Experimental Determination of Transport Parameters for Binary Electrolyte Solutions for Use in Numerical Simulations

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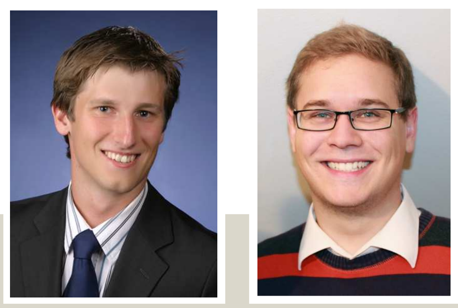


Motivation

Advanced numerical simulation tools are important for both the improvement of existing battery systems as well as the development of superior future battery systems such as Li-air batteries. To provide insight into physical and chemical aspects of such battery systems, it is necessary to develop computer models based on

- thermodynamically consistent models for ion-transport in porous media consisting of electrolyte solution, active and electrically conducting electrode materials and non-conducting materials
- accurate and reliable geometrical parameters and transport parameters

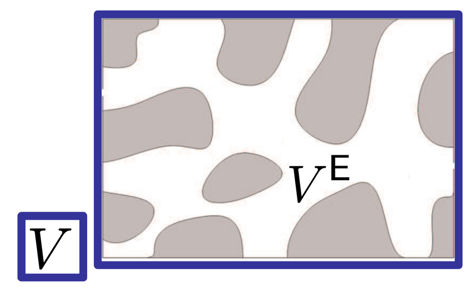
Mathematical model

Ion transport in porous separator filled with electrolyte solution [1] governed by

$$\frac{\partial \varepsilon \bar{c}^{\,\mathrm{E}}}{\partial t} - \nabla \cdot \left(\frac{\varepsilon}{\tau} D_{\pm}(c) \nabla \bar{c}^{\,\mathrm{E}} \right) + \nabla \cdot \left(\frac{t_{+}(c)}{F z_1 \nu_1} \bar{\boldsymbol{i}} \right) = 0$$

$$\nabla \cdot \bar{\boldsymbol{i}} = 0$$

$$\bar{\boldsymbol{i}} = -\frac{\varepsilon}{\tau} \kappa(c) \nabla \bar{\phi}^{\mathrm{E}} + \frac{RT}{F} \frac{\varepsilon}{\tau} \kappa(c)\, g_{\phi}\, \nabla \ln \bar{c}^{\,\mathrm{E}}$$



$$\bar{c}^{\,\mathrm{E}} = \frac{1}{V^{E}} \int_{\Omega^{\mathrm{E}}} c \, \mathrm{d} V^{\mathrm{E}}$$

Experimental determination of transport parameter for binary electrolyte solutions

Experimental setup

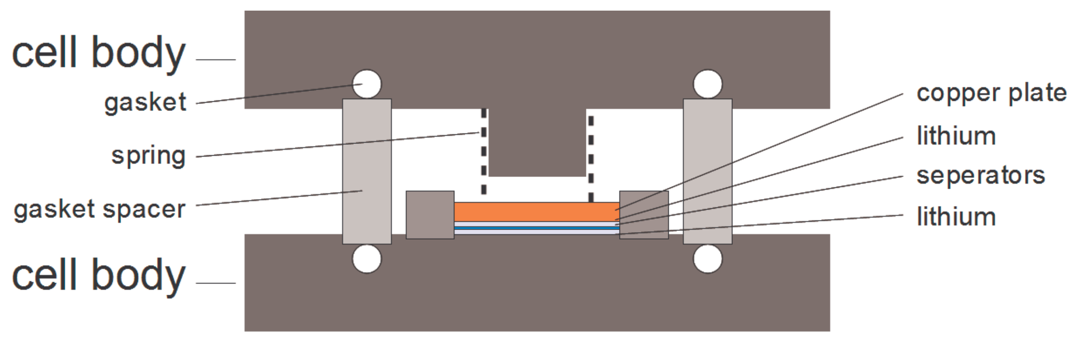


Fig. 1: schematic of experimental test cell

- 0.01M, 0.1M and 1.0M $LiClO_4$ in EC:DEC (1:1wt%)
- 10 layers of Cellgard® 2500, 25 μm, $\varepsilon = 0.55$
- geometrical parameter:
  - tortuosity τ of the porous medium
- transport parameters:
  - conductivity κ
  - diffusion coefficient $D_{\pm}$
  - transference number t_{+}
  - thermodynamic factor $f_{\pm}$

