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Modelling of the Mass Transport Phenomena in Li-ion Battery Electrolytes

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Lithium-Ion Batteries

Two types of commercial batteries:

- **Conventional lithium-ion batteries**, commercialised 1991 (80% of the market)

- **Lithium-ion polymer batteries**, commercialised around 1996 (20% of the market)

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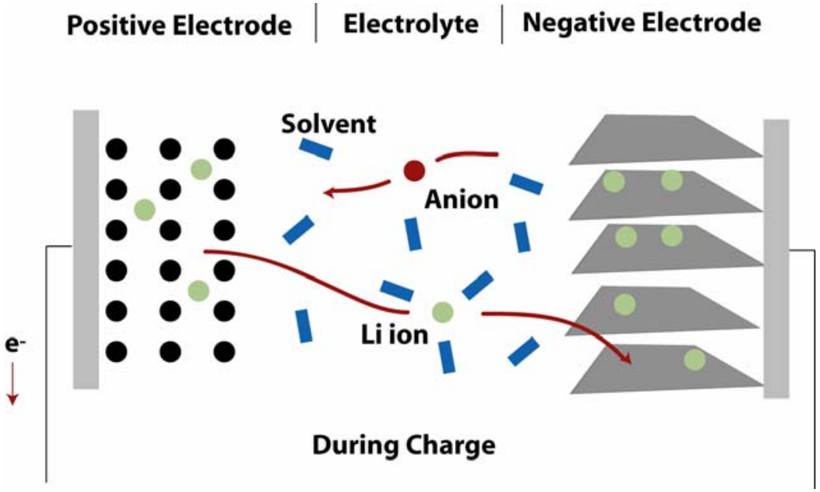
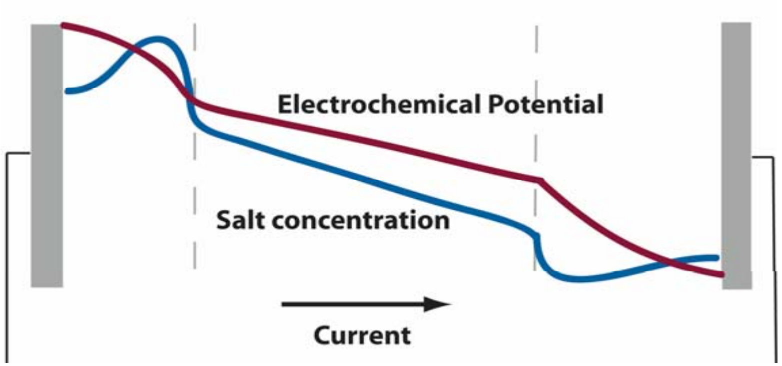
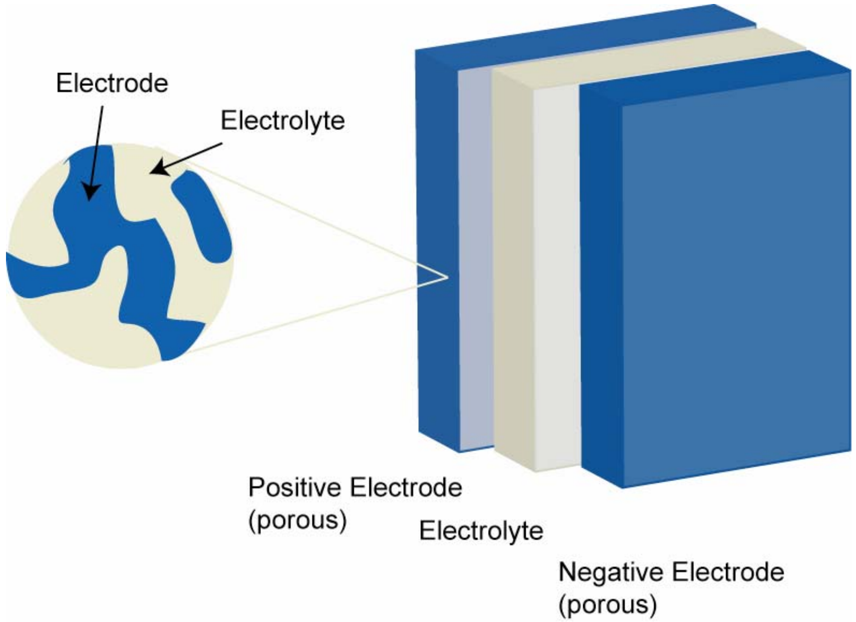
The Lithium-Ion Battery







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$v_{Li+} \approx 250$ nm/s

Electrolyte

- **$LiPF_6$** dissolved in **ethylene carbonate** (EC), **propylene carbonate** (PC) and **poly(vinylidene fluoride-co-hexafluoropropylene)** (PVdF-HFP)

  EC:PC (6:4)
  Random P(VdF-HFP)

