FROM RESEARCH TO INDUSTRY

TWO-DIMENSIONAL MODEL OF A LITHIUM IRON-PHOSPHATE SINGLE PARTICLE

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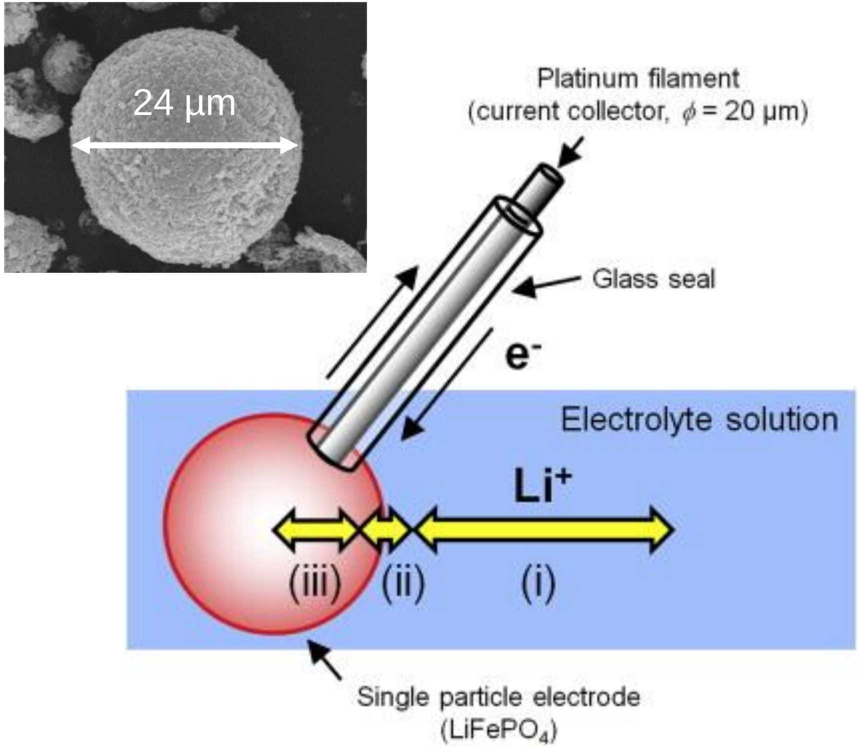
- **CONTEXT**

  - Single particle technique employed by Dokko *et al.** to investigate the intrinsic electrochemical properties of $LiFePO_4$
  - Spherical secondary single particle of 24 µm composed of a plurality of primary particles with diameter ranging from 100 to 200 nm
  - Application of the regular solution model for homogeneous free energy density proposed by Bai *et al.*** to address phase-separation dynamics under the experimentally relevant conditions of constant applied current

