DE LA RECHERCHE À L'INDUSTRIE

INSTITUT NATIONAL DE L'ENERGIE SOLAIRE

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF A $LiFePO_4/Li$ HALF-CELL

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SUMMARY

INTRODUCTION

ABOUT THE SPEAKER

- ☐ Mikael Cugnet is currently a project manager specialist in Lead-acid and Lithium-ion batteries modeling and diagnostic at the French National Institute for Solar Energy (INES), mainly operated by the Atomic and Alternative Energy Commission (CEA)

ABOUT THE TALK

- ☐ Hybrid and electric vehicles (HEV & EV) need a reliable and safe battery on board
- ☐ Battery Management Systems (BMS) are designed to protect the battery, to predict the vehicle range, and to update the prediction depending on the driving conditions
- ☐ Battery models used in BMS are often derived from Electrochemical Impedance Spectroscopy (EIS), which is a widely used technique to characterize batteries
- ☐ However, there is a gap between the physical equations characterizing the batteries and the meaning of the electrical component used in the equivalent circuit models

Batteries are intrinsically non linear …
But people still want to model them with linear model because it’s easier

CONTEXT AND MODEL DESCRIPTION

DESIGN OF A $LiFePO_4/Li$ COIN CELL (HALF-CELL)

- Open and separate the constitutive materials of the commercial cell
- Scrape off the selected active material from one face of its current collector
- Punch the electrode with a die-cutter
- Clean the electrode with DMC[1]
- Dry the electrode
- Assemble the half-cell with a separator, a lithium foil, and a proper electrolyte

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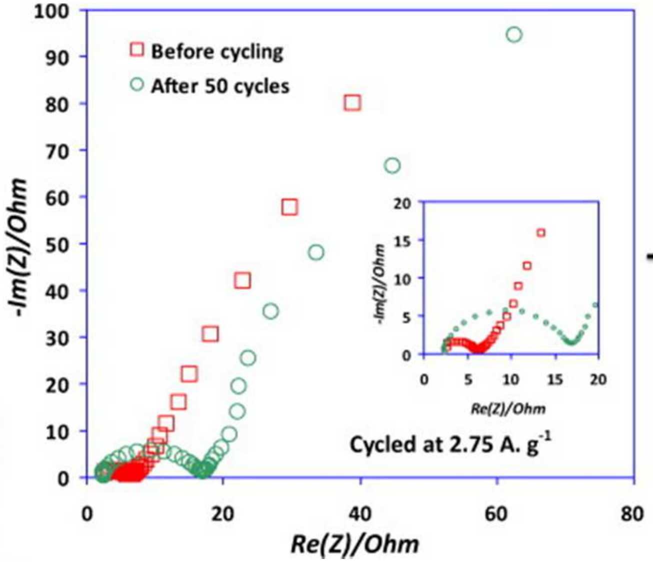
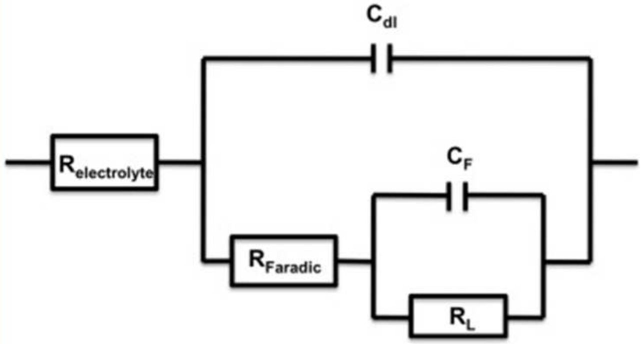
[1] DMC : Dimethyl carbonate ($C_3H_6O_3$) is an organic solvent

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

- EIS is a commonly used technique to characterize various battery technologies
- The impedance spectrum is converted into equivalent circuit models
- Equivalent circuit models (ECM) are then integrated into embedded battery management systems to ensure a safe and reliable operation of electric vehicles