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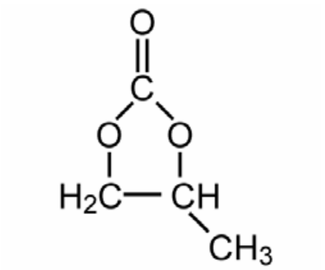
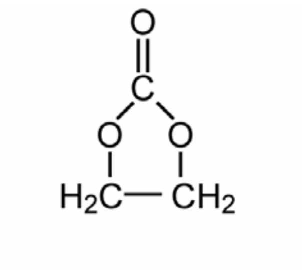
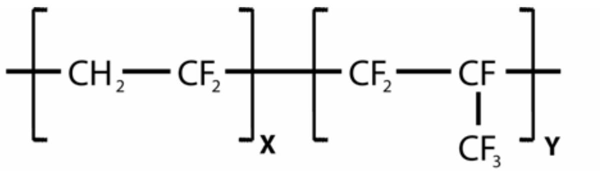


Propylene carbonate (PC)



Ethylene carbonate (EC)



PVdF-HFP
Poly(vinylidene diflouride co hexafluoropropylene)

Li^+ PF_6^-

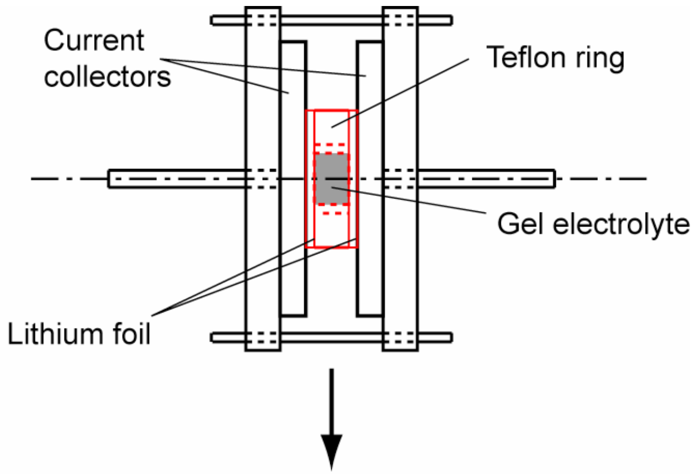
Lithium hexafluorophophate

Model

$$\frac{c_i}{RT}\frac{\partial \mu_i}{\partial x} = \sum_{k \neq i} \frac{c_i c_k}{c_{tot} D_{ik}} (v_k - v_i)$$

$$\sum_i c_i V_i^m = 1$$

$$i = \quad Li^+, PF_6^-, EC/PC \;\&\; P(VdF-HFP)$$



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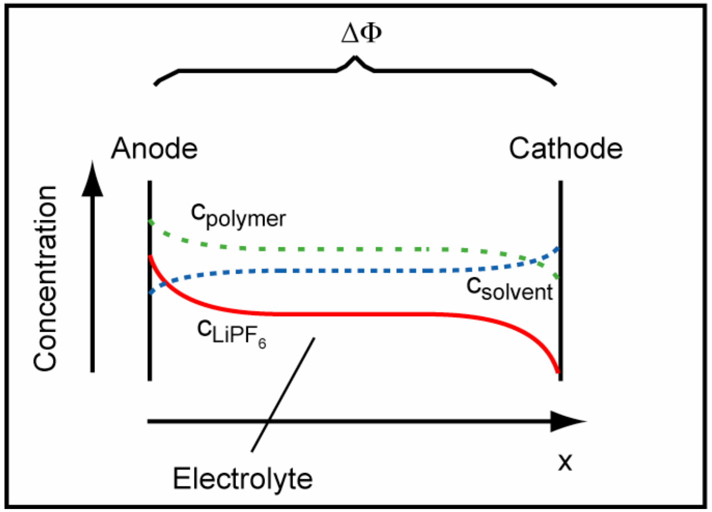
$$i_F = F\left(N_{Li^+} - N_{PF_6^-}\right)$$

$$c_{Li^+} = c_{PF_6^-} = c_{LiPF_6}$$

$$\mu_{Li^+} = F\Phi$$



Model

$$\begin{bmatrix} N_{LiPF_6} \\ N_{EC-PC} \end{bmatrix} = -\begin{bmatrix} D^{salt}_{salt} & d_{salt} \cdot D^{salt}_{solv} \\ d_{solv} \cdot D^{solv}_{salt} & D^{solv}_{solv} \end{bmatrix} \begin{bmatrix} \frac{\partial c_{LiPF_6}}{\partial x} \\ \frac{\partial c_{EC-PC}}{\partial x} \end{bmatrix} + \begin{bmatrix} -\frac{(1-t_+)i}{F} \\ \frac{t_{solv} i}{F} \end{bmatrix}$$

$$\frac{\partial \Phi}{\partial x} = -\frac{i}{\kappa} + \eta_1 \frac{\partial c_{LiPF_6}}{\partial x} + \eta_2 \frac{\partial c_{EC-PC}}{\partial x}$$

$$\frac{\partial c_i}{\partial t} = -\frac{\partial N_i}{\partial x} + R_i$$

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Model

- Galvanostatic polarization model
  Uniform concentration at t=0
  Fluxes at the boundaries are known: $N_{PF6-}=N_{EC:PC}=0$

- Solvent and salt diffusion model
  Uniform concentration at t=0
  Concentrations at the boundaries are known

