

A Fully Optimized Electrowinning Cell for Achieving a Uniform Current Distribution at Electrodes Utilizing Sampling-Based Sensitivity Approach

Nak-Sun Choi*, Dong-Wook Kim*, Jeonghun Cho** and Dong-Hun Kim[†]

Abstract – In this paper, a zinc electrowinning cell is fully optimized to achieve a uniform current distribution at electrode surfaces. To effectively deal with an electromagnetically coupled problem with multi-dimensional design variables, a sampling-based sensitivity approach is combined with a highly tuned multiphysics simulation model. The model involves the interrelation between electrochemical reactions and electromagnetic phenomena so as to predict accurate current distributions in the electrowinning cell. In the sampling-based sensitivity approach, Kriging-based surrogate models are generated in a local window, and accordingly their sensitivity values are extracted. Such unique design strategy facilitates optimizing very complicated multiphysics and multi-dimensional design problems. Finally, ten design variables deciding the electrolytic cell structure are optimized, and then the uniformity of current distribution in the optimized cell is examined through the comparison with existing cell designs.

Keywords: Electrochemistry, Electromagnetics, Finite element analysis, Kriging method, Optimization, Sensitivity analysis.

1. Introduction

Since the development of the hydrometallurgical zinc production, electrochemical deposition of metals is widely used in various industry fields. Production of noble metals such as Cu, Ni, and Zn traditionally involves electro-winning as the last process, where anodic dissolution and electrodeposition on a cathode occurs. The process is carried out in a cell house typically consisting of many electrowinning cells, cooling towers and electrolyte storage. It is revealed that the zinc cell house is responsible for approximately 80% of the energy used by an electrolytic zinc refinery. Thus, intensive research has been conducted to lower energy consumption or increase current efficiency per mass of zinc produced [1-6].

Several studies have examined optimal conditions for zinc electrowinning [3-5]. They utilized a variety of experimental cells and electrodes to test the effect of variables on cell performance. Even though they are reliable methods to analyze the electrowinning cell, the number of required experimental permutations rapidly increases as the number of manipulated variables is getting larger. Therefore, it is difficult to define a global optimum for the cell house. Meanwhile, Bouzek et al. in [6] investigated the effects of current distribution flowing through an electrolyte between

the anode and cathode on zinc electrodeposition, mathematically and experimentally. It is concluded that the quantity and morphology of electrodeposits strongly depends on the current distribution between electrodes. Even though good electrode alignment is maintained, the nonuniformity of the current distribution is caused by various design factors, such as spacing, thickness, and position of electrodes and their insulating edge strips. Such nonuniform current distribution generates local dendrites on the cathode surface or decrease available electrode surface areas for zinc deposition. The growing dendrite or effective electrode area reduction specifically occurring at the edges of cathodes can give an increased tendency to short circuits or loss in current efficiency.

The objective of this paper is to find an optimized cell structure for zinc electrowinning, which can enhance the uniformity of electrode current distribution. To accurately predict the current distribution between electrodes, a highly tuned numerical model is introduced. The complicated interrelations between electrochemical and electromagnetic phenomena are taken into account. An efficient optimization method, called sampling-based sensitivity approach, is applied to the multiphysics design problem of an electrowinning cell. The method basically generates a Kriging-based surrogate model in a local window, and accordingly its sensitivity value is extracted. Such unique design strategy facilitates integrating very complex multiphysics systems into the optimization process. Finally, an electrolytic cell with ten design variables is optimized under the assumption of a steady-state secondary current distribution. Then the uniformity of current distribution in the optimized cell is

[†] Corresponding Author: Dept. of Electrical Engineering, Kyungpook National University, Korea (dh29kim@ee.knu.ac.kr).

* Dept. of Electrical Engineering, Kyungpook National University, Korea. ({nakedsun98, bloodkdw}@nate.com).

** School of Electronic Eng., Kyungpook National University, Korea. (bloodkdw@nate.com).

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investigated through the comparison with two conventional cell designs (i.e. initial and empirically obtained ones).

2. Mathematical Model

A zinc cell house consists of electrolytic cells, where plate-shaped anodes and cathodes are suspended alternately as shown in Fig. 1. Fresh electrolyte enters the house at one end, passes along the cell in the direction normal to the electrodes, and the depleted solution leaves the tank at the opposite end. Electrochemical reactions involve the transfer of electrons across the interface between an electrode and electrolyte. When electrodes are connected to the power supply, hydrated metal ions receive electrons from the electrode, and the resulting metal is deposited at the cathode surface.

