A thermodynamically consistent model for electric double layers in Li-all-solid-state batteries

S. Braun[1,2], A. Latz[1,2,3] and C. Yada[4]

[1] German Aerospace Center, Stuttgart, Germany
[2] Helmholtz Institute for Battery Research Ulm, Ulm, Germany
[3] Ulm University, Ulm, Germany
[4] Toyota Motor Europe NV/SA, Zaventem, Belgium

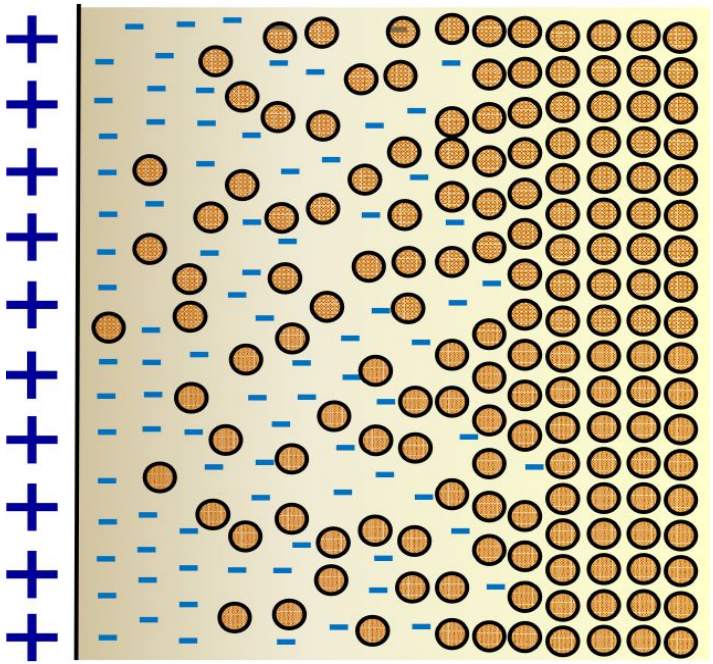
November 27th, 2014

DLR

Outline

- Motivation: Lithium-deficient layers in solid electrolytes
- The mathematical model
  - General properties
  - 1D stationary boundary value problem
- Results: Cation and potential distributions
- Conclusions & Outlook

Motivation:
Lithium-deficient layers (LDLs) in solid electrolytes



Applied external el. potential:

- Anode:
  - Li ions vacate region near electrode
  - Area partially or totally void of Li ions develops (LDL)
- Cathode:
  - Vacancies fill up with Li ions
  - Area with few or no vacancies develops
- In space charge regions:
  high electric fields, reduced conductivity

Limits the performance of the battery!

Numerical study: Ideas for improved battery concepts leading to higher power density?

Properties of the model (I)

What properties should the model have?

- As general as possible (e.g., material independent)
- Usable in a full-cell model
- Easily extendable to include more physics
- Accurately describe dynamics inside LDL
- Consistent with laws of physics and thermodynamics [1]!

[1] W. Dreyer et al, *Phys. Chem. Chem. Phys.* **15**, 7075 (2013)

Properties of the model (II)

ρ … mass density
α … particle index
$\boldsymbol{v}$ … velocity
$\boldsymbol{T}$ … stress tensor
$\boldsymbol{b}$ … body force
ϵ … energy density
$\boldsymbol{q}$ … heat flux
$\boldsymbol{E}$ … electric field
$\boldsymbol{D}$ … electric displacement
h … body heat
s … entropy density
$\boldsymbol{J}_s$ … entropy flux
ϑ … temperature
k_B … Boltzmann constant
n_α … density of particle α
$\nu = 1 - n_a$

How is the model realised mathematically/physically?