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- PDE-mode in Comsol Multiphysics
  One-dimensional
  Time dependent solver

- The models were compared to experimental data

Experimental Techniques

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Techniques used in this study:

- Density measurements
- Conductivity measurements
- Concentration Cells
- Galvanostatic Polarisation
- Solvent and salt diffusion measurements

Other Techniques:

- Hittorf's method
  transport numbers referenced to the Hittorf frame
- Electrophoretic NMR
  velocities of species
- PFG-NMR
  self-diffusion coefficient
- Raman Spectroscopy
  time dependent concentration profiles

Concentration Cells and EIS

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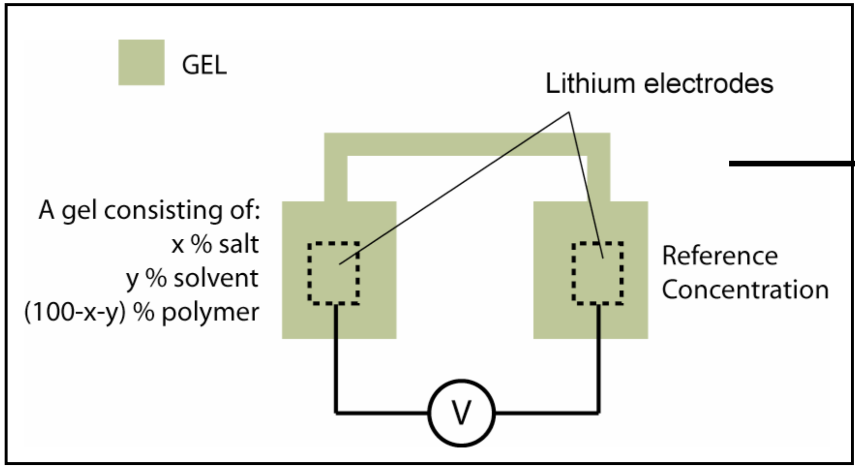
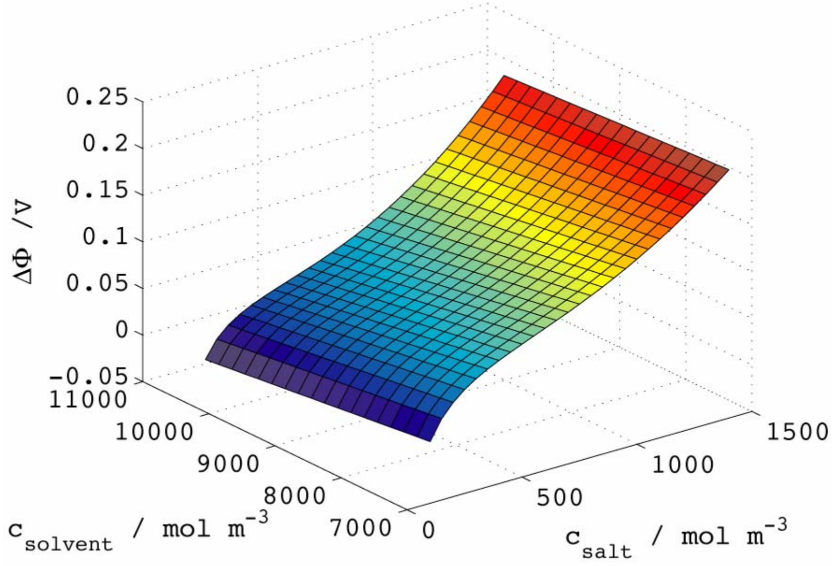
Concentration Cell