Due to the geometrical symmetry, the area marked with a red box in Fig. 1 is selected for a two-dimensional finite element analysis. The geometry is a unit cell containing an electrolyte domain, where the anodes and cathodes are modeled as electrode surfaces on the boundaries. The ends of the electrodes are isolated using edge strips of isolating material.

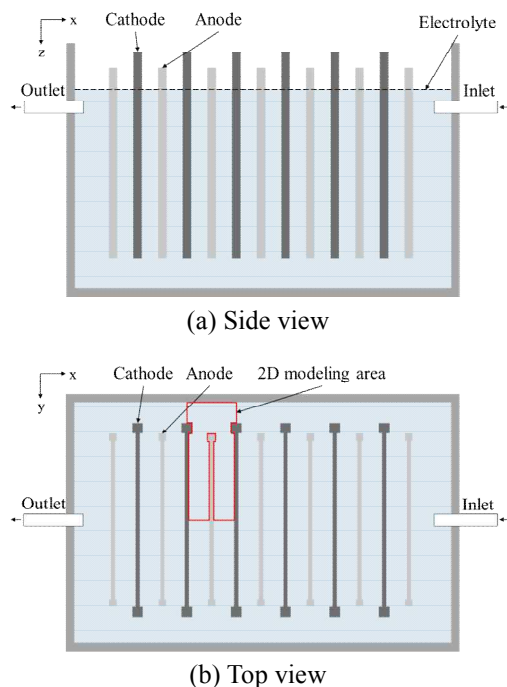


Fig. 1. A schematic view of a zinc electrowinning cell

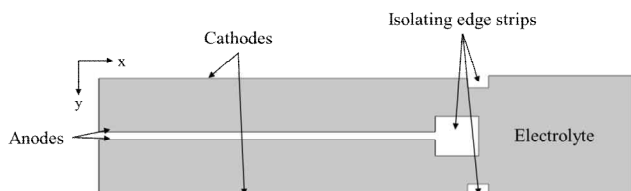


Fig. 2. A two-dimensional finite element model

To predict the distribution of the galvanic potential ϕ_l in the interelectrode space and the current density at the electrodes, the Laplace equation of (1) has to be solved with several electrochemical boundary conditions.

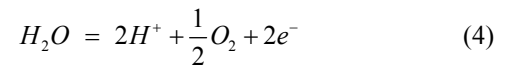
$$\nabla^2 \phi_l = 0 \quad (1)$$

A steady-state secondary current distribution at both anodes and cathodes is considered under the assumption that the electrolyte has a constant conductivity of 36.2 S/m.

At the cathode, the zinc deposition and simultaneous hydrogen occur as follows:



On the other hand, oxygen is evolved on the anode.



The total current passing through an electrode is the sum of the currents arising from all reactions occurring on its surface. The Butler-Volmer expression of (5) is used to establish a quantitative relationship between the electrode reaction kinetics and its current [1, 6, 7].

$$j = j_0 \left(\exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right) \quad (5)$$

where j is the *electrode* current density, j_0 is the exchange current density, α_a and α_c are the anodic and cathodic charge transfer coefficients respectively, F is the Faraday constant, R is the gas constant, T is the temperature in Kelvin, and η is the overpotential for the electrode reactions.

The overpotential is the principal factor determining the current density for the three reactions from (2) to (4), and its value is given by

$$\eta = \phi_s - \phi_l - E_{eq} \quad (6)$$

where ϕ_s and E_{eq} denote the potential externally applied to the *electrode* and the equilibrium potential due to the electrochemical reactions, respectively. The equilibrium potential is calculated from the Nernst equation of (7), which is the basis of all thermodynamic calculations for electrochemical processes.

$$E_{eq} = E^0 - \frac{RT}{nF} \ln \frac{a_o}{a_r} \quad (7)$$

where E^0 is the equilibrium potential in a normal state, n is the number of electrons, and a_o is the activity of the

oxidized species, and a_r is the activity of the reduced species. The above equation implies that the equilibrium potential due to the electron transport is related to the cell temperature and the activities of the oxidized and reduced species.

