

Charge Transfer Enhancement by the Second Redox Mediator

Graduate School of Engineering, Osaka Univ.¹, Textile Research Institute Gunma Pre. Gov.²

°Huanwen Han¹, Kazuyuki Nobusawa², Ting-Chieh Chu, Ichiro Yamashita¹

E-mail: huanwen@pmdp.arl.eng.osaka-u.ac.jp

Introduction.

Electrochemical Impedance Spectroscopy (EIS) is a method widely used for interface measurement and has high potential in biomolecules detection. The impedances can monitor the charge-transfer between electrode and electro-chemical redox probes. Magnifying of the charge transfer process will lead to high measurement performance. [1] The selection of the redox probe depends on various parameters. $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, p-benzoquinone/hydroquinone are widely used to monitor the charge transfer. [2, 3] 1 - 10 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ is the most frequently used as a redox probe pair. Recently, we have discovered that the addition of a small amount of second redox probe to the popular ferricyanide/ferrocyanide results in a significant improvement in charge-transfer.

Experimental.

We employed 1 mM ferricyanide and 1 mM ferrocyanide redox pair in our EIS system. Commercial glassy carbon electrodes, commercial gold electrode and carbon screen printed electrodes (SPE) were used. The glassy carbon electrodes were polished with Al_2O_3 and sonicated in ethanol and pure water 5 minutes before use. EIS measurements were carried out in a 10mM Tris pH 8.0, 50 mM KCl, 1.5 mM MgCl_2 , and 1mM $\text{K}_3[\text{Fe}(\text{CN})_6] / \text{K}_4[\text{Fe}(\text{CN})_6]$, with frequency scan of 10k Hz to 0.1 Hz, applied voltage 10 mVac and open potential Vdc. After EIS measurement, the cyclic voltammetry was measured from 1 V to -1 V with scan rate 100 mV/s. Sequentially, the second redox probe $1\mu\text{M Ru}(\text{bpy})_2\text{DPPZ}^{2+}$ were added and the previous measuring process was repeated. The same measurements were carried out using other types of electrodes after appropriate washing.

Result and Discussion.

Figure 1. shows the result. Without the second redox probes, the Nyquist plot shows a typical semicircle, the diameter was approximately the charge transfer resistance (Rct). Upon addition of the second probe with 1/1,000 concentration of the first redox probe, the Rct, originally 15k Ohm, decreased significantly down to 1.8 k Ohm. The $\text{Ru}(\text{bpy})_2\text{DPPZ}^{2+}$ ion concentration was too small that $\text{Ru}(\text{bpy})_2\text{DPPZ}^{2+}$ ions are the direct cause of the charge transfer increase. This is supported by the cyclic voltammetry of $\text{Ru}(\text{bpy})_2\text{DPPZ}^{2+}$ that does not have peak near the redox peaks of the ferri/ferrocyanide. This phenomenon has been confirmed in graphite electrodes, SPEs and gold electrodes. This phenomenon looks like occur in a wide range of electrodes. The mechanism elucidation is in progress.

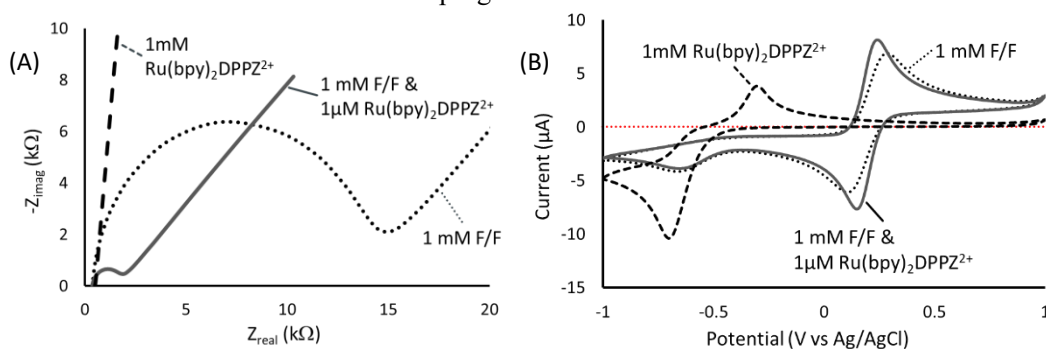


Figure 1. The second redox mediator effected the Rct decreasing. F/F is ferricyanide/ferrocyanide.

Reference

1. Belluzo et. al., **Sensors**: 8(3): 1366-1399, 2008.
2. Chang, B. and Park, S., **Annu. Rev. of Ana. Chem.:** 3(1):207-229, 2010.
3. Sander et. al., **Env. Sci. and Tech.:** 49(10): 5862-5878, 2015.