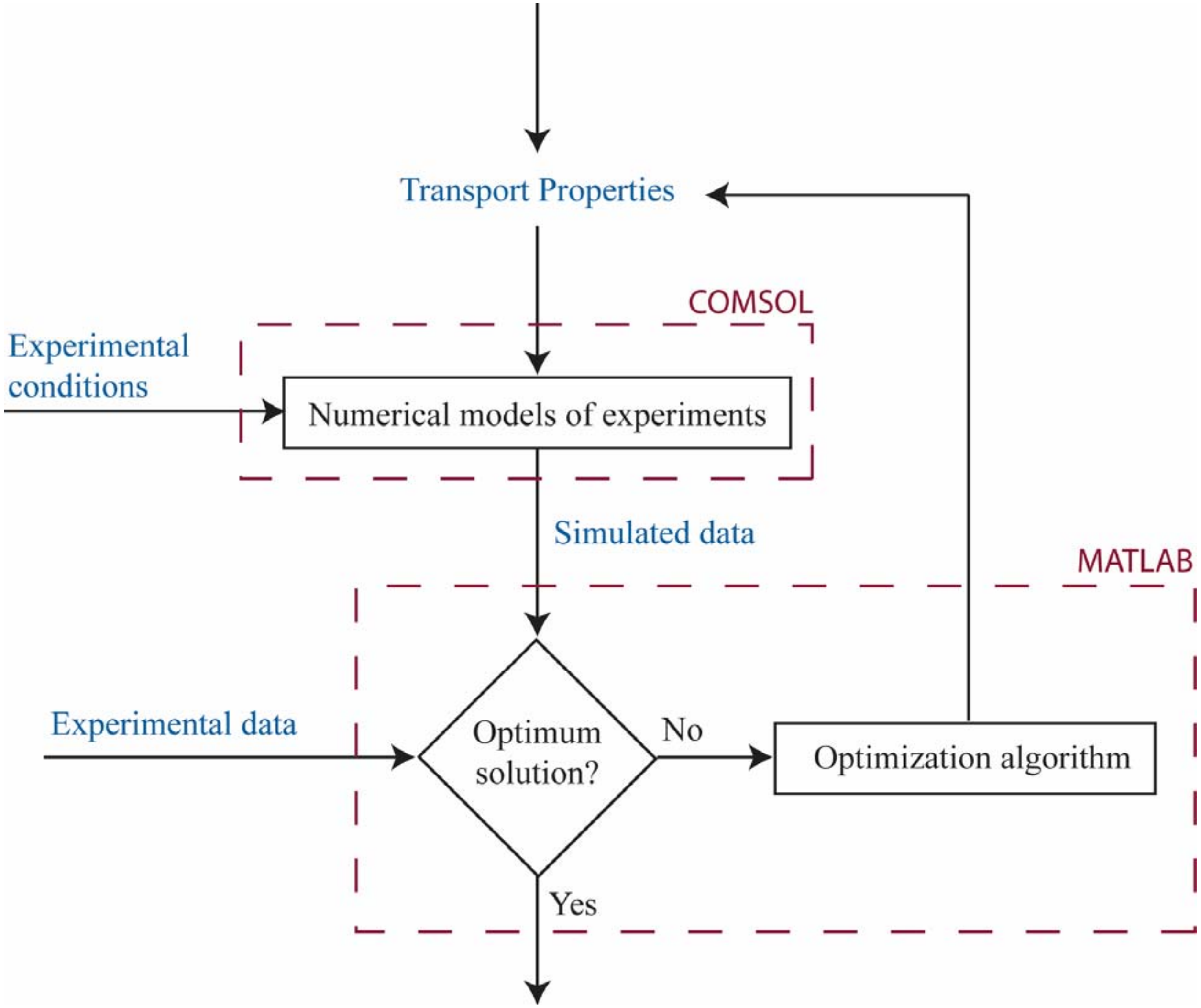




Electrochemical Impedance Spectroscopy

$$\frac{\partial \Phi}{\partial x} = -\frac{i}{\kappa} + \eta_1 \frac{\partial c_{salt}}{\partial x} + \eta_2 \frac{\partial c_{solv}}{\partial x}$$