BioLogic® VMP3® battery tester

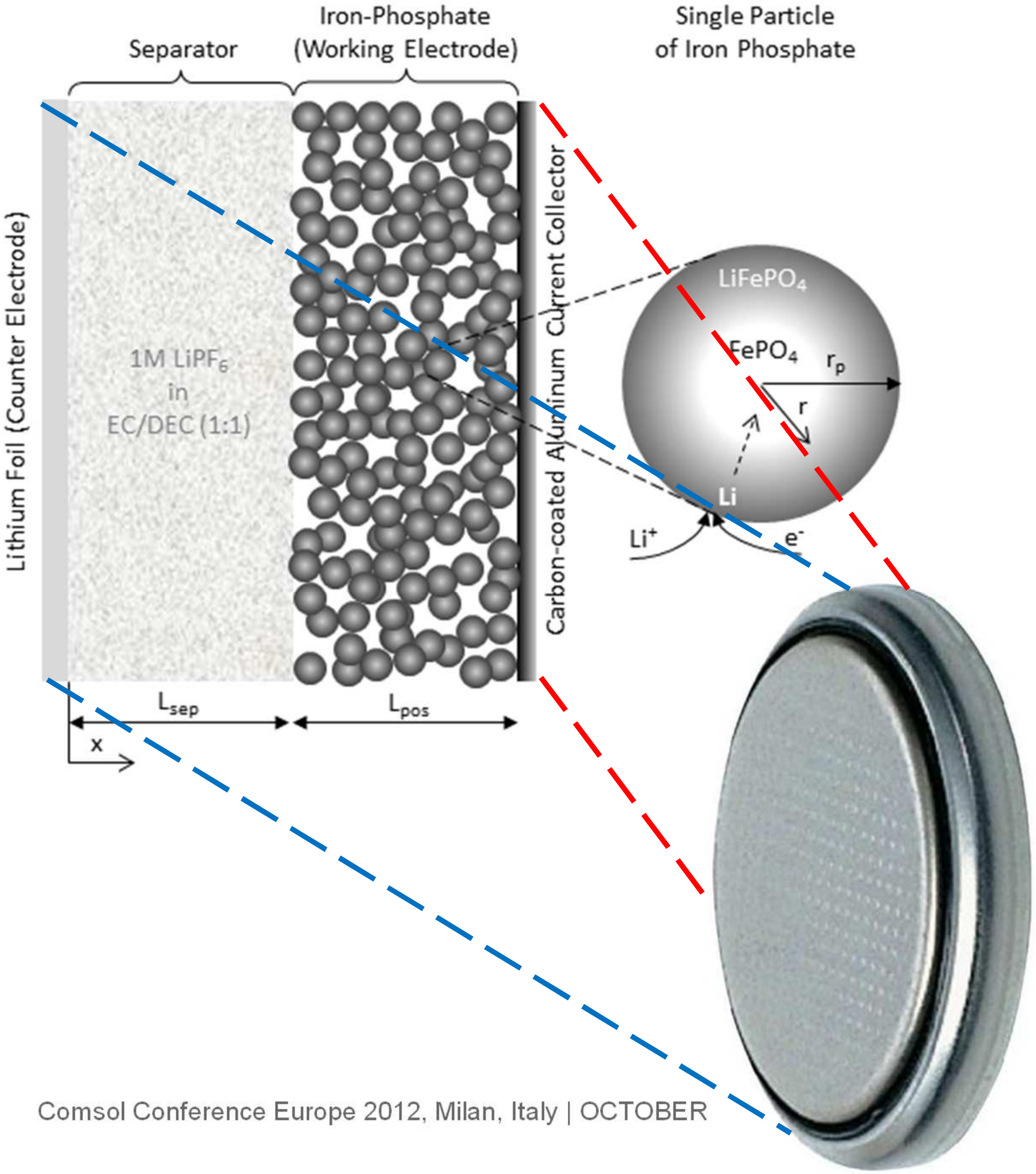




EIS and ECM from Tummala, Guduru and Mohanty, *J. Power Sources,* **209** (2012) 44

CAN COMSOL® HELP US MODEL THE CELL ?

