Synthesis and Electrochemical Analysis of 1-Butyl-3-methylimidazolium tetrafluoroborate

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Abstract

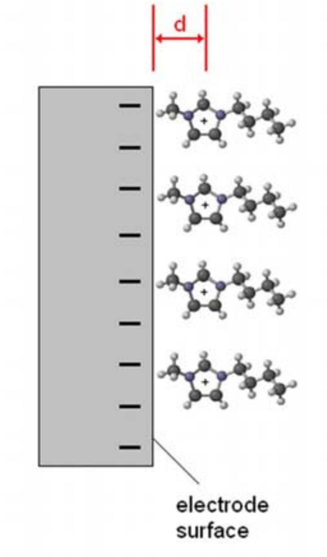
The purpose of this study was to determine the correlation between temperature and the double layer capacitance of the ionic liquid- electrode interface. In this study, 1-Butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF4] was synthesized and purified. Cyclic voltammetry was used to determine the purity and the electrochemical window. Impedance measurements were taken every 200 mV from -1000 mV to 600 mV at 0°C, 20°C, 40°C, and 60°C. This data was then modeled using an equivalent circuit to determine the capacitance of the ionic liquid-electrode interface, modeling as a parallel-plate capacitor. From this capacitance, the thickness of the double-layer, and the PZC were determined.

Electrochemical Analysis of 1-Butyl-3-methylimidazolium tetrafluoroborate

Introduction

1-Butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF_4], is a room-temperature ionic liquid, meaning that it is completely composed of ions yet it is a liquid at room-temperature. Ionic liquids are often referred to as molten salts, yet ionic liquid describes more specifically ionic substances that are liquid at room temperature.[1] Ionic liquids are usually comprised of an organic cation with an inorganic anion. Some fairly common cations are imidazolium, pyridinum, and ammonium; common anions include BF_4^-, PF_6^-, $AuCl_4^-$, $CF_3SO_2^-$, and $(CF_3SO_3)_2N^-$.[1] The general properties of ionic liquids include non-volatility, non-flammibilty, relatively high ion conductivity, wide liquidus range, thermal stability, chemical stability, and a large electrochemical window.[2] These characteristics depend somewhat on the chosen cation and anion. These properties of ionic liquids indicate possible applications as solvents, in lithium batteries, capacitors, solar cells, and fuel cells.[2]

Electrochemistry was the focus of this study. Cyclic voltammetry was used to determine the purity of the sample and the electrochemical window. Cyclic voltammetry measures the current of a sample as various voltages are scanned. The peaks of a voltammogram represent when the sample is either being oxidized or reduced.[3] As mentioned above, ionic liquids have a large electrochemical window, meaning that there is a large range of voltages applied that cause no current flow. During this voltage window the charge is stored in the electrode surface. Any peaks in the electrochemical window indicate contamination, which often is water and/or gases. The slightest contamination can have a large effect on the properties of an ionic liquid.[4] Although it is hard to compare cyclic voltammograms due to the use of different electrodes and quasi-electrodes, they are useful for determining purity in ionic liquids.



Impedance is the total complex resistance encountered when a current flows through a circuit containing resistances, capacitors and/or coils. Impedance is measured by applying AC potential to an electrochemical cell and observing the current flow. [5] The ionic liquid-electrode interface can be modeled after a parallel plate capacitor as illustrated on the left. If the electrode is negatively charged as it is in the diagram, then the $[BMIM]^+$ ion is attracted to the surface and the $[BF_4]^-$ ion is repelled into the bulk of the liquid. When the electrode becomes positively charged, the $[BMIM]^+$ tilts away from the electrode surface allowing the $[BF_4]^-$ to move closer to the electrode surface.[6] This interface can be modeled according to a Helmholtz description.[6,8,9]

Procedure

Synthesis of 1-Butyl-3-methylimidazolium tetrafluoroborate

The synthesis of 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4] for short) occurred in two steps. In the first step, amounts of 1-methylimidazole and 1-chlorobutane were combined in a 1:1.1 ratio to produce 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) (Figure 1). Approximately 40 ml of 1-methylimidazole was combined with approximately 59 ml of 1-chlorobutane in a round bottom flask. A magnetic stirrer was placed in the flask and constantly stirred the reaction. The flask was attached to a condenser, through which nitrogen gas was flowed to remove oxygen gas that may interfere with the reaction. The temperature of the flask was kept around 60°C through the completion of the reaction, which took about 108 hours.

