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ABSTRACT

AC impedance spectroscopy is an important method for evaluating ionic, electronic, and dielectric properties of materials. In conventional analysis of AC impedance spectra, the selection of an equivalent circuit model and its initial parameters are *visually* determined from a Nyquist plot; this visual determination can be both inefficient and inaccurate. Thus, analysis based on a rigorous mathematical method is highly desirable. Here, we demonstrate the analysis of AC impedance spectra using Bayesian statistics. We apply the method to artificial AC impedance spectra generated from resistance (R) and capacitance (C) circuits, obtaining a high accuracy ratio (>90%) in model selection when the ratio of the time constants of two RC parallel circuits exceeds 3. Furthermore, this method is applied to an actual electrical circuit comprising a resistance and two RC parallel circuits, yielding highly accurate model selection and parameter estimation. The results demonstrate the effectiveness of the proposed method for AC impedance spectra.

INTRODUCTION

AC impedance spectroscopy is a popular method for analyzing the ionic, electronic, and dielectric properties of materials.[1] During AC impedance measurements, an AC voltage is applied to a sample at different frequencies, and the electrical current is measured. This method enables the quantitative analysis of intra- and inter-grain electrical conductivity as well as the evaluation of each elementary process in devices, including fuel cells,[2,3] supercapacitors,[4,5] lithium batteries,[6] and solar cells.[7,8]

In the analysis of AC impedance spectra of dielectrics and ionic/electronic conductors, the physical and chemical processes are modeled with equivalent circuits that generally include resistance (R), capacitance (C), and constant phase element components. When an equivalent circuit contains an RC parallel circuit, a semicircle appears on the Nyquist plot. In the conventional analysis of dielectrics and ionic/electronic conductors, the number of RC parallel circuits and the initial model parameters are *visually* determined from the Nyquist plot; however, this visual determination can be both inefficient and inaccurate. Therefore, development of quantitative methods based on adequate mathematical formulations is necessary.

In this study, we present a method for analyzing AC impedance spectra based on Bayesian statistics. Although analyses of other types of spectra using Bayesian statistics are available,[9–12] Bayesian statistics have not been applied for model selection in the analysis of impedance spectra. For artificial AC impedance data generated from RC parallel circuits connected in series, the proposed analysis predicted the correct number of circuits and parameters at rates exceeding 90%. Furthermore, our analysis succeeded with high accuracy when applied to an actual electrical circuit. These results indicate that the proposed method is suitable for AC impedance spectra analysis, opening the way to unambiguous and systematic analysis of such data.

METHODS

In order to determine the number of circuits and circuit parameters (R and C values) from the impedance spectra using Bayesian statistics, we used the same formulation as in Ref. 12. For a circuit with resistance (R_0) and few RC parallel circuits connected in series, the impedance $z(\omega)$ is expressed as

$$z(\omega) = \sum_{k=0}^{K} \frac{R_k}{1 + i\omega R_k C_k} = R_0 + \sum_{k=1}^{K} \frac{R_k}{1 + i\omega R_k C_k}, \tag{1}$$

where K is the number of RC parallel circuits, ω is the angular frequency, and R_k and C_k are the resistance and capacitance of the k-th parallel circuit, respectively. By definition, $C_0 = 0$. We assume that the experimental AC impedance spectra Z_i at angular frequency ω_i are observed as the sum of the true impedance function $z(\omega)$ and noise ϵ_i,

$$Z_i = z(\omega_i) + \epsilon_i. \tag{2}$$

In Bayesian inference, parameters R_k and C_k are assumed to be stochastic variables. Assuming that the noise ϵ_i is a Gaussian random number with zero mean and variance σ^2, the likelihood (the probability of observing impedance Z_i at frequency ω_i when the number of circuits K and the parameter values are fixed at specific values) is

$$p(Z_i|\omega_i, R_1, C_1, R_2, C_2, \ldots) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2\sigma^2}|Z_i - z(\omega_i)|^2\right). \tag{3}$$

