Design Requirement for 2nd Generation Fourier Transform Electrochemical Impedance Spectroscopy (FT-EIS): Rise time and Applied Potential

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The effect of the rise time on a second generation Fourier transform Electrochemical Impedance Spectroscopy (2G FT-EIS) system was investigated using a COMSOL simulation and a numerical analysis. Chronoamperometry with either a non-ideal or an ideal step function was simulated by manipulating the rise time (transition zone in COMSOL). First, EIS data were obtained from (1) the differentiation of both step function and the current response, after which (2) the subsequent fast Fourier transform (FFT) of the derivatives in reversible electrode system. A longer rise time (ms order) caused more noise in the high frequency region compared to a shorter rise time (μs order). Second, the noise in a slower charge transfer system was analyzed with different rise times. The noise level, however, is tolerable over the practical frequency range with a long rise time. Third, 2G FT-EIS behavior upon an unconventionally large potential amplitude on a quasi-reversible system was simulated. With an overpotential increase, the 2G FT-EIS system deviated from linear approximation due to a change in the charge transfer resistance, indicating that the decision to allow the maximum stimulating potential should depend on electrode kinetics. These simulation results here suggest the proper design requirements for the 2G FT-EIS instrument.

1. INTRODUCTION

Currently we are in an era of electrochemistry, with many researchers studying electrochemistry in order to develop technologies such as secondary batteries, fuel cells, electrolyzers, supercapacitors and solar fuels [1]. Researchers have been characterizing electrochemical systems by classical voltammetric techniques such as cyclic voltammetry (CV) and linear sweep voltammetry (LSV) [2]. Quantitative and precise estimations of voltammetry, however, are not straightforward, and researchers

trained in other disciplines may reach misleading conclusions unintentionally. Electrochemical impedance spectroscopy (EIS) is an alternative quantitative method for an electrochemical system. Although it also requires equivalent circuits corresponding to experimental data to extract physical meaning, well-developed software helps with proper interpretations of experimental data. Recently, our group introduced a simple method by which to acquire 2nd generation Fourier transform Electrochemical Impedance Spectroscopy (2G FT-EIS) from chronoamperometry using a commercial potentiostat without complex modifications of hardware or software [3]. In order to acquire high-quality EIS data from simple chronoamperometry, (1) a high sampling rate of the signals (up to tens of kHz) and (2) a fast rise time so that the potential step is close to the ideal step (Heaviside) function are mandatory. The former requirement is easily satisfied even with an old potentiostat. The latter, however, is questionable due to the unclear specifications for EIS. A quantitative analysis of the rise time for EIS has not yet been reported to the best of the authors' knowledge, although the effects of the former requirement on the frequency range of EIS are available in the literature [4].

The aim of this paper is to reveal the influence of the rise time and of the amount of applied potential in order to establish the design requirements for 2G FT-EIS. A theoretical simulation of chronoamperometry with various rise times deviating from the ideal step function was conducted while assuming an ideal electrode reaction kinetics and one-dimensional diffusion of the macroelectrode. Our approach using a simulation provides the precise control of the rise time in the step function, for which it is difficult to adjust the parameters in experimental electrochemistry. The amounts of applied potential with various standard rate constants (k_0) for the electrode reaction were also investigated.

2. EXPERIMENTAL

Electrochemistry Module in COMSOL Multiphysics 5.4 was employed to simulate the electrochemical response upon the potential step. The Butler-Volmer model was selected for solvation of simple 1D diffusion system as a charge transfer reaction. The standard reduction potential for two species of Oxidation and Reduction was postulated to be 0 V. One-electron transfer between Ox/Red redox couples with different k_0 were investigated. The transition zone parameter was adjusted for controlling rise time. The diffusion coefficient of Ox and Red were set as $D_{Ox}=D_{Red}=D=1\times10^{-9}$ m^2/s at T=293.15 K. Double layer capacitance was set as 0.2 F/m^2. Initial concentration of Ox and Red were set at 1 mM. The variable relative tolerance in solver was set manually to control conversion accuracy. The data from COMSOL simulation were analyzed by MATLAB.

