Integrated Electroplating System Modeling and Simulation for Near Zero Discharge of Chemicals and Metals

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The optimality of design and operation of an electroplating system determines largely coating quality, productivity, and waste reduction efficiency. Industrial practice shows that, in a usual operation, the solution loss from an electroplating unit through drag-out can be as high as 30% of overall consumption. This has dramatically increased operating cost as well as waste treatment cost. On the other hand, plating quality in terms of coating thickness on workpieces is always a concern in plants. To improve the economic and environmental performance, a key step is to have a deep understanding of the system. Model-based simulation has proven to be a cost-effective approach along this venue. This paper introduces a fundamental-based general modeling methodology for characterizing an integrated electroplating system that consists of a plating unit and a solution recovery subsystem. The methodology allows detailed system analysis and complete process information integration, which will be crucial for optimal design and operation of a closed-loop electroplating for prevention of plating solution loss and assurance of coating thickness on workpieces. A case study on an alkali zinc electroplating system will demonstrate the efficacy of the model-based design and operation approach.

Introduction

Virtually all manufacturing of precious metal products involves electroplating. In the nation, there are over 8000 electroplating plants that provide numerous types of plated parts to the electronics, automotive, aerospace, and other manufacturing industries.[1,2] These plants have been generating huge amounts of waste in the forms of wastewater, sludge, and spent solutions.[3,4] The waste usually contains over 100 chemical, metal, and nonmetal contaminants.[5,6] A continuous generation of these wastes has led the industry to the second most regulated one in the nation.[2,7,8]

A usual electroplating line consists of different types of cleaning, many steps of rinsing, and a core operation of electroplating. In an electroplating unit, a selected type of metal is electrochemically deposited onto the surface of workpieces. In operation, the workpieces, loaded either in barrels or on racks, are immersed in the electrolyte. The metal deposition thickness, a key indicator of plating quality, is largely determined by electrolyte composition, current density, and plating time.[9,10] It is known that the workpiece rejection rate due to coating thickness problems is frequently above 5% in usual production. The rework of the rejected workpieces may involve costly stripping and replating. In addition to the quality issue, plating solution loss in operation is a very serious problem. Industrial practice has shown that the loss through drag-out can be commonly as high as 30% of overall consumption.[11] In a case study on a zinc acid plating line with the production rate of 11 barrels per hour (220 lbs of

workpieces per barrel), the solution loss was about 104 000 gallons per year, on a basis of 300 production days per year.[12] The lost solutions usually enter wastewater streams from relevant rinse units. Note that plating solution contains a number of valuable chemicals and metals, and the treatment of the wastewater stream containing those chemicals and metals is always very expensive. Thus, the prevention of solution loss into wastewater is of great economic and environmental significance.[13−15]

The reduction of chemical/metal loss through drag-out from plating units has drawn great attention over the past two decades.[2,16] Various drag-out reduction approaches have been practiced in plants, such as the use of a longer drainage time, a higher solution temperature, a lower surface tension, and an improvement of barrel design.[6,11] However, the exact relationships of these parameters with plating quality and solution reduction are unknown.[17−19] In addition to drag-out reduction, a reversed-drag-out technique was introduced a decade ago.[11] By this technique, the rinse unit immediately after a plating step need be designed for static rinse. In operation, a barrel or rack of workpieces is rinsed in the static rinse unit immediately after plating. The solution-containing rinse water in the unit is then periodically pumped back to the plating unit. While this technique sounds attractive, the system design and operation are only experience based. There are various technical difficulties yet to overcome, which are related to the effectiveness of solution loss reduction and the assurance of plating quality. As such, this technique has not been well adopted in plants.[20]

This paper introduces a general integrated system modeling methodology for characterizing the dynamic behavior of a closed-loop plating−rinsing system that can recover very effectively the lost chemical/metal-containing solution from the plating unit due to drag-

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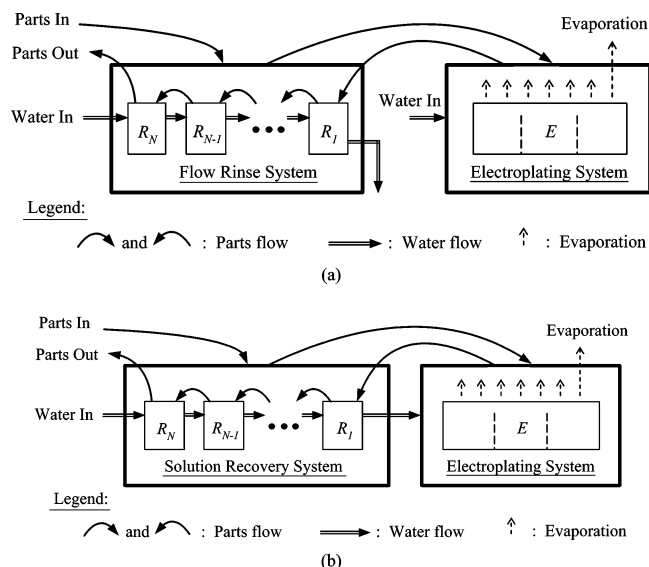* To whom all correspondence should be addressed. Tel.: 313-577-3771. Fax: 313-577-3810. E-mail: yhuang@wayne.edu.

Figure 1. Design schemes for electroplating and rinsing.