According to (7), the equilibrium potential values of 1.247 V and 0.016 V are respectively obtained for the two cathodic reactions of (2) and (3), while the other value for the anodic reaction of (4) is -0.797 V. The Laplace equation of (1) is solved with the electrolyte-electrode boundary interface of (5), above electrode reactions and applied potential value ϕ_s of 3.597 V. The other detailed simulation conditions comply with [6] and [7].

3. Sampling-Based Sensitivity Approach

The optimization of the electrowinning cell requires somewhat complicated electrochemical analysis described in the previous chapter, and also deals with the multi-dimensional design variables, of which the number usually is more than ten. To obtain an optimum structure of the electrowinning cell, a sampling-based sensitivity approach is employed. The method consists of the local window concept and Kriging-based surrogate modeling. In this section, the two key components are briefly explained.

3.1 Hyper-cubic local window

The global window generates sampling points over the whole design space, while the local window samples a very small region at the center of a nominal design point. Consequently, the concept of the local window is much more suitable for obtaining the accurate sensitivity value of a surrogate model than the global window. The local window size, R_i , is given by

$$R_i = c(d_i^U - d_i^L) \quad i = 1, 2, \dots, nd \quad (8)$$

where c is the coefficient which is usually between 2~5%, d_i is the i th design variable in a nd -dimensional space, and the superscripts, U and L , are the upper and lower bounds, respectively. After deciding the local window, evenly distributed N_r initial samples are generated on the window based on the Latin Centroidal Voronoi Tssellation [8, 9].

A surrogate model is created based on the responses at samples and universal Kriging (UKG) method. The accuracy of the model is checked with a certain criterion. If unsatisfied, additional samples are inserted in the window. The design sensitivity at the center of a design point of interest is extracted from approximated functions of the surrogate model. Fig. 3 explains how to explore an optimum in a design space with the proposed sampling-based sensitivity approach. In the illustration, only two design variables, d_1 and d_2 , are involved along with two constraint conditions, g_1 and g_2 . It is also assumed that an

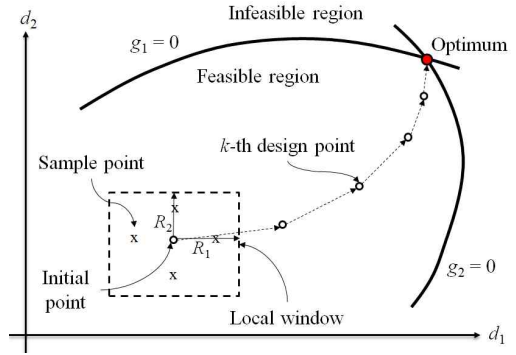


Fig. 3. Illustration of a hyper-cubic local window and its sensitivity-based searching technique

objective function monotonically decreases as the design variable values are increased. Starting with an initial point, an elaborate surrogate model is produced in the hyper-cubic local window depicted in Fig. 3. Accordingly an accurate design sensitivity value at the initial point is calculated. A next improved design is obtained with the aid of a gradient-based searching technique. The above process is repeated until an optimum is found out.

3.2 Surrogate model and its sensitivity

In the Kriging method [9-11], the outcomes are considered as a realization of a stochastic process. The goal is to estimate a response $y = [y(x_1), y(x_2), \dots, y(x_n)]^T$ with $y(x_i) \in \mathbf{R}^1$ based on n samples, $\mathbf{x} = [x_1, x_2, \dots, x_n]^T$ with $x_i \in \mathbf{R}^m$. The response consists of a summation of two parts as:

$$\mathbf{y} = \mathbf{F}\boldsymbol{\beta} + \mathbf{e} \quad (9)$$

The first term of the right side of (9), called the mean structure of the response, is intended to follow the general tendency of the function to be modeled. It is generally composed of the first/second-order basis functions \mathbf{F} and the regression coefficient vector $\boldsymbol{\beta}$, which is obtained from the generalized least square method. The second term \mathbf{e} is a realization of the stochastic process, and its mean is assumed zero. The covariance of \mathbf{e} is defined by

$$\text{Cov}(e(\mathbf{x}_i), e(\mathbf{x}_j)) = \sigma^2 R(\boldsymbol{\theta}, \mathbf{x}_i, \mathbf{x}_j) \quad (10)$$

where σ^2 is the process variance, $\boldsymbol{\theta}$ is the correlation parameter vector estimated by applying the maximum likelihood estimator (MLE). The symbol R denotes the correlation function of the stochastic process. The term \mathbf{e} makes it possible to follow the fluctuations around the general tendency. In most engineering applications, the correlation function is set to be a Gaussian form expressed as follows

$$R(\boldsymbol{\theta}, \mathbf{x}_i, \mathbf{x}_j) = \prod_{l=1}^{nr} \exp(-\theta_l (x_{i,l} - x_{j,l})^2) \quad (11)$$

where $x_{i,l}$ is the l th component of variable \mathbf{x}_i .