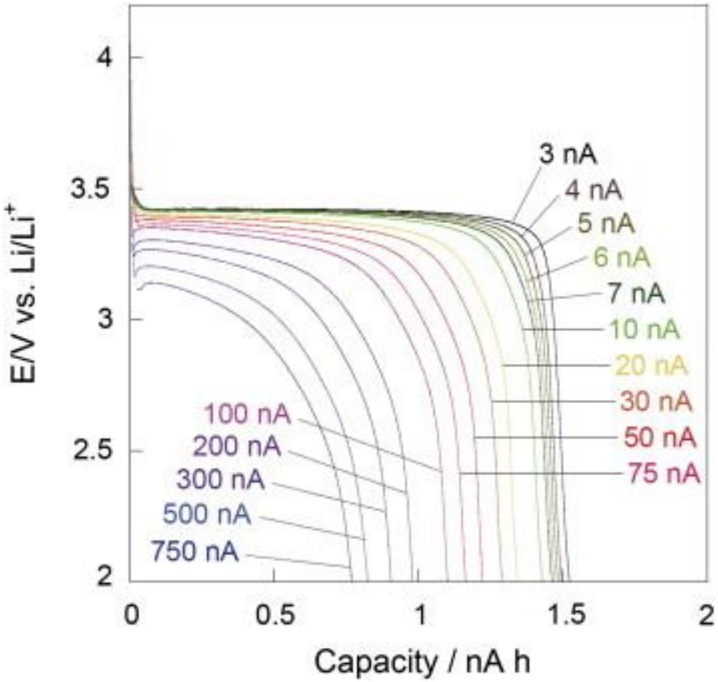


from H. Munakata *et al. J. Power Sources* **217** (2012) 444

* K. Dokko *et al. J. Power Sources* **189** (2009) 783
** P. Bai *et al. Nano Lett.* **11** (2011) 4890

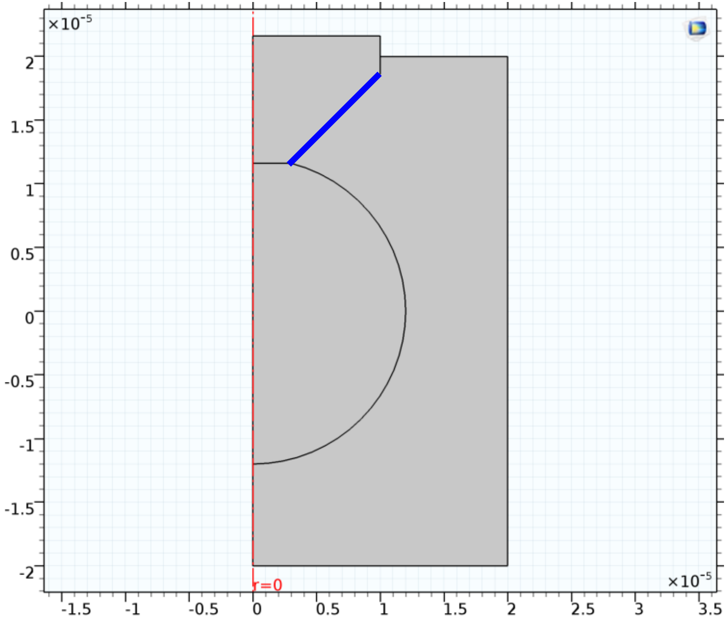
- **EXPERIMENTAL DATA**

  - Discharge capacity of the secondary particle at low rate (2C): 1.5 nAh at 30°C
  - The particle was discharged galvanostatically at a constant current ranging from 3 nA (2C) to 750 nA (500C) down to 2 V vs. Li/Li+
  - Recharge was performed at 3 nA up to 4.2 V
  - Even at 500C, more than 50 % of the full capacity was maintained