Figure 2. Chemical/metal flows of an electroplating unit.

out. To characterize the process behavior in each operational step of the system, a first-principles-based general integrated system model is developed. Model-based simulation can enable identifying optimal design and operational strategy and determining the efficiency of solution recovery under plating quality constraints.[21] The modeling methodology is detailed through studying an alkali zinc plating system, where general design and operational strategies are generated.[22]

Integrated Electroplating System Basics

A typical electroplating−flow rinse system is depicted in Figure 1a. In operation, barrels or racks of workpieces periodically enter the flow rinse system and then the plating unit. The plated workpieces then return to the rinse system where the drag-out solutions from the plating unit will be washed off. By comparing with this traditional system design, an integrated electroplating system (IES) is proposed in Figure 1b. The IES consists of an electroplating subsystem (EPS) that may have a number of plating slots in the plating unit, depending on desired production rate, and a solution recovery system (SRS) that may contain a number of static rinse units, determined by desired recovery efficiency and production rate. A major difference of the designs is that the IES adopts static rinse instead of flow rinse. This also requires different operational strategies as the IES uses periodic water adding in a cascade mode. That is, freshwater is periodically fed into rinse unit R_N, and the solution-containing rinse water in R_N then flows to R_{N-1}, ..., and R_1 periodically. Finally, the solution-containing rinse water in R_1 is periodically pumped into plating unit E. Note that since the bath solution temperature is higher than the ambient temperature, the plating unit has a continuous evaporation of water. Hence, the amount of freshwater fed into R_N periodically should be equal to the amount evaporated in the plating unit.

The effectiveness of solution recovery and product quality assurance is largely determined by the system configuration and operational strategy of an IES. From the design and operation point of view, the use of more rinse units in the SRS can help recover more lost solutions, but at the same time the capital cost will be increased and the production efficiency will be decreased
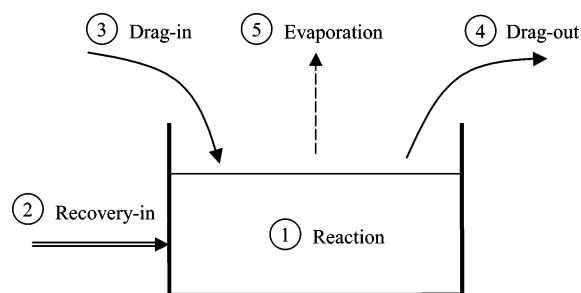
if the total rinse time is increased. The relationships among the productivity, quality, and waste reduction can be understood through developing a fundamental-based integrated system model. Note that in real production the temperature of the electroplating tank can be readily maintained, and the temperature change of the rinse tanks is negligible. Thus, energy balance is not considered.

General System Modeling

As an IES consists of two entirely different subsystems, the modeling methods will be presented as two separate efforts. The construction of an integrated model will be presented according to system configuration.

Electroplating Subsystem (EPS) Modeling. In an electroplating unit, a direct electric current passes through the solution so that chemical reactions take place. This will lead to the deposition of a thin layer of metal on the negative electrode (cathode, which is always workpieces to be plated). Note that the positive electrode (anode) can be either a metal, possibly impure, that is dissolved through chemical reactions into the solution in operation or a material that is not dissolved but is for the passage of the current, acting as an "inert" anode.[22] A number of first-principles-based modeling methods have been introduced for characterizing various types of metal plating.[23−25] However, all the available models are steady state based, which are naturally incapable of describing time-variant changes about metal deposition and solution composition.

To effectively design an IES, a dynamic plating model must be developed. Such a model must consist of two types of submodels: the one for characterizing solution composition changes of all involved chemicals and metal and the one for describing metal deposition on workpieces.

Chemical/Metal Dynamics. Figure 2 illustrates a general plating unit where system component balance related factors are depicted: (i) chemical reaction related, (ii) recovered solution related, (iii) solution drag-in related, and (iv) solution drag-out related. Note that chemical/metal loss through evaporation can be safely omitted, as the evaporation contains almost all water. With these analyses, a general chemical dynamics model can be structured as follows:

$$V^E \frac{dC_j^E(t)}{dt} = f_j(R_a(t),R_c(t))\, A_p i (U(t - t_{is}^E) -$$

$$U(t - t_{os}^E)) + F_r C_j^{R_1}(t) + D \sum_{k=1}^{N} (y^k C_j^{R_k}(t_{ini,os}^{R_k}))(U(t - t_{is}^E) -$$

$$U(t - t_{ie}^E))) - DC_j^E(t)(U(t - t_{os}^E) - U(t - t_{oe}^E)) \quad (1)$$
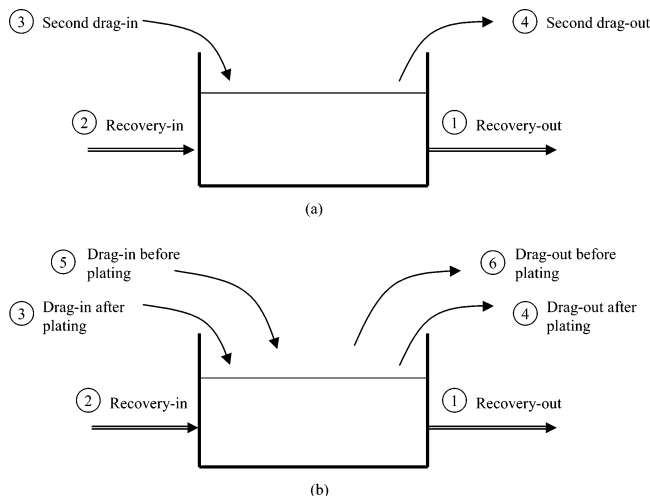
Figure 3. Chemical/metal flows of a solution recovery system.

where $C_j^E(t)$ is the concentration of component j in the plating unit, mol/L; $C_j^{R_k}(t)$ the concentration of component j in the kth rinse unit, mol/L; $f_j(R_a(t),R_c(t))$ the reaction rate function of component j, mol/C; $R_a(t)$ the current efficiency of the anode; $R_c(t)$ the current efficiency of the cathode; V^E the volume capacity of electroplating unit, L; A_p the total surface area of the workpieces, m²; i the current density, A/m²; j the component species index; k the rinse unit index; F_r the flow rate of recovery, L/min; D the flow rate of drag-in or drag-out, L/min; y^k the binary variable; $U(t - t_a)$ the unit step function occurred at the time instant, t_a; $t_{ini,os}^{R_k}$ the starting time of the initial drag-out from the kth rinse unit, min; t_{is}^E, t_{ie}^E the starting and ending time of drag-in to the plating unit, respectively, min; t_{os}^E, t_{oe}^E the starting and ending time of drag-out from the plating unit, respectively, min; and N the number of rinse units.