- Yes, either you use the existing Li-ion battery model available in the “Batteries & Fuel Cells Module”
- Or, you can also develop your own from scratch depending on how familiar you are with the equations
- The button cell is composed of two models with different scales
- The macroscopic model is made up of two domains (separator and working electrode)
- The microscopic model is a spherical particle of iron phosphate (the main component of the working electrode active material) = 1 domain



FEATURES OF THE MULTIPHYSICAL MODEL

MACROSCOPIC MODEL EQUATIONS

- **Ohm's law** (current conservation) for the electronically conducting solid phase

$$\nabla\cdot\left(-\frac{\kappa_1^{eff}}{L_i}\nabla\phi_1\right)=-i_{loc}S_iL_i$$

- **Ohm's law** (current conservation) for the ionically conducting liquid phase

$$\nabla\cdot\left(-\frac{\kappa_2^{eff}}{L_i}\left(\nabla\phi_2-\frac{K_{junc}}{c_2}\nabla c_2\right)\right)=i_{loc}S_iL_i$$

- **Material balance** on the salt LiPF$_6$ dissolved in the liquid phase

$$\varepsilon_{2,i}L_i\frac{\partial c_2}{\partial t}+\nabla\cdot\left(-\frac{D_2^{eff}}{L_i}\nabla c_2\right)=i_{loc}S_iL_i\frac{1-t_+}{F}$$

MICROSCOPIC MODEL EQUATION

- **Fick's law** in spherical coordinates characterizing solid-state diffusion of the reduced-lithium species in the particle

$$y^2r_p\frac{\partial c_1}{\partial t}+\nabla\cdot\left(-\mathbf{D}_1\nabla c_1\right)=0$$

Butler-Volmer equation for kinetics

$$i_{loc}=k_{pos}(c_1^{\max}-c_1)^{\alpha_{pos}}c_1^{1-\alpha_{pos}}c_2^{\alpha_{pos}}$$
$$\times\left[\exp\left(\frac{\alpha_{pos}F}{RT}(\phi_1-\phi_2-E_{pos})\right)\right.$$
$$\left.-\exp\left(-\frac{(1-\alpha_{pos})F}{RT}(\phi_1-\phi_2-E_{pos})\right)\right]$$
$$+C_{dl,pos}\left(\frac{\partial\phi_1}{\partial t}-\frac{\partial\phi_2}{\partial t}\right)$$

Electrical double layer

MODEL IMPROVED WITH LiveLink™ for MATLAB®

PREPROCESSING DATA

- ❑ EIS data are extracted from their original measurement files and converted into a suitable Matlab format