Next, the [BMIM][Cl] was washed with ethyl acetate to remove any excess reactants and any contaminates. The [BMIM][Cl] was mixed with about 20 ml of ethyl acetate in a separatory funnel and shook together. After a few minutes, the mixture separated into two distinct layers. The top layer was ethyl acetate and all of the contaminants. The bottom layer was [BMIM][Cl]. The bottom layer was saved in the original flask and the top layer, which was discarded later, was poured into a clean beaker. This washing procedure was repeated four times.

The next step of the synthesis of [BMIM][BF_4] was the addition of tetrafluoroboric acid (HBF_4). The BF_4^- ion replaces the chloride ion in the [BMIM][Cl] to produce [BMIM] [BF_4] and hydrochloric acid (Figure 2). 65 ml of HBF_4 were added to the [BMIM][Cl] in a round bottom flask. A few ml of water were also added. The flask was covered with Teflon, and stirred overnight.

The [BMIM][BF_4] also needed to be washed to get rid of any contaminants. First, the water, [BMIM][BF_4], and dichloromethane – each in their own container – were cooled in an ice bath for a few hours. These were cooled to minimize the dissolving of the [BMIM][BF_4] in the water. Dichloromethane was added to the [BMIM][BF_4] in the separatory funnel. After adding water, two phases appeared. The top phase was water and the bottom phase was [BMIM][BF_4] mixed with dichloromethane. The sample was washed using water five times. The water from the washing was tested for the presence of chloride with silver nitrate and no precipitate formed, indicating that no chloride was present. The [BMIM][BF_4] was attached to the rotary evaporator (rotovap) and put it in a hot water bath until all of the dichloromethane vaporized.

Nuclear magnetic resonance (NMR) spectroscopy was taken on the sample (Figure 3). The NMR showed that the sample was fairly clean, but there was one peak at 2.26 ppm which indicated some contamination, probably water. The peak at 1.94 ppm is the peak from acetonitrile, which was used as the solvent.

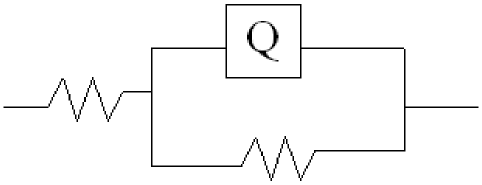
The [BMIM][BF_4] was purified with activated carbon. Ethanol was used to dissolve the [BMIM][BF_4], then three small scoops of activated carbon were added. The mixture was heated and stirred for three hours. After filtering out the carbon and rotovaping out the ethanol, the [BMIM][BF_4] was poured into a glass cell and attached it to the vacuum pump line. It was pumped down to 5.2E-5 Torr. A diagram of the vacuum pump line is shown in Figure 4.

Electrochemistry with [BMIM][BF4]
Cyclic Voltammetry was used to determine the purity of the sample and its electrochemical window. The cell used for cyclic voltammetry is pictured in Figure 5. Two platinum electrodes were used for the counter and working electrodes and a silver wire was used as a quasi-reference electrode. The platinum electrodes were cleaned by soaking in nitric acid and the silver electrode was soaked in ammonium hydroxide for two hours. Next, the electrodes were rinsed with water very well and sonicated. A little bit of [BMIM][BF_4] was transferred from the glass cell into the cell used for electrochemistry, using a Pasteur pipette. Both of the platinum electrodes were flame annealed and cooled in an atmosphere of argon gas. The surface area of the working electrode was about 0.1 cm^2. The screws connecting the electrodes to the cell were tightened and the cell was attached to the vacuum line. Each electrode had a Kalrez O-ring to make the seal vacuum tight. After pumping the [BMIM][BF_4] down to 5.2E-5 Torr, cyclic voltammetry was performed. The cyclic voltammogram is shown in Figure 5. Two sweeps were taken at 100 mV/s with a maximum of 100μA. Voltage limits of –100mV to 100 mV were started with and then increased until oxidation or reduction began to occur. The potential window is about 2.50 V. The cyclic voltammetry was taken using PineChem 2.7.9a. The cyclic voltammogram was plotted using Origin Pro 7.0.

