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Effect of Artifactual Impedance on Impedance Spectrum in High Frequency Range

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Electrochemical impedance spectroscopy technique is able to discriminate several time-constants involved in electrode reactions. The electrochemical impedance was usually measured with the three electrode electrochemical cell. It is well known that the impedance spectrum in the high frequency range was unstable because of the highly resistive RE. Herrmann *et al*.[1] proposed the dual reference electrode to eliminate the problem of the transient behavior of a standard high impedance reference electrode and in addition acts as an adequate filter for power-line frequency noise. It consists in coupling a platinum wire in series with a capacitor of 0.01 μF to the standard reference electrode. Some reports also used the dual reference electrode in order to measure the impedance spectrum without high frequency distortion [2, 3]. However, the details of the measurement of distorted impedance spectrum were not clarified yet. Recently, Trans *et al.* [4] investigated the high frequency EIS measurements in high-conductivity solutions from experiments in 1 M H_2SO_4 solutions and simulations based on the equivalent circuit of the cell and of the electrode potential measurement device. They reported that high frequency artifacts are due to the high impedance of the RE, to the stray capacitance of the cable connected to the voltage amplifier, and to the input capacitance of this amplifier. They clarified the mechanism of the dual RE with a Pt wire in series with a capacitor connected to the RE in addition to the strong influence of the position of the Pt wire relative to the RE and to the WE. Our group [5] reported that the impedance spectrum of air battery cathode (gas diffusion electrode) described the distorted semicircle in the high frequency range due to the saturated KCl/Ag/AgCl electrode with salt bridge. The impedance spectra of gas diffusion electrode for air battery cathode were shown in Fig. 1. The impedance spectra in Fig. 1 showed the capacitive loop in high frequency range, 45 degrees straight line in middle frequency range and a part of large semicircle in low frequency range when Ag wire was used as a reference. On the other hand, the impedance spectrum described a part of large semicircle crossing over imaginary axis. This error of semicircle is related to the highly resistive RE. Thus, the purpose of this study is to investigate the effect of artifactual impedance on impedance spectrum in high frequency range.

The electrical equivalent circuit of the electrochemical cell is shown in Fig. 1. The details of parameters are as follows: the gain of voltage amplifier (G_V), the gain of current amplifier (G_I), the output signal of the voltage amplifier (S_V), the output signal of the current amplifier (S_I), the impedance of the working electrode (Z_w), the impedance of the reference electrode (Z_{RE}), the floating capacitance of the reference electrode (Z_{in}), the potential of the reference electrode (V_{RE}), the input voltage follower connected to the reference electrode (V_{Gv+}). The measured impedance Z_{meas} was expressed as follows.

$$Z_{meas} = \frac{G_I}{G_V}\frac{S_V}{S_I}R_{range} = \frac{Z_{in}}{Z_{RE}+Z_{in}}Z_{WE} \qquad (1)$$

In this study, we proposed the reference electrode to avoid the distorted impedance spectrum in the high frequency range. The various arrangements of electrochemical cell and their equivalent circuits were discussed.

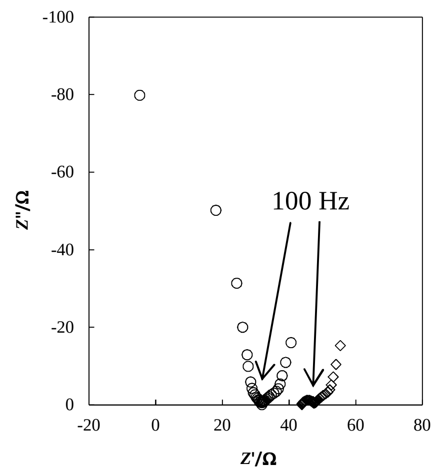

Fig. 1 The impedance spectra of air battery cathode (gas diffusion electrode). The reference electrode is: (◇) Ag wire, (○) saturated KCl/Ag/AgCl electrode with salt bridge.

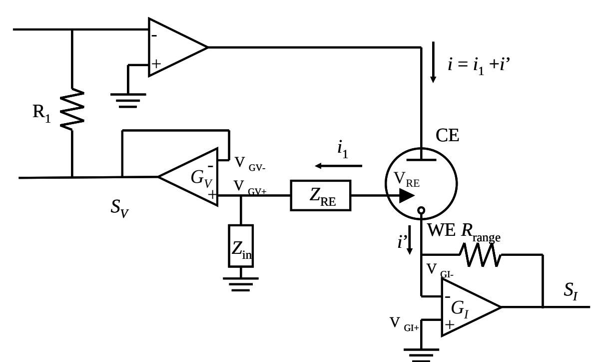

Fig. 2 The electrical equivalent circuit of the electrochemical cell.

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