Conductivity

Fig. 2: conductivity cell 1100+

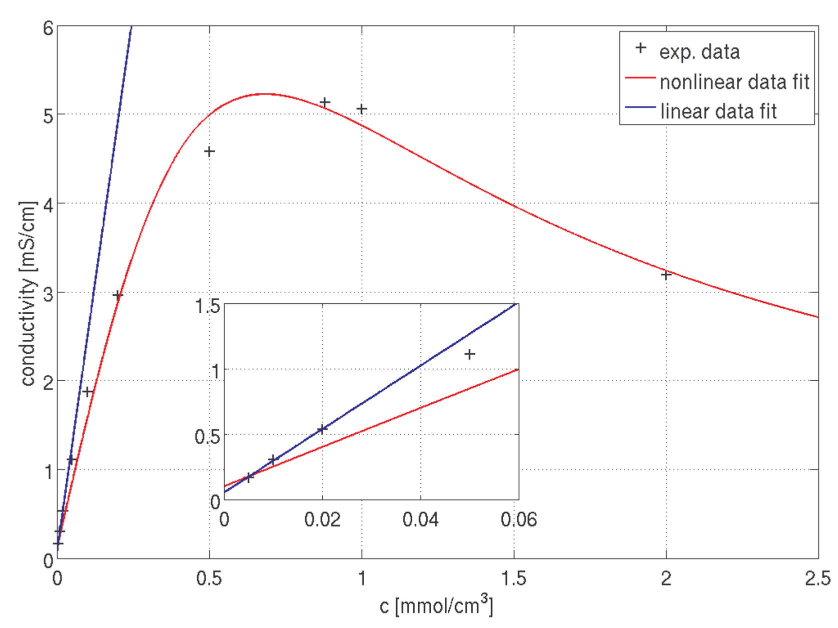


Fig. 3: experimentally determined conductivity

Diffusion coefficient

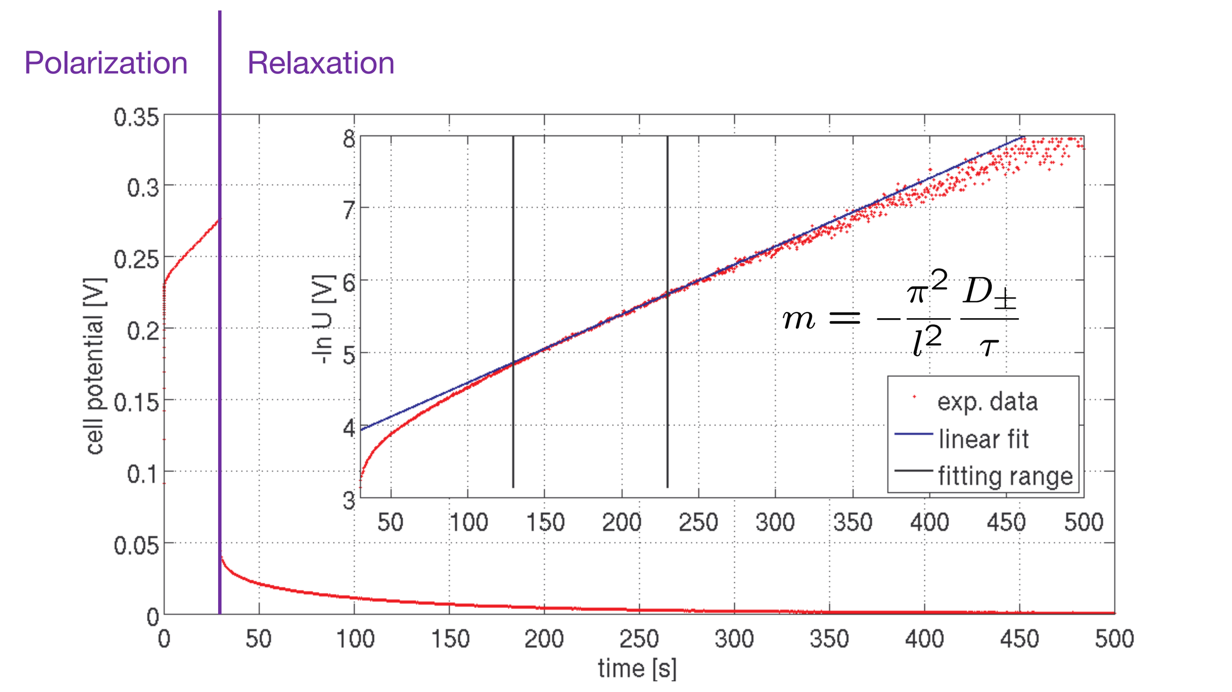


Fig. 4: determination of diffusion coefficient (0.01M $LiClO_4$) [2]

c [M]	0.01	0.1	1.0
$D_{\pm}$ [cm²/s]	1.36e-6 (±0.7%)	1.44e-6 (±4.8%)	6.87e-7 (±2.6%)