Under the decomposition of (9) and the optimal θ to maximize MLE, the noise-free unbiased response \hat{y} at a new point of interest denoted by \mathbf{x}_0 is written as a linear predictor

$$\hat{y}(\mathbf{x}_0) = \mathbf{w}_0^T \mathbf{y} \quad (12)$$

where $\mathbf{w}_0 = [w_1(\mathbf{x}_0), w_2(\mathbf{x}_0), \dots, w_n(\mathbf{x}_0)]^T$ means the $n \times 1$ weight vector for prediction at the point. It is obtained using the unbiased condition $E[\hat{y}(\mathbf{x}_0)] = E[y(\mathbf{x}_0)]$ as

$$\mathbf{w}_0 = \mathbf{R}^{-1} \left(\mathbf{r}_0 + \frac{1}{2\sigma^2} \mathbf{F} \boldsymbol{\lambda} \right) \quad (13)$$

where \mathbf{R} is the symmetric correlation matrix with the ij th component $R_{ij} = R(\theta, \mathbf{x}_i, \mathbf{x}_j)$, $\mathbf{r}_0 = [R(\theta, \mathbf{x}_1, \mathbf{x}_0), \dots, R(\theta, \mathbf{x}_n, \mathbf{x}_0)]^T$ is the correlation vector between \mathbf{x}_0 and samples \mathbf{x}_i , and $\boldsymbol{\lambda}$ is the Lagrange multiplier.

After substituting (13) into (12), the prediction of Kriging model which interpolates the n sample points is expressed as

$$\hat{y}(\mathbf{x}_0) = \mathbf{w}_0^T \mathbf{y} = \left(\mathbf{r}_0 + \frac{\mathbf{F} \boldsymbol{\lambda}}{2\sigma^2} \right)^T \mathbf{R}^{-1} \mathbf{y} = \mathbf{f}_0^T \boldsymbol{\beta} + \mathbf{r}_0^T \mathbf{R}^{-1} (\mathbf{y} - \mathbf{F} \boldsymbol{\beta}) \quad (14)$$

where $\sigma^2 = 1/n(\mathbf{y} - \mathbf{F} \boldsymbol{\beta})^T \mathbf{R}^{-1} (\mathbf{y} - \mathbf{F} \boldsymbol{\beta})$ and $\boldsymbol{\beta} = (\mathbf{F}^T \mathbf{R}^{-1} \mathbf{F})^{-1} (\mathbf{F}^T \mathbf{R}^{-1} \mathbf{y})$ are obtained from the generalized least square regression. Finally, the derivative \hat{y}' of the prediction model at \mathbf{x}_0 is extracted from (14) like

$$\hat{y}'(\mathbf{x}_0) = \mathbf{J}_f^T \boldsymbol{\beta} + \mathbf{J}_r^T \mathbf{r}_0 \quad (15)$$

where \mathbf{J}_f^T and \mathbf{J}_r^T denote the Jacobian transformation of \mathbf{f}_0 and \mathbf{r}_0 , respectively.

4. Results

The nonuniform current distribution on electrode surfaces is liable to cause the locally growing dendrite or effective electrode area reduction, which can lead to the short circuit in electrowinning cells or loss in current efficiency. To achieve the uniformity of cathodic current distribution, a previous work in [6] performed a parametric study based on an empirical way, and obtained an improved cell design. There, the only effect of the edge strip locations of cathodes was investigated, whereas other geometric parameters relating to the whole cell structure were fixed.