MODEL CONVERSION

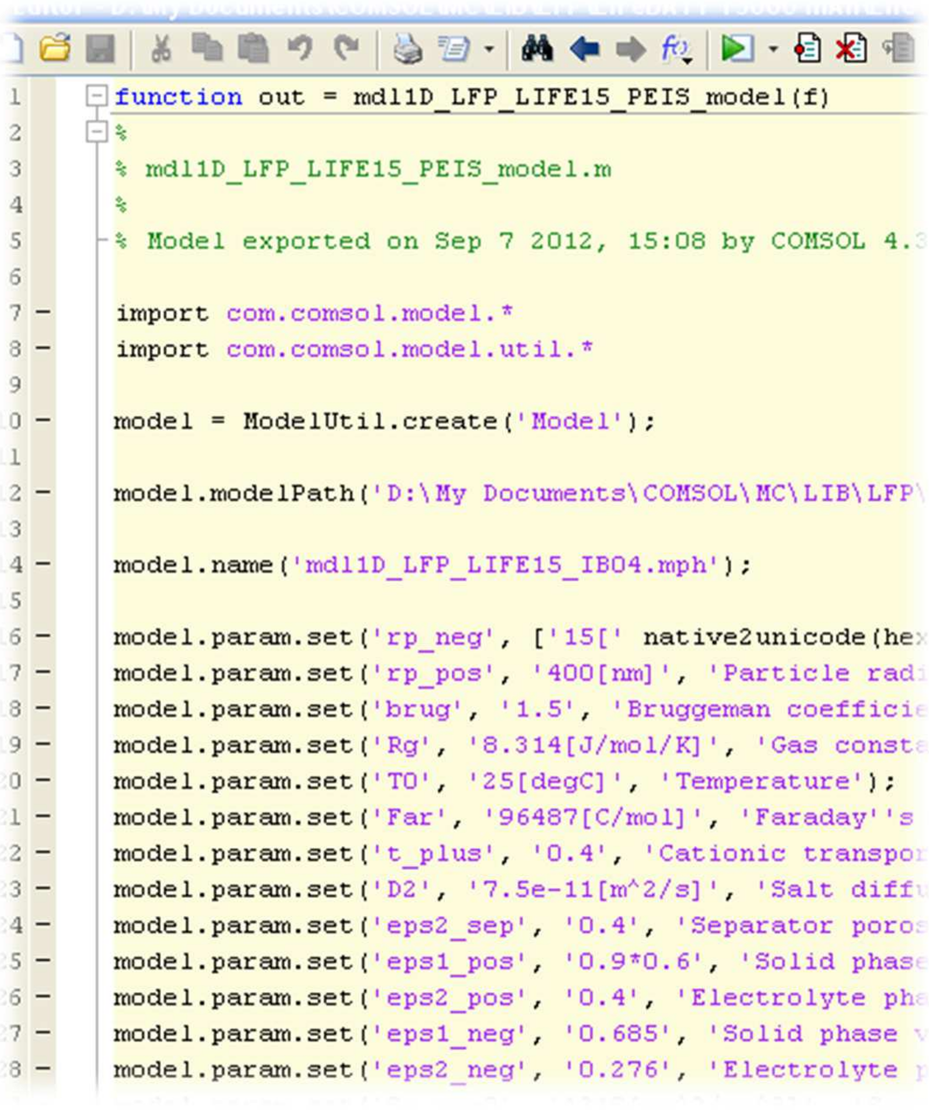
- ❑ The half-cell model is converted into a user-defined function whose argument is the frequency of the voltage input

PARAMETER OPTIMIZATION

- ❑ Model parameters are optimized with a chosen function from the “Optimization toolbox” provided by Matlab

POSTPROCESSING DATA

- ❑ Model results are displayed as well as the sensitivity analysis of the model output to the key parameters



```
function out = mdl1D_LFP_LIFE15_PEIS_model(f)
%
% mdl1D_LFP_LIFE15_PEIS_model.m
%
% Model exported on Sep 7 2012, 15:08 by COMSOL 4.

import com.comsol.model.*
import com.comsol.model.util.*

model = ModelUtil.create('Model');

model.modelPath('D:\My Documents\COMSOL\MC\LIB\LFP\

model.name('mdl1D_LFP_LIFE15_IB04.mph');

model.param.set('rp_neg', ['15[' native2unicode(he
model.param.set('rp_pos', '400[nm]', 'Particle rad
model.param.set('brug', '1.5', 'Bruggeman coeffici
model.param.set('Rg', '8.314[J/mol/K]', 'Gas const
model.param.set('T0', '25[degC]', 'Temperature');
model.param.set('Far', '96487[C/mol]', 'Faraday''s
model.param.set('t_plus', '0.4', 'Cationic transpo
model.param.set('D2', '7.5e-11[m^2/s]', 'Salt diff
model.param.set('eps2_sep', '0.4', 'Separator poro
model.param.set('eps1_pos', '0.9*0.6', 'Solid phas
model.param.set('eps2_pos', '0.4', 'Electrolyte ph
model.param.set('eps1_neg', '0.685', 'Solid phase
model.param.set('eps2_neg', '0.276', 'Electrolyte
```