Transference number & thermodynamic factor

concentrated solution theory: $g_{\phi} = 2\left(1 + \frac{\mathrm{d}\ \ln f_{\pm}}{\mathrm{d}\ \ln c}\right)(1 - t_{+})$

for small concentration variation: $g \approx g_{\phi}(1 - t_{+}) \frac{1}{D_{+-}} = 2\left(1 + \frac{\mathrm{d}\ \ln f_{\pm}}{\mathrm{d}\ \ln c}\right)(1 - t_{+})^2 \frac{1}{D_{+-}}$

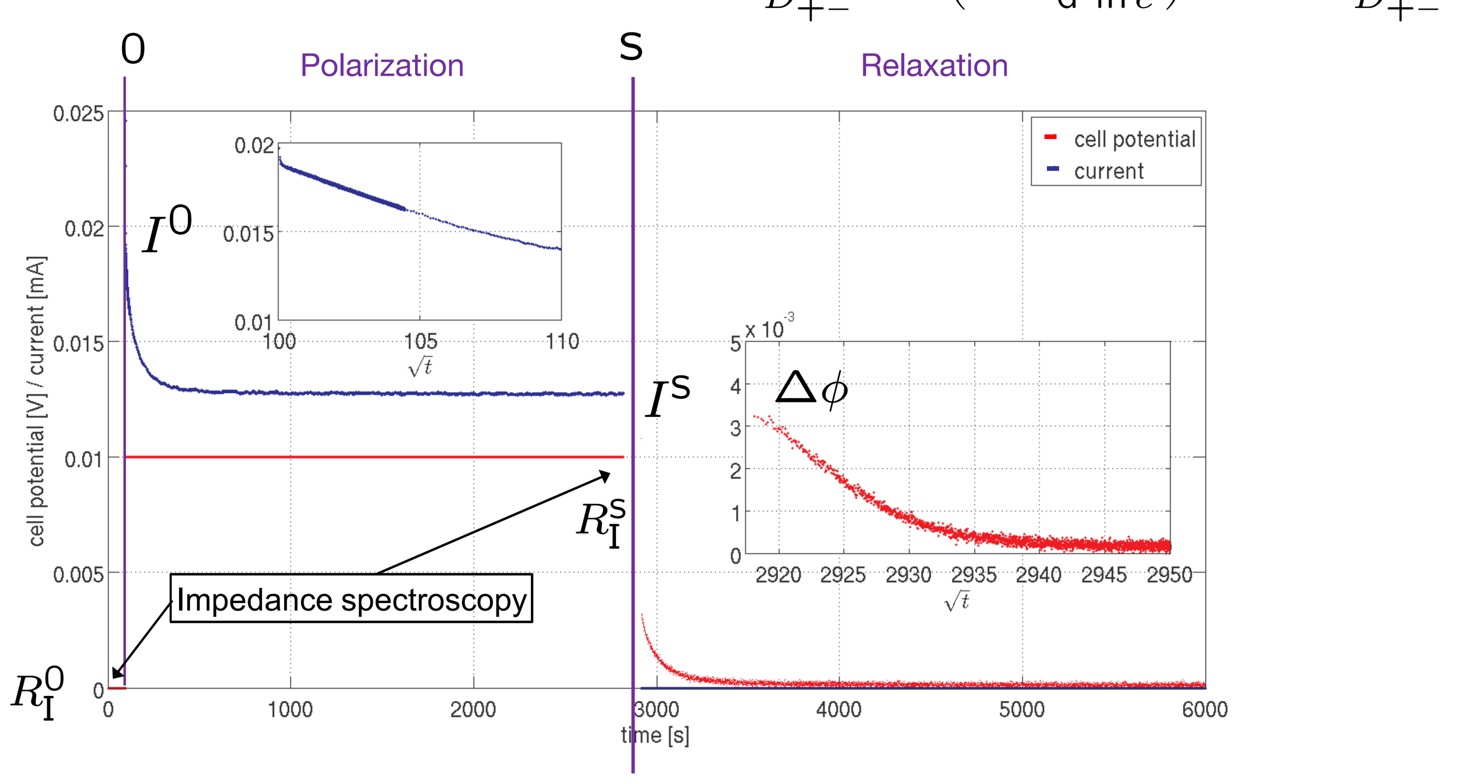


Fig. 5: determination of transference number and thermodynamic factor (0.01M $LiClO_4$)

$$g = \left[1 - \frac{I^s(U - R_I^0 I^0)}{I^0(U - R_I^s I^s)}\right] \frac{(U - R_I^s I^S)}{\frac{RT}{F^2}\frac{l}{c_0}\frac{I^S}{A}} \qquad g = \frac{F^2}{RT}\frac{c_0}{l} A \frac{\Delta\phi}{I^s}$$

c [M]	0.01		0.1		1.0	
g * $D_{\pm}$ [-]	0.306	0.309	0.052	0.050	0.016	-

Factor g_{ϕ} can be determined in a concentration cell [4]: $\nabla \phi = \frac{RT}{F} g_{\phi} \nabla \ln c$