- Li ions and vacancies modeled as a continuum
- Simplifications:
  - Isothermal condition
  - Only one type of vacancies
- Based on first principles only:
  - Mass conservation: $\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \boldsymbol{v}_\alpha) = 0$
  - momentum conservation: $\rho \dot{\boldsymbol{v}} = \nabla \cdot \boldsymbol{T} + \rho \boldsymbol{b}$
  - Energy conservation: $\rho \dot{\epsilon} = \nabla(\boldsymbol{T}^T \boldsymbol{v}) + \rho \boldsymbol{v} \cdot \boldsymbol{b} - \nabla \cdot \left(\boldsymbol{q} - \boldsymbol{E} \times (\boldsymbol{v} \times \boldsymbol{D})\right) + \rho h$
  - Entropy inequality: $\rho \dot{s} + \nabla \cdot \boldsymbol{J}_s - \rho \frac{h}{\vartheta} \geq 0$
- Free-energy functional constitutes closure of the system:

$$\rho\psi = \rho\psi_R + \rho\psi_p + \rho\psi_{pol} + k_B\vartheta \left(n_c \ln\left(\frac{n_c}{\nu}\right) + (\nu - n_c) \ln\left(\frac{\nu - n_c}{\nu}\right)\right)$$

DLR

Properties of the model (II)

How is the model realised mathematically/physically?

- Li ions and vacancies modeled as a continuum
- Simplifications:
  - Isothermal condition
  - Only one type of vacancies
- Based on first principles only:
  - Mass conservation: $\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \boldsymbol{v}_\alpha) = 0$
  - momentum conservation: $\rho \dot{\boldsymbol{v}} = \nabla \cdot \boldsymbol{T} + \rho \boldsymbol{b}$
  - Energy conservation: $\rho \dot{\epsilon} = \nabla(\boldsymbol{T}^T \boldsymbol{v}) + \rho \boldsymbol{v} \cdot \boldsymbol{b} - \nabla \cdot \left(\boldsymbol{q} - \boldsymbol{E} \times (\boldsymbol{v} \times \boldsymbol{D})\right) + \rho h$
  - Entropy inequality: $\rho \dot{s} + \nabla \cdot \boldsymbol{J}_s - \rho \frac{h}{\vartheta} \geq 0$
- Free-energy functional constitutes closure of the system:

$$\rho\psi = \rho\psi_R + \rho\psi_p + \rho\psi_{pol} + k_B\vartheta \left(n_c \ln\left(\frac{n_c}{\nu}\right) + (\nu - n_c) \ln\left(\frac{\nu - n_c}{\nu}\right)\right)$$

Li ion hopping

ρ ... mass density
α ... particle index
$\boldsymbol{v}$ ... velocity
$\boldsymbol{T}$ ... stress tensor
$\boldsymbol{b}$ ... body force
ϵ ... energy density
$\boldsymbol{q}$ ... heat flux
$\boldsymbol{E}$ ... electric field
$\boldsymbol{D}$ ... electric displacement
h ... body heat
s ... entropy density
$\boldsymbol{J}_s$ ... entropy flux
ϑ ... temperature
k_B ... Boltzmann constant
n_α ... density of particle α
$\nu = 1 - n_a$

Properties of the model (II)

How is the model realised mathematically/physically?

- Li ions and vacancies modeled as a continuum
- Simplifications:
  - Isothermal condition
  - Only one type of vacancies
- Based on first principles only:
  - Mass conservation: $\partial_t \rho_\alpha + \nabla \cdot (\rho_\alpha \boldsymbol{v}_\alpha) = 0$
  - momentum conservation: $\rho \dot{\boldsymbol{v}} = \nabla \cdot \boldsymbol{T} + \rho \boldsymbol{b}$
  - Energy conservation: $\rho \dot{\epsilon} = \nabla(\boldsymbol{T}^T \boldsymbol{v}) + \rho \boldsymbol{v} \cdot \boldsymbol{b} - \nabla \cdot \left(\boldsymbol{q} - \boldsymbol{E} \times (\boldsymbol{v} \times \boldsymbol{D})\right) + \rho h$
  - Entropy inequality: $\rho \dot{s} + \nabla \cdot \boldsymbol{J}_s - \rho \frac{h}{\vartheta} \geq 0$
- Free-energy functional constitutes closure of the system:

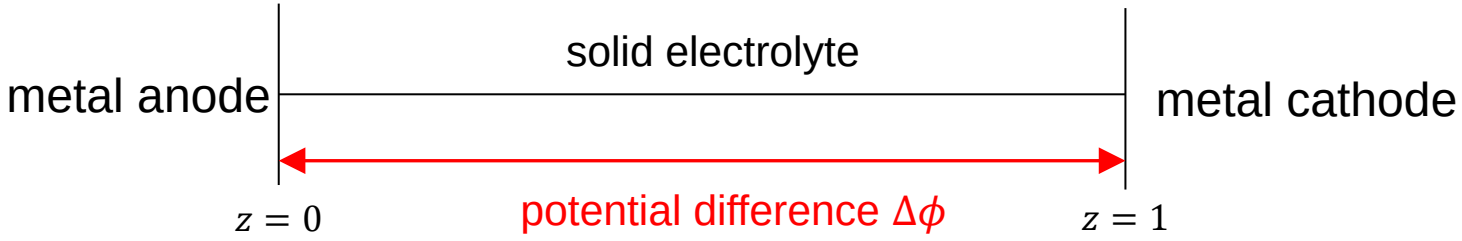
$$\rho\psi = \rho\psi_R + \rho\psi_p + \rho\psi_{pol} + k_B \vartheta \left(n_c \ln\left(\frac{n_c}{\nu}\right) + (\nu - n_c) \ln\left(\frac{\nu - n_c}{\nu}\right)\right)$$

Thermodynamic consistency!

Li ion hopping

ρ ... mass density
α ... particle index
$\boldsymbol{v}$ ... velocity
$\boldsymbol{T}$ ... stress tensor
$\boldsymbol{b}$ ... body force
ϵ ... energy density
$\boldsymbol{q}$ ... heat flux
$\boldsymbol{E}$ ... electric field
$\boldsymbol{D}$ ... electric displacement
h ... body heat
s ... entropy density
$\boldsymbol{J}_s$ ... entropy flux
ϑ ... temperature
k_B ... Boltzmann constant
n_α ... density of particle α
$\nu = 1 - n_a$

1D stationary boundary value problem



Set of equations:

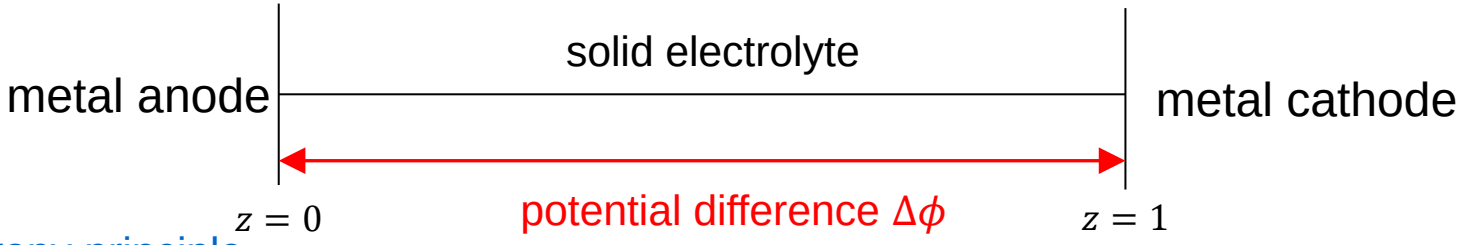
$$\partial_z \left(\mu_c - \frac{m_c}{m_a} \left(\mu_a - \frac{\nu}{n_a} \mu_\nu \right) \right) + \left(z_c - \frac{m_c}{m_a} z_a \right) \partial_z \phi = 0$$

$$a^2 \partial_z p = -n^F \partial_z \phi$$

$$\lambda^2 \partial_{zz} \phi = -n^F$$

μ_α ... chemical potential
n^F ... charge density
ϕ, p ... el. potential and pressure
z_α, m_α ... particle charge and mass
a, λ, ϵ ... parameters
$F(n^F), H(n^F)$ ... coefficient functions

1D stationary boundary value problem



from entropy principle

Set of equations:

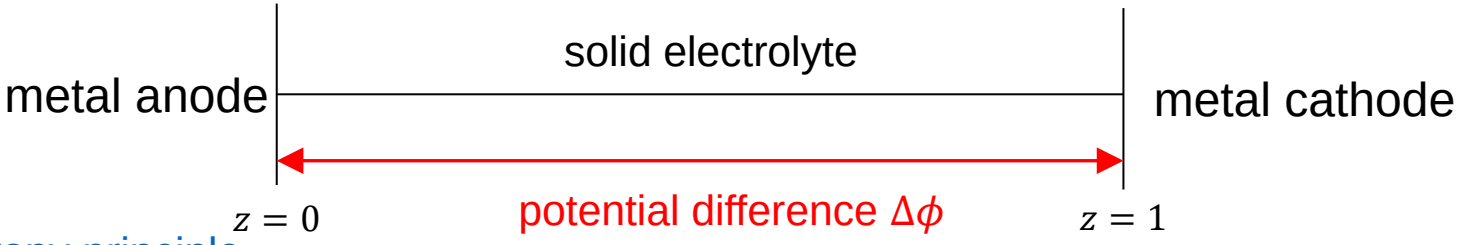
$$\partial_z\left(\mu_c - \frac{m_c}{m_a}\left(\mu_a - \frac{\nu}{n_a}\mu_v\right)\right) + \left(z_c - \frac{m_c}{m_a}z_a\right)\partial_z\phi = 0$$

$$a^2\partial_z p = -n^F\partial_z\phi$$

$$\lambda^2\partial_{zz}\phi = -n^F$$

μ_α ... chemical potential
n^F ... charge density
ϕ, p ... el. potential and pressure
z_α, m_α ... particle charge and mass
a, λ, ϵ ... parameters
$F(n^F), H(n^F)$ ... coefficient functions

1D stationary boundary value problem



from entropy principle

Set of equations:

$$\partial_z\left(\mu_c - \frac{m_c}{m_a}\left(\mu_a - \frac{\nu}{n_a}\mu_\nu\right)\right) + \left(z_c - \frac{m_c}{m_a}z_a\right)\partial_z\phi = 0$$

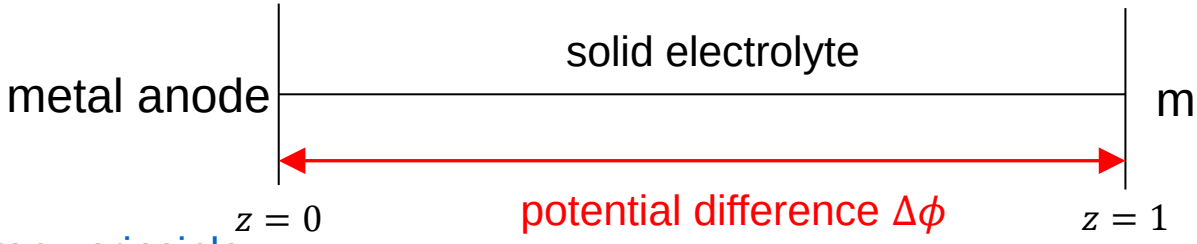
$$a^2\partial_z p = -n^F\partial_z\phi$$ ← momentum balance

$$\lambda^2\partial_{zz}\phi = -n^F$$

μ_α ... chemical potential
n^F ... charge density
ϕ, p ... el. potential and pressure
z_α, m_α ... particle charge and mass
a, λ, ϵ ... parameters
$F(n^F), H(n^F)$ ... coefficient functions