The posterior distribution $p(R_1, C_1, R_2, C_2, \ldots|D, K)$ of parameters $R_1, C_1, R_2, C_2, \ldots$, given data D (which contains n measurements of impedance at various frequencies), can be expressed using Bayes' theorem as follows:

$$p\left(R_1, C_1, R_2, C_2, \ldots|\omega^n, Z^n, K\right) = \frac{1}{p(D|K)} p(R_1, C_1, R_2, C_2, \ldots|K) \times \prod_{i=1}^{n} p(\omega_i, R_1, C_1, R_2, C_2, \ldots, K), \tag{4}$$

where $p(R_1, C_1, R_2, C_2, \ldots|K)$ is the prior distribution of the circuit parameters and $p(D|K) = p(Z^n|\omega^n, K)$ is a normalization constant called marginal likelihood or evidence. In this study, the Markov chain Monte Carlo (MCMC) with the parallel tempering method was used for sampling the posterior distribution and estimating the parameters (see the supplementary material). The function $-\log p(D|K)$ was approximately evaluated using the widely applicable Bayesian information criterion (WBIC)[13] and minimized for the determination of K[9,14,15] (see the supplementary material).

Analysis of artificial impedance data

We first analyzed the artificial impedance spectra to evaluate the effectiveness of our method. Artificial data were generated from the sum of the impedance of three circuits ($K = 3$) [Fig. 1(a)]. Figure 1(b) shows the Nyquist plot of the artificial impedance spectra with Gaussian noise (standard deviation $\sigma = 10^3$). The number of impedance datasets n for Bayesian inference was 150. The prior distributions of the resistance $p(R_j)$ and capacitance $p(C_j)$ were selected as uniform distributions in a positive region:

$$p(R_j) = \begin{cases} \text{const.} & (0 < R_j < \infty) \\ 0 & (\text{otherwise}), \end{cases}$$

$$p(C_j) = \begin{cases} \text{const.} & (0 < C_j < \infty) \\ 0 & (\text{otherwise}). \end{cases}$$

The prior distribution for K, $p(K)$, was a discrete uniform distribution within $K = 1$–8. The details of the calculations [temperature, initial values, iteration, and WBIC_K calculation (Fig. S1)] are presented in the supplementary material. We implemented our method in MATLAB and performed the calculations using the TSUBAME3.0 at the Tokyo Institute of Technology [CPU: Intel Xeon E5-2680 V4 Processor (Broadwell-EP, 7 cores, 2.4 GHz), RAM: 60 GB]. The wall time was about 5 min following the selection of a model.

Figure 1(c) depicts the model-selection accuracy using our method. The correct answer $K = 3$ was selected at a frequency of 90% (45 times out of 50). Subsequently, we confirmed the accuracy of the estimated circuit parameters for $K = 3$. The trace plots and posterior distributions of the circuit parameters for $K = 3$ calculated using the MCMC with the parallel tempering method are displayed in Figs. 1(d) and 1(e), respectively. The convergence of the posterior distributions is observable in all the trace plots; the posterior distributions exhibit a maximum in the vicinity of the true value, as shown in Figs. 1(f) and 1(g). Table I shows the parameters estimated using our method. The estimated Nyquist plot is depicted in Fig. 1(b); the results [red solid line in Fig. 1(b)] are in good agreement with the artificial data [black dots in Fig. 1(b)]. It should be noted that the difference between the estimated value and true parameters was less than 1% for each parameter (Table I). Additionally, the model selection accuracy for circuits with various R and C ratios was investigated (Fig. S2, Table S1). The correct answer $K = 2$ was selected at a frequency of ~90% for various R and C ratios (Table S2).

Model selection accuracy for circuits with different time constants

Next, we investigated the accuracy of our method in circuits with proximate time constants (where the time constant is defined as $\tau = RC$). This investigation is important because parameter estimation becomes difficult when the difference between the time constants is smaller. Artificial impedance spectra with various time constant ratios (τ_1/τ_2) ranging from 2 to 7 were prepared by changing the capacitance (C_1, C_2) of the circuit with $K = 2$ [Figs. 2(a)–2(g)], where the values of R_1 and R_2 were fixed to 100 kΩ and 50 kΩ, respectively. The values of circuits parameters are summarized in Table S3. All the artificial spectra included Gaussian noise with