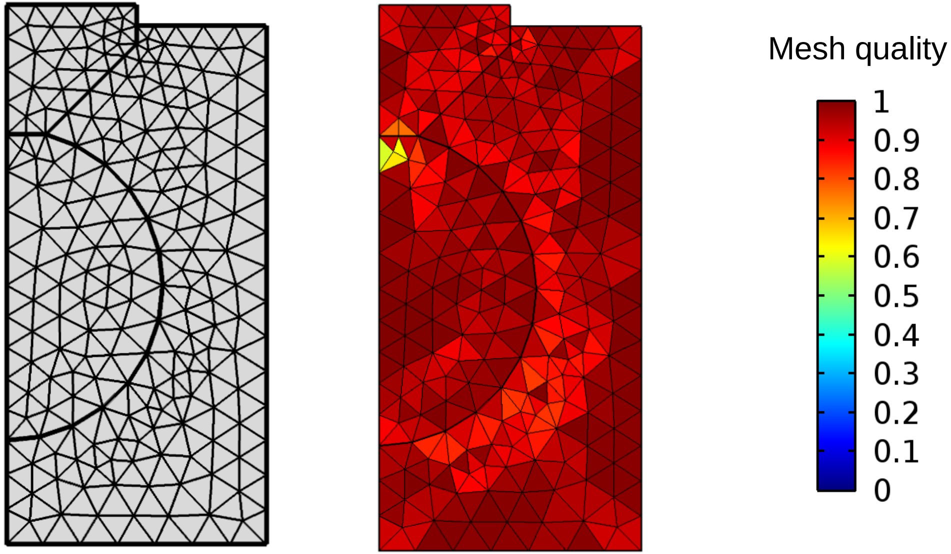


Picture from H. Munakata *et al.* *J. Power Sources* **217** (2012) 444

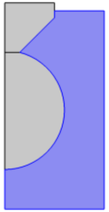
- **GEOMETRY**
  - 2D axisymmetric model



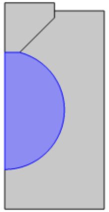
- **MESH**
  - Physics-controlled mesh (size: normal)
  - Use of a **chamfer** to improve the mesh



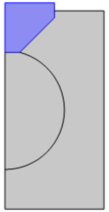
- **MATERIALS**
  - Electrolyte (mix 1:1 in volume)
    - Ethylene Carbonate (EC)
    - Propylene Carbonate (PC)
    - Lithium Perchlorate (1M $LiClO_4$)



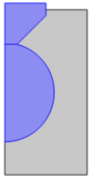
  - Iron phosphate ($FePO_4$)
    - Accessible $FePO_4$ represents only 34 % of the particle volume



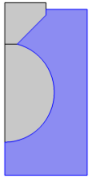
  - Current collector (Pt)



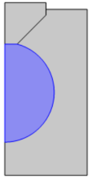
- **PHYSICS**
  - Electric currents (Ohm's law in solids)



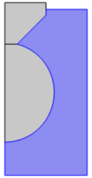
  - Electric currents (Ohm's law in liquids)



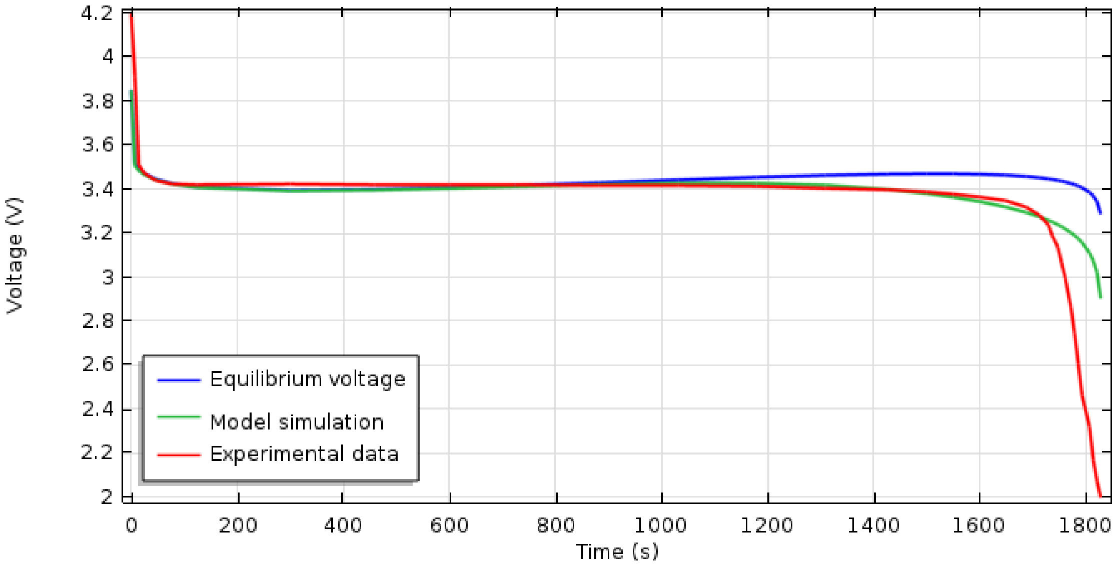
  - Transport of diluted species (Fick's law for intercalated Li)



  - Transport of diluted species (Fick's law for Li^+ ion)