RESULTS AND ANALYSIS

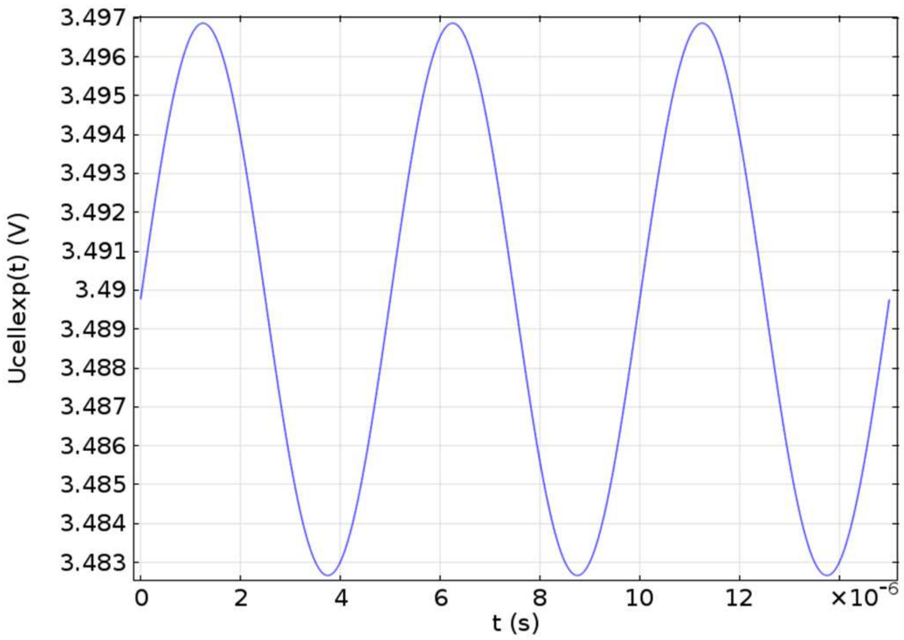
MODEL INPUTS/OUTPUTS – Example at f = 200 kHz

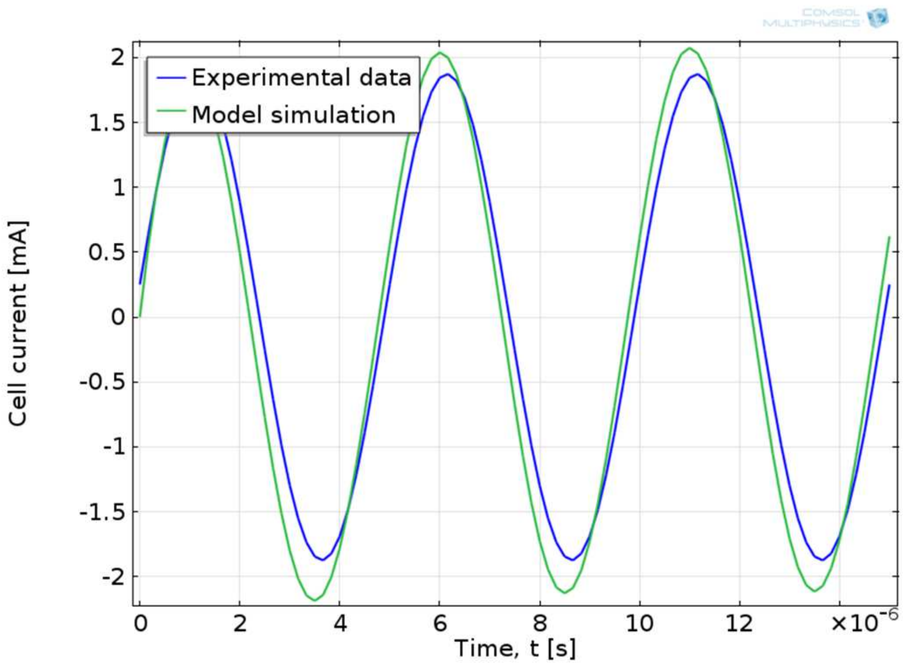
MODEL INPUTS

- **Cell state of charge (SOC):** 100 %
- **Magnitude of the sinusoidal excitation voltage:** 7.1 mV around the equilibrium potential (3.490 V)
- **Frequency of the sinusoidal excitation voltage:** from 10 mHz to 200 kHz (3 periods per frequency)