Note that y^k is a binary variable for rinse unit R_k (equal to 1 if R_k is selected for rinse before plating; 0 otherwise). Since only one rinse unit can be designed for rinse before plating (see Figure 1b), the following constraint should be satisfied:

$$\sum_{k=1}^{N} y^k = 1 \qquad (2)$$

Equation 1 contains a number of pulse functions in the form of $U(t - t_a) - U(t - t_b)$ (with magnitude of 1 in the time period between t_a and t_b, or 0 otherwise). Thus, a phenomenon occurring only in a specific time interval can be expressed by the product of a function describing the phenomenon and the pulse function for the specific time interval. For instance, the last term on the right-hand side of eq 1 indicates that the drag-out, D, lasts in the time interval between t_{os}^E and t_{oe}^E only. Also note that in eq 1 the reaction rate function, $f_j(R_a(t),R_c(t))$, is always nonlinear and is determined by the current efficiencies of the anode and the cathode, $R_a(t)$ and $R_c(t)$, and the chemical/metal species involved in the reactions.

Solution Recovery Subsystem (SRS) Modeling. The lost solution from the EPS is recovered in the SRS, which is essentially a multistep rinse system as depicted in Figure 1b. A general SRS model can be developed on the basis of the models for each rinse unit. The rinse units can be functionally classified into two types: one

for rinsing after plating only and the other for rinsing both before and after plating. Figure 3 illustrates the two types where chemical/metal flows in each are plotted. Note that evaporation of chemicals/metal in each rinse unit can be safely neglected, particularly due to the rinse water at room temperature. In any case, the component balance is determined by the recovered solution into and out of the unit and the amounts of drag-in and drag-out. If the unit is used also for rinse before plating, then that drag-in and drag-out should all be counted. Therefore, a general dynamics model for a rinse unit can be formulated as follows.

$$V^R \frac{dC_j^{R_k}(t)}{dt} = F_r(C_j^{R_{k+1}}(t) - C_j^{R_k}(t)) + DC_j^{R_{k-1}}(t_{os}^{R_{k-1}})(U(t - t_{is}^{R_k}) - U(t - t_{ie}^{R_k})) - DC_j^{R_k}(t)(U(t - t_{os}^{R_k}) - U(t - t_{oe}^{R_k})) - \sum_{k=1}^{N} (y^k DC_j^{R_k}(t)(U(t - t_{ini,os}^{R_k}) - U(t - t_{ini,oe}^{R_k}))) \quad (3)$$

$$C_j^{R_0}(t) = C_j^E(t) \qquad (4)$$

$$C_j^{R_{N+1}}(t) = 0 \qquad (5)$$

where V^R is the capacity of each rinse unit, L; $t_{is}^{R_k}$, $t_{ie}^{R_k}$ the starting and ending time of the drag-in to the kth rinse unit, respectively, min; $t_{os}^{R_k}$, $t_{oe}^{R_k}$ the starting and ending time of the drag-out from the kth rinse unit, respectively, min; and $t_{ini,oe}^{R_k}$ the ending time of the initial drag-out from the kth rinse unit, min

Equation 4 suggests that the drag-in solution to R_1 is actually from plating unit E, while eq 5 means that the solution flowing into R_1 comes from the freshwater that is usually chemicals/metals free. The unit-based model in eq 3 can be used to construct a system model for a SRS that may contain any number of rinse units. The general IES modeling is an extension of the existing rinse system modeling work by Zhou et al.,[26,27] where no plating solution is involved and each rinse unit is only for the rinse either before or after plating, but not both.

Modeling of an Alkali Zinc Plating System

Alkaline zinc plating has been widely used to deposit a thin layer of zinc metal on numerous types of workpieces. The IES modeling method is used to study this particular type of plating system for solution recovery. It is to show how the information generated from the integrated model can help design and operate a most effective IES or, more specifically, determine a system configuration and develop operational strategies so that the solution lost from the plating unit can be recovered to the maximum extent, while the plating quality can be ensured. The IES exemplified here is the one with a plating unit E and three rinse units: R_1 for both pre- and postplating rinse and R_2 and R_3 for postplating rinse. Figure 4 provides a processing procedure of the workpieces either in barrel or on rack for this IES. It shows that for any barrel or rack of workpieces it is rinsed in R_1 first and then plated in E. After plating, it is rinsed in R_1, R_2, and R_3 in sequence. The time instants for each operation are defined in the figure. For instance, the duration between t_{is}^E and t_{os}^E is the plating
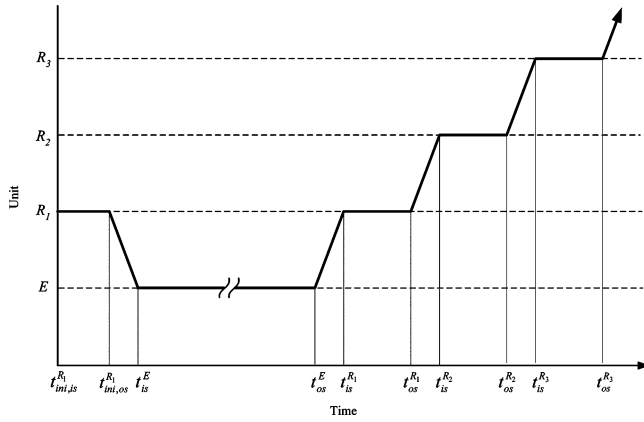
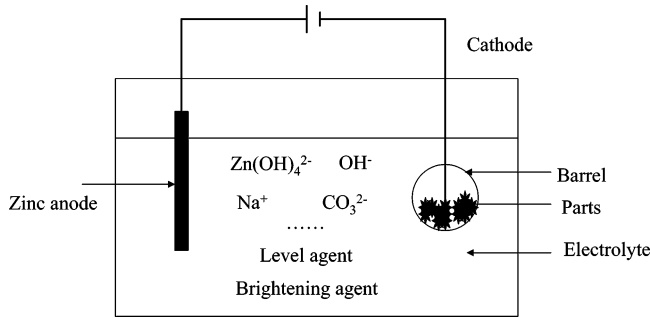**Figure 4.** Example of workpiece processing sequence in a one-plating–three-rinse system.
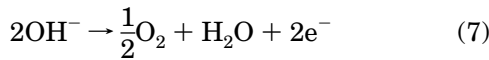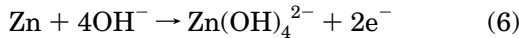