- **PARTICLE VOLTAGE CURVE IN DISCHARGE AT THE LOWEST RATE (2C)**



- The OCV* is derived from the homogeneous chemical potential

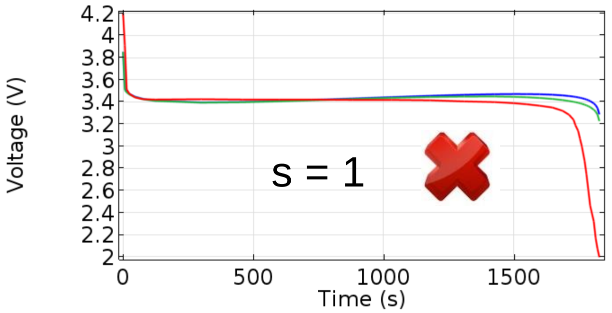
$$\mu_{hom} = \Omega\,(1-2x_1) + 2k_BT\ln\left(\frac{x_1}{1-x_1}\right)$$

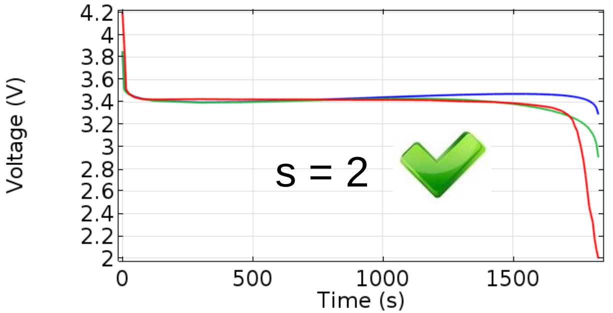
with Ω = 0.183 eV in agreement with the $LiFePO_4$ phase diagram**

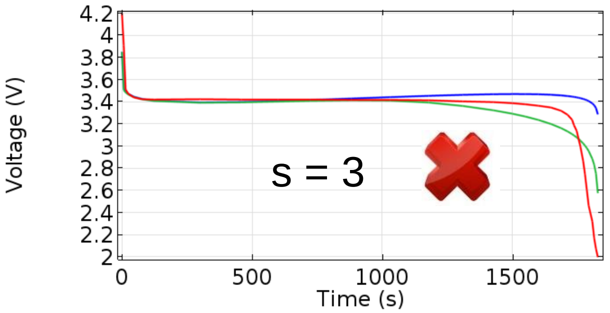
- The knee of the particle voltage curve is obtained by considering the apparent volumetric capacity of the $LiFePO_4$ particle: 34 % of the theoretical volumetric capacity

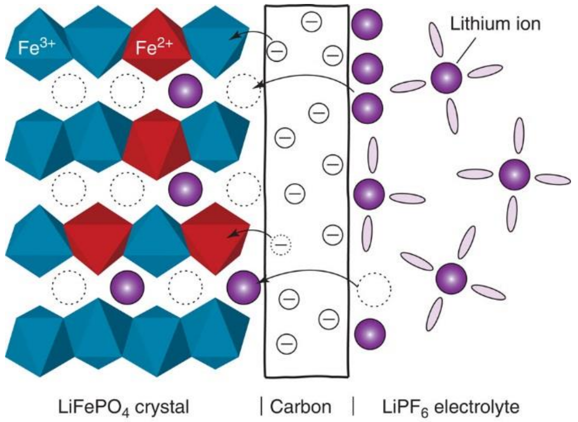
* OCV = Open Circuit Voltage
** A. Yamada *et al. Electrochem. Solid-State Lett.* **8** (2005) A409