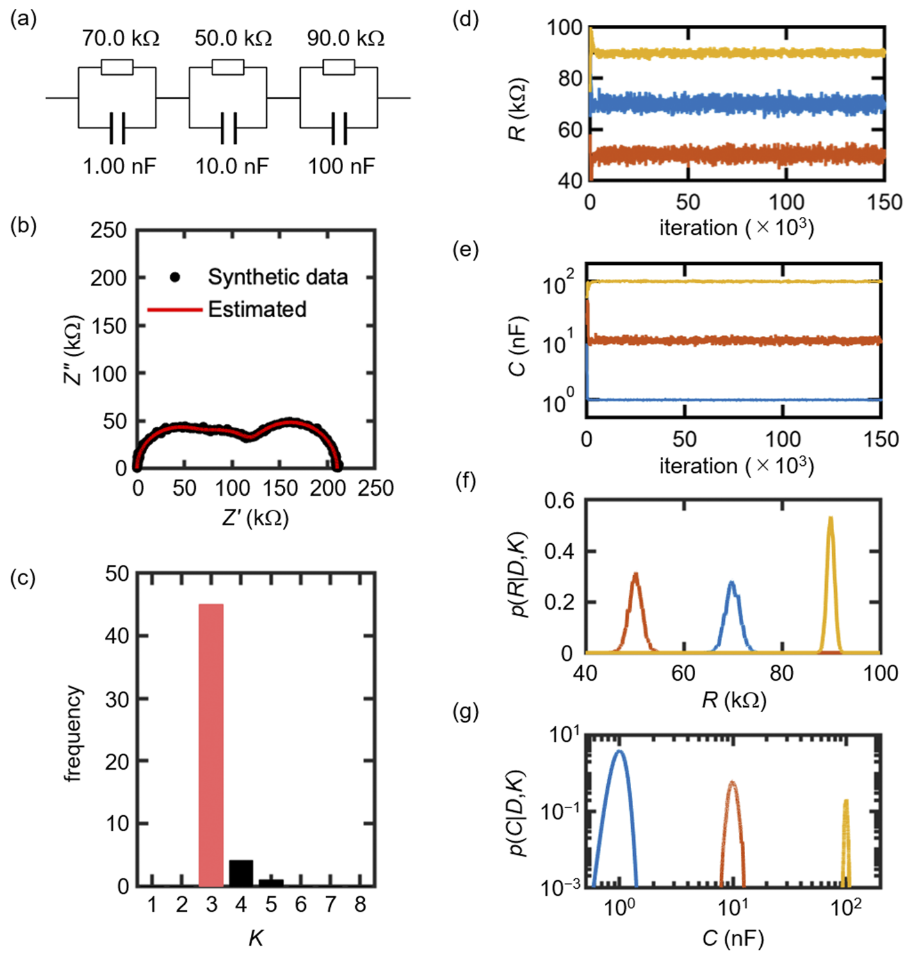

FIG. 1. (a) Schematic of a circuit with three resistance (R) and capacitance (C) parallel circuits connected in series. (b) Artificial impedance spectra calculated from the circuit shown in (a), indicated by black dots. Gaussian noise is superimposed on the artificial spectra. The red solid line denotes the predicted spectra using Bayesian statistics. The estimated circuit parameters are summarized in Table I. (c) Model selection accuracy. The horizontal axis indicates the number of RC parallel circuits K, whereas the vertical axis indicates the frequency at which the corresponding equivalent circuit model is selected. The red histogram shows the frequency at which the true equivalent circuit model is selected. [(d)–(g)] Trace plots and posterior distributions of the circuit parameters for K = 3, calculated using the MCMC with parallel tempering.

TABLE I. True parameters of the circuit shown in Fig. 1(a) and estimated parameters for K = 3. The estimated parameters were determined by calculating the maximum *a posteriori* probability estimation (see the supplementary material).

	R_1 (kΩ)	C_1 (nF)	R_2 (kΩ)	C_2 (nF)	R_3 (kΩ)	C_3 (nF)
True parameters	70.0	1.00	50.0	10.0	90.0	100
Estimated parameters for K = 3	69.8	1.00	50.5	9.94	89.9	101

a standard deviation $\sigma = 10^3$; the calculation conditions were the same as those described above except for the number of trials (100 times). Although the accuracy rapidly decreased when $\tau_1/\tau_2 < 3$, the accuracy rate remained above 90% when $\tau_1/\tau_2 \geq 3$ [Fig. 2(h), Table II]. Additionally, when $\tau_1/\tau_2 \geq 3$, the differences between the estimated values and true parameters were less than 5% for each parameter (Table S3).

