82.5	3.578	2.683	-	-
Nd/Nd ³⁺	-67.9	2.944	2.049	1.812	0.237
Pu/Pu ³⁺	-62.4	2.706	1.811	1.543	0.268
U/U ³⁺	-55.2	2.394	1.499	1.233	0.266
Cd/Cd ²⁺	-32.3	1.400	0.505	-	-
Cl-/Cl ₂	0	0	-0.895	-	-
Ag/Ag+	-20.6	0.895	0	-	-

*Difference=Calculated value-Kobayashi's data

Table 2. Kinetic parameters of metal in liquid cadmium and LiCl-KCl molten salt.

Metal	Z	Rate const. [#/cm]	Transfer coeff.		Diffusion Coeff.[$\times 10^{-5}$ cm ² /s]	
			α	β	LiCl-KCl	Cd
U	3	0.1*	0.5*	0.5*	0.686 [#]	1.5*
Pu	3	0.1*	0.5*	0.5*	1.083 [#]	1.5*
Nd	3	0.1*	0.5*	0.5*	1.208 [#]	1.5*
Li	1	0.1*	0.5*	0.5*	2.5*	1.5*
K	1	0.1*	0.5*	0.5*	2.5*	1.5*
Cd	2	0.1*	0.5*	0.5*	2.23 [#]	1.5*
Cl	-1	0.1*	0.5*	0.5*	2.5*	1.5*

* assumed value [#] from reference [11]

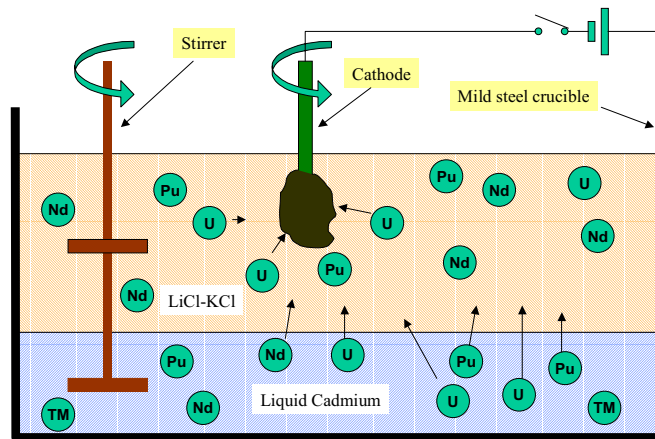


Figure 1. Schematics of electrorefiner with liquid cadmium anode and LiCl-KCl molten salt.

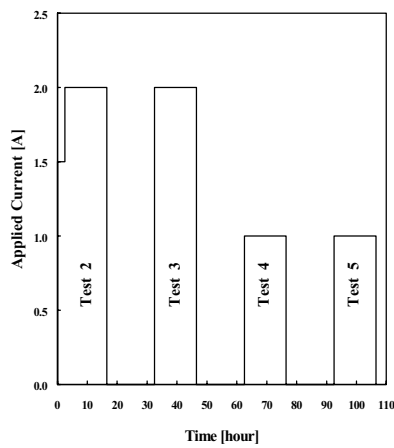


Figure 2. Applied current history of Tomczuk et al.'s electrorefining experiment campaign.[4]

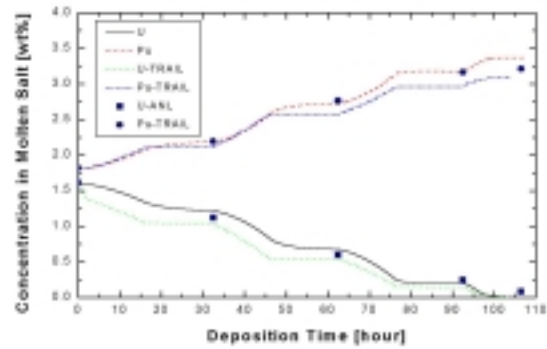


Figure 4. Calculated concentration changes of U, Pu, and Nd in molten salt. Calculation results are compared with experimental results and TRAIL calculation results.

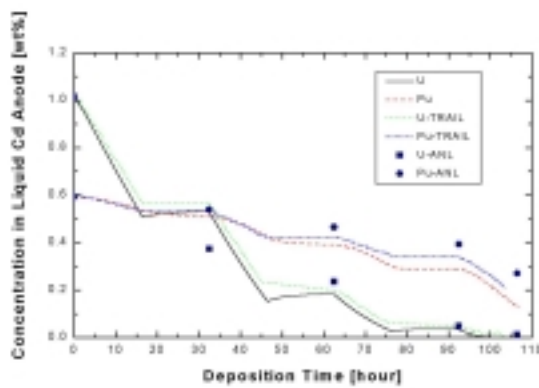


Figure 3. Calculated concentration changes of U, Pu, and Nd in liquid cadmium anode. Calculation results are compared with experimental results and TRAIL calculation results.

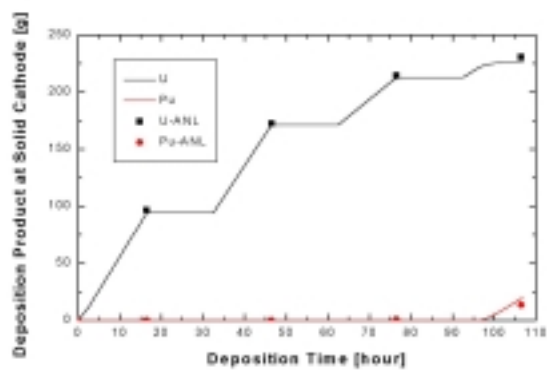


Figure 5. Calculated deposition history of U and Pu compared with corresponding experimental results.