3. RESULTS AND DISCUSSION

As a reminder, a brief summary of 2G FT-EIS is shown in Scheme 1. A small potential step of 10 mV is applied to the electrochemical cell indicated by the black arrow in Scheme 1. This step function involves the integration of the Dirac δ function, which is composed of the superposition of harmonic

waves at all frequencies with identical phases. Electrochemical systems do not respond linearly to such an infinite quantity of the δ function; hence, this integration form of the step function acts as a stimulus. The current as a response is measured during this potential step, referred to as conventional chronoamperometry. Based on the linearity of the system, the first derivative of both the potential and current against time represents the current behavior with the δ function, as shown by the green arrow in Scheme 1. Finally, the impedance at each frequency is estimated simply with Ohm's law [5, 6]. At this stage, two questions arise. First, what is the practical limit of deviation from the ideal step function? Second, is the linearity of an electrochemical system valid with a larger potential step?
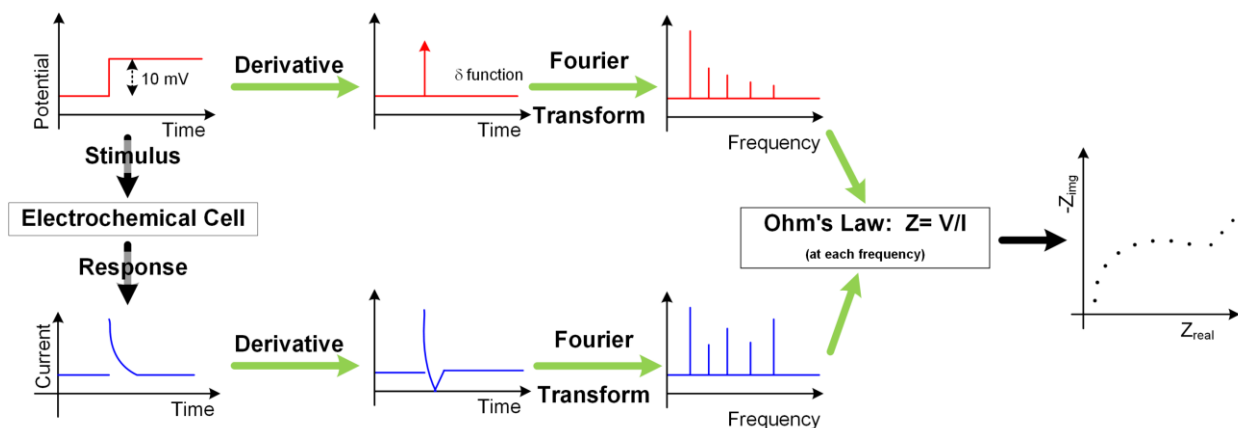
Scheme 1. Illustration of 2G FT-EIS acquisition.

In this report, we investigate the effects of the rise time on a reversible system with a k_0 value of 10^{-4} m/s by controlling the "transition zone" parameter in COMSOL, with chronoamperometry also estimated numerically. A simulation is a good tool to characterize the non-ideal step function with a controlled rise time, compared to an experimental technique using a potentiostat. Figure 1A and 1B show the step functions with different rise times (transition zones) and the current signals from the COMSOL 1D simulation, respectively. There is a clear difference in the rise time depending on the transition zone. The exceptionally large initial current caused by the electrical double layer is obvious with a shorter transition zone approaching the ideal step function. To obtain a Nyquist plot of the electrochemical system, the potential and current signals were differentiated (Figures 1C and 1D, respectively). The derivative of the potential at 10^{-4} in the transition zone is as ideal as the Dirac delta function, while the result at 10^{-2} appears to be an impulse. Similar behaviors were observed with the derivative of the current response. The derivatives of signals with a slow rise time show a small and broad response. Next, fast Fourier transform (FFT) was carried out to convert the time domain into the frequency domain. Subsequently, the FFT of dV/dt was divided by the FFT of dI/dt. As a result, the Nyquist plots shown in Figures 1F and 1E were obtained. A higher noise level in the high-frequency range with a longer rise time can be observed in Figure 1F compared to that with a short rise time in Figure 1E. The amplitude of each frequency contributing to the stimulation potential strongly depends on the rise time. Specifically, potential step with a shorter rise time contains the harmonic wave with a higher frequency. Accordingly, this noise at a high frequency appears to be reasonable. Yoo et al. reported a specially

