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On-line Identification of Electro-Conductivity in Electrolytic Solutions

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***Abstract*— An on-line method is proposed to identify electro-conductivity in electrolytic solutions. The method uses a model of a cell of electrolytic solutions in a micro reactor modeled by an electronic circuit. The circuit consists of a cell part with a resister and a capacitor connected in series and a measurement part having a resister. Then the resistance and the capacitance of the cell part are identified to calculate the electro-conductivity. The identification scheme is the least-square method with a forgetting factor calculated on-line. To avoid the effect of differentiation of measured signals, a filter is added to the identification method. The effectiveness of the proposed control scheme is shown by numerical simulation.**

Index Terms- Conductivity, Parameter identification, Electrolytic solutions

I. Introduction

Measuring the electric resistance of electrolytic solutions and electric conductivity is important in chemical field. The electro-conductance means that how much electricity can be transformed, and it is defined as the inverse of the electric resistance.

Electric conductivity, which is proportionate to its concentration, is determined by the density of electrolyte solving into water. Therefore, if the concentration of electrolyte is large, the value of electric conductivity is large as well.

One example of application is that the electric conductivity is used to know the amount of saline component in hydroponics cultivation. Another example is that, it is utilized as an indicator of water pollution, that is, the electric conductivity in a polluted river becomes larger by sewage from an inorganic-creating factory, also the conductivity can be used to measure how acidic acid rain is.

Generally, the method to measure electric conductivity is first to input an alternating current between the two poles in conductivity cell filled with electrolytic solutions and the resistance of the liquid is measured. However the method requires another electrolytic solution for calibration and batch calculation. In application there are many cases with no calibration solutions and requiring on-time calculation.

This paper proposes a method to identify on-line the conductivity of an electrolytic solution cell without using calibration solutions. The method uses a model of the cell given by an electronic circuit.

Meraz et al [1] also proposed a method using an electronic circuit model. Their method identifies the parameters in the circuit by using resonance to sinusoidal wave inputs and is not on-line calculation, but batch calculation.

The modeling circuit in this paper consists of two parts; a cell part to model the electrolytic solution cell and a measurement part to model current to voltage (I-V) conversion. The cell part has a resister and a capacitor with unknown resistance and capacitance. The measurement part is a resister with known resistance.

The estimation of the conductivity is calculated from the identified values of the resistance and the capacitance of the cell part. The identification is obtained by using on-line least-square method with a forgetting factor. The method uses input and output measured signals to the circuit model.

Since the circuit model includes differentiation, the least-square method also requires differentiation of the measured signals. But usually measured signals contain measurement noise and the noise is enlarged by the differentiation, hence in the identification process, the differentiation should be avoided. In this paper, a new method is proposed to avoid the differentiation. In the method a signal filter is added and the differentiation is replaced by integration.

This paper consists of the following sections. The electrolytic solution cell to be measured is explained in section 2. Following this, the model of the system is given. In section 4, we propose the least square in discrete time that does not contain the element of differential. Finally, the effectiveness of the proposed method is proved by simulation.

II. Electrolytic solution

In case of measuring the electric resistance of a metal, we generally use the circuit tester. The circuit tester applies a direct-current voltage to the metal and measures a value of current, then the circuit tester calculates the value of resistance by using Ohm's law.

On the other hand, in measuring the conductivity of electrolytic solutions, if the direct-current voltage is applied to the solution with the electrodes, ions in solution polarize to each electrode over time. Finally, the electric resistance of the solution reaches an infinite value owing to complete polarization. Thus, the alternating current voltage is used in the case of electrolytic solution. Recently, many devices to

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measure the electric resistance and conductivity of electrolytic solutions are on the market. However, with these devices, it is difficult to measure the conductivity to observe variation of the conductivity in time. In this paper a new method is proposed to control the measurement with computers.

A. Conductivity cell

The part to measure the electro-conductivity of a solution is called the conductivity cell. We show the image of the conductivity cell in Fig. 1 and Fig. 2.