Optimization



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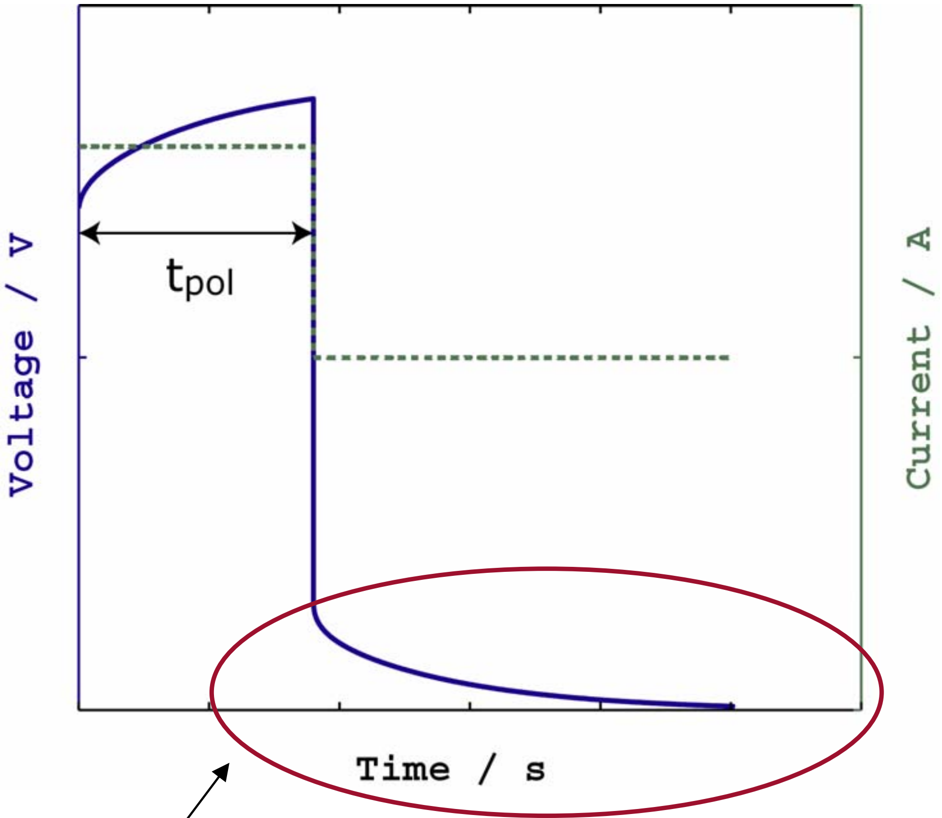
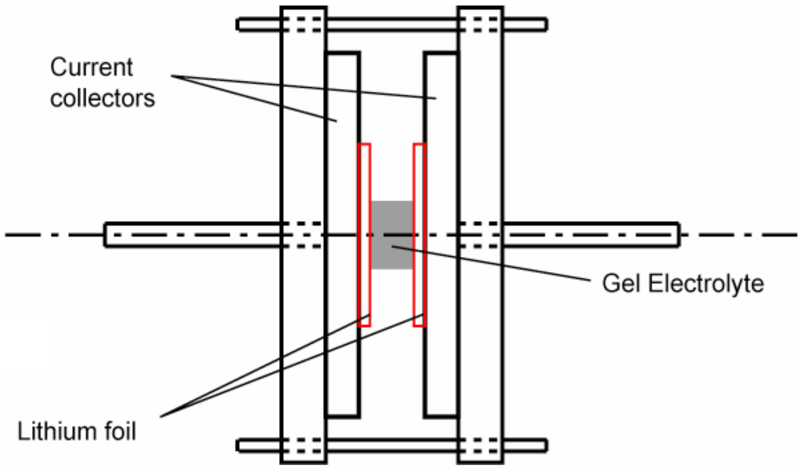
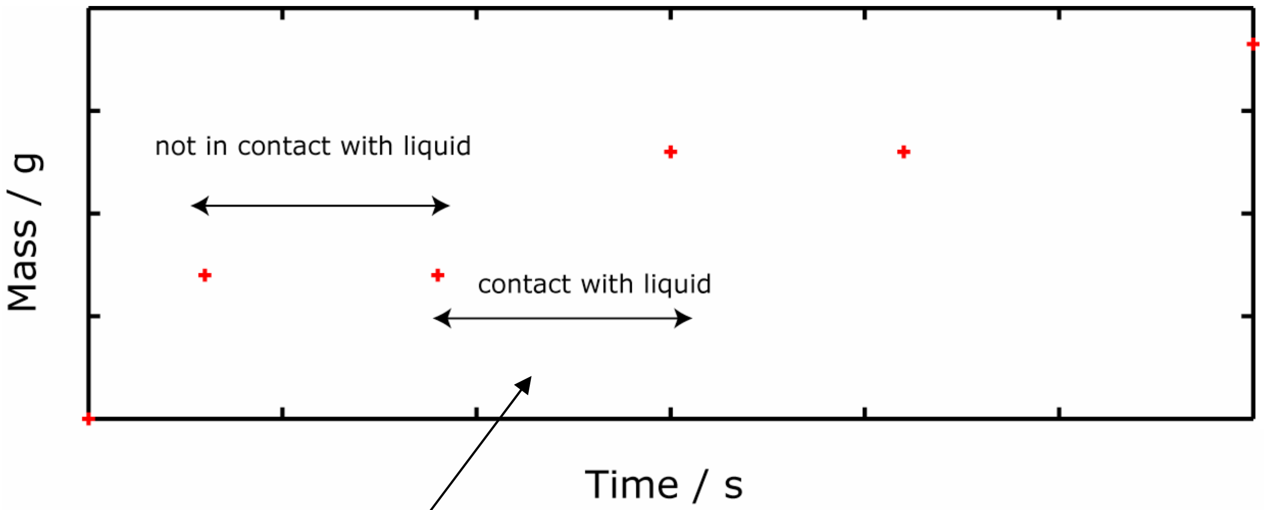
Galvanostatic Polarisation Experiments