Analysis of experimental impedance data obtained from an electrical circuit

Furthermore, we analyzed the experimental impedance spectra obtained from an actual electrical circuit [Figs. 3(a) and 3(b)]. The data were collected using potentiostat Biologic SP-150. Different from the artificial data, the variance σ^2 of the Gaussian noise in the experimental impedance spectra is unknown, and several hundred or thousand independent observations are required to determine σ. However, σ can be optimized using WBIC because σ is also a parameter of the Bayesian probability model. In this study, we estimated the most probable σ using Bayesian statistics before the selection of the equivalent circuit model (see the Appendix; Fig. S3). We used an electrical circuit in which the number of RC parallel circuits (K) and the circuit parameters (R, C) were already known. Thus, the correctness of σ estimation can be confirmed by comparing the estimated parameters with the true ones. The number of impedance datasets n for the Bayesian inference was 98. The prior distributions of the

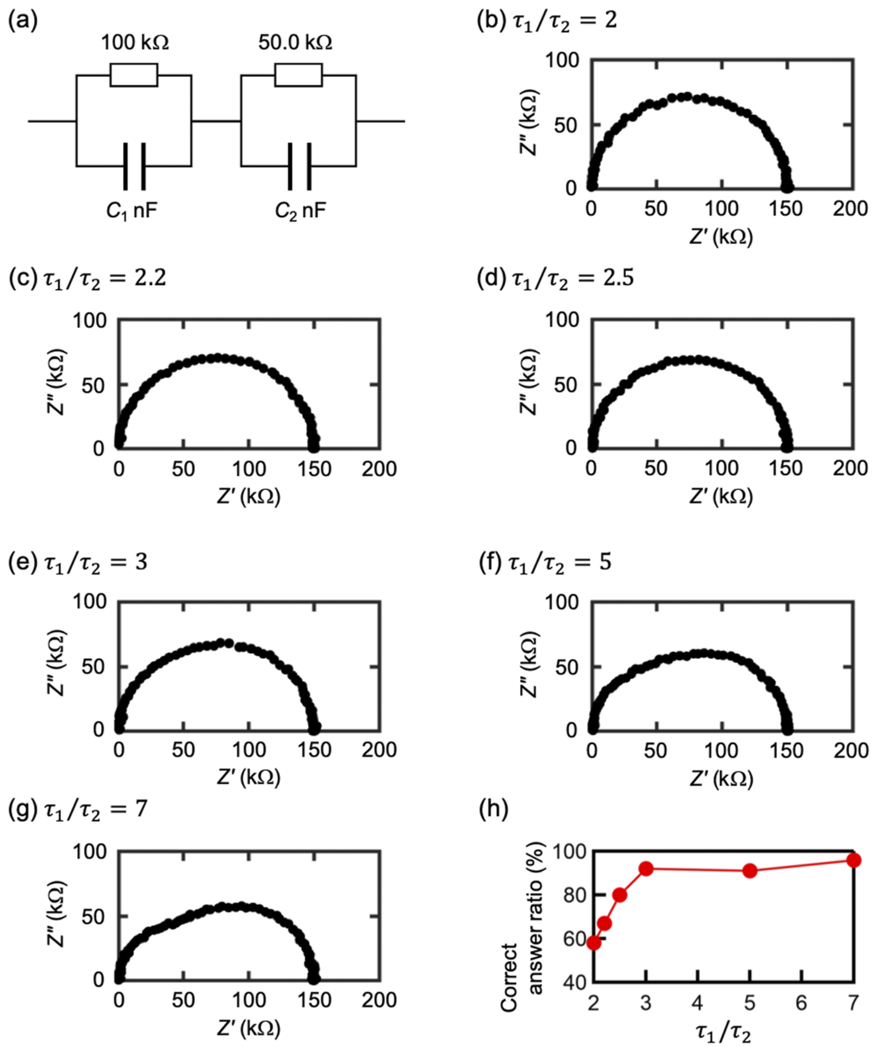

FIG. 2. (a) Schematic of a circuit with two RC parallel circuits connected in series, in which the time constant ratio (τ_1/τ_2) is varied by changing the capacitance values (C_1, C_2). [(b)–(g)] Artificial impedance data spectra with different time constant ratios (τ_1/τ_2) ranging from 2 to 7 prepared by changing the capacitance of the circuit with K = 2. The estimated circuit parameters are summarized in Table I. (h) Correct-answer ratios for the time constant (τ_1/τ_2) ratios.

resistance $p(R_j)$ and capacitance $p(C_j)$, K, $p(K)$ were the same as those used for the calculation of the artificial impedance spectra. The details of the calculations [temperature, initial values, iteration, and the WBIC$_K$ calculation (Fig. S4)] are presented in the supplementary material.

