

Transference number determination using Bruce & Vincent method

Transference/transport number is dimensionless parameter which informs about the contribution of the particular charged species present in the electrolyte (ions and electrons!) to the overall charge transport across the cell. In case of a simple binary electrolyte comprising of completely dissociated salt C^+A^- , it can be expressed as follows:

$$t_c = \frac{I_c}{I_c + I_A}$$

t_c – cation transference number

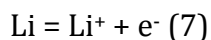
I_c – current carried by cations

I_A – current carried by anions

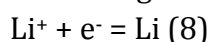
Allowed values of transport numbers are believed to lay exclusively in the range from 0 to 1, however it is discussed whether negative values are possible and physically meaningful. When one applies potentiostatic signal to a cell, several different processes can take place simultaneously:

- Presence of the electric field produces a driving force for charged species to migrate (Coulomb force).
- Disturbance of the equilibria at the electrode / electrolyte interface (double layer) results in its charging and charge transfer across it (if reversible vs. any of the charged species present in the electrolyte).

Let us consider simple symmetrical cell $Li|Li^+X^-, solvent|Li$. The electrodes are reversible only versus lithium. When small potentiostatic signal is applied (for example 20mV vs lithium) across the cell, ions start to move. This effect is caused by the Coulomb force (migration under electric field which is a driving force). On positive electrode lithium oxidation will take place (according to eq. 7):



on the negative reduction of lithium cation (according to eq. 8):



Thanks to these reactions lithium cations can move constantly from one electrode to the other one; in other words provide ion's current passage through the electrolyte. In most cases anions can also move and that is also the case of the system under our study. However Li electrodes are not reversible vs. anions and once they arrive near the electrode they remain there unchanged (i.e. charged, unlike lithium ions that are depolarized and become an uncharged metal phase). In order to keep the environment neutral (uncharged in the macroscopic scale) some of lithium cations have to follow the anions to balance the charge accumulated there.

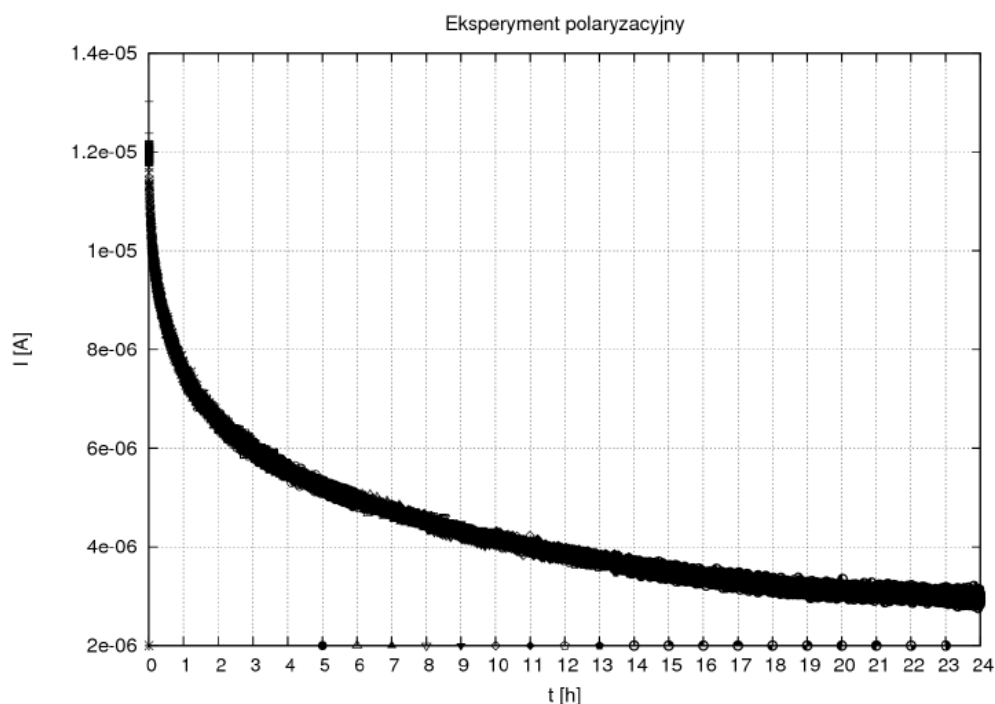
As a result a salt (both Li^+ and X^-) concentration gradient develops athwart the cell. Once the concentration gradient starts to develop, an opposite process starts to take place, i.e. diffusion described by Fick's laws (already mentioned before) that tends to equalize the salt concentration in the electrolyte.

These two processes (migration of ions in external electric field and diffusion resulting from concentration gradients) are antagonistic therefore after sufficiently long time

steady state should be reached, i.e. concentration profile resulting from the superposition of both factors remaining stable in time.