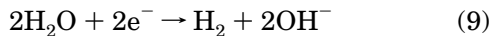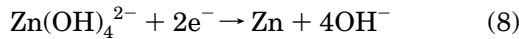**Figure 5.** Sketch of an electroplating unit.

time, and the duration between t_{os}^E and $t_{is}^{R_1}$ is the time for moving the workpieces from plating unit E to rinse unit R_1.

Electrochemical Reactions and Plating System Modeling. Figure 5 gives a sketch of an alkaline zinc plating unit, where the reactions take place around the electrodes, with the main ones as follows:[28−31]

anode reactions:

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \tag{6}$$

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \tag{7}$$

cathode reactions:

$$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^- \tag{8}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{9}$$

The above electrochemistry shows that there is a net depletion of zinc and an evolution of oxygen at the anode and an evolution of hydrogen and a net depletion of water at the cathode. When a substantial external current goes through the plating solution, zinc will be continuously dissolved into the electrolyte from the anode. Meanwhile, an almost equivalent amount of zinc will leave the solution and be deposited on the cathode. Note that the combined effects of the electrode reactions and electrolyte ion migration result in composition change of electrolyte in different scales. At the local scale, the regions surrounding the anode and the cathode and the central region (solution) have complex chemical/metal concentration distributions. Process modeling in this work focuses on the distributions at the global scale.

Table 1. Component Concentration Ranges in the Plating System

component (mol/L)	electroplating unit			rinsing unit		
	C_{lb}	C_o	C_{ub}	R_1	R_2	R_3
Zn^{2+}	0.15	0.21	0.27	0.0299	0.0049	0.0007
NaOH	2.50	3.25	4.00	0.4627	0.0753	0.0108
Na_2CO_3	0.00	0.28	0.57	0.0399	0.0065	0.0009

Electrolyte Concentration. The concentrations of chemicals/metal in the plating unit are determined by the rate of dissolution at the anode and the rate of deposition at the cathode, as well as those dragged into and out of the plating unit. It is assumed that the solution in the plating unit has a perfect mixing. The dynamics of dissolved zinc in the plating unit can be described as

$$V^E \frac{dC_{Zn}^E(t)}{dt} = \left(\frac{R_a(t) - R_c(t)}{2F}\right) A_p i (U(t - t_{is}^E) - U(t - t_{os}^E)) + F_r C_{Zn}^{R_1}(t) + DC_{Zn}^{R_1}(t_{ini,os}^{R_1})(U(t - t_{is}^E) - U(t - t_{ie}^E)) - DC_{Zn}^E(t)(U(t - t_{os}^E) - U(t - t_{oe}^E)) \tag{10}$$

where $C_{Zn}^E(t)$ is the concentration of Zn^{2+} in plating unit E, mol/L; and F is Faraday's constant (96 485 C/mol).

Note that caustic is also consumed during the reaction. On the basis of the cathode and anode reactions in (6) through (9), the dynamics of its concentration can be described by a similar model structure to that for zinc.

$$V^E \frac{dC_{OH}^E(t)}{dt} = \left(\frac{1 + R_c(t) - 2R_a(t)}{F}\right) A_p i (U(t - t_{is}^E) - U(t - t_{os}^E)) + F_r C_{OH}^{R_1}(t) + DC_{OH}^{R_1}(t_{ini,os}^{R_1})(U(t - t_{is}^E) - U(t - t_{ie}^E)) - DC_{OH}^E(t)(U(t - t_{os}^E) - U(t - t_{oe}^E)) \tag{11}$$

where $C_{OH}^E(t)$ is the concentration of NaOH in plating unit E, mol/L.

Note that Na_2CO_3 is not involved in reactions 6−9. The dynamics of the concentration of this component can be described as follows:

$$V^E \frac{dC_{Na_2CO_3}^E(t)}{dt} = F_r C_{Na_2CO_3}^{R_1}(t) + DC_{Na_2CO_3}^{R_1}(t_{ini,os}^{R_1})(U(t - t_{is}^E) - U(t - t_{ie}^E)) - DC_{Na_2CO_3}^E(t)(U(t - t_{os}^E) - U(t - t_{oe}^E)) \tag{12}$$

where $C_{Na_2CO_3}^E(t)$ is the concentration of Na_2CO_3 in plating unit E, mol/L.

