EIS Charge Transfer Enhancement by the Electrochemical Mediator “Methylene Blue”

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Electrochemical Impedance Spectroscopy (EIS) is a method wildly used for interface measurement. This has great potential for biomolecular detection due to the capacity to operate under high salt conditions. The impedances monitor the charge-transfer between electrode and electrochemical redox probes. Amplifying the charge-transfer process will achieve high measurement performance.[1] The selection of redox probe depends on various parameters, among which 1 - 10 mM $[Fe(CN)_6]^{3-/4}$ is the most frequently chosen in EIS experiments, and we use this redox pair as well. We have discovered that adding a small amount of second redox probe could enhance the charge transfer between electrode and hexacyanoferrate strongly, as $[Ru(bpy)_2DPPZ]^{2+}$.[2] $[Ru(bpy)_2DPPZ]^{2+}$ is a DNA intercalator with 2 positive charges, and wildly used for luminescent signals in chemosensors. Methylene Blue is known as a DNA intercalator with electrochemical activity. Since MB has a different affinity for ssDNA and dsDNA, it has been widely used for DNA hybridization monitor. Besides the MB-guanine interaction. MB could also bind the DNA surface through the electrostatic interaction or intercalative interaction between G-C pair.[3] We change the Ru complex to methylene blue and carry out the EIS measurement and found a similar effect. The EIS were measured with commercial glassy carbon electrode and the electrolyte was PBS with 1 mM $K_3[Fe(CN)_6]$ /$K_4[Fe(CN)_6]$. After stabilization, we added the MB from 0.01 μM, 0.05 μM, 0.1 μM, 0.5 μM, 1 μM, and 2 μM in sequence. Figure 1 shows the result of the Nyquist plot. After increasing the MB concentration to 0.5 μM, very small semicircles are shown on the plot and the Rct is almost no change with concentration increase. This phenomenon looks like occur in a wide range of electrodes and DNA intercalator and need more studies to clear.

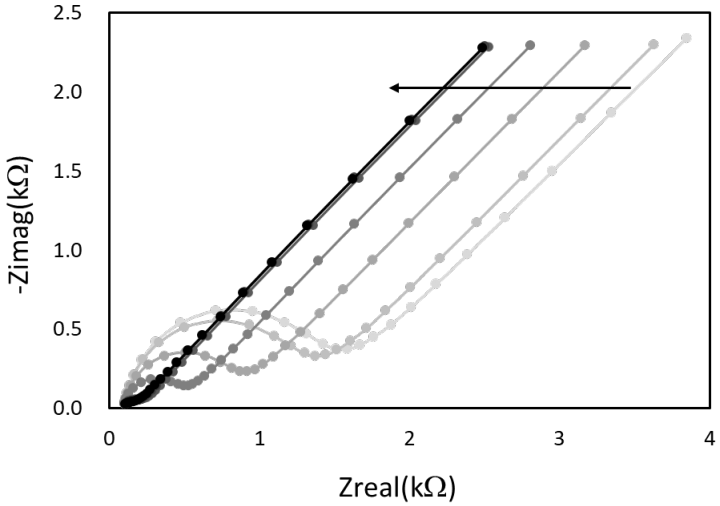

Figure 1. The Nyquist of Methylene blue from 0.01 μM, 0.05 μM, 0.1 μM, 0.5 μM, 1 μM, and 2 μM. With the MB concentration increase, the Rct decrease like Ru complex.

Reference

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3. Rashid, J and Yusof, N, **Sensing & Bio-sensing Res.** 2017, (16):19-31.