Figure 3(c) shows the accuracy of the equivalent circuit model selection using our method. The correct answer $K = 2$ was selected at a frequency of 92% (46 times out of 50). Subsequently, we confirmed the accuracy of the estimated circuit parameters for $K = 2$. Similar to the analysis of the artificial data, the convergence of the posterior

TABLE II. Model selection frequency for the impedance spectra with time constant ratios (τ_1/τ_2) ranging from 2 to 7. The boldface numbers correspond to the correct answer (K = 2).

	Frequency of the model selections								Correct answer ratio (%)
τ_1/τ_2	$K = 1$	$K = 2$	$K = 3$	$K = 4$	$K = 5$	$K = 6$	$K = 7$	$K = 8$	
2	0	**58**	20	7	5	0	8	2	**58**
2.2	0	**67**	23	6	2	0	2	0	**67**
2.5	0	**80**	15	3	1	0	1	0	**80**
3	0	**92**	8	0	0	0	0	0	**92**
5	0	**91**	8	1	0	0	0	0	**91**
7	0	**96**	2	1	1	0	0	0	**96**

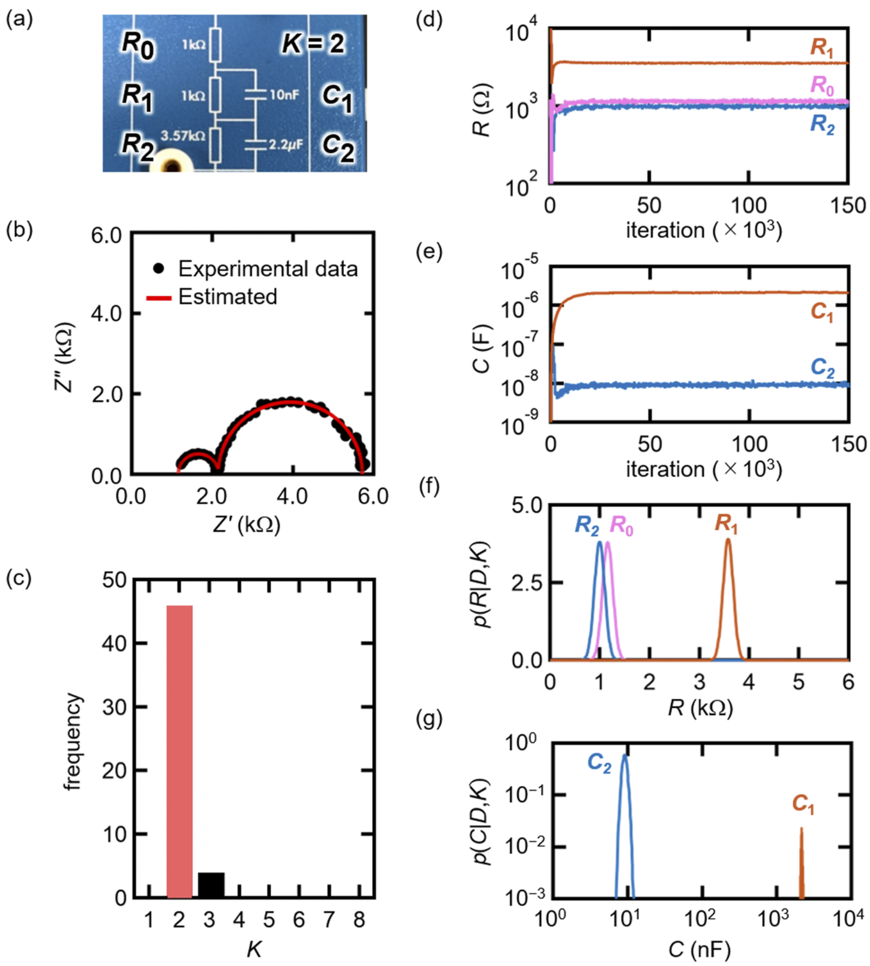

FIG. 3. (a) A schematic of the electrical circuit. (b) Experimental impedance spectra obtained from the circuit shown in (a) are indicated by black dots. The red solid line shows the predicted spectra using Bayesian statistics. The estimated circuit parameters are summarized in Table III. (c) Model selection accuracy. The horizontal axis indicates the number of RC parallel circuits K, whereas the vertical axis indicates the frequency at which the corresponding equivalent circuit model is selected. The red histogram shows the frequency at which the true equivalent circuit model is selected. [(d)–(g)] Trace plots and posterior distributions of the circuit parameters for $K = 2$ calculated using the MCMC with parallel tempering.

distributions for $K = 2$ is observable in all the trace plots [Figs. 3(d) and 3(e)]. The maxima of the calculated posterior distributions are almost identical to the actual values, as shown in Figs. 3(f) and 3(g). The estimated parameters for $K = 2$ are summarized in Table III. The estimated Nyquist plot [red solid line in Fig. 3(b)] is in good agreement with the experimental data [black dots in Fig. 3(b)]. These results indicate that the estimation of σ is also accurate and confirm that our Bayesian statistics approach can be applied to experimental AC impedance spectra.

Comparison with conventional AC impedance spectra analysis

We compare the proposed method with conventional AC impedance spectra analysis. In the latter, the equivalent circuit model and initial parameters are determined *visually* from Nyquist plots. Subsequently, the circuit parameters are determined using the nonlinear least squares method, which has several problems in this context. First, since the number of RC circuits must be

TABLE III. True parameters of the circuit shown in Fig. 3(a) and estimated parameters for $K = 2$. The estimated parameters were decided by the maximum *a posteriori* probability estimation (see the supplementary material).