designed potentiostat with a rise time of 1 V/50 ns [7], while Huang et al. constructed a slower potentiostat of ~ 1V/μs with a tradeoff between the stability and the sampling rate [8]. The latter also showed more noise in the high-frequency region, in good agreement with Figure 1F. Previous reports, however, did not provide any theoretical background with regard to the rise time requirements. Our results depending on the transition zone clearly demonstrate that a conventional potentiostat is sufficient for 2G FT-EIS.
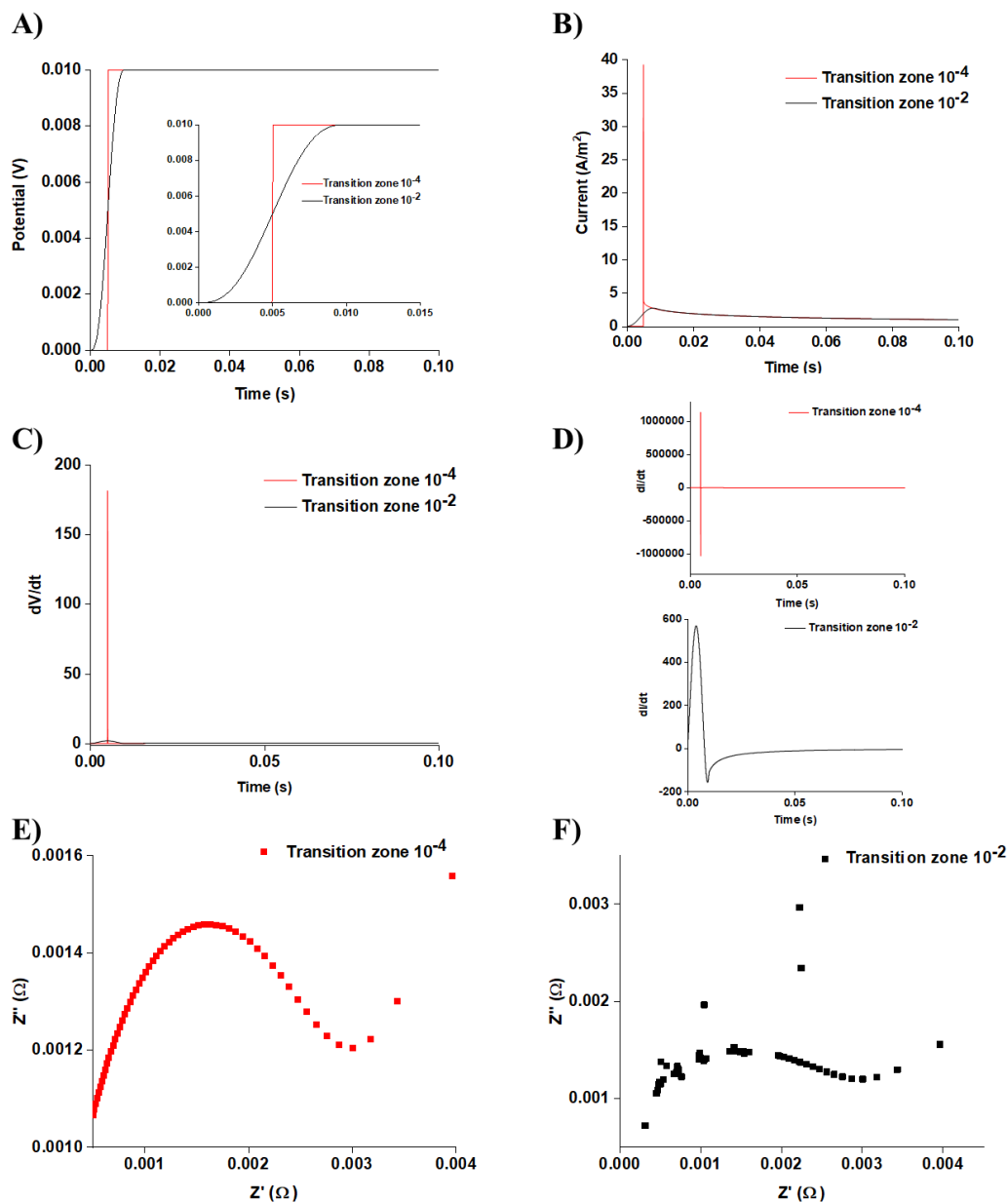
Figure 1. (A) Potential steps with different transition zone. (B) Current responses of the steps. (C) and (D) the first derivative of (A) and (B). (E) and (F) Nyquist plots from for 2nd Generation FT-EIS. (parameters: k_0: 10^{-4} m/s (reversible system), transition zone: 10^{-2} and 10^{-4}, step function: 10 mV)