MODEL OUTPUTS

- **Cell current** in response to the voltage
- **Potentials** in electronically conducting solid phase and ionically conducting liquid phase
- **Concentrations of Lithium ions (Li^+)** in solid (microscopic model) and liquid (macroscopic model) phases





IMPEDANCE SPECTRUM from 10 mHz to 200 kHz

EXPERIMENTAL DATA

- ❑ Application of the Potentiostatic EIS (PEIS) technique of the BioLogic® VMP3® battery tester to the half-cell
- ❑ Impedance values directly calculated by the BioLogic® EC-lab® software

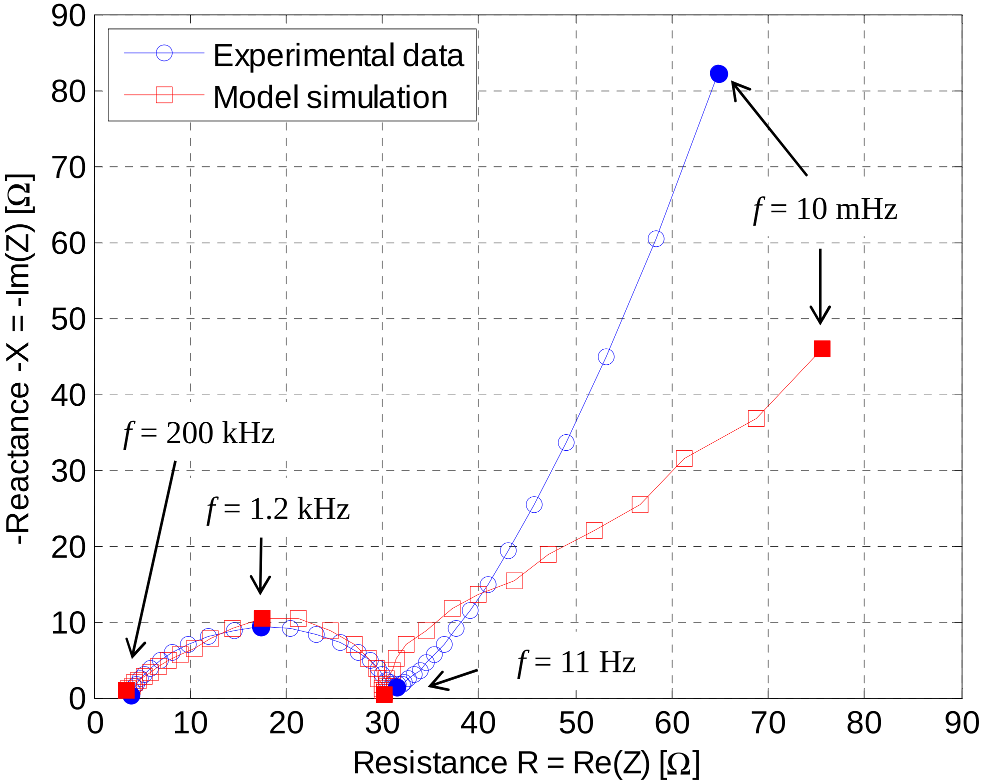
MODEL SIMULATION

- ❑ Selection of the third period of the sinusoidal current response to achieve steady-state
- ❑ Calculation of the impedance:

$$U = |U| e^{j(\omega t + \varphi_U)}$$

$$I = |I| e^{j(\omega t + \varphi_I)}$$

$$\boxed{Z = R + jX = |Z| e^{j(\omega t + \theta)} = \frac{|U|}{|I|} e^{j(\omega t + \varphi_U - \varphi_I)}}$$



The comparison of our model simulation with experimental data shows quite a good fit !