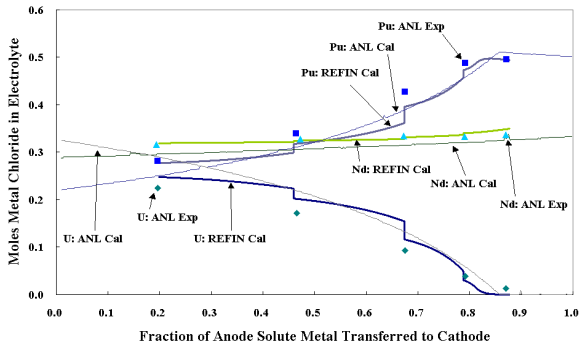


Figure 6. Concentration changes in molten salt predicted by REFIN compared with thermodynamic model calculation results.

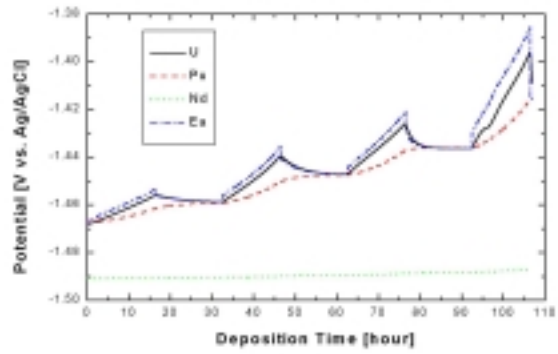


Figure 10. Surface potential drop, E_a and equilibrium potential.

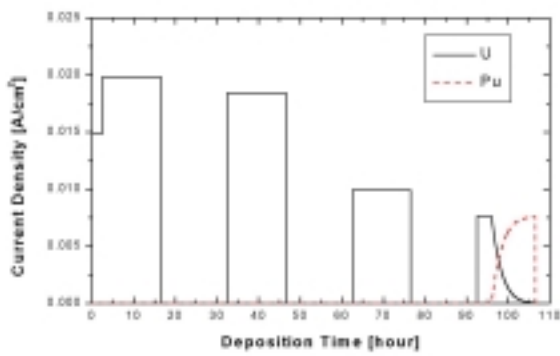


Figure 7. Current densities at cathode.

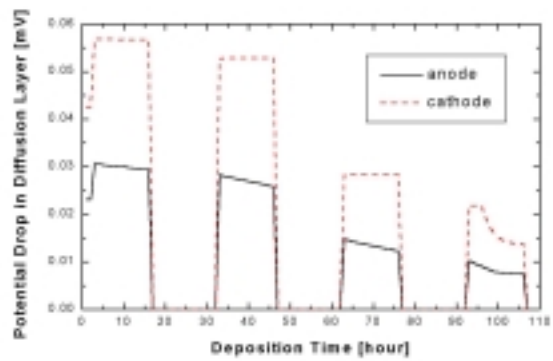


Figure 11. Potential drop in diffusion layer.

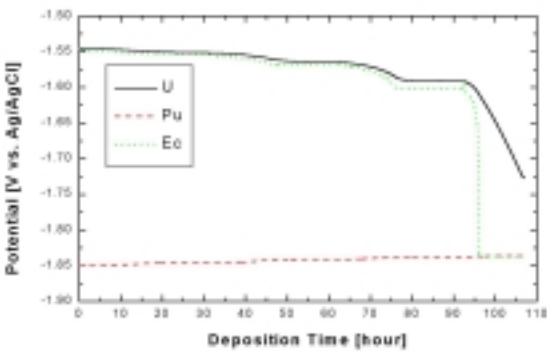


Figure 8. Surface potential drop, E_c and equilibrium potentials at cathode.

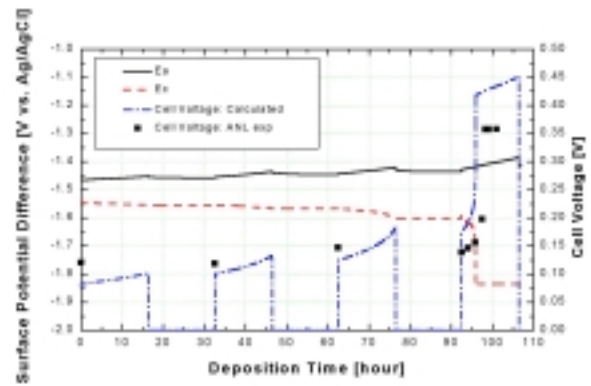


Figure 12 Cell potential, surface potential drops at anode and cathode.

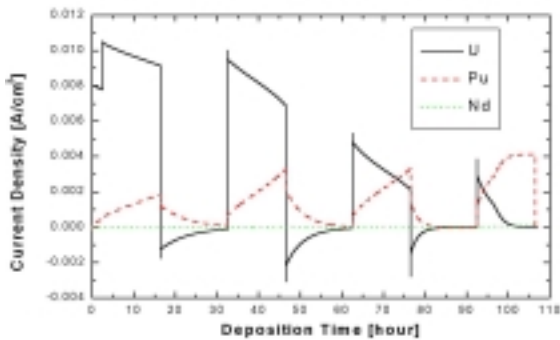


Figure 9. Current densities at anode.