An analysis of drifts and nonlinearities in electrochemical impedance spectra

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ABSTRACT

The response of an electrochemical reacting system to potential perturbations during electrochemical impedance spectrum measurement is investigated using numerical simulation. Electrochemical metal dissolution via an adsorbed intermediate species is analyzed and it is shown that applying the potential perturbation causes the average surface coverage to drift. For high frequency perturbations, the final value of the average surface coverage depends mainly on the kinetic parameters and the amplitude of the applied perturbation. Acquiring the data during the first few cycles of perturbations leads to an incorrect calculation of the impedance, particularly for large amplitude perturbations. Repeating the experiments will not identify this drift, while Kramers–Kronig Transform (KKT) can successfully detect this problem. The correct experimental methodology to overcome this effect and obtain the impedance spectra is also described. Another reaction with two adsorbed intermediates is also investigated and it is shown that in certain cases, the violations of linearity criteria can also be detected by KKT. The results illustrate the importance of validating the impedance data with KKT before further analysis.

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1. Introduction

Electrochemical systems are inherently nonlinear, but small amplitude electrochemical impedance spectroscopy (EIS) is frequently used to characterize them with the assumption that the system can be approximated by a linear system [1,2]. In a typical EIS experiment, the frequency of the perturbation is varied, and the system response is recorded [3–6]. Once the measurement at one frequency is completed, an excitation at the next frequency is commenced. Gabrielli et al. analyzed the effect of this change in perturbation frequency [7]. It was shown that the fast swept sinusoidal excitation causes a systematic error. They also showed that the error can be reduced by "keeping the initial phase of the input signal zero or by delaying every measurement for several times the longest system time constant" [7]. The electrochemical system may be examined in quasi potentiostatic or quasi galvanostatic mode. Many electrochemical reactions are reported to occur via one or more adsorbed intermediates [8–11]. In the absence of any passivating film, diffusion limited processes and significant solution resistance, the electrochemical system can be modeled

by a double layer capacitance in parallel with the Faradaic process [12]. The high-frequency impedance is determined mainly by the double layer capacitance and the low-frequency impedance is determined mainly by the Faradaic process, while both double layer and Faradaic process play a role in determining the mid-frequency impedance. The equations of impedance for the Faradaic processes involving the adsorbed intermediates can be obtained analytically if it is assumed that the system response is linear [8,9,13].

One of the assumptions used in the analysis is that the system is stable, "in the sense that it returns to its original state after the perturbation is removed" [14]. There are limited investigations of EIS under nonlinear conditions [13,15–20] or with stability issues [21–25]. Recently we reported the results of the numerical solution of the nonlinear impedance equations for a reaction with an adsorbed intermediate, under stable and unstable conditions [25]. In this work, we extend it to analyze the effect of applying sinusoidal potential perturbation to the system and show that the surface coverage changes with time due to the perturbation itself. The case of reactions with one or two adsorbed intermediates is analyzed. We also evaluate the implications of this drift on different methods of acquiring EIS data. The ability of the Kramers–Kronig Transform (KKT) to identify the drifts as well as violations of linearity is analyzed. While EIS may be acquired under quasi potentiostatic or quasi galvanostatic mode, in this work EIS acquisition in the quasi potentiostatic mode is considered with the electrode at 500 mV anodic with respect to the open circuit potential.

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2. Theory

It is assumed that the kinetic parameters depend exponentially on the voltage and that Langmuir isotherm model is applicable. Consider the dissolution of a metal via an adsorbed intermediate given by the following equation

$$
M \xrightarrow{k_1} M^+_{ads} + e^-
$$
$$
M^+_{ads} \xrightarrow{k_2} M^+_{sol}
\tag{1}
$$

Here, M represents the bare metal site, M^+_{ads} the adsorbed intermediate species and M^+_{sol} the dissolved metal ion. In addition, k_1 and k_2 are the reaction rate constants which depend on the overpotential as $k_i = k_{i0}e^{b_i V}$. Here k_{i0} is the rate constant pre-exponent and V is the overpotential. The exponent b_i is given by the formula $b_i = \alpha_i F/RT$ where α_i is the transfer coefficient with a value between 0 and 1, F is the Faraday constant, R is the universal gas constant and T is the temperature. The current corresponding to this reaction is given by

$$
i = Fk_1(1 - \theta_{M^+})
\tag{2}
$$

where θ_{M^+} is the surface coverage of M^+_{ads} and the surface coverage of bare metal sites can be denoted by $\theta_M = 1 - \theta_{M^+}$. The mass balance equation is given by

$$
\tau \frac{d\theta_{M^+}}{dt} = k_1(1 - \theta_{M^+}) - k_2\theta_{M^+}
\tag{3}
$$

where τ corresponds to the total number of sites at monolayer coverage and t is the time. In the absence of any perturbation, the steady state surface coverage is given by

$$
\theta_{M^+}^{SS} = \frac{k_{1DC}}{k_{1DC} + k_{2DC}} = \frac{1/k_{2DC}}{\sum_{i=1}^{2}(1/k_{iDC})}
\tag{4}
$$

Here k_{iDC} refers to the rate constant at the overpotential V_{dc}, given by $k_{iDC} = k_{i0}e^{b_i V_{dc}}$. During impedance measurement, an ac potential of angular frequency ω and amplitude V_{ac0} is superimposed on the dc overpotential V_{dc} and the total potential applied is given by $V = V_{dc} + V_{ac0}\sin(\omega t)$. The frequency f is related to ω by the equation $\omega = 2\pi f$. It is assumed that before the beginning of the EIS measurement, the system is in steady state.