Impedance was measured at temperatures 0 ºC, 20 ºC, 40 ºC, and 60 ºC. The cell was placed in a water bath to reach each temperature. The Impedance measurements were taken from -1000mV to 600mV, every 200 mV. The Nyquist diagram from the impedance results for 60 ºC is shown in Figure 7.

Results and Conclusions

The data from the impedance measurements was analyzed using various circuit models. The circuits tested were RQ, RQR, R(QR), RC, RCR, R(CR), R(Q(RW)), R(C(RW)). The circuit model R(QR), pictured to the left, was the best fit based on χ^2 and the lowest percent error. Using Z SimpWin Demo Version 3.20, the impedance data for each temperature at each voltage was modeled with this circuit. The values for CPE (constant phase element), which is represented by Q in the diagram, were determined by the modeling. A plot of the CPE vs. the applied voltage for each temperature is shown in Figure 8. The CPE was then converted to capacitance using the equation:



$$C = Q_o\,(2\pi\, f_{max})^{n-1}$$

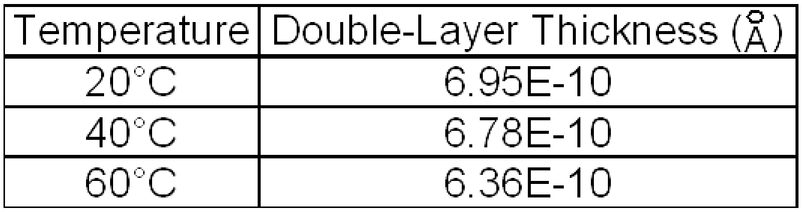
C is capacitance, Q_o is CPE, f_{max} is frequency corresponding to the maximum of an RQ loop, modeled using the initial fitting parameters, and n is the frequency power.

The values for Q_o, f_{max}, and n were determined when the impedance data was fit to the circuit model. A graph of capacitance vs. voltage is shown in Figure 9. The data for 0°C was unable to be converted to capacitance since the fitting showed no f_{max} due to the extremely large size of the resistor in parallel with the CPE.

The calculated capacitance was then converted to the double-layer thickness, based on the Helmholtz model using this equation:

$$d = \frac{\varepsilon\varepsilon_0}{C}$$

d is the double-layer thickness
ε is the dielectric constant; 11.7 for [BMIM][BF4][7]
ε_0 is the permittivity of free space; 8.85419E-12 F/m [8]
C is the capacitance



Temperature	Double-Layer Thickness (Å)
20°C	6.95E-10
40°C	6.78E-10
60°C	6.36E-10

The capacitance of the PZC (potential of zero charge) was used to calculate the double-layer thickness since it is the point at which the double-layer thickness is the minimum.[9] PZC is defined as the potential at which the excess charge density on the metallic and solution sides is zero.[8] The PZC does not vary with temperature. As the data shows, there is very little difference in the double-layer capacitance and thickness at different temperatures, but some general trends were observed. The double-layer capacitance varies directly with temperature and the double-layer thickness varies inversely with temperature. Since the thickness is of the magnitude 10^{-10} m, this indicates that the double-layer is one-ion thick since the dimensions of the ions fall in the range of 3 to 10 Å. This organization of ions on the electrode surface follows the Hemholtz model.[6,8,9]

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Appendix

Figure 1.