The current efficiencies, $R_c(t)$ and $R_a(t)$, are largely determined by electrolyte compositions. Wery et al. identified a regression expression as follows:[30]

$$R_c(t) = 0.927 + 0.037C_{Zn}^E(t) - 0.031C_{OH}^E(t) - 1.3C_{Na_2CO_3}^E(t) + 3.4C_{Zn}^E(t)C_{OH}^E(t) + 3.4C_{Zn}^E(t)C_{Na_2CO_3}^E(t) - 2.0C_{OH}^E(t)C_{Na_2CO_3}^E(t) + 1.4C_{Zn}^E(t)C_{OH}^E(t)C_{Na_2CO_3}^E(t) \tag{13}$$

This expression is restricted to a certain concentration range of each component in the plating unit. Table 1 gives the lower and upper boundaries, C_{lb} and C_{ub},

respectively, of these components. A simple way for deriving $R_a(t)$ can be as follows:

$$R_a(t) = (1 + \alpha)R_c(t) \qquad (14)$$

where α is a constant.

Thickness Dynamic Model. According to Faraday's law, zinc deposition dynamics can be obtained as follows::[10]

$$\frac{dm(t)}{dQ} = \frac{R_c(t)M}{2F} \qquad (15)$$

where $m(t)$ is the mass of zinc deposited on the cathode, kg; M the molecular weight of zinc, kg/mol; and Q the amount of charge, C. Note that

$$dQ = A_p i \, dt \qquad (16)$$

If the zinc deposition is assumed uniform on the workpiece surfaces during plating, a simplified zinc thickness dynamic model is derived:

$$\frac{d\theta(t)}{dt} = \left(\frac{R_c M}{2F\rho}\right)i \qquad (17)$$

where $\theta(t)$ is the deposit thickness, m; and ρ is the zinc density, kg/m^3. It is worth noting that earlier studies provided the relationship of plating thickness vs operating parameters in the stand-along electroplating tank. However, there is no integrated dynamic model to exploit the intrinsic relationship between plating and rinsing. Hitherto, plating solution loss reduction is only based on experience, and it is far from optimal.

Modeling for Solution Recovery. In operation, the workpieces in barrel or on rack are first dipped in rinse unit R_1 and then loaded into plating unit E. After plating, the workpieces are rinsed in rinse units R_1, R_2, and R_3 in sequence. In this subsystem, freshwater is fed into rinse unit R_3, with the amount of F_r equal to the evaporation loss from plating unit E. To avoid the potential accumulation of salts from municipal water, deionized water is recommended. The amount of rinse water same as that of freshwater is pumped from R_3 to R_2, from R_2 to R_1, and finally from R_1 to E. This is a three-step solution recovery mechanism that is operated periodically. The model for each rinse step is as follows.

unit R_1:

$$V^R \frac{dC_j^{R_1}(t)}{dt} = F_r(C_j^{R_2}(t) - C_j^{R_1}(t)) + DC_j^E(t_{os}^E)(U(t - t_{is}^{R_1}) - U(t - t_{ie}^{R_1})) - DC_j^{R_1}(t)(U(t - t_{os}^{R_1}) - U(t - t_{oe}^{R_1})) - DC_j^{R_1}(t)(U(t - t_{\text{ini},os}^{R_1}) - U(t - t_{\text{ini},oe}^{R_1})) \quad (18)$$

unit R$_2$:

$$V^R \frac{dC_j^{R_2}(t)}{dt} = F_r(C_j^{R_3}(t) - C_j^{R_2}(t)) + DC_j^{R_1}(t_{os}^{R_1})(U(t - t_{is}^{R_2}) - U(t - t_{ie}^{R_2})) - DC_j^{R_2}(t)(U(t - t_{os}^{R_2}) - U(t - t_{oe}^{R_2})) \quad (19)$$

unit R_3:

$$V^R \frac{dC_j^{R_3}(t)}{dt} = F_r C_j^{R_3}(t) + DC_j^{R_2}(t_{os}^{R_2})(U(t - t_{is}^{R_3}) - U(t - t_{ie}^{R_3})) - DC_j^{R_3}(t)(U(t - t_{os}^{R_3}) - U(t - t_{oe}^{R_3})) \quad (20)$$

where subscript j is designated for Zn^{2+}, NaOH, and Na$_2$CO$_3$.

System Model. The IES model for this particular plating system consists of eqs 10−14 and eqs 17−20. Since there are three components in each rinse unit, the alkali zinc plating system model contains a total of 15 equations. The system model can be used to describe the dynamic behavior of electrodeposition and chemical/metal concentration changes in the plating and rinse units for the production of any number of barrels or racks of workpieces.

System Simulation and Analysis

A main focus of the model-based simulation is to demonstrate the ability of an IES for near zero discharge of chemicals and metals as compared to the traditional design. To facilitate identification of an optimal IES design, different design and operational strategies need to be studied in detail. The study is also expected to generate general guidelines for design and operation of the most effective IES for solution recovery and coating quality control in electroplating systems.

Parameter Setting. In the dynamic simulation, initial conditions, such as component compositions, are set to the nominal values. Table 1 lists those for the plating unit (see the column for C_0 values). However, it is relatively difficult to set the initial conditions for the three rinse units. A suggested method is to calculate them based on the mass balance of units R_1, R_2, and R_3 at steady state, such as follows.

for unit R_1:

$$2F_{Do}^{R_1}C_{j,0}^{R_1} + F_r TC_{j,0}^{R_1} = F_{Di}^{R_0}C_{j,0}^E + F_r TC_{j,0}^{R_2} \qquad (21)$$

for unit R_2:

$$F_{Do}^{R_2}C_{j,0}^{R_2} + F_r TC_{j,0}^{R_2} = F_{Di}^{R_1}C_{j,0}^{R_1} + F_r TC_{j,0}^{R_3} \qquad (22)$$

for unit R_3:

$$F_{Do}^{R_3}C_{j,0}^{R_3} + F_r TC_{j,0}^{R_3} = F_{Di}^{R_2}C_{j,0}^{R_2} \qquad (23)$$

where

$$F_{Di}^{R_k} = D(U(t - t_{is}^{R_k}) - U(t - t_{ie}^{R_k})) = D(t_{ie}^{R_k} - t_{is}^{R_k}) \qquad (24)$$

$$F_{Do}^{R_k} = D(U(t - t_{os}^{R_k}) - U(t - t_{oe}^{R_k})) = D(t_{oe}^{R_k} - t_{os}^{R_k}) \qquad (25)$$