The signal-to-noise ratio in FT-EIS also depends on the charge transfer kinetics on the electrode because the total impedance of an electrochemical cell is strongly affected by the electrode kinetics. For

a charge transfer ten times slower with a k_0 value of 10^{-5} m/s value, 2G FT-EIS was simulated with different transition zones. Figures 2A and 2B show the Nyquist plots for 10^{-4} and 10^{-2} in the transition zones, respectively. This is similar to the reversible electrode system shown in Figure 1, EIS data with a slow rise time are noisier at a higher frequency.
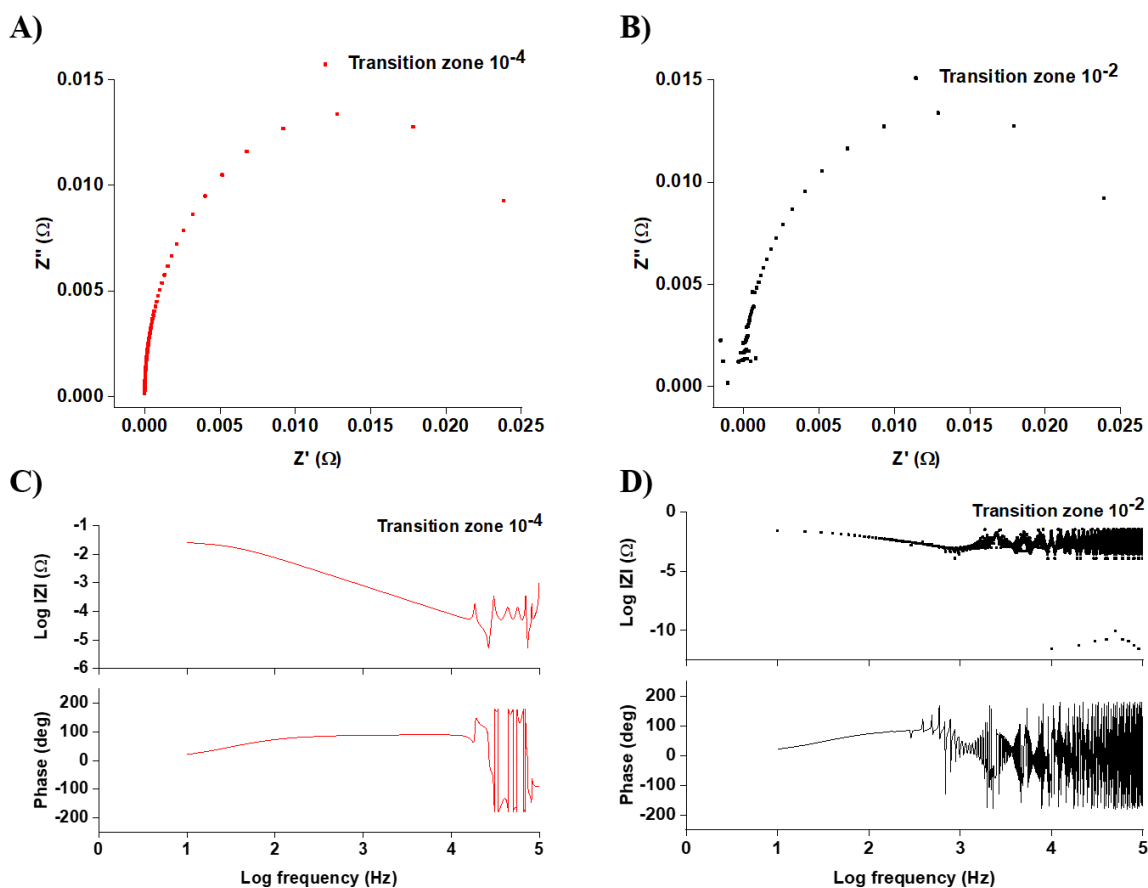