In this paper, all geometric parameters deciding the cell structure in Fig. 4 are selected and optimized as design variables. The design goal is to find a fully optimized cell structure, which can yield a more uniform cathodic current

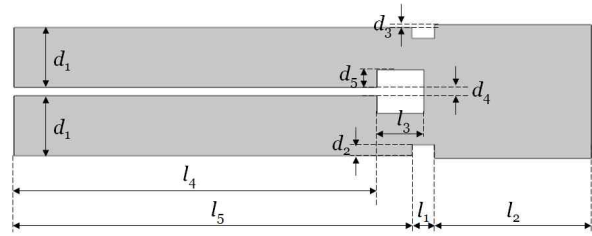


Fig. 4. Ten design variables shaping an electrowinning cell

distribution. The objective function f is mathematically defined as follows

$$\text{minimize } f(\mathbf{d}) = \int_L (j_n(\mathbf{d}) - 1)^2 dl \quad (16)$$

where \mathbf{d} is the design variable vector, L is the integral path along the cathode surface, and j_n is the normalized cathodic current density. The proposed sampling-based sensitivity approach was implemented by means of Matlab functions and application programming interface language [12]. The electrochemical simulations at samples were executed with a commercial multiphysics software package, called COMSOL [7].

For comparison with conventional cell designs, the optimization started with the same initial design as the empirical design method used in [7]. After 16 iterative designs requiring total 673 finite element simulations, an optimized cell design was sought out. Design variable values between three different designs of the initial, empirically obtained, and fully optimized cells are compared with each other in Table 1. In the empirical method, only two design variables of l_2 and l_5 in Fig. 4 were tuned through examining the impact of changing the edge strips of cathodes.

Table 1. Comparison of design variables between three different designs (unit: mm)

	Lower bounds	Initial design	Empirical method	Proposed method	Upper bounds
d_1	34	44	44	34	54
d_2	4	8	8	11.97	12
d_3	1	2	2	3.32	5
d_4	3	6	6	3	9
d_5	3	13	13	3	20
l_1	7	17	17	9.72	27
l_2	107	117	137	126.63	147
l_3	25	35	35	37.84	45
l_4	200	271	271	286.20	350
l_5	200	297	277	290.82	350

The galvanic potential and current distributions in the electrolyte solution for the three different cells are compared in Fig. 5 and 6, respectively. It is clear that the current uniformity around the edge strips of anode as well as cathodes of the optimized cell is much improved when compared with the initial and the empirical ones. Moreover, Fig. 6 shows that the current density value around the

electrode center in the optimized cell is increased by more than 20% of those in two other cells. Fig. 7 presents the normalized current density distributions along the cathode surface for the three cells. It is observed that the uniformity of cathodic current distribution in the optimized cell is enhanced specifically around the edge strip, which is located at about 290 mm. In Fig. 8, three different cell structures are compared with each other.