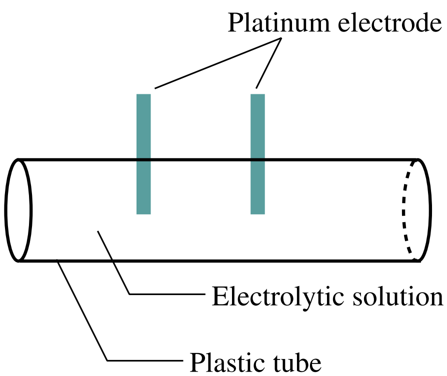

Fig. 1. Conductivity cell

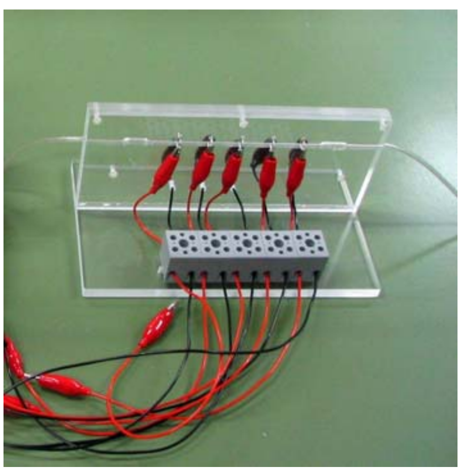

Fig. 2. Conductivity cell

In the cell, two platinum electrodes run into the plastic tube filled with a electrolytic solution of which conductivity is measured.

B. Electrical characteristic

The whole of measurement system is shown in Fig. 3. It consists of the alternating current oscillator, current amplifier, commutator, V-I and I-V converters, digital IO board and AD/DA converter.

Alternating current oscillator
The alternating current oscillator is used to generate an

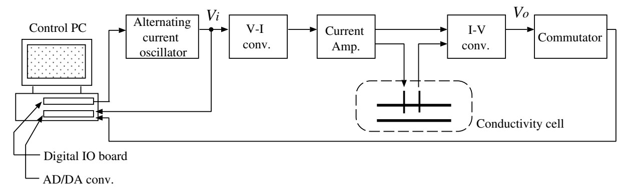

Fig. 3. Measurement system

alternating current voltage to apply the electrodes.

Current amplifier
The output current from the alternating current oscillator is amplified to a suitable value for measurement with the current amplifier.

Commutator
The signal provided for the control PC should be direct current, and the measured signal is alternating current. Hence, a commutator is used to convert the alternating current into direct current.

V-I and I-V converters
Both input and output signals for the control PC are voltage signals. In contract, current signals are used in the measuring device. Thus, we need V-I and I-V converters.

Digital IO board
The digital IO board is used to specify the frequency of alternating current with a control computer.

AD/DA converter
All processing in the control computer is treated by the digital signals. But the analog signals are used in the measurement system. Hence, it requires the AD/DA converter in the control computer.

III. Circuit model

It has been shown that a model expressing a conductivity cell for many electrolytic solutions well is the electrolyte resistance R_s, with the capacitance C_s in series, corresponding to the electrode-solution cell[1]. The circuit based on the model with measurement part for I-V converter is shown in Fig. 4. Resistence R_s and Capacitance C_s are unknown and after identification of R_s and C_s, the estimation of conductivity is given by $\frac{1}{R_s+i\frac{C_s}{\omega}}$.

In this figure, V_i is a sine-wave voltage, frequency ω [Hz] and the voltage V_o through the known resistance R_p is the output. Moreover, we assume that the current passing through the circuit is i. Then $V_o = -R_p i$ and the relation between the input voltage V_i and the output voltage V_o is shown by the following formula.

$$V_o = \frac{1}{C_s}\int_0^t i dt + R_s i + V_i \tag{1}$$

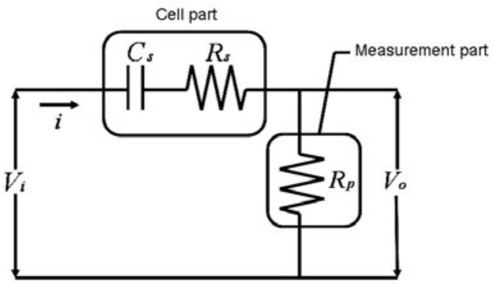

Fig. 4. The equivalent circuit of the conductivity cell

IV. Parameter identification

From (1), measured input signal V_i and output signal V_o have the next relation

$$C_s(R_p + R_s)\frac{di}{dt} - i = C_s\frac{dV_i}{dt}. \tag{2}$$

In this relation, differentiation signals of measured signals $i = -\frac{1}{R_p}V_o$ and V_i are included. In actual measurement, measured signals are contaminated by noise. To avoid the effect of noise, it is necessary to remove differentiation in the identification procedure. To remove the differentiation, a filter is added in the procedure by the following.