DLR

1D stationary boundary value problem



from entropy principle

Set of equations:

$$\partial_z\left(\mu_c - \frac{m_c}{m_a}\left(\mu_a - \frac{\nu}{n_a}\mu_\nu\right)\right) + \left(z_c - \frac{m_c}{m_a}z_a\right)\partial_z\phi = 0$$

$$a^2\partial_z p = -n^F\partial_z\phi$$ momentum balance

Poisson equation

$$\lambda^2\partial_{zz}\phi = -n^F$$

Electroneutrality:

$$\int_0^1 n^F dz = 0$$

Boundary conditions:

$$\phi(z=0) = \phi_L; \phi(z=1) = \phi_R$$

$$p(z=0) = p_0$$

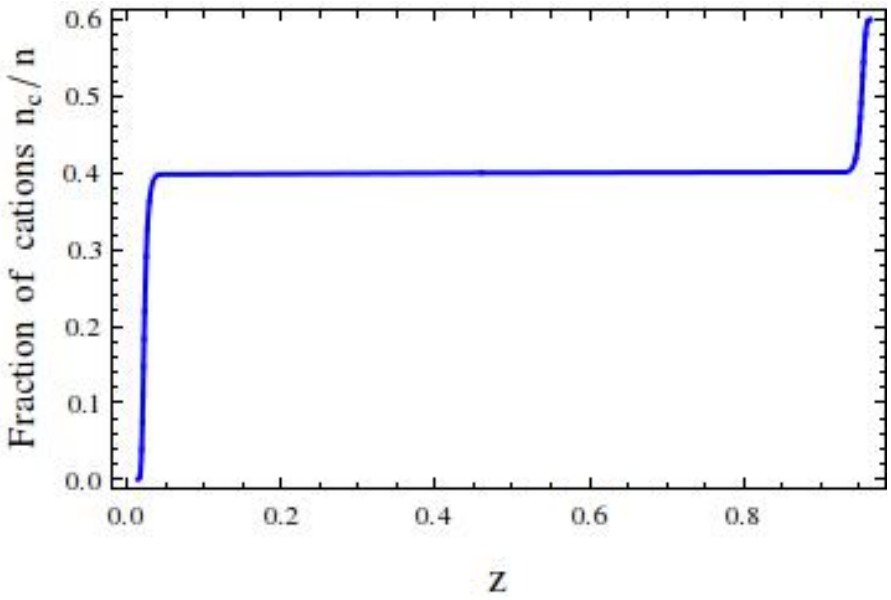
Semi-analytical solution:

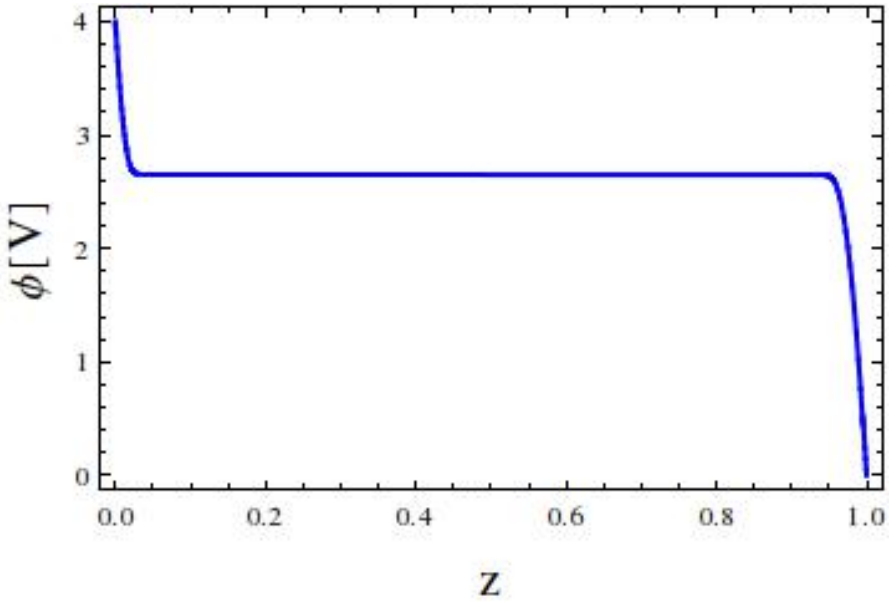
$$z = \int_{n_0^F}^{n_1^F} \frac{F(\tilde{n}^F)d\tilde{n}^F}{\sqrt{\epsilon + 2/\lambda^2(H(0) - H(\tilde{n}^F))}}$$