Figure 2. (A), (B) Nyquist plots and (C), (D) Bode plots from for 2nd Generation FT-EIS. (parameters: k_0: 10^{-5} m/s (quasi-reversible system), transition zone: 10^{-2} and 10^{-4}, step function: 10 mV)

Nonetheless, researchers can extract physical meaning from the corresponding equivalent circuit, consisting of the charge transfer resistance (R_{ct}) and a simple capacitor (C_{dl}) in a parallel fashion because the semicircle is obvious in both Figure 2A and Figure 2B. Bode plots are another type of diagrams that can depict the noise level depending on the frequency in each transition zone. Figure 2C presents a Bode plot at 10^{-4} in a transition zone, with the impedance in good agreement with the experimental value within the practical frequency ranging from the mHz scale to tens of kHz. At a slower rising time, Figure 2D shows that noise occurs above ca. 300 Hz and becomes dominant over the signal above ca. 1 kHz. The rise time is defined as the time for a signal to rise from 10% to 90% in terms of the amplitude. The rise time for 10^{-2} in a transition zone corresponds to ca. 9 ms, while that in most commercial potentiostats is less than a few μs. Although a slow rise time of a few ms evokes noise above 1 kHz, most practical ranges for EIS experimentally are less than 1 kHz. Therefore, a modern electrochemical instrument, i.e., potentiostat, can be applied to acquire 2G FT-EIS for case of slower charge transfer kinetics at least. It

should also be noted that these results assume an ideal measurement of the current in the simulation. Practically, a weak current signal from a slower charge transfer may contain relatively more noise in a current-voltage converter [9]. The results also indicate that 2G FT-EIS can be applied to dynamic measurements of relatively slow processes, such as those in a lithium battery [10, 11].