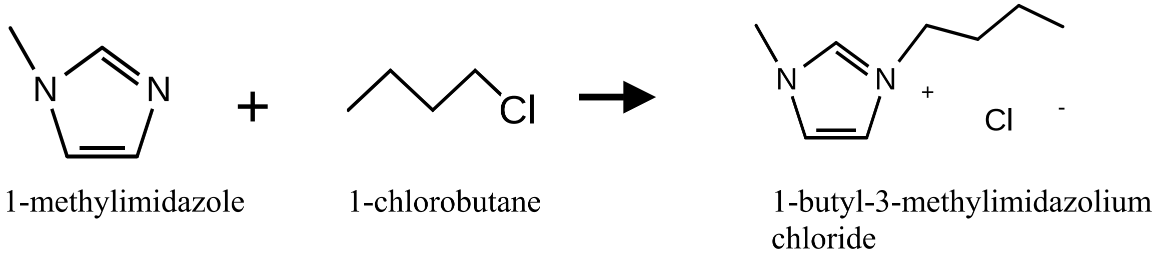


Figure 2.

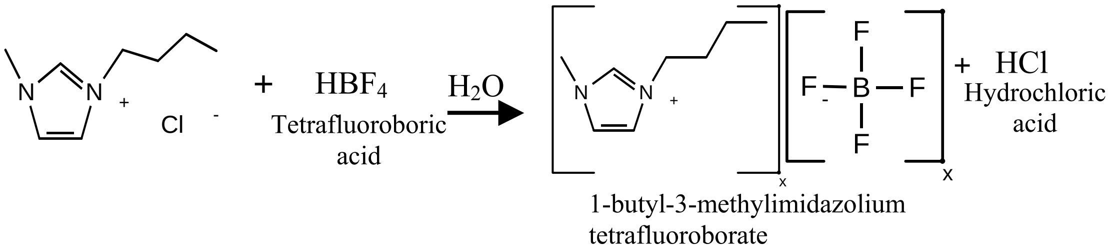
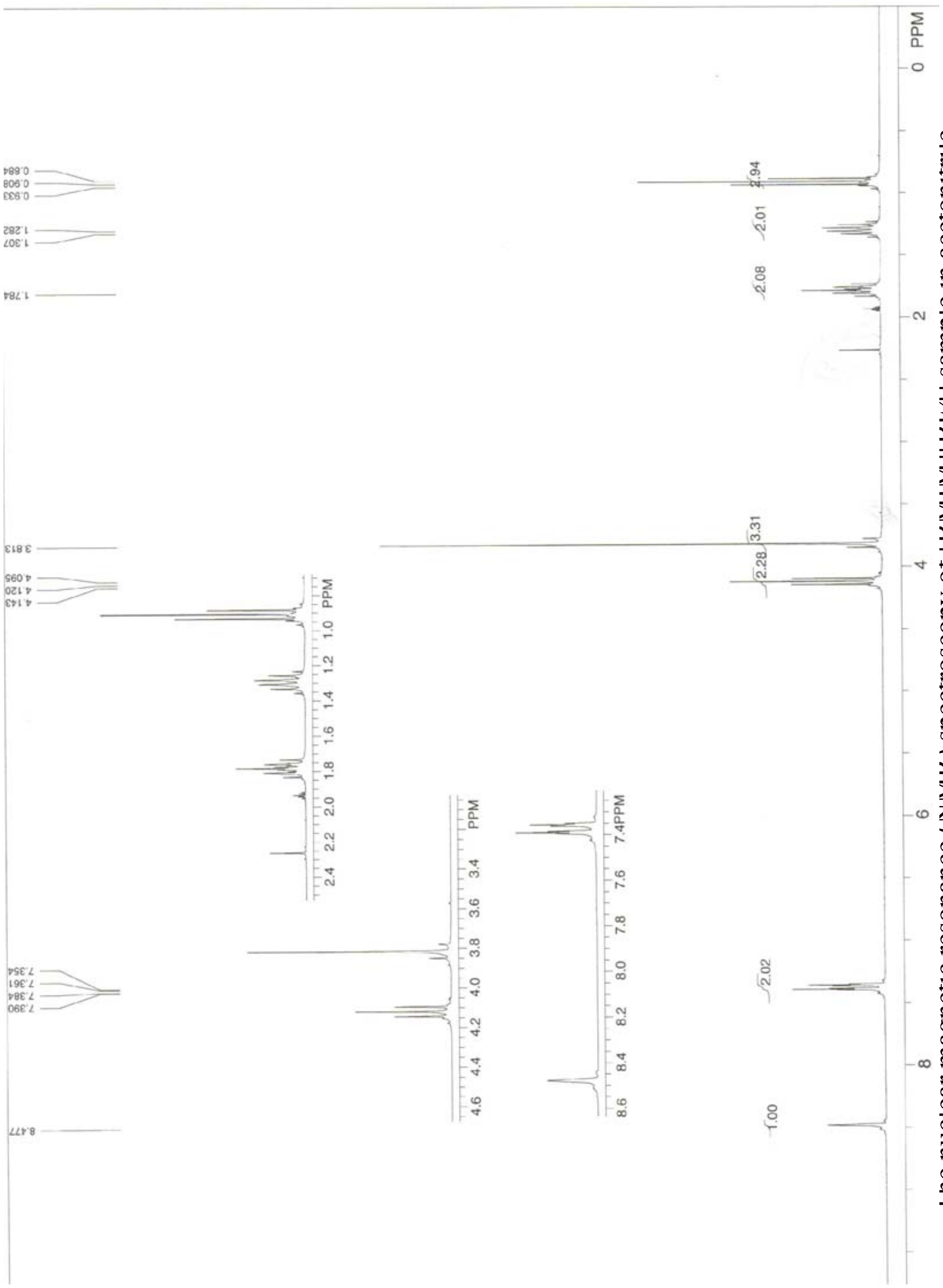