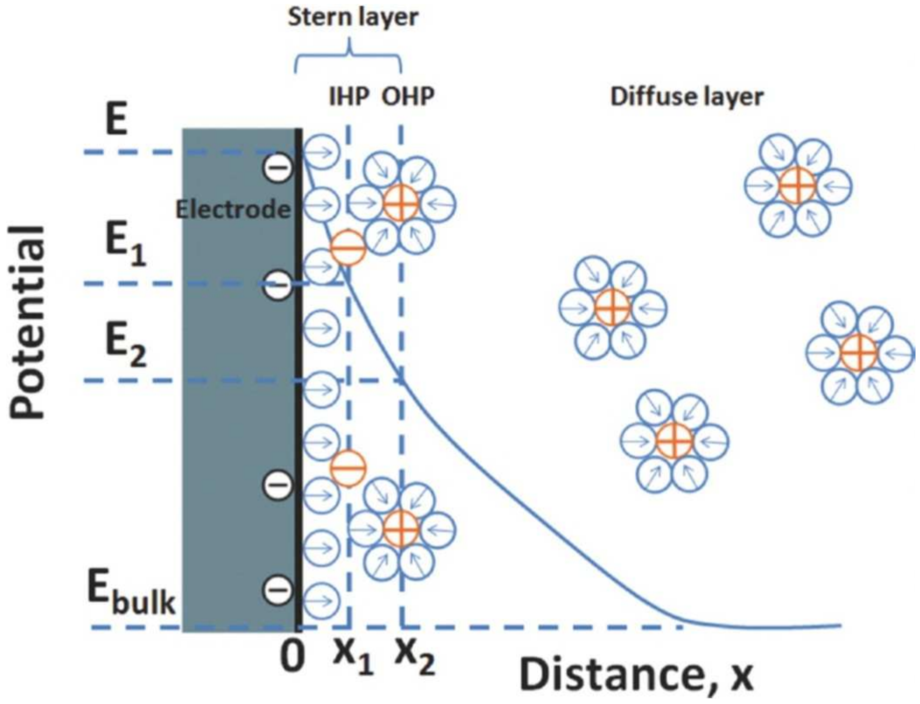
NEED FOR AN ELECTRICAL DOUBLE LAYER (EDL)

- In all the Li-ion battery models published in the literature, the current density localized at the particle-surface/liquid interface i_{loc} includes only the Butler-Volmer equation for the electrode kinetics

Butler-Volmer equation for kinetics

$$
\begin{aligned}
i_{loc} = k_{pos}\,(c_1^{\max} - c_1)^{\alpha_{pos}}\, c_1^{1-\alpha_{pos}}\, c_2^{\alpha_{pos}} \\
\times \left[\exp\left(\frac{\alpha_{pos} F}{RT} (\phi_1 - \phi_2 - E_{pos}) \right) \right. \\
\left. - \exp\left(-\frac{(1-\alpha_{pos}) F}{RT} (\phi_1 - \phi_2 - E_{pos}) \right) \right] \\
+ C_{dl,pos} \left(\frac{\partial \phi_1}{\partial t} - \frac{\partial \phi_2}{\partial t} \right)
\end{aligned}
$$

Electrical double layer



- In most of the cases, battery models are used to simulate full discharges and charges, during which EDL plays a minor role
- In this work, the EDL is taken into account, because it is known to have an impact on the cell behavior in high frequencies