With $\theta_1 = -\frac{1}{C_s R_s}$, $\theta_2 = \frac{1}{R_s}$ and using $s = \frac{d}{dt}$ and a positive value $\alpha > 0$, (2) is

$$(s+\alpha)i = (\theta_1 + \alpha)i + \theta_s s(V_o - V_i). \tag{3}$$

Dividing by $(s+\alpha)$,

$$i = (\theta_1 + \alpha)\frac{1}{s+\alpha}i + \theta_2\frac{s}{s+\alpha}(V_o - V_i). \tag{4}$$

Using $\theta_1' = \theta_1 + \alpha$, and filtered signals

$$\begin{aligned} \phi_1 &= \frac{1}{s+\alpha}i, \qquad \dot{\phi}_1 = -\alpha\phi_1 + i, \\ \phi_2 &= \frac{s}{s+\alpha}(V_o - V_i) = \phi_{21} + \phi_{22}, \\ \phi_{21} &= V_o - V_i, \\ \phi_{22} &= -\frac{\alpha}{s+\alpha}(V_o - V_i), \quad \phi_{22}' = -\alpha\phi_{22} - \alpha(V_o - V_i), \end{aligned}$$

then (4) becomes

$$i = \theta_1'\phi_1 + \theta_2\phi_2. \tag{5}$$

This relation does not include differentiation. Using this relation, we can identify unknown parameters θ_1' and θ_2 by least square method. The calculation of the least square method is as follows,

$$\begin{aligned} \hat{\Phi}_{k+1} &= \hat{\Phi}_k - \frac{R_k^{-1}Z_{k+1}(Z_{k+1}^T\hat{\Phi}_k - i_{k+1})}{\lambda + Z_{k+1}^T R_k^{-1} Z_{k+1}} && (6) \\ R_{k+1}^{-1} &= \frac{1}{\lambda}(R_k^{-1} - \frac{R_k^{-1}Z_{k+1}Z_{k+1}^T R_k^{-1}}{\lambda + Z_{k+1}^T R_k^{-1} Z_{k+1}}) && (7) \\ \hat{\Phi}_k &= \begin{pmatrix} \hat{\theta}_1' \\ \hat{\theta}_2 \end{pmatrix}_k && (8) \\ Z_k &= \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}_k && (9) \end{aligned}$$

where, λ is the forgetting factor $(0 < \lambda \le 1)$, $\hat{\theta}_1'$ and $\hat{\theta}_2$ are the identified values of θ_1' and θ_2 and $(*)_k$ denotes sampled value of signal * at sampling time k.

V. Simulation

A. Simulation condition

Model expression (2) is shown by the following differential equations.

$$didt = -\frac{1}{C_s(R_p + R_s)}i - \frac{1}{R_p + R_s}\frac{d}{dt}V_i \tag{10}$$

Simulation is conducted under the following condition: R_s and C_s change from one value to another value linearly.

$$R_s: \begin{cases} 0.1 \times 10^4 \ [\Omega] & 0 \le t < 4 \\ 0.25 \times (t-4) \times 10^4 + 0.1 \times 10^4 \ [\Omega] & 4 \le t < 6 \\ 0.6 \times 10^4 \ [\Omega] & 6 \le t \end{cases}$$

$$C_s: \begin{cases} 1 \times 10^{-5} \ [F] & 0 \le t < 4 \\ -0.25 \times (t-4) \times 10^{-5} + 1 \times 10^{-5} \ [F] & 4 \le t < 6 \\ 0.5 \times 10^{-5} \ [F] & 6 \le t \end{cases}$$

R_p: 4500 $[\Omega]$

Fig. 5 shows the current i received from the simulation.

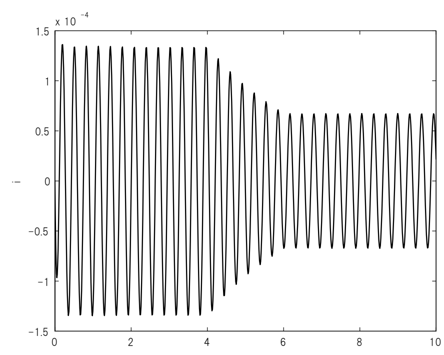

Fig. 5. The current i for the parameter identification

B. Simulation result

The signals ϕ_1 and ϕ_2 generated from measured value are obtained solving the following equations. Fig. 6 shows filtered signals ϕ_1 and ϕ_2.

