Salt diffusion coefficient determination

Diffusion is a parameter which informs about transport of molecules from a region of higher concentration to one of lower concentration by random molecular motion. Driving force of diffusion is concentration gradient. This effect was described by Adolf Fick in 1855 his first law relates the diffusive flux to the concentration field. The rate is proportional to the concentration gradient. In one dimension diffusion can be written as:

$$J = -D\frac{\partial c}{\partial x} \qquad (1)$$

J – diffusion flux $\frac{mol}{m^2 s}$

D – diffusion coefficient $\frac{m^2}{s}$ (length, time)

c - concentration

x – position (length)

Second Fick's law correlate with time and can be written as:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \qquad (2)$$

t – time

The experiment consists of constant current passage through a symmetrical Li|electrolyte|Li cell for a short period of time t. This time should be long enough to make electrolyte concentration gradients develop in the vicinity of both electrodes and, as a result, produce measurable potential difference between both electrodes (concentration cell). The excess salt on one side of the call and depleted salt on the other side refer to Nernst equation. Current flow thru the cell should not be too long, so that we avoid changes of the concentration in the centre of the cell ($t_i << L^2 /D$). Under these conditions, the experiment can be modeled as a semi-infinity diffusion problem. According to second Fick's law for diffusion in one dimension x, can be written by eq. 2.
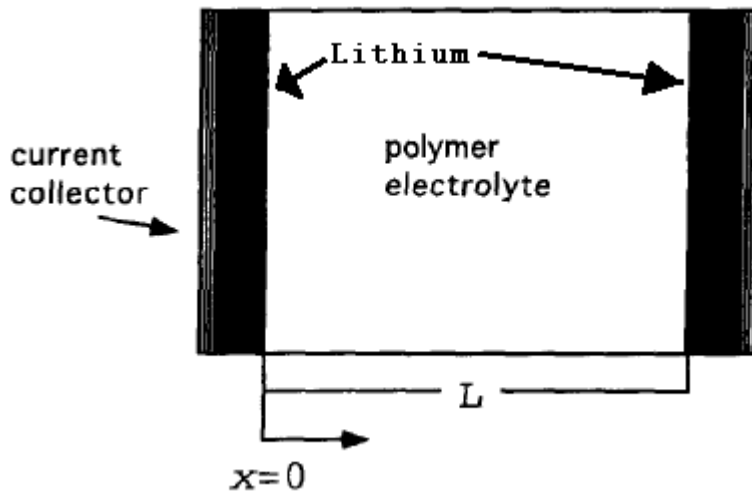
Fig 1

Figure 1 provides a diagram of a cell.

In case of semi-infinite diffusion, boundary conditions are:

$$\frac{\partial c}{\partial x}(x = 0) = -\frac{I(1-t_+^0)}{FD} \qquad (3)$$

coming from the assumption that reaction (4) is the only one taking place at the electrode:

Li = Li⁺ + e- (4).

Second boundary condition is:

$$c_{(t=0 \ and \ x=\infty)= c_\infty} \qquad (5)$$

This implies a thick cell, assuming that far from the electrode (in the centre of the cell) salt concentration is not altered during the experiment.

According to Nernst eq. in our cell:

$$\varphi(L, t) = \varphi^0 + \frac{RT}{F} ln \frac{c_{electrolyte}^0}{c(L,t)} \qquad (6)$$

$\varphi(L, t)$- equilibrium potential of the electrode

$c_{electrolyte}^0$- concentration of electrolyte at the surface of the electrode

$c(L, t)$- concentration of electrolyte at x=L in electrolyte.

The solution of eq. (2) which is local derivative with uniform boundary conditions with reference with eq. (6) gives us a final linear equation with logarithmic scale. Mathematical simplifications and inquiring final solution was neglected.

Typical linear plot of OCV of cell after current interruption is presented on figure 2.
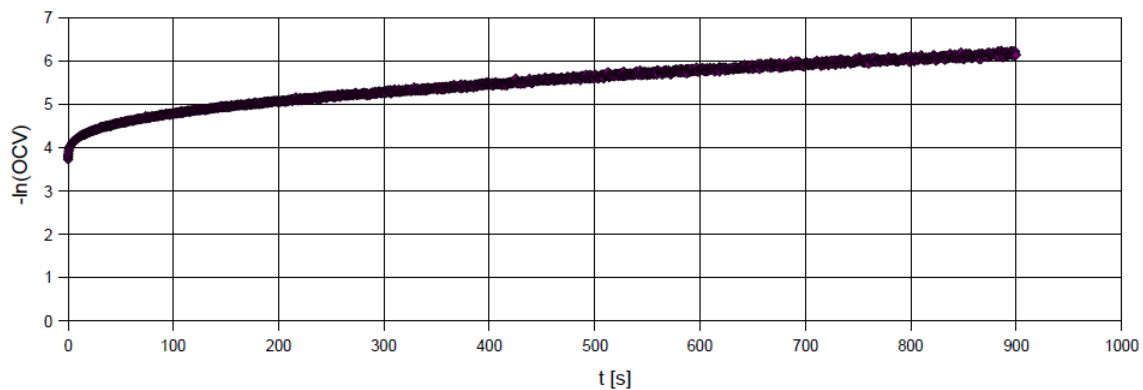

Figure 2

The experimental difficulty is that *I* value has to be known *a priori* or determined heuristically so that all the assumptions are fulfilled. Fortunately VMP potentiostat-galvanostat enables the user to modify experimental conditions even while it is ongoing. In this exercise we will make use of this feature and determine the polarization current by hit-or-miss approach i.e. start with some safely low value and increase the polarization current step by step if the concentration gradient develops too slowly). On the other hand, polarization time can be determined by iteration, i.e. after polarizing the cell for some time, let's say a minute, measure OCV of just generated concentration cell and in case it is too low, go on and polarize the cell again. Once sufficiently large OCV is generated, its decay after switching the polarization off will be recorded.

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 electrodes in swagelock type cassis. The cell has to be assembled in glove box due to highly reactive nature of metallic lithium.
3. Connect assembled cell to VMP potentiostat.
4. Apply sequence of galvanostatic pulses in order to develop concentration cell until OCV equals 10 - 20mV. The single step should consist of 1 minute of galvanostatic polarization with 100 µ*A* and 3 seconds of OCV of control.
5. Stop the polarization and record OCV vs. time for at least 15 minutes.
6. Plot -ln(OCV) vs. time (express OCV in [V] and time in [s]).

7. The curve obtained should be linear with some distortion near *t=0* which is related to double layer discharge. The slope of the linear part is related to the diffusion coefficient according to equation:

$$A = -\frac{\pi^2 D}{L^2}$$

A- slope of the linear part of the plot

D – Diffusion coefficient

L – thickness of tar cell

References:

1. Yanping Ma, Marc Doyle, Thomas F. Fuller, Marca M. Doeff, Lutgard C. Jonghe, and John Newman "The Measurement of a Complete Set of Transport Properties for a Concentrated Solid Polymer Electrolyte Solution"
2. Qing Wang, Hong Li, Xuejie Huang, and Liquan Chen "Determination of Chemical Diffusion Coefficient of Lithium Ion in Graphitized Mesocarbon Microbeads with Potential Relaxation Technique"