- **IMPACT OF THE TRANSITION STATE (TS) MODEL ON THE VOLTAGE CURVE AT 2C**









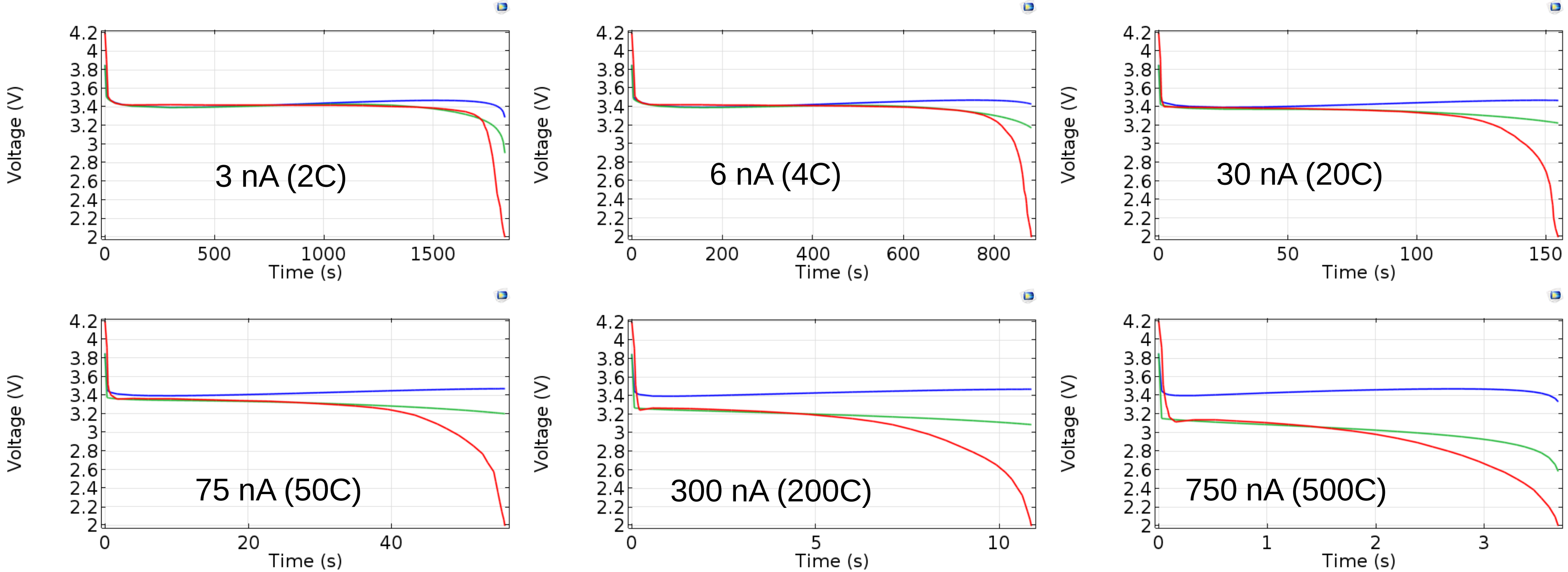
- Reaction rate corresponds to a certain choice of model for the activity coefficient of the TS:

$$\mu_{\ddagger}^{ex} = k_B T \ln \gamma_A = -s k_B T \ln(1 - x_1) + E_{\ddagger}$$

- The transition state may exclude more than one site if we take into account the solvation shell*

* M. Bazant *Acc. Chem. Res.* **46** (5) (2013) 1144
Picture from Bai et al. *Nat. Commun.* **5** (2014) 3585

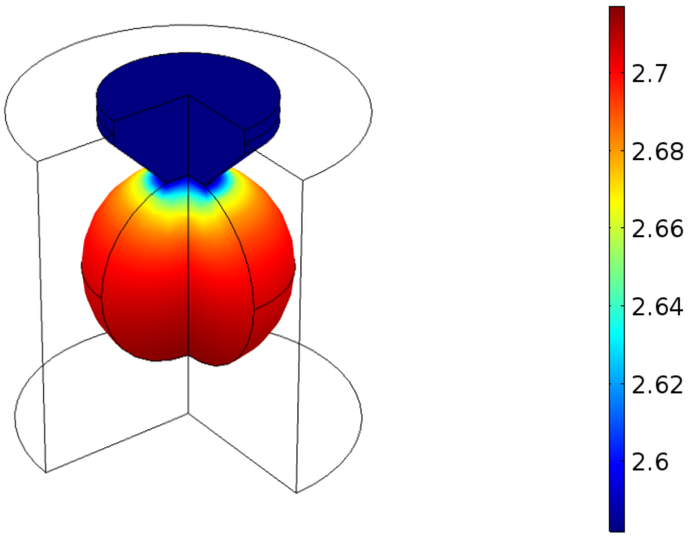
- **PARTICLE VOLTAGE CURVES IN DISCHARGE AT VARIOUS RATES**