The surface coverage θ at any time is obtained by solving Eq. (3) numerically with the initial condition given by Eq. (4). For the second example, the following reaction with two adsorbed intermediate species is considered.

$$
M \xrightarrow{k_1} M^+_{ads} + e^-
$$
$$
M^+_{ads} \xrightarrow{k_2} M^{2+}_{ads} + e^-
$$
$$
M^{2+}_{ads} \xrightarrow{k_3} M^{2+}_{sol}
\tag{5}
$$

where the rate constants k_i's are defined as before. Here, M^{2+}_{ads} denotes the adsorbed intermediate species with two charges, distinct from the bare metal site M and the adsorbed intermediate with a single charge M^+_{ads}. The corresponding mass balance equations are

$$
\tau \frac{d\theta_{M^+}}{dt} = k_1(1 - \theta_{M^+} - \theta_{M^{2+}}) - k_2\theta_{M^+}
$$
$$
\tau \frac{d\theta_{M^{2+}}}{dt} = k_2\theta_{M^+} - k_3\theta_{M^{2+}}
\tag{6}
$$

where the surface coverage of the two species M^+_{ads} and M^{2+}_{ads} are θ_{M^+} and $\theta_{M^{2+}}$ respectively. The surface coverage of the bare metal sites can be denoted by $\theta_M = 1 - \theta_{M^+} - \theta_{M^{2+}}$

The steady state surface coverage values of these two species are given by

$$
\theta_{M^+}^{SS} = \frac{1/k_{2DC}}{\sum_{i=1}^{3} 1/k_{iDC}}
$$
$$
\theta_{M^{2+}}^{SS} = \frac{1/k_{3DC}}{\sum_{i=1}^{3} 1/k_{iDC}}
\tag{7}
$$

while the current is given by

$$
i = F(k_1(1 - \theta_{M^+} - \theta_{M^{2+}}) + k_2\theta_{M^+})
\tag{8}
$$

The current component at the fundamental and other harmonics can be extracted by applying fast Fourier transform [25]. The methodology can be employed for analyzing other reactions such as reversible reactions and for other adsorption isotherms such as Frumkin isotherm model. The source code, written in Matlab® programming language, can be obtained by contacting the corresponding author.

3. Results and discussion

3.1. Reaction with one adsorbed intermediate

3.1.1. Surface coverage drift

Fig. 1 shows the average surface coverage ($\theta_{M^+}^{av}$) and transient surface coverage (θ_{M^+}) as a function of time, for 10 mV perturbation amplitude and four different frequencies. The starting point (at $t = 0$) corresponds to the surface coverage at steady state conditions ($\theta_{M^+}^{SS}$) given by Eq. (4). The $\theta_{M^+}^{av}$ is calculated by averaging the transient surface coverage over one complete cycle and the average is assigned to the time corresponding to the middle of the cycle. The transient surface coverage values for the frequencies 10 Hz and 100 Hz are shown in the inset. For 100 mHz and 1 Hz perturbations, θ_{M^+} and the $\theta_{M^+}^{av}$ values are presented in the same plot. The relevant kinetic parameters are given in the figure caption. For 1 Hz or higher frequencies, $\theta_{M^+}^{av}$ clearly moves away from the initial value of approximately 0.5975 and settles at a final value of approximately 0.5986. The final $\theta_{M^+}^{av}$ is the same for all the frequencies, as long as the frequency is above 1 Hz. At 100 mHz, the final value of $\theta_{M^+}^{av}$ is approximately 0.5983, which is slightly lower compared to that observed for high frequencies. The duration needed for $\theta_{M^+}^{av}$ to settle about the final value does not depend on the frequency employed. Simulations with different starting values for the surface coverage show that the final $\theta_{M^+}^{av}$ value is always the same for a given set of parameter values (results not shown). Fig. 1 also shows that a wait time of 20 s is sufficient for $\theta_{M^+}^{av}$ to stabilize around its final value for this system. Fig. 2 shows the final $\theta_{M^+}^{av}$ values for $V_{ac0} = 10$ mV and 100 mV for various frequencies. It is clear that as long as the frequency is 1 Hz or more, the final value is independent of the frequency. It is also strongly dependent on the V_{ac0} employed.

We have not been able to get the exact analytical solution to Eq. (3) when the ac potential is superimposed on the dc potentials. However, the solution in limiting cases can be calculated. Using the Fourier series expansion of $e^{\alpha \sin(\omega t)}$ [26]

$$
e^{\alpha \sin(\omega t)} = I_0(\alpha) + 2\sum_{m=0}^{\infty}(-1)^m I_{2m+1}(\alpha)\sin\{(2m+1)\omega t\}
$$
$$
+ 2\sum_{m=1}^{\infty}(-1)^m I_{2m}(\alpha)\cos\{2m\omega t\}
\tag{9}
$$