To analyze the origin of the higher noise level at a higher frequency, the power spectrum of the derivative of the potential stimulus is shown in Figure 3. The potential at 10^{-4} in the transition zone possessed the more components over the entire frequency range compared to that with a slower rise time, resulting in the noise-free Nyquist plot shown in Figure 1E and Figure 2A. However, the amplitudes of the potential at 10^{-2} in the transition zone are small and are grouped at a specific frequency, as shown in Figure 3. Considering the frequency range for a Bode plot of Figure 2D, noise level is more severe above 500 Hz. The first band in Figure 3(B) shows the small component above that frequency which may be the origin of the noise in EIS while the amplitude of the first band in the low-frequency region is tolerable. The poor rise time up to a few ms, however, is sufficient to perform 2G FT-EIS owing to the highest frequency range of a few kHz and slower charge transfer kinetics in a typical EIS experiment. In contrast to previous reports that utilized a fast potentiostat [6], our results demonstrate that the rise time itself is not the dominant noise source in 2G FT-EIS. Other parameters such as the sampling rate of the signals and quantization noise during digital sampling may be more critical issues when the designing an electrochemical instrument for 2G FT-EIS [12].
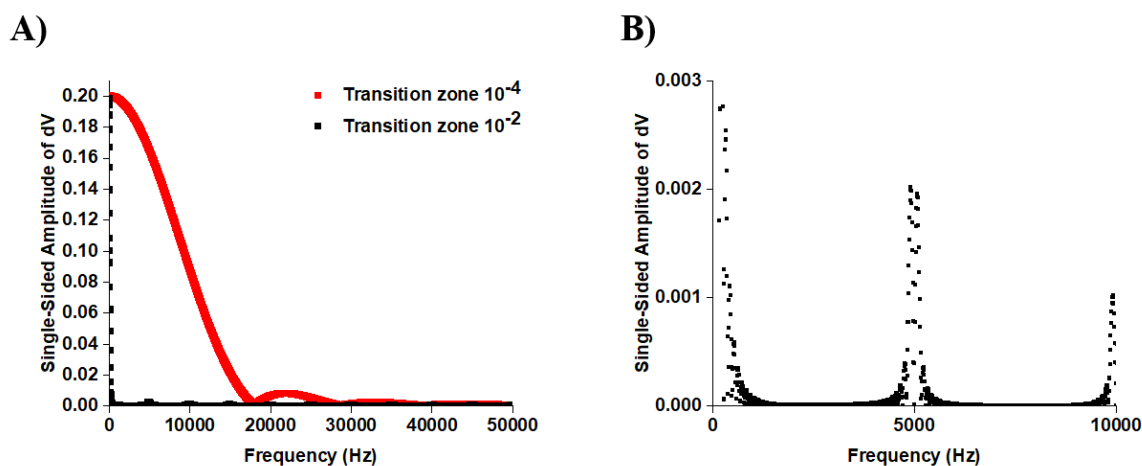
Figure 3. (A) Power spectrum of derivative of potential. (B) Zoom image of (A). The condition is same with Figure. 1.

To circumvent the noise, an increase in the amplitude of the potential may enhance the signal-to-noise ratio of the potentiostat by creating a larger current signal in chronoamperometry at least experimentally. The typical amplitude of EIS is either 5 mV or 10 mV in order to guarantee a linear response from the Butler-Volmer model. Thus, one should choose the largest amplitude where linear approximation is valid and the current signal is increased. We attempted to several amplitudes starting from the conventional figure of 10 mV, as shown in Figure 4, with a quasi-reversible electrode system at 10^{-3} in the transition zone to mimic a very poor potentiostat with a rise time of ca. 1 ms. A Bode plot from 20 mV is consistent with that from 10 mV. However, 50 mV of applied potential distorts the