- Adjustable parameters: exchange current density, diffusion coefficient in solid phase, material resistance

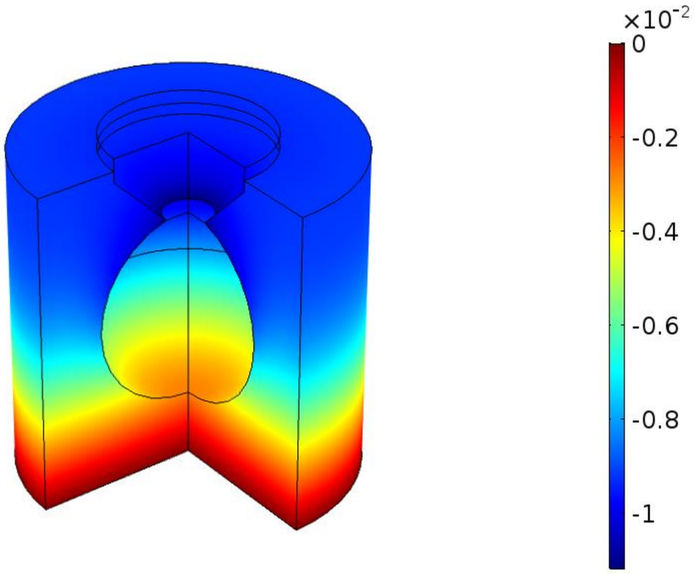
- **LOCAL POTENTIALS AT THE END OF DISCHARGE AT THE HIGHEST RATE (500C)**

  - Potential in the solid phases (V)



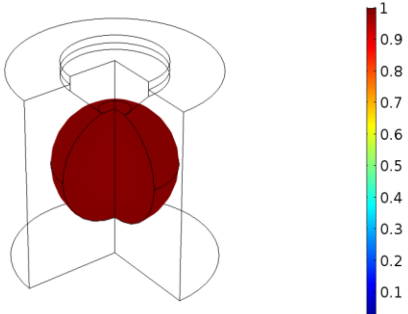
  - Conductivity of carbon coated iron phosphate set to 5 mS/cm to fit the experimental voltage

  - Potential in the liquid phase

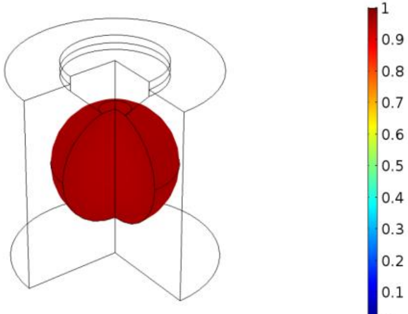


  - Conductivity of electrolyte assumed to be equal to the one of lithium hexafluorophosphate

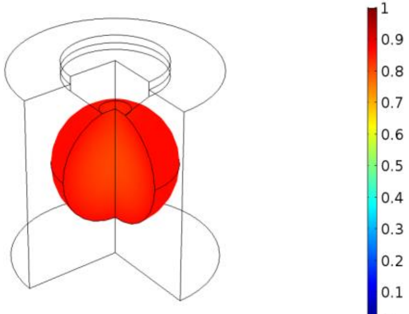
- **LOCAL FILLING FRACTION OF THE PARTICLE AT THE END OF DISCHARGE**



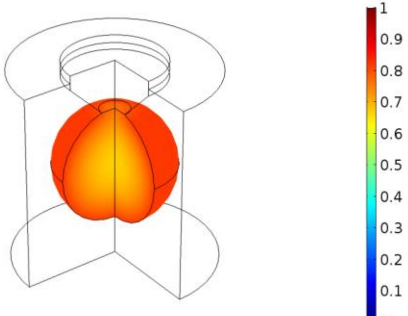
3 nA (2C)