μ_α ... chemical potential
n^F ... charge density
ϕ, p ... el. potential and pressure
z_α, m_α ... particle charge and mass
a, λ, ϵ ... parameters
$F(n^F), H(n^F)$ ... coefficient functions

DLR

Results (I): Cation and potential distributions





- Potential variation on same length scale as density variation
- $Li_{1+x+3z}Al_x(Ti,Ge)_{2-x}Si_{3z}P_{3-z}O_{12}$ [1] at $4.0V$: space charge layers $\sim 400 - 600$ nm

Classical PNP-theory:
LDL $\sim 1 - 10$ Å

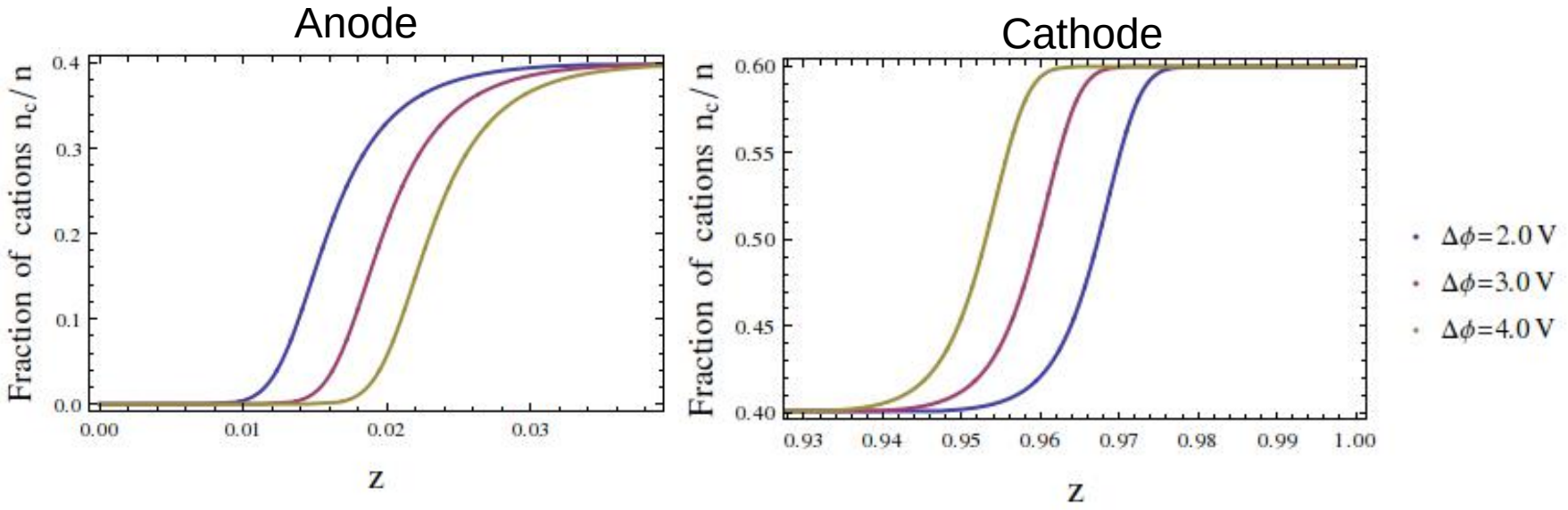
$\Leftrightarrow$

Experiments by Yamamoto et al [2]:
LDL $\sim 1\mu$m (for $Li_{1+x+y}Al_yTi_{2-y}Si_xP_{3-x}O_{12}$)

[1] Courtesy Y. Inda, Ohara Inc. [2] K. Yamamoto et al, *Angew. Chem. Int. Ed.* **49**, 4414-4417 (2010)

DLR

Results (II): different electrode potentials

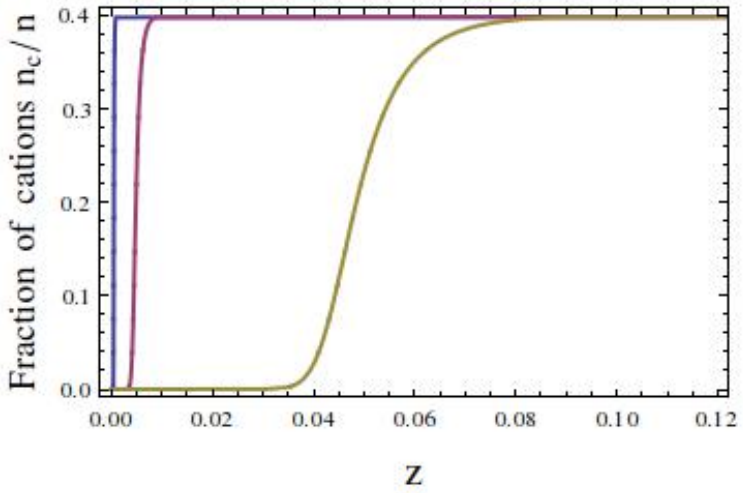


$Li_{1+x+3z}Al_x(Ti,Ge)_{2-x}Si_{3z}P_{3-z}O_{12}$:

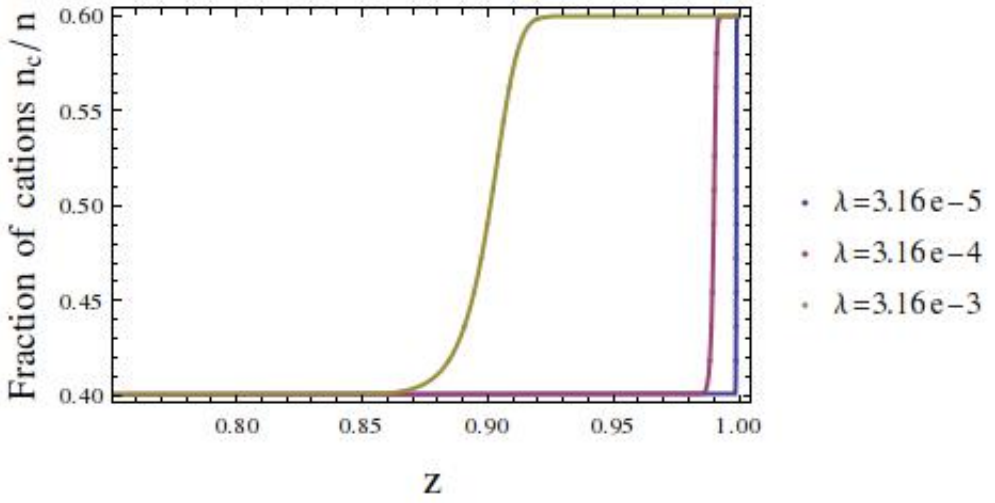
- electrode potentials were varied between $\Delta\phi = 2.0V, 3.0V, 4.0V$
- Changes of the order of a factor ~2 in a real battery possible

Results (III): different material parameters (varying λ)

Anode



Cathode



- $\lambda = \sqrt{\frac{k_B T\, \epsilon_0 (1+\chi)}{n_R e_0^2 L_R^2}} \sim \frac{\text{Debye length}}{\text{system length}}$
- λ mainly determined by dielectric properties of the material (χ)
  (χ can differ by orders of magnitude! $La_{0.5}Li_{0.5}TiO_3$: $\chi \sim 10^5$, $LiPO_3$: $\chi \sim 10^2$)
- LDL $\sim 10\,\lambda$ (in a fluid: $\sim \lambda$!)

⇨ Dielectric properties are main influencing factor for LDL!

Conclusions

- A thermodynamically consistent model for ion transport in a solid electrolyte was derived
- Predictions for the width of the LDL are roughly of the same order of magnitude as experimental findings for similar parameters
- Main influencing factor are the dielectric properties,
  external potential difference and other factors plays only minor role

Outlook

- Numerical implementation for solution of full time-dependent problem under way
- Possibility to “tailor” materials regarding dielectric properties

Thank you!

DLR