Now let us consider the current evolution is response of the system to the applied constant potential. At $t=0$ both types of ions move and contribute to the current flow. Hence the initial current should be close to that calculated according to Ohm's law with the electrolyte conductance and applied potential as input values. Previous considerations led us to conclusion, that after steady state is reached, only ions that can be depolarized can move and provide the current flow from one electrode to another. In other words the number of active charge carriers is decreased and as a result current value should decrease similarly.

Current decay in DC polarization experiment.



The first approximation is to assume, that the current carried by lithium ions is the same at the beginning of the experiment ($t=0$) and in steady state ($t=\infty$) and furthermore are the only species that carry charge in the steady state. In such case one could calculate the Li transference number from the formula:

$$t_{Li} = \frac{I_{ss}}{I_0}$$

where:

I_0 - initial current

I_{ss} - steady state current

The real system is a little bit more complicated. First of all there are species different from Li that contribute into charge transfer reactions on the electrodes (traces of water, oxygen, solvent molecules and impurities). Furthermore reactions of these species lead in most cases to deposition of passivating products onto the electrode(s) surface and alteration of cell parameters during the experiment, and their constancy is assumed in this simple formula.

In order to make DC polarization experiments more meaningful a correction factor must be introduced into this simple formula. One of the simplest and most commonly used is the so-called Bruce & Vincent method/formula. They proposed to characterize the cell (passivation layer) before and after polarization (after reaching the steady state) by means of Electrochemical Impedance Spectroscopy (EIS) and correct the formula by the factor pertaining to the alteration of cell parameters that can be easily obtained from the simple impedance spectrum.

$$t_{Li} = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})}$$

where:

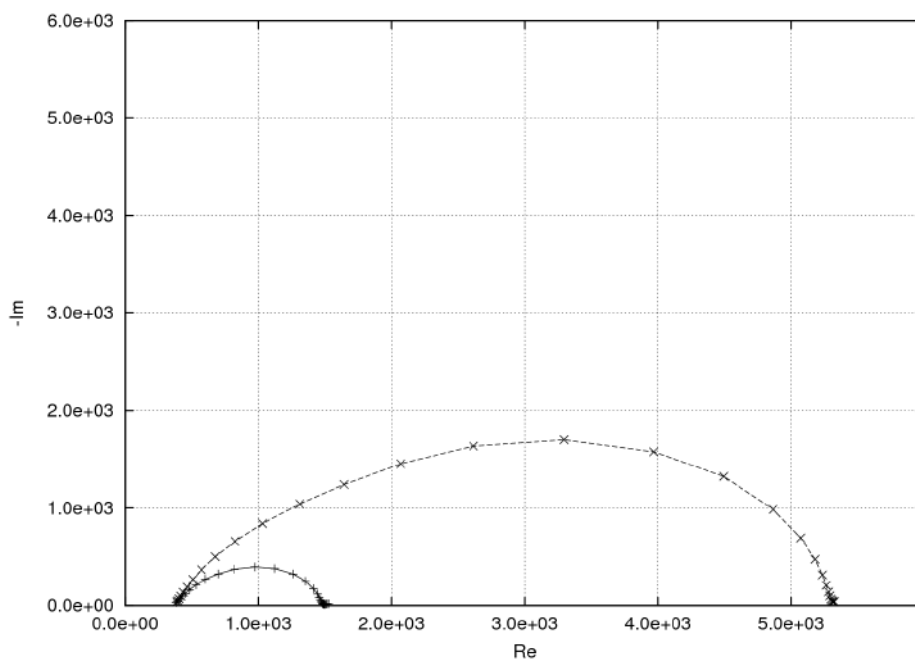
t_{Li} – lithium transference number

V – applied potential

R_0 – initial resistance of the passivation layer

R_{ss} – resistance of the passivation layer (steady state)

An example of cell spectra before and after DC polarization experiment.



Way to determine the Diffusion coefficient:

1. Preparation of all necessary equipment to work in glove box (pumping in sluice)
2. Prepare symmetrical cell Li|electrolyte|Li with lithium metal electrodes in so-called swagelock type configuration. The cell has to be assembled in glove box due to highly reactivity of metallic lithium towards air constituents.
3. Connect prepared cell to the VMP potentiostat.
4. Record EIS spectrum in range of frequencies 100kHz-1Hz

5. Apply potentiostatic polarization to the cell (potential should be in range of 10-20mV vs. lithium). Follow current evolution until a steady state is reached (sometimes it can take even tens of hours!).
6. Once you consider the current stabilized, stop the polarization and record another impedance spectrum (similarly as in point 3).
7. Calculate transference number using Bruce-Vincent formula according to the eq 10

Reference:

1. Fiona M. Gray "Solid Polymer Electrolytes Fundamentals and Technological Applications"
2. Peter G. Bruce, Colin A. Vincent Steady state current flow in solid binary electrolyte cells, *J. Electroanal. Chem.*, 255 (1987) 1-17
3. Peter G. Bruce, James Evans And Colin A. Vincent, Conductivity and transference number measurements on polymer electrolytes, *SSI* 28-30 (1988) 918-922