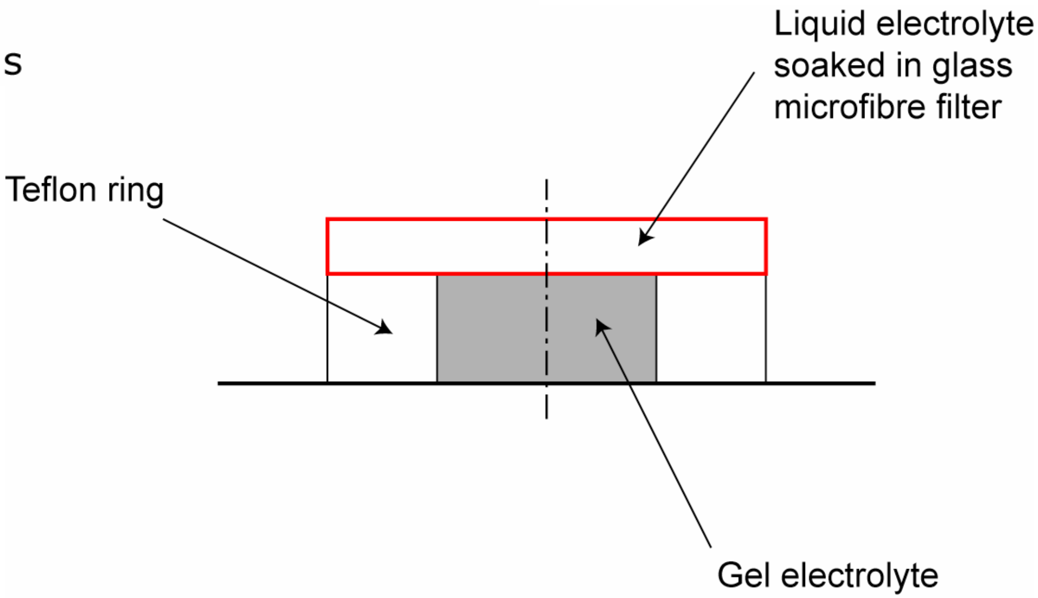


Information about the transport phenomena

Diffusion Experiments

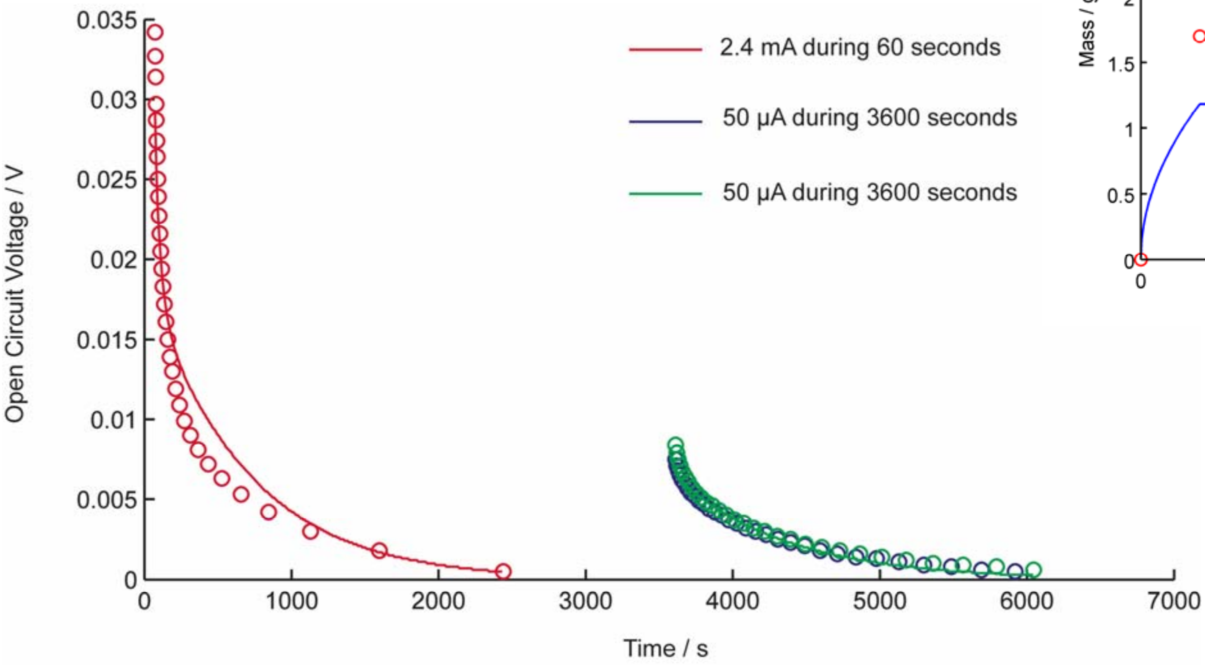


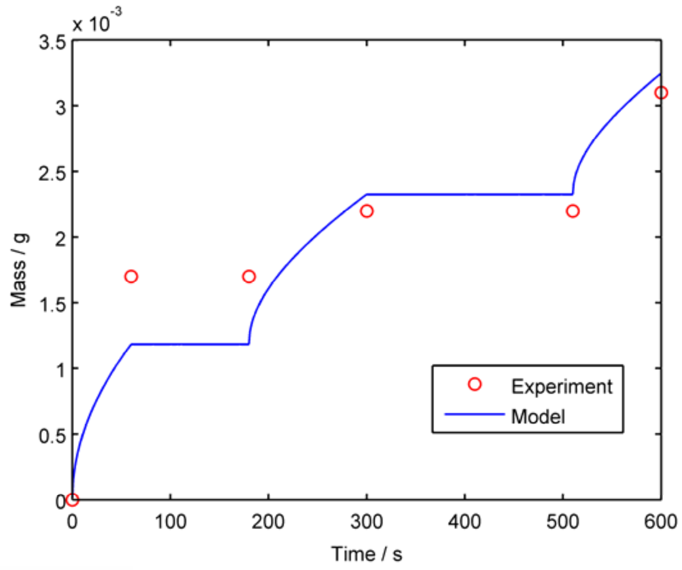
Information about the transport phenomena



Results

Galvanostatic polarization experiments





Solvent diffusion experiments

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Results

κ	D^{salt}_{salt}	D^{solv}_{solv}	t_+
0.17 S/m	$10^{-9.80}$ m^2/s	$10^{-9.11}$ m^2/s	0.25
t_{solv}	d_{salt}	d_{solv}	
-0.65	-0.78	-0.22	
η_1		η_2	
$1.23 \cdot 10^{-4}$ Vm^3/mol		$-9.43 \cdot 10^{-6}$ Vm^3/mol	

