



Electrochemical Impedance Spectroscopy #4 Measurement of the Conductivity of Polymer Electrolytes

Purpose

There is much interest in using ionically conducting lithium-salt polymers as electrolytes for solid state lithium batteries, as well as for other electronic devices. One important parameter that determines whether a given polymer is suitable as an electrolyte is its conductivity.

Reference

Ionic Conductivity of Polymer Complexes Formed by Poly(ethylene succinate) and Lithium Perchlorate, M. Watanabe, M. Rikukaawa, K. Sanui, N. Ogata, H. Kato, T. Kobayashi and Z. Ohtaki, *Macromolecules* 17 (1984) 2902-2908.

Method

Although other techniques are available for the measurement of solution conductivity, the advantage of electrochemical impedance spectroscopy (EIS) is that the effect of solution resistance can be readily separated from the effects of other impedances present.

Results

EIS measurements of conductivity are typically performed using a two electrode cell. The electrodes are made of an inert material, which essentially inhibits any charge transfer reaction between the electrodes and the lithium ions. The dominant impedance of the cell is that due to the electrolyte between the electrodes. In addition to its bulk resistance, the electrolyte also has an associated geometric capacitance. It can therefore be represented as a parallel combination of the resistance R_b and the capacitance C_g , and hence it gives rise to a semi-circle in the Nyquist plot. The high frequency and low frequency intercepts with the real axis should lie at the origin and R_b , respectively.

The Nyquist plot for a layer of poly(ethylene succinate)/lithium perchlorate between two platinum elec-

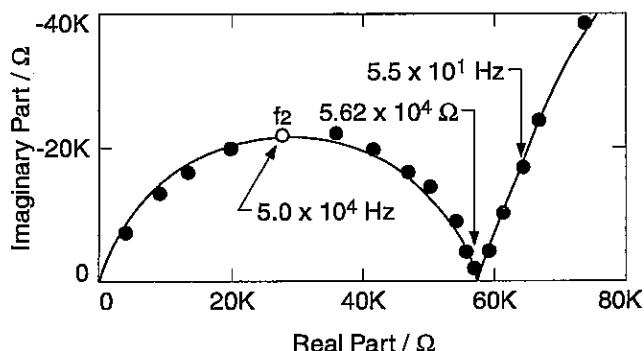


Figure 1. Nyquist plot for poly(ethylene succinate)/lithium perchlorate electrolyte using platinum electrodes. Figure adapted from primary reference.

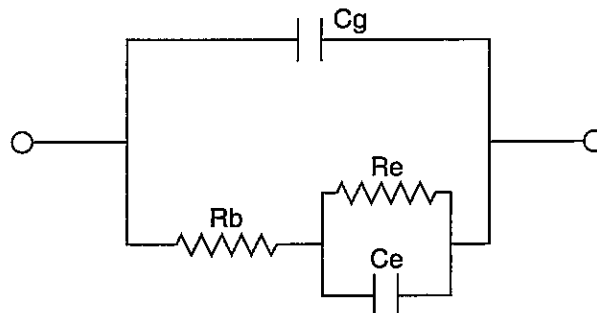


Figure 2. Equivalent circuit for the cell discussed in this Capsule.

trodes is shown in F1. As expected, the dominant feature is the semi-circle due to the C_g/R_b combination. However, there is another arc at low frequencies which can be attributed to the combination of the double-layer capacitance (C_{dl}) and the charge-transfer resistance (R_{ct}) (these are shown in the equivalent circuit in F2). The complete semi-circle is not evident, as the value for R_{ct} is so large (due to the very slow electron transfer kinetics). It is interesting to contrast the Nyquist plot shown in F1 with the Nyquist plot for a cell in which the polymer electrolyte is sandwiched between two lithium electrodes (F3) (i.e., the electron transfer kinetics are now more

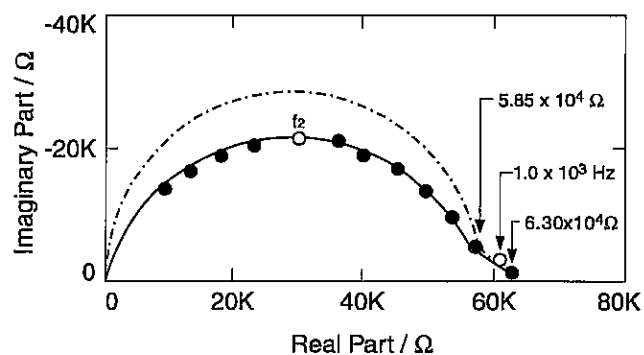


Figure 3. Nyquist plot for poly(ethylene succinate)/lithium perchlorate electrolyte using lithium electrodes. Figure adapted from primary reference.

rapid). In the latter cell, a poorly-resolved semi-circle is evident at low frequencies, which is consistent with the more facile electron transfer kinetics.

It is important to note that, for many cells, the semi-circle associated with the electrolyte may lie at frequencies beyond the experimental limit. For such cells, C_g is generally eliminated from the equivalent circuit; that is, only the resistance of the electrolyte is considered.