	R_0 (kΩ)	R_1 (kΩ)	C_1 (nF)	R_2 (kΩ)	C_2 (nF)
True parameters	1.00	1.00	10.0	3.57	2.20
Estimated parameters for $K = 2$	1.15	1.00	10.0	3.58	2.15

determined visually beforehand, the validity of the circuit model is highly ambiguous in the conventional analysis using the nonlinear least squares method. Next, the fitting result obtained using the nonlinear least squares method often depends on the initial values of the parameters used in the search. Therefore, there is no guarantee that nonlinear least squares will converge to the parameters which globally minimize the errors.[16] These problems are undesirable for accurate analysis of AC impedance spectra.

Apart from the nonlinear least squares method, the distribution of relaxation times (DRT) method is often employed to analyze AC impedance spectra analysis.[17–20] In the DRT method, a continuous distribution of the relaxation times corresponding to infinite RC parallel circuits are calculated from the AC impedance data. As each RC circuit shows a characteristic relaxation time, the determination of the relaxation time distribution assists in model selection and circuit parameter determination. However, the DRT method requires a proper regularization parameter to obtain the relaxation time distribution. Furthermore, the analyst eventually needs to determine the equivalent circuit model and initial parameters based on the relaxation time distribution. Thus, although the DRT method provides a guideline for AC impedance analysis, the analyst is vital for determining the equivalent circuit model and initial parameters.

In contrast to existing methods, the proposed approach based on Bayesian statistics automatically provides the most probable equivalent circuit model. Subsequently, the circuit parameters are estimated from the posterior distributions without requiring an analyst. These features are favorable for analysis of AC impedance spectra.

CONCLUSIONS

In this study, we proposed a Bayesian statistics method for the quantitative analysis of AC impedance spectra. The proposed method was applied to artificial AC impedance data generated from RC parallel circuits, achieving a high accuracy rate (>90%) in determining the number of circuits and associated parameters. Although the model selection accuracy was affected by the proximity of the circuit time constants, the accuracy rate still exceeded 90% when the time constant ratio was greater than three. Moreover, the method was effective when applied to an actual electrical circuit. The proposed Bayesian method is therefore a highly promising method for the analysis of AC impedance measurements and can be expected to lead to unambiguous and automated analysis of electrochemical data in the future.

SUPPLEMENTARY MATERIAL

See the supplementary material for the experimental details of AC impedance spectra analysis.

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