Figure 3.



The nuclear magnetic resonance (NMR) spectroscopy of [BMIM][BF4] sample in acetonitrile.

Figure 4.

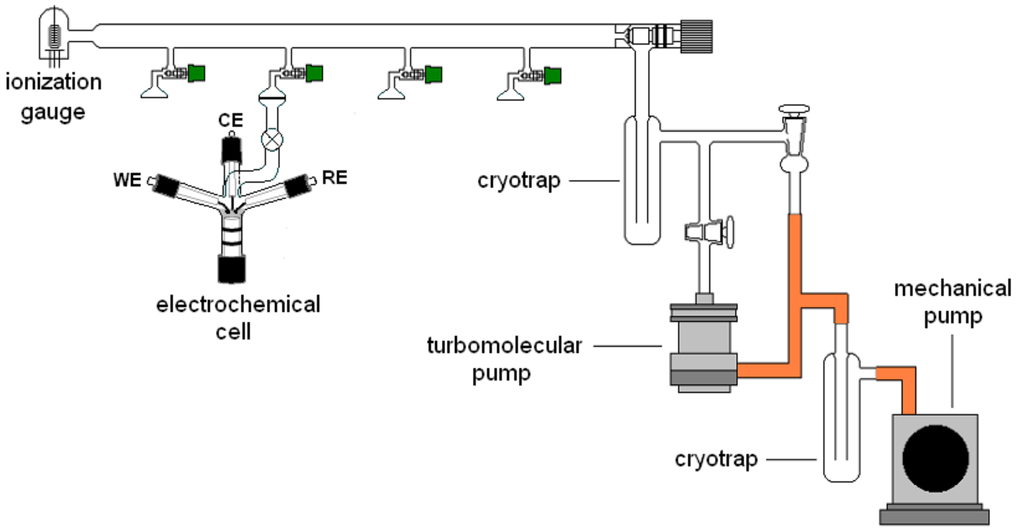


Figure 5.