Tortuosity – impedance spectroscopy

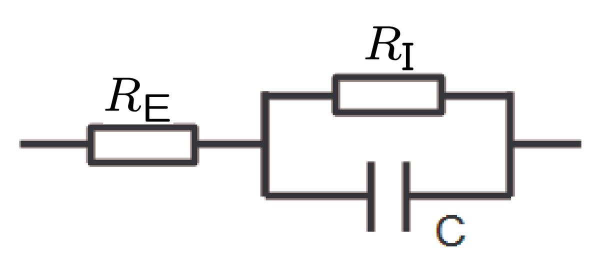


Fig. 6: equivalent circuit

$$\tau = \frac{\kappa}{\kappa_{\mathrm{eff}}} \varepsilon \qquad \kappa_{\mathrm{eff}} = \frac{1}{R_E} \frac{l}{A}$$

c [M]	0.01	0.1	1.0
τ [-]	1.12	2.03	2.47
τ [-] *	2.13	2.12	-

* without Li- electrode

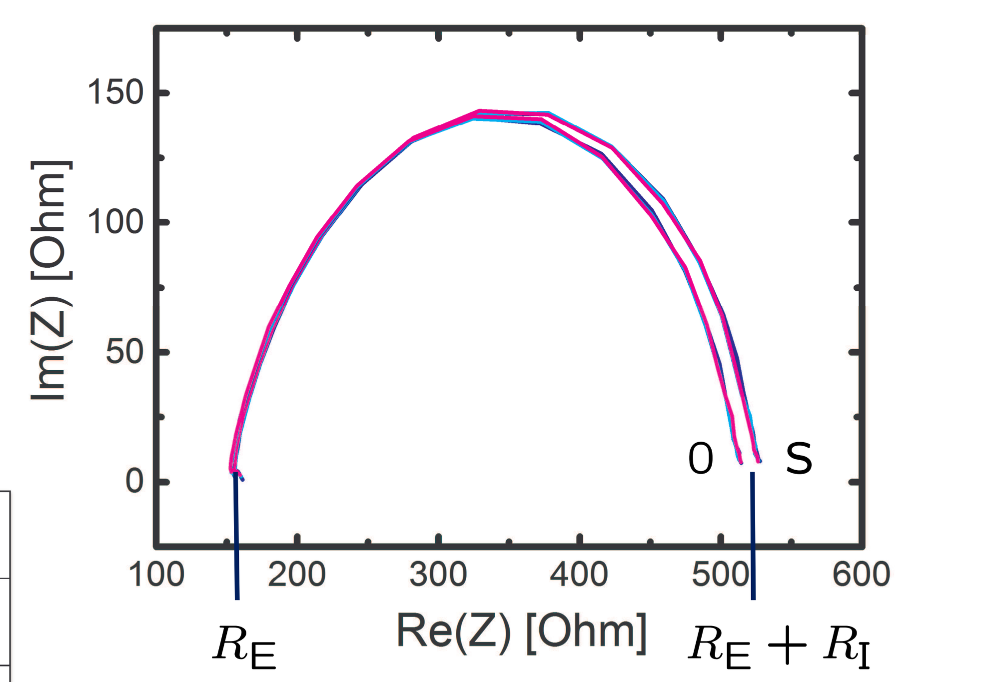


Fig. 7: impedance spectroscopy for transference number determination at 0 and s (0.01M $LiClO_4$)

Future work

- Numerical validation of determined parameters
- Determination of physically motivated transport parameters for
  - tertiary electrolyte solutions
  - ionic liquids

  based on thermodynamically consistent transport equations

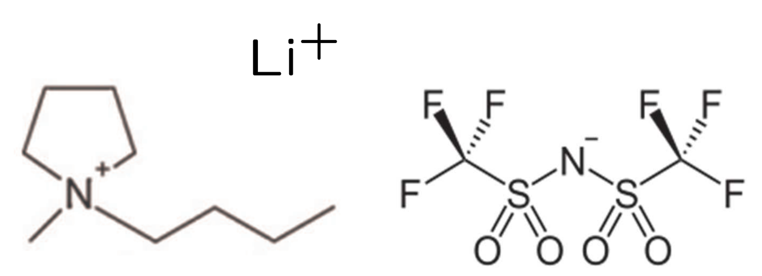


Fig. 8: ionic liquid consisting of Pyr_{14} (left), TFSI (right) and Lithium ions.

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