For simplicity, reasonable assumptions can be made as follows:

$$\Delta t_D = t_{ie}^{R_k} - t_{is}^{R_k} = t_{oe}^{R_k} - t_{os}^{R_k} \qquad (26)$$

$$F_D = F_{Di}^{R_k} = F_{Do}^{R_k} \qquad (27)$$

Table 2. Simulation Related Parameters

processing parameter	F_r	D	V^E	V^R	i	M	ρ	α	Δt_D	T
value	0.2 L/min	20 L/min	1200 L	1200 L	100 A/m^2	0.0654 kg/mol	7140 kg/m^3	0.1	0.1 min	55.6 min
operating time	$t_{ini,is}^{R_1}$	$t_{ini,os}^{R_1}$	t_{is}^E	t_{os}^E	$t_{is}^{R_1}$	$t_{os}^{R_1}$	$t_{is}^{R_2}$	$t_{os}^{R_2}$	$t_{is}^{R_3}$	$t_{os}^{R_3}$
traditional design	0	2.0	2.2	52.4	52.6	53.4	53.6	54.2	54.4	54.6
design A	0	2.0	2.2	52.4	52.6	53.4	53.6	54.2	54.4	54.6
design B	0	2.0	2.2	52.4	52.6	53.5	53.7	54.6		
design C	0	2.0	2.2	52.4	52.6	54.6				

Solving eqs 21−27 gives

$$C_{j,0}^{R_1} = \cfrac{F_D C_{j,0}^E}{2F_D + F_r T - \cfrac{F_D F_r T}{F_D + F_r T - \cfrac{F_D F_r T}{F_D + F_r T}}} \quad (28)$$

$$C_{j,0}^{R_2} = \cfrac{F_D C_{j,0}^{R_1}}{F_D + F_r T - \cfrac{F_D F_r T}{F_D + F_r T}} \quad (29)$$

$$C_{j,0}^{R_3} = \frac{F_D C_{j,0}^{R_2}}{F_D + F_r T} \quad (30)$$

When $C_{j,0}^E$ is given, $C_{j,0}^{R_1}$, $C_{j,0}^{R_2}$, and $C_{j,0}^{R_3}$ can be determined uniquely. Table 1 shows the calculated initial values for the three rinse units.

Simulation-Based Design Comparison. The comparison is conducted through simulating four designs: a traditional design (with three rinse tanks) and the IES's with three rinse units (design A), two rinse units (design B), and one rinse unit (design C). For all the four designs, the total flow rinse time is fixed for 2 min so that the production rates are the same. Each system runs for processing 120 barrels of workpieces, and the production periods are the same. The operational parameters other than the rinsing time assignments are the same for all the designs (see Table 2, part A). In addition, it is assumed that the volume of drag-out solution from the plating unit is 2 L per barrel.

Comparison of Design A with the Traditional Design. Design A has been extensively simulated. As shown in Figure 6a−c, the concentration of Zn^{2+} is increased nearly linearly from 0.21 to 0.232 mol/L, while the concentrations of NaOH and Na$_2$CO$_3$ are decreased gradually from 3.251 and 0.280 mol/L to 3.21 and 0.277 mol/L, respectively. Note that all these three curves are not smooth; this is because every time when a barrel is loaded into unit E, the drag-in solution from unit R_1 has the concentrations of all three components much lower than those in unit E, which dilutes the plating solution initially. When each barrel leaves unit E, the component concentration is increased to a certain level. This situation repeats for every barrel of processing. As to the final coating thickness of the workpieces in 120 barrels, it is maintained almost the same (12.0 μm), which indicates excellent plating quality (see Figure 6d).

In the rinse units, it is expected that the concentration of each component be decreased. These general trends are confirmed in Figures 7−9, except for Figure 7a. In Figure 7a, the Zn^{2+} concentration is decreased initially, and at around the 5000th minute, the concentration moves back slowly. This indicates that the initial Zn^{2+} concentration set for simulation is too high. The simulation also shows that each rinse step can significantly reduce the concentration of each component. For in-