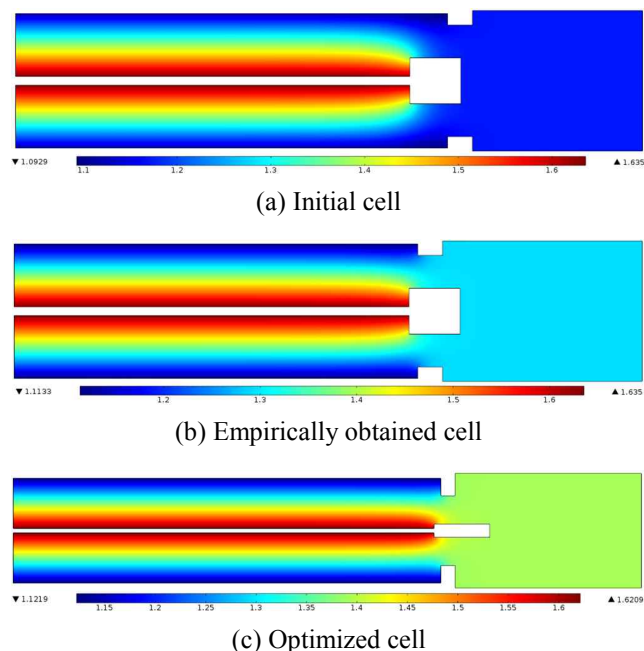


Fig. 5. Potential distributions between three different cell designs

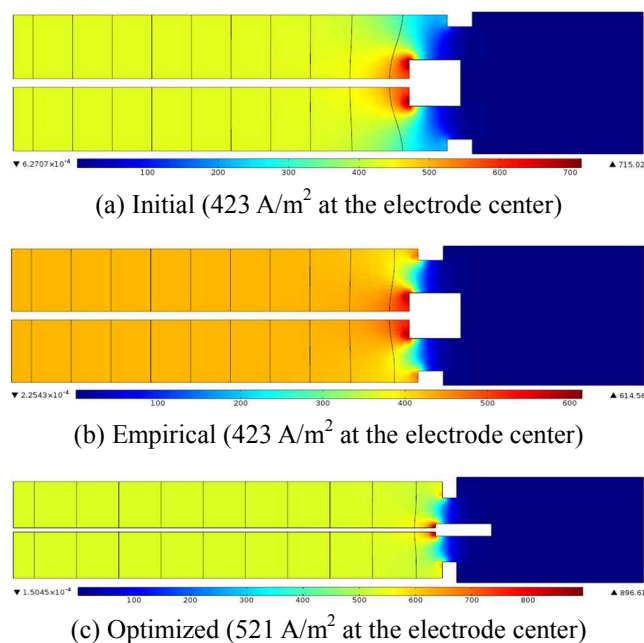


Fig. 6. Current density distributions between three different cell designs

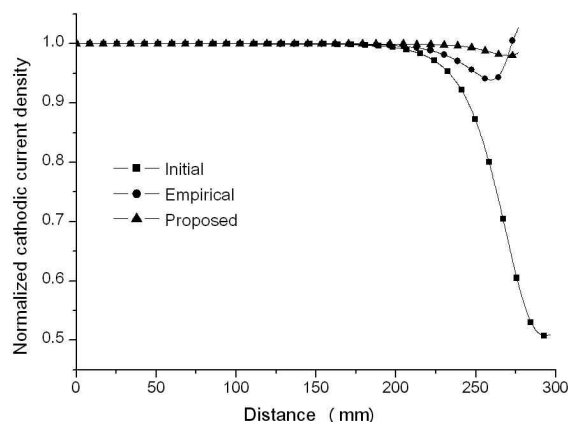


Fig. 7. Current density distributions between three different cell designs

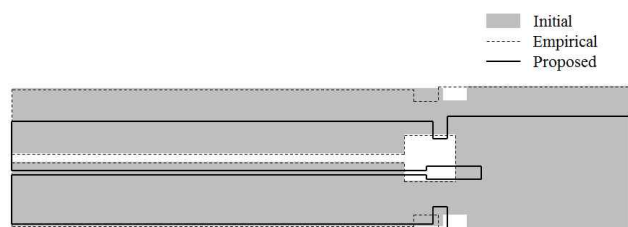


Fig. 8. Three different cell structures

5. Conclusion

The sampling-based sensitivity approach was successfully combined with the multiphysics simulator to optimize the whole cell structure for zinc electrowinning. The results show that the optimized cell provides a higher uniformity of cathodic current distribution when compared with the empirically obtained design. It is inferred that the proposed cell design will be very useful for improving the current efficiency and preventing the local dendrites in the electrowinning process.

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Dong-Wook Kim was born in Korea in 1982. He received his B.S. and M.S. degrees in Electrical Engineering from Kyungpook National University, Daegu, Korea, in 2009 and 2011, respectively. Currently, he is on his Ph.D. course at Kyungpook National University.



Jeonghun Cho received his M.S. and Ph.D. degrees in Electrical Engineering from Korea Advanced Institute of Science and Technology, Daejeon, Korea, in 1998 and 2003, respectively. He was a senior researcher at MCU Application Team of Hynix Semiconductor Inc. in Cheongju, Korea, from 2003 to 2005.

He is currently an associate professor at the School of Electronics Engineering in Kyungpook National University, Daegu, Korea. His main interests include automotive embedded systems, model-based design, and HW/SW codesign.



Dong-Hun Kim received his M.S. and Ph.D. degrees in Electrical Engineering from Seoul National University, Seoul, Korea, in 1994 and 1998, respectively. He was a senior researcher at the Digital Appliance Research Center of LG Inc. in Seoul, Korea, from 1998 to 2001. He continued his research at the

University of Southampton in United Kingdom as a research fellow for two years (2002 - 2003). He is currently an associate professor at the Department of Electrical Engineering in Kyungpook National University, Daegu, Korea. His main interests include electromagnetic field analysis, design optimization of electrical appliances, and biomedical application.



Nak-Sun Choi was born in Korea in 1979. He received his M.S. and Ph. D. degrees in Electrical Engineering from Kyungpook National University, Daegu, Korea, in 2006 and 2009, respectively. He is currently a senior researcher at the Defense Agency for Technology and Quality.