TRANSPORT PROPERTIES OF ELECTROLYTES

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1. Aim of the unit:

Aim of the unit is to get knowledge about determination of two important parameters related to the transport properties of the electrolyte – cation transference number and cation diffusion coefficient..

2. Calculations based on the experimental work:

2.1 How to determine the transference number 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 a proper range of frequencies
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. $t_{Li} = \frac{I_{SS}(V - I_0 R_0)}{I_0(V - I_{SS} R_{SS})}$

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)

2.2 How 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 -15 minute(s) of galvanostatic polarization with 100 µA 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:

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

where:

A- slope of the linear part of the plot

D – Diffusion coefficient

L – thickness of tar cell

3. Additional calculations:

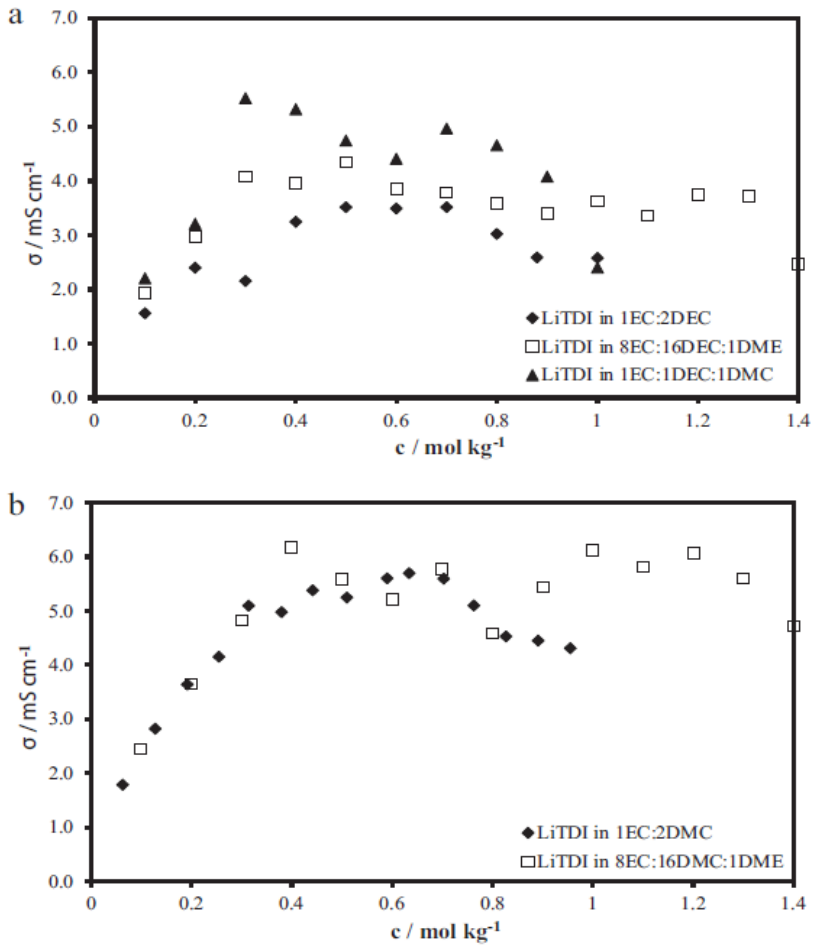


Fig. 2. Ionic conductivity dependence of LiTDI concentration in: a) EC:DEC (1:2 weight ratio), EC:DEC:DME (8:16:1 weight ratio) and EC:DEC:DMC (1:1:1 weight ratio) mixtures; b) EC:DMC (1:2 weight ratio) and EC:DMC:DME (8:16:1 weight ratio) mixtures.

Data on the ionic conductivity of the solution combined with the lithium cation transfer number can be used to obtain a value for the so-called lithium cation ionic conductivity (σ_{Li+}). ***This parameter is obtained by multiplying the conductivity value for a given sample by the value of the lithium cation transfer number obtained for a given sample.***

Below is a summary of the lithium cation transfer numbers.

0.3 mol kg−1 LiTDI in EC:DEC:DMC (1:1:1)	t_{Li+}=0.333
0.7 mol kg−1 LiTDI in EC:DEC:DMC (1:1:1)	t_{Li+}=0.497
0.4 mol kg−1 LiTDI in EC:DEC (1:2)	t_{Li+}=0.601
0.7 mol kg−1 LiTDI in EC:DEC (1:2)	t_{Li+}=0.563
0.31 mol kg−1 LiTDI in EC:DMC (1:2)	t_{Li+}=0.622
0.63 mol kg−1 LiTDI in EC:DMC (1:2)	t_{Li+}=0.553
0.3 mol kg−1 LiTDI in EC:DEC:DME (8:16:1)	t_{Li+}=0.614
0.5 mol kg−1 LiTDI in EC:DEC:DME (8:16:1)	t_{Li+}=0.850
1.2 mol kg−1 LiTDI in EC:DEC:DME (8:16:1)	t_{Li+}=0.666
0.4 mol kg−1 LiTDI in EC:DMC:DME (8:16:1)	t_{Li+}=0.648
1.0 mol kg−1 LiTDI in EC:DMC:DME (8:16:1)	t_{Li+}=0.731

3.1 Using the data from Fig. 2, determine the conductivity of the lithium cation for the above samples.

3.2 Based on the results obtained, please determine which of the above electrolytes is the best for use in cells? Please justify your answer.

3.3 Does a higher salt concentration always guarantee better transport parameters of lithium cations in the solution?