stance, at the time instant of the 5000th minute, the concentrations for Zn^{2+}, NaOH, and Na$_2$CO$_3$ are about 0.0298, 0.448, and 0.0386 mol/L, respectively, in unit R_1. In unit R_2, these concentrations are reduced to
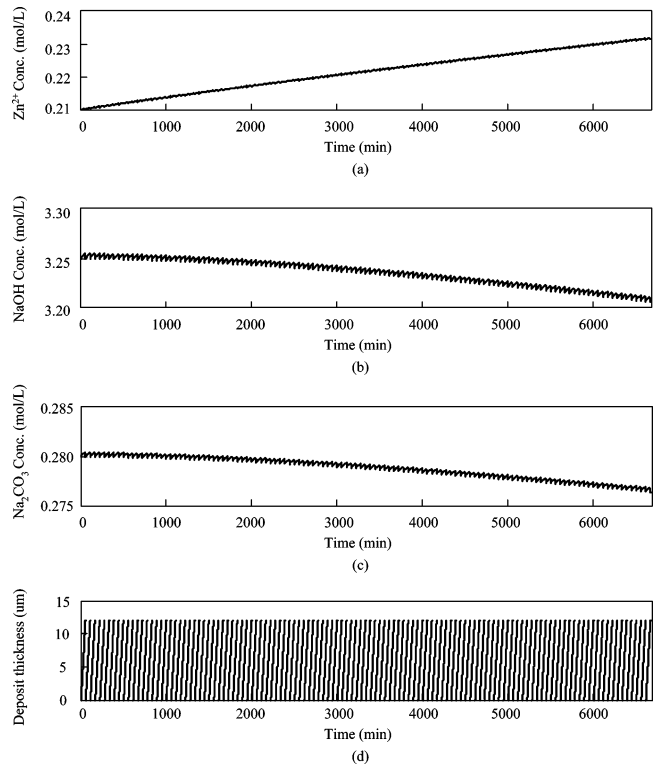
Figure 6. Dynamics of electroplating unit E in design A.
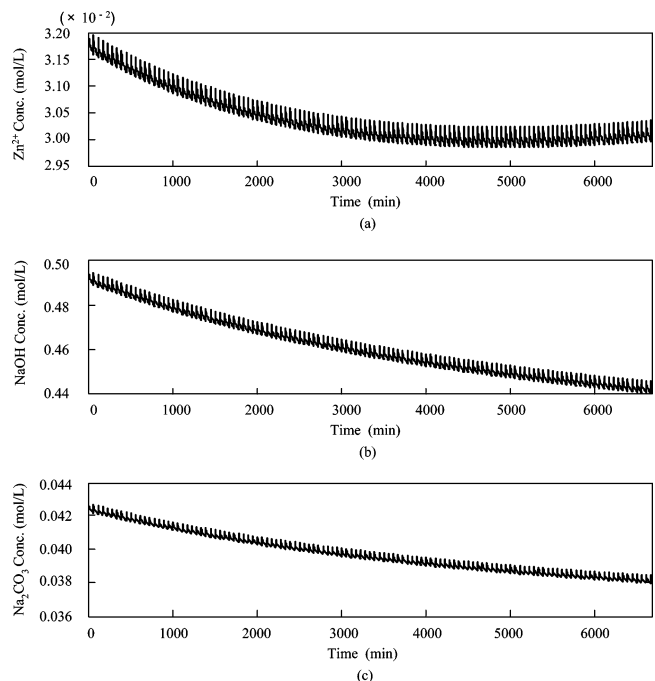
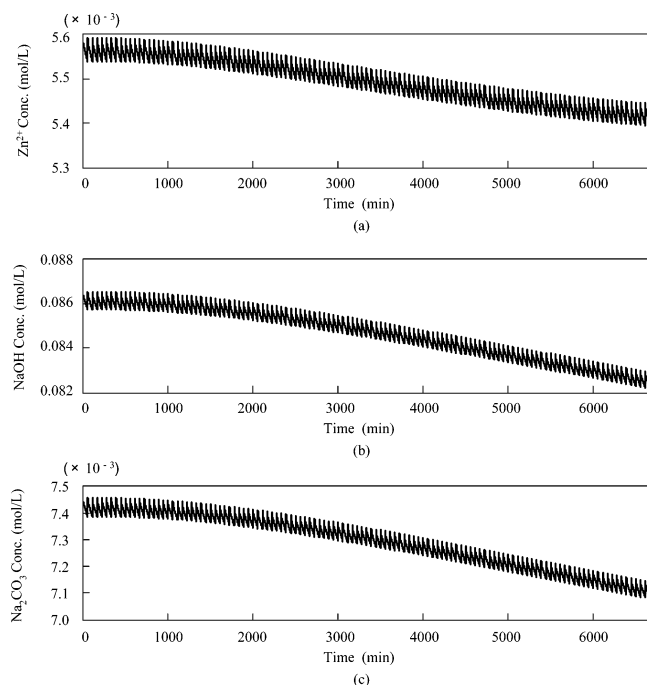
Figure 7. Dynamics of rinse unit R_1 in design A.

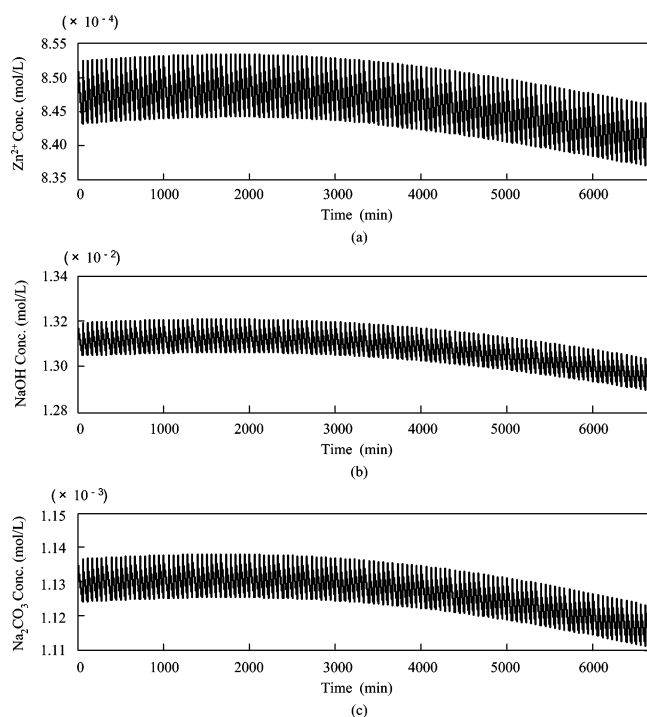**Figure 8.** Dynamics of rinse unit R_2 in design A.

Figure 9. Dynamics of rinse unit R_3 in design A.

0.00543, 0.0834, and 0.0072 mol/L, respectively. In unit R_3, these concentrations are further reduced to 0.000 841,

0.0130, and 0.001 12 mol/L, respectively. All these indicate that each rinse step can reduce the concentration of each component by 81−85%. Almost equivalently, the chemical and metal loss after each rise step is reduced by 81−85%.

