

Modeling of ionic liquids as electrolyte for Lithium batteries



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Ionic liquids

Properties of ionic liquids:

- High chemical and thermal stability
- Broad electrochemical stability window
- Low vapor pressure
- Non-flammability
- But so far: low capacities and current densities
- Potential electrolyte for future electrochemical storage applications, such as e.g., Li-ion, Li-S or Li-O₂ batteries

Modeling of ionic liquids:

- More complex mass transport due to interacting ions and absence of solvent
- Concentration-dependent physical properties
- Key for accurate numerical simulation: exact determination of potentially concentration-dependent diffusion coefficients and transference numbers
- First step: concentration-independent diffusion coefficients for binary electrolyte solutions in aprotic solvent

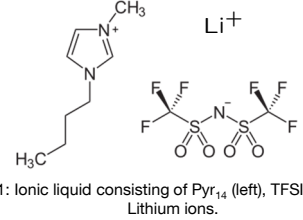


Fig. 1: Ionic liquid consisting of Pyr₁₄ (left), TFSI (right) and Lithium ions.

Determination of diffusion coefficients for binary electrolyte solutions

1) Experimental determination of limiting current

Experimental setup "Lithium pump":

- Anode & cathode: Lithium foil
- Porous separator: 2 layers Celgard 3500
- Binary electrolyte: 0.1 M LiTFSI in PC

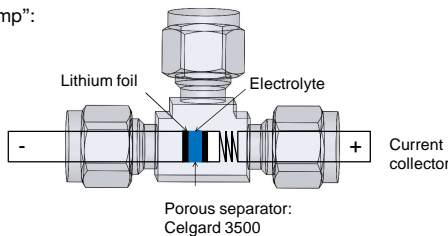


Fig. 2: Experimental setup of a Lithium-ion cell (lithium pump).

Galvanostatic experiments:

- Swagelok™ T-cell
- Current cycle shown in Fig. 3
- Electrochemical impedance spectroscopy (EIS) measurement with Biologic VMP3 in the end of each interval (see Fig. 3)

Theoretical resistance of binary electrolyte solutions (Fig. 4):

$$\frac{R}{R_{\text{bulk}}} = \frac{1}{2 \frac{z}{z_{\text{Li}^+}} \ln \left(\frac{1 + \frac{z}{z_{\text{Li}^+}}}{1 - \frac{z}{z_{\text{Li}^+}}} \right)}$$

Experimental results (see Fig. 4):

- Evaluation of mass transport limited current density i_{lim} based on the resistance ratio R/R_{bulk} of the electrolyte solution
- High variability of the experimental results for the initial bulk resistance R_{bulk} and R
- Restricted to concentration - independent diffusion coefficients and dilute solutions

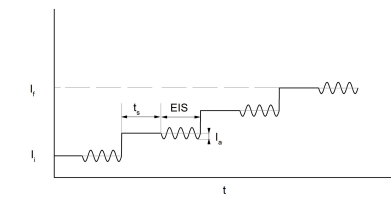


Fig. 3: Current cycle for galvanostatic experiments.

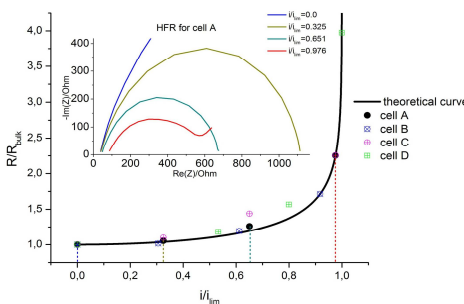


Fig. 4: Resistance ratio and electrochemical impedance spectra for different current densities in various cells.

2) Computation of effective separator length

- Effective separator length δ_{eff} : including the effect of reduced diffusion coefficients as a result of porous diffusion media
- $\delta_{\text{eff}} = l \epsilon^{1.5}$
- Conductivity measurement of pure electrolyte solution (Schott LF 1100+)
- Compression of cell changes porosity ϵ of separator
- Effective separator length based on bulk resistance determined with impedance measurements and conductivity κ of the electrolyte solution: $\delta_{\text{eff}} = R_{\text{bulk}} \kappa A$

3) Computation of diffusion coefficients

Diffusion coefficients of Lithium and TFSI computed based on limiting current i_{lim} , conductivity κ and effective separator length δ_{eff} :

$$D_{\text{Li}^+} = \frac{i_{\text{lim}}}{2z_{\text{Li}^+} F} \frac{\delta_{\text{eff}}}{c_{\text{bulk}}} \quad D_{\text{TFSI}^-} = \frac{RT}{z_{\text{Li}^+} F^2 c_{\text{bulk}}} \kappa - D_{\text{Li}^+}$$

4) Numerical simulation

General multi-ion transport equation:

- Dilute solution theory & concentration-independent physical transport properties
- $D_{\text{Li}^+} = 9.8 \text{e-}5 \text{ mm}^2/\text{s}$ (see, e.g., [3]), $D_{\text{TFSI}^-} = 18.0 \text{e-}5 \text{ mm}^2/\text{s} \rightarrow t_+ = 0.35$
- Mass conservation and electroneutrality condition (see, e.g., [2]):

$$\frac{\partial c_k}{\partial t} + \mathbf{u} \cdot \nabla c_k + \nabla \cdot \mathbf{N}_k^{d+m} = 0; \quad \sum_{k=0}^m z_k c_k = 0$$

• Ionic flux:

$$\mathbf{N}_k^{d+m} = -D_k \nabla c_k - \frac{F}{RT} z_k D_k c_k \nabla \Phi$$

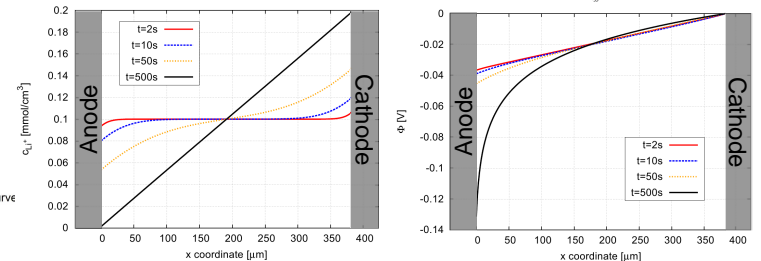
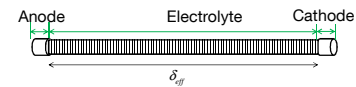


Fig. 5: Geometry, concentration and potential profile in the electrolyte for a one-dimensional "Lithium pump" at limiting current $i_{\text{lim}}=0.99 \text{ mA/cm}^2$ during charge.

- Linear potential profile in the beginning (no concentration gradient)
- Logarithmic potential profile in the end (linear concentration profile)
- Experimentally measured cell potential not reproducible (also not by including Nernst potential or Butler-Volmer equation)

Future work

- Improvement of currently developed method for binary electrolyte solutions
- Investigation of a "lithium pump" based on ionic liquids
- Development of a framework based on experiments and numerical simulations to determine potentially concentration-dependent physical properties as, e.g., diffusion coefficients and transference numbers
- Ionic flux of cation in concentrated solutions or molten salts as defined in [4]:

$$\mathbf{N}_1 = -\frac{\nu_1^A \nu_3^B D(c)}{RT} c_A \nabla \mu_A + \frac{t_1^c(c)}{z_1 F} \mathbf{i}_2 + c_1 \mathbf{u}_3$$

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Acknowledgement

N. Tsiouvaras gratefully acknowledges scholarship from the Alexander von Humboldt foundation