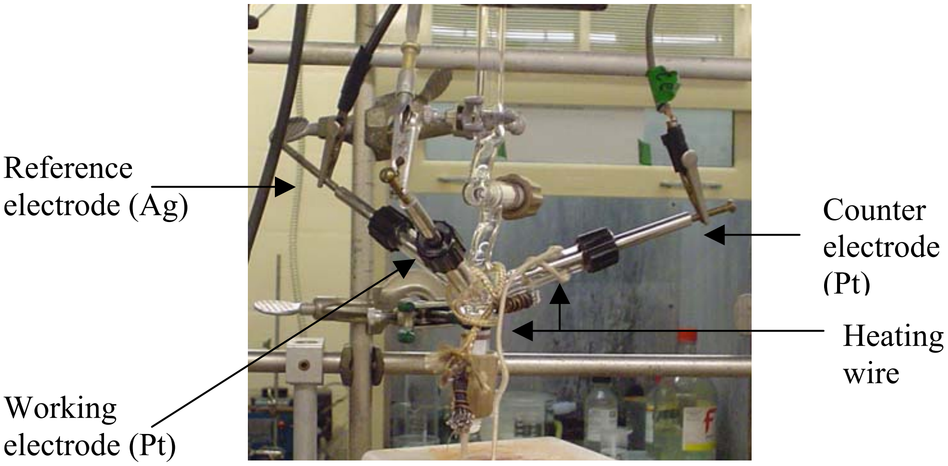


Figure 6.

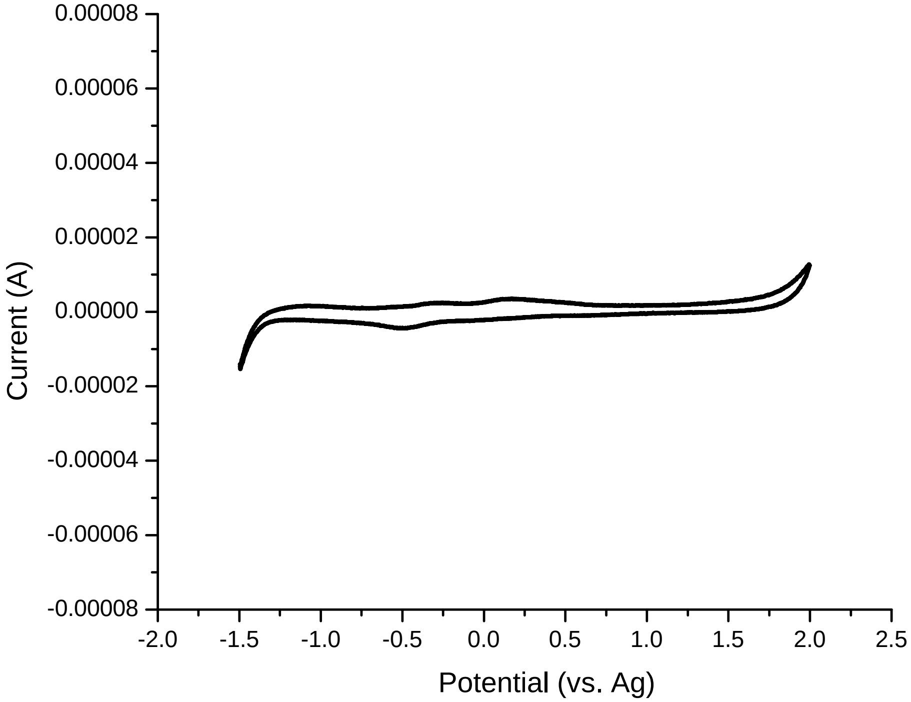


Figure 7.