The traditional design is also simulated on the same basis as design A. Table 3 (columns 3 and 4) lists the chemical/metal loss and recovery data for the two designs. As shown, the recoveries of Zn^{2+}, NaOH, and Na_2CO_3 by design A are at least 99.5%. Obviously, design A has demonstrated the capability of near zero discharge of chemicals and metals.

Further Study. While design A gives superior performance for chemical/metal recovery, a simplified IES (with a reduced number of rinse units) can also provide very impressive results. In this study, design B (with two static rinse units) and design C (with one static rinse unit) are simulated. The processing parameter values for the traditional design and design A shown in Table 2 are also used for designs B and C. Table 2 also lists the unit processing times for each of these two new designs.

The system model for designs B is the same as that for design A, except for excluding eq 20, while the model for design C should exclude eqs 19 and 20. The model-based simulation results have been listed in Table 3 (columns 5 and 6). It shows that the chemical/metal loss by designs B and C can be reduced by at least 97.6% and 86.2%, respectively, regardless of the types of chemicals and metals. Although the chemical and metal recovery efficiency of either of these designs is not as impressive as design A, the capital cost for the SRS can be reduced by 33.3% (design B) or 66.5% (design C). Figure 10 summarizes the general trend for chemical/metal loss of an IES with the increasing number of rinse units.

In these simulations, a Runge−Kutta method[21] was proven efficient. If an IES is more complicated, e.g., if the reactions in the electrolyte are very complicated, then some other numerical methods might be deployed.[32,33]

General Guidelines. With the case studies shown above, several general conclusions can be made as follows:

(a) The design of the SRS of an IES with three rinse units after plating should be preferred since it can gives a truly near zero discharge of valuable plating solutions, if the physical accommodation of these units, associated with their cost, is not an issue.

(b) An SRS with more than three rinse units is not recommended for two reasons: (i) the gain for further reduction of chemical/metal loss becomes negligible, (ii) it is usually not practical to expect any plant to have the space to accommodate four rinse units after plating, and (iii) it becomes very difficult for production scheduling.

Table 3. Comparison of Solution Loss and Recovery Rate among the Four Designs[a]

component	solution loss and recovery	traditional design	design A	design B	design C
Zn^{2+}	loss (mol/barrel)	0.446	0.0017	0.0094	0.053
	recovery (%)		99.6	97.9	88.1
NaOH	loss (mol/barrel)	6.49	0.026	0.13	0.81
	recovery (%)		99.6	97.9	87.5
Na_2CO_3	loss (mol/barrel)	0.507	0.0023	0.012	0.070
	recovery (%)		99.5	97.6	86.2

[a] Note: (1) Results are based on the production of 120 barrels of parts. (2) The cycle time is 55.6 min for each design. (3)The recovery percentage is based on the traditional design.
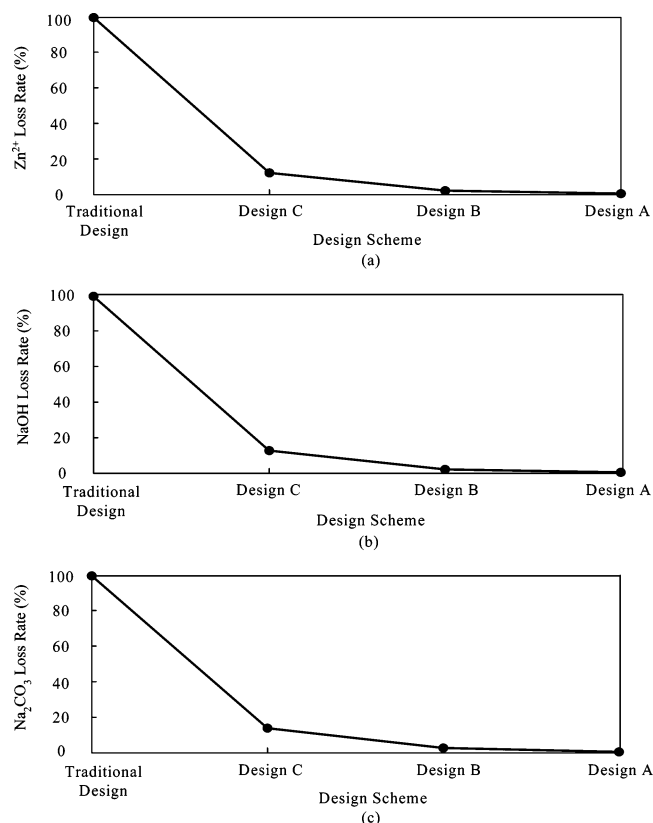
Figure 10. Comparison of chemical/metal loss reductions by different designs.

(c) In any case, the commonly used electroplating system with flow rinse after plating should be replaced by an IES. As shown, an IES with only one rinse unit can still recover at least 80% of the solution otherwise to be lost into the wastewater system. As we all know, to treat wastewater stream with high chemical/metal concentration is always expensive, and if the recovery of those chemicals and metals from the wastewater is required, then additional economic burden will be even more expensive.

Concluding Remarks

Chemical and metal loss in electroplating systems is always significant, which has caused tremendous profit loss and environmental burden. This paper has introduced a general modeling methodology for characterizing dynamically the operations of electroplating and rinsing. The modeling methodology plays a key role in developing an integrated electroplating system (IES) that consists of an electroplating subsystem (EPS) and a solution recovery subsystem (SRS). Extensive model-based simulations have clearly demonstrated that the integrated IES modeling method can greatly help identify an economically and environmentally highly desirable system design and operational strategy. This modeling and simulation methodology is general and can be employed for any type of electroplating system.

Acknowledgment

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