semicircle by making it smaller, indicating a deviation from the linear assumption. This deviation is obvious in a plot with 100 mV, where the charge transfer resistance clearly decreases due to the large overpotential. These results show that 20 mV is the maximum potential for EIS experiments with a quasi-reversible system. The maximum potential depends on the electrode kinetics. Carbonnier et al. reported less noise in the high-frequency region at larger amplitudes, though the authors provided a caution regarding the maximum amplitude under the assumption of linear behavior without specific values [13]. Our investigation reveals that the slower the electrode kinetics is, the larger the maximum potential can be allowed. Because the current by the redox reaction during a slow charge transfer is less sensitive to the overpotential, the electrochemical response upon a larger amplitude level as a type of excitation may still show linear behavior, which can potentially be applied to the characterization of lithium-ion batteries [14]. Details of the relationship between k_0 and the maximum potential may be studied in future.
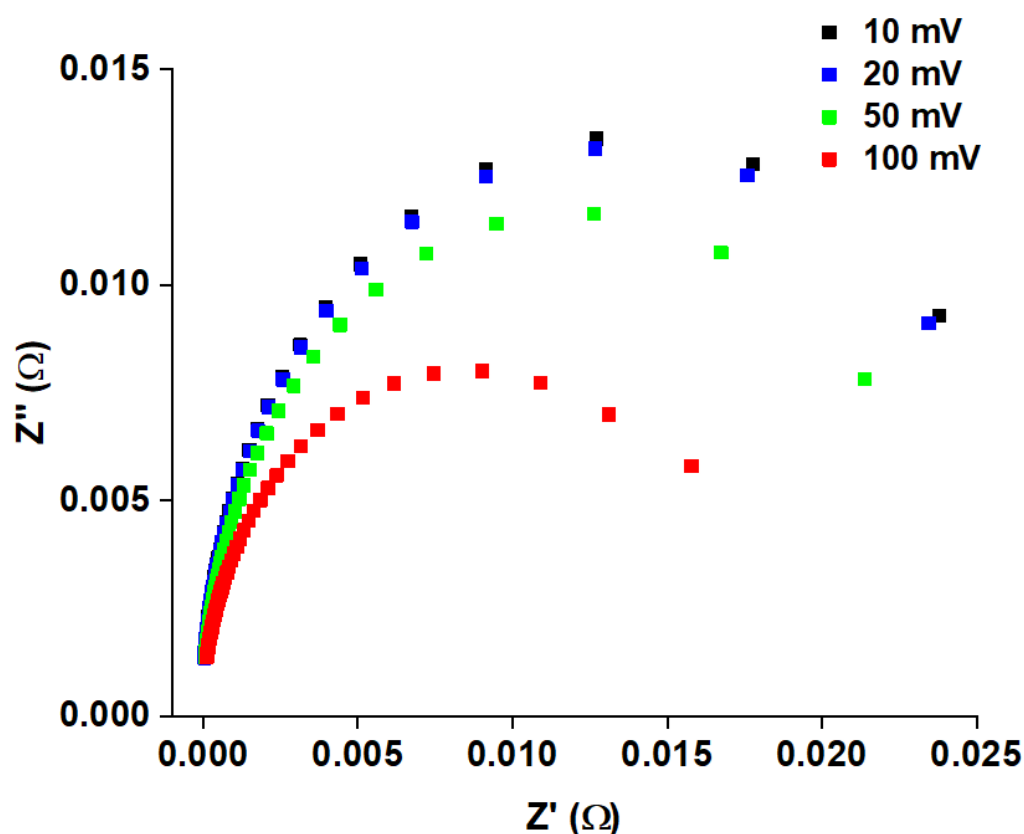
Figure 4. Nyquist plots from for 2nd Generation FT-EIS. (parameters: k_0: 10^{-5} m/s (quasi-reversible system), transition zone: 10^{-3}, step function: 10, 20, 50, 100 mV)

4. CONCLUSIONS

The effect of rise time and stimulating potential on a 2G FT-EIS was investigated using COMSOL simulation. The large rise time (ms order) raised the noise in high frequency region compared with EIS data with the small rise time (μs order). Nonetheless Bode plot even with noise contains sufficient information to extract the physical meaning with equivalent circuit model. The noise from

slow rise time came from the smaller amplitude in high frequency region of applied potential in our simulation, assuming that measuring instrument in potentiostat works perfectly. The large amplitude of potential may circumvent the noise by large current signal in experiment. The large stimulating signal, however, may violate the hypothesis of linear assumption of Butler-Volmer model in EIS. Our simulation shows that Bode plots with less than 20 mV are consistent for the quasi-reversible electrode reaction with 1 ms in rise time. Above 20 mV, the charge transfer resistance is diminished, indicating a deviation from the linear approximation. Our results give the design requirement for 2G FT-EIS instrument; The faster rise time of potentiostat is, the higher signal-to-noise in high frequency region is. Most of modern electronics will be available because even rise time of a few ms provides the conventional Bode plots when the suitable and large applied potential is selected.

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