Transport properties for a P(VdF-HFP)-EC-PC-$LiPF_6$ gel. 5 % $LiPF_6$, 40 % P(VdF-HFP) and 60 % EC-PC (by weight)

$$\begin{bmatrix} N_{LiPF_6} \\ N_{EC-PC} \end{bmatrix} = -\begin{bmatrix} D^{salt}_{salt} & d_{salt} \cdot D^{solv}_{salt} \\ d_{solv} \cdot D^{salt}_{solv} & D^{solv}_{solv} \end{bmatrix} \begin{bmatrix} \frac{\partial c_{LiPF_6}}{\partial x} \\ \frac{\partial c_{EC-PC}}{\partial x} \end{bmatrix} + \begin{bmatrix} -\frac{(1-t_+)i}{F} \\ \frac{t_{solv} i}{F} \end{bmatrix}$$

$$\frac{\partial \Phi}{\partial x} = -\frac{i}{\kappa} + \eta_1 \frac{\partial c_{LiPF_6}}{\partial x} + \eta_2 \frac{\partial c_{EC-PC}}{\partial x}$$

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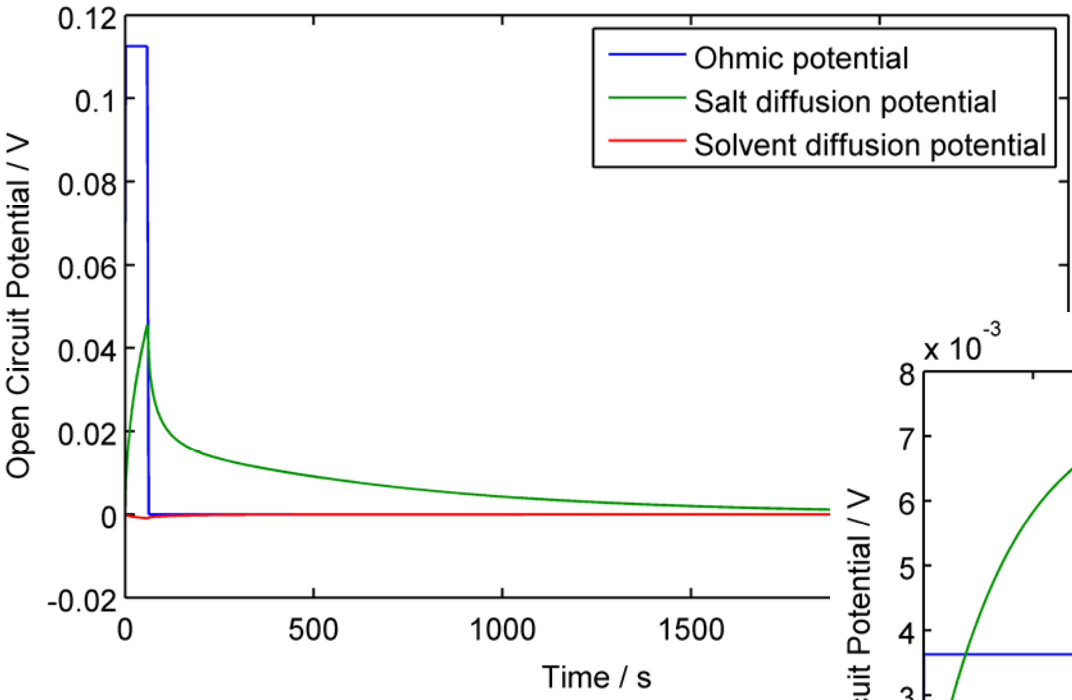
Results



Polarization with 2.4 mA during 60 s

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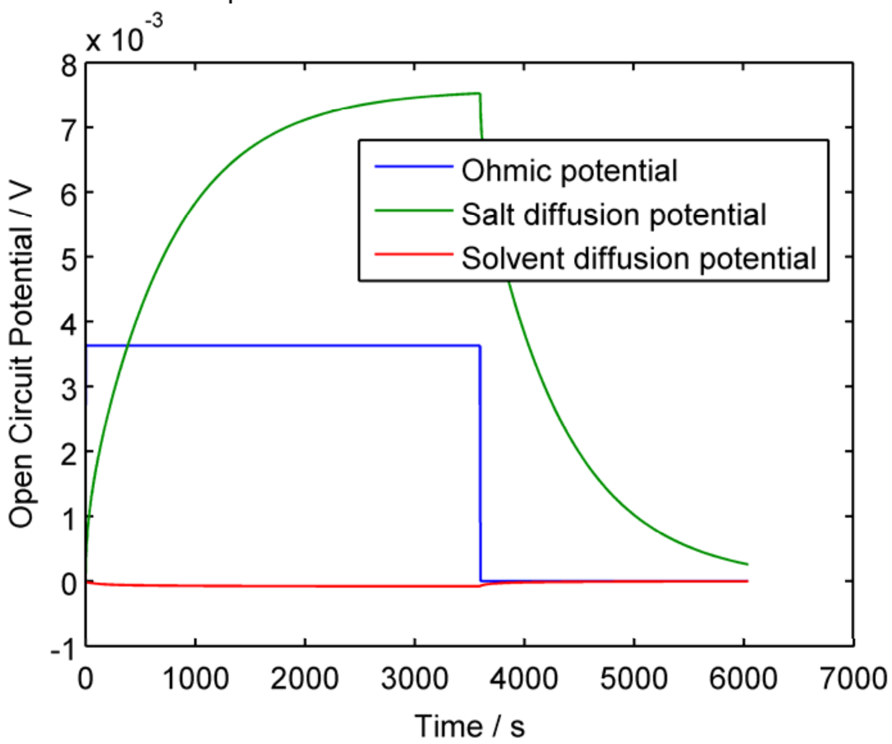