$$\dot{\phi}_1 = -\alpha\phi_1 - \frac{1}{R_p}V_o \quad (11)$$

$$\dot{\phi}_3 = -\alpha\phi_3 + \alpha(V_o - V_i) \quad (12)$$

$$\phi_2 = V_o - V_i - \phi_3 \quad (13)$$

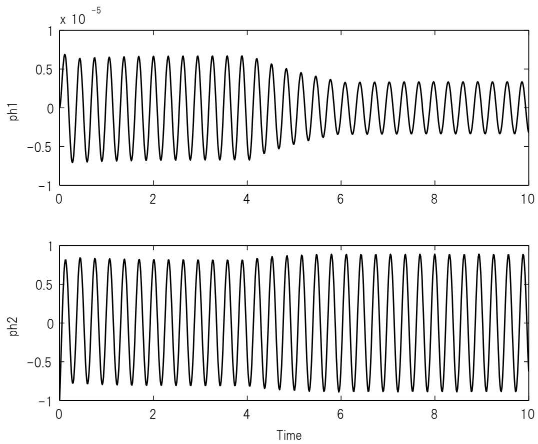

Fig. 6. Time variation of ϕ_1 and ϕ_2

In Fig. 6, ph1 and ph2 show ϕ_1 and ϕ_2 respectively.

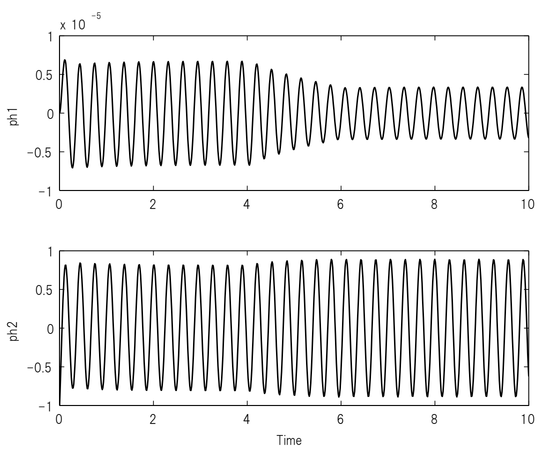

Fig. 7. The simulation data $\hat{\theta}_1'$ and $\hat{\theta}_2$

Fig. 7 shows the simulation result. th1 and th2 show $\hat{\theta}_1'$ and $\hat{\theta}_2$ respectively. The identified values of R_s and C_s follow the change of true values of R_s and C_s in $4 \leq t < 6$. The graphs of Rs and Cs are shown in Figs. 8 and 9.

VI. Conclusion

An estimation method for conductivity of electrolytic solutions is proposed in this paper. The method estimates the conductivity on-line and does not need calibration solutions. The least square method with a forgetting factor is used and to avoid differentiation of measured signals and to reduce the effect of measurement noise, the method uses an additional filter. A simulation result shows the effectiveness of the proposed method.

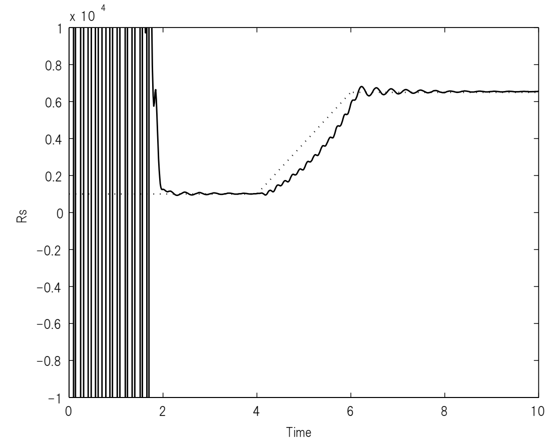

Fig. 8. The presumption value of Rs

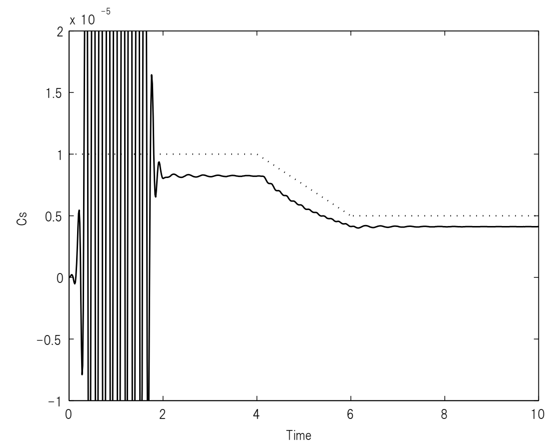

Fig. 9. The presumption value of Cs

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