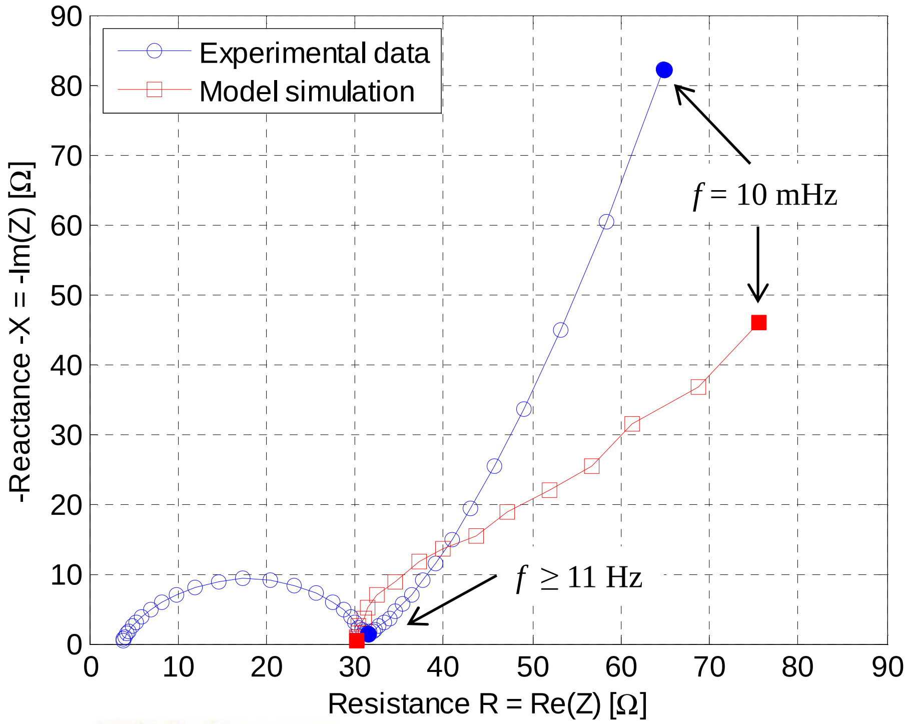
IMPACT OF THE ELECTRICAL DOUBLE LAYER (EDL)

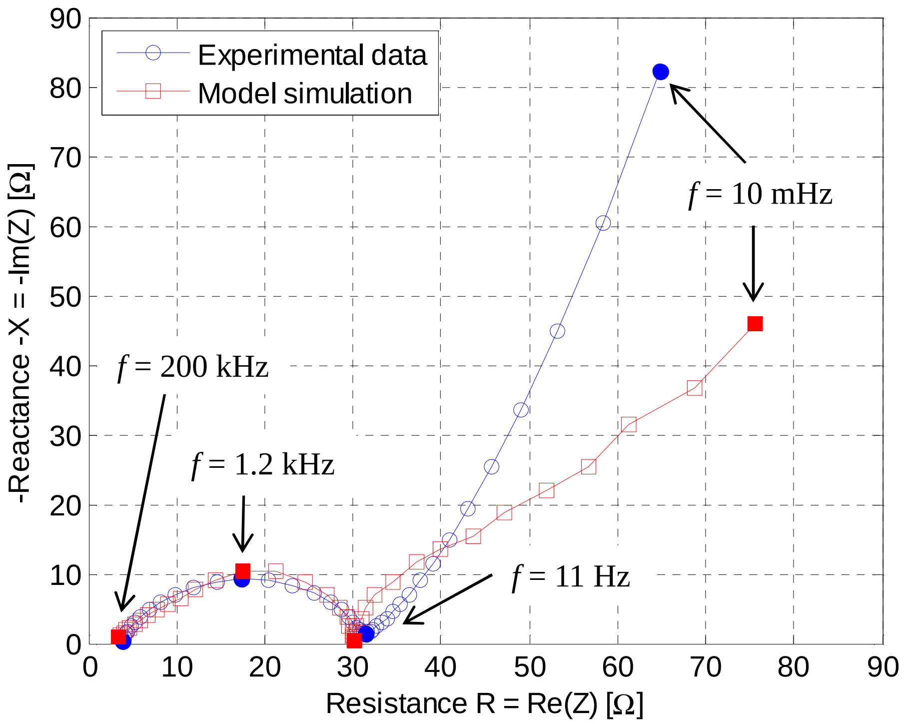
IMPEDANCE WITHOUT EDL

- ☐ The semi-circle characterizing the charge transfer does not appear as in the experimental data despite the use of the Butler-Volmer equation for kinetics

IMPEDANCE WITH EDL