Polarization with 50 µA during 1 h

Summary

- The mass transport phenomena of a $LiPF_6$-EC-PC-P(VdF-HFP) gel was characterized and modeled at 298 K.
- Two types of models were implemented in Comsol. A galvanostatic polarization model (constant fluxes at the boundaries) and a salt and solvent diffusion model (constant concentrations at the boundaries).
- Two diffusion coefficients, two transport numbers and two drag coefficients were all calculated by fitting the models to experimental data.
- The conductivity was obtained from electrochemical impedance measurements while the two diffusion potential coefficients were directly calculated from concentration cell data.
- The solvent diffusion potential was relative small compared to the ohmic potential drop and the salt diffusion potential.

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Acknowledgements

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VETENSKAPSRÅDET
SWEDISH RESEARCH COUNCIL

Transport Properties and Thermodynamic Properties

$$\frac{\partial c_{LiPF_6}}{\partial t} = -\frac{\partial}{\partial x}\left(\begin{aligned} &-\left(\left(1 - V_m^{LiPF_6} c_{LiPF_6}\right)\hat{D}_{11} - \left(V_m^{EC-PC} c_{LiPF_6}\right)\hat{D}_{21}\right)\frac{\partial c_{LiPF_6}}{\partial x} \\ &-\left(\left(1 - V_m^{LiPF_6} c_{LiPF_6}\right)\hat{D}_{12} - \left(V_m^{EC-PC} c_{LiPF_6}\right)\hat{D}_{22}\right)\frac{\partial c_{EC-PC}}{\partial x} \\ &-\left(\left(1 - V_m^{LiPF_6} c_{LiPF_6}\right)\left(1 - t_+^0\right) + \left(V_m^{EC-PC} c_{LiPF_6}\right)t_{EC-PC}^0\right)\frac{i}{F} \end{aligned} \right)$$

$\longrightarrow$

$$\hat{D}_{11}$$
$$\hat{D}_{12}$$
$$\hat{D}_{21}$$
$$\hat{D}_{22}$$
$$t_+^0$$
$$t_{EC-PC}^0$$
$$\kappa$$

$$\frac{\partial c_{EC-PC}}{\partial t} = -\frac{\partial}{\partial x}\left(\begin{aligned} &-\left(\left(1 - V_m^{EC-PC} c_{EC-PC}\right)\hat{D}_{21} - \left(V_m^{LiPF_6} c_{EC-PC}\right)\hat{D}_{11}\right)\frac{\partial c_{LiPF_6}}{\partial x} \\ &-\left(\left(1 - V_m^{EC-PC} c_{EC-PC}\right)\hat{D}_{22} - \left(V_m^{LiPF_6} c_{EC-PC}\right)\hat{D}_{12}\right)\frac{\partial c_{EC-PC}}{\partial x} \\ &+\left(\left(1 - V_m^{EC-PC} c_{EC-PC}\right)t_{EC-PC}^0 + \left(V_m^{LiPF_6} c_{EC-PC}\right)\left(1 - t_+^0\right)\right)\frac{i}{F} \end{aligned} \right)$$

$$\Delta\Phi = \int \frac{RT}{c_{LiPF_6}F}\left(2\left(1 - t_+^0\right)\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c_{LiPF_6}}\right) - t_{EC-PC}^0 \frac{\partial \ln f_{EC-PC}}{\partial \ln c_{LiPF_6}}\right) dc_{LiPF_6} +$$
$$\int \frac{RT}{c_{EC-PC}F}\left(2\left(1 - t_+^0\right)\frac{\partial \ln f_\pm}{\partial \ln c_{EC-PC}} - t_{EC-PC}^0\left(1 + \frac{\partial \ln f_{EC-PC}}{\partial \ln c_{EC-PC}}\right)\right) dc_{EC-PC}$$

$\longrightarrow$

$$V_m^{LiPF_6}$$
$$V_m^{EC-PC}$$
$$\left(1 + \frac{\partial \ln f_\pm}{\partial \ln c_{LiPF_6}}\right)$$
$$\frac{\partial \ln f_\pm}{\partial \ln c_{EC-PC}}$$
$$\frac{\partial \ln f_{EC-PC}}{\partial \ln c_{LiPF_6}}$$
$$\left(1 + \frac{\partial \ln f_{EC-PC}}{\partial \ln c_{EC-PC}}\right)$$

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