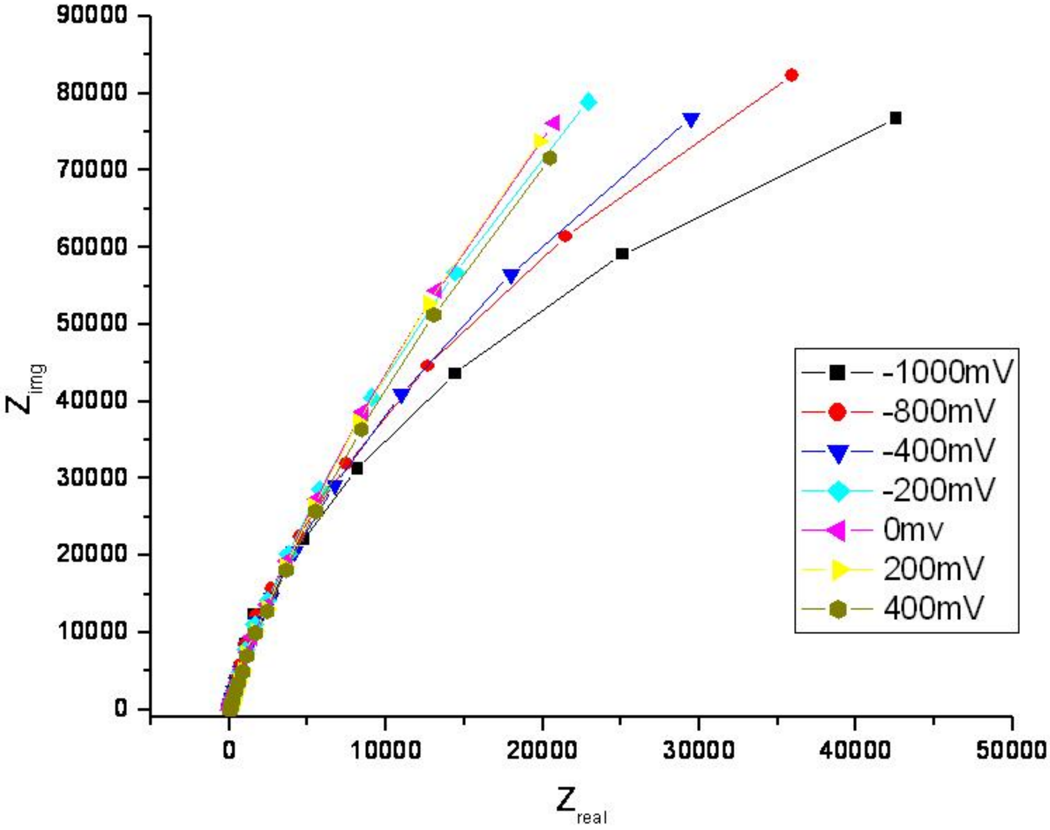


Figure 8.

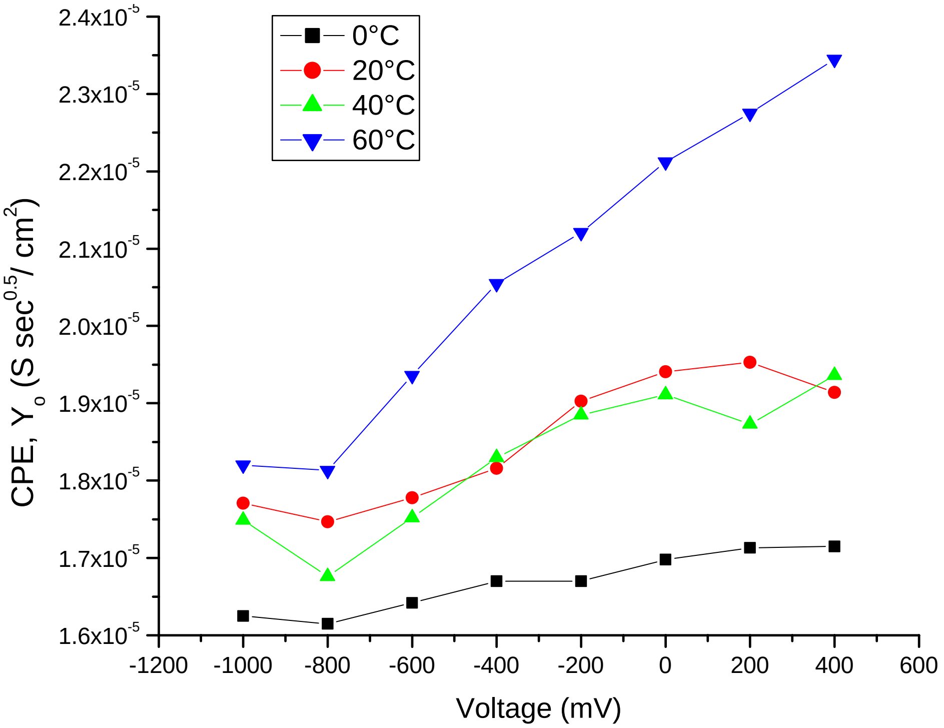


Figure 9.