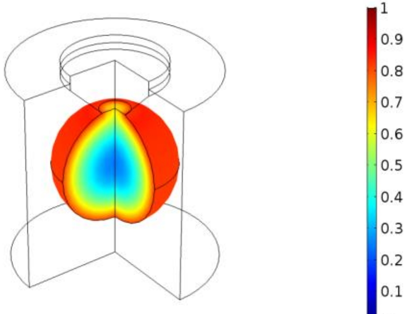
6 nA (4C)



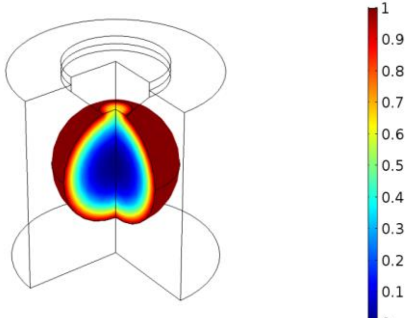
30 nA (20C)



75 nA (50C)



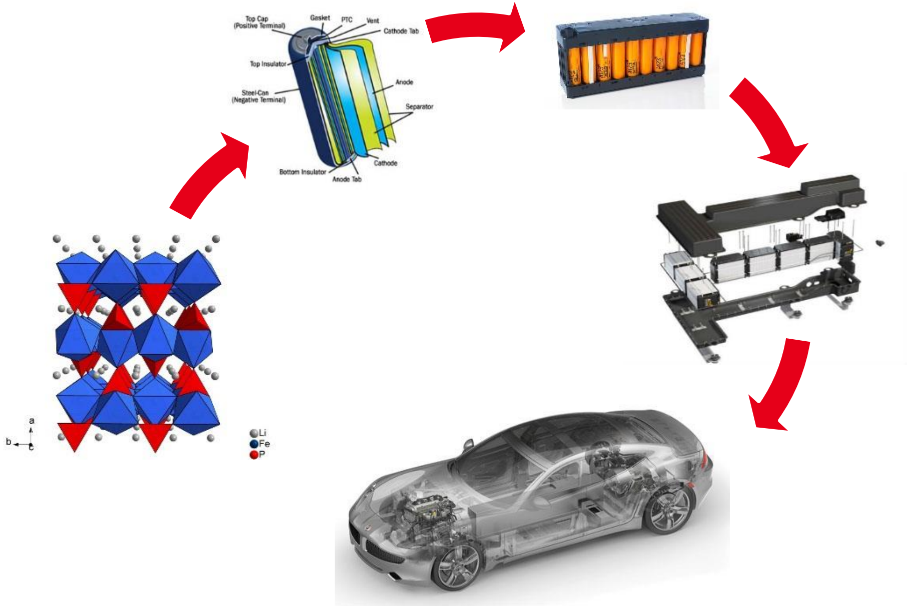
300 nA (200C)



750 nA (500C)

CONCLUSIONS AND PERSPECTIVES

- The 2D axisymmetric model of the $LiFePO_4$ secondary particle was particularly suitable for evaluating the pertinence of the regular solution model (voltage curve simulations)
- Fast computation time: 15 s for full discharge
- Revolution 2D provides nice cut views of the local particle filling clearly showing a limitation due to Li diffusion in the solid phase at high rate of discharge
- Phase-field model of such a particle could be done successfully with Comsol in a next study involving a better model for both the chemical potential and the transition state



Thank you for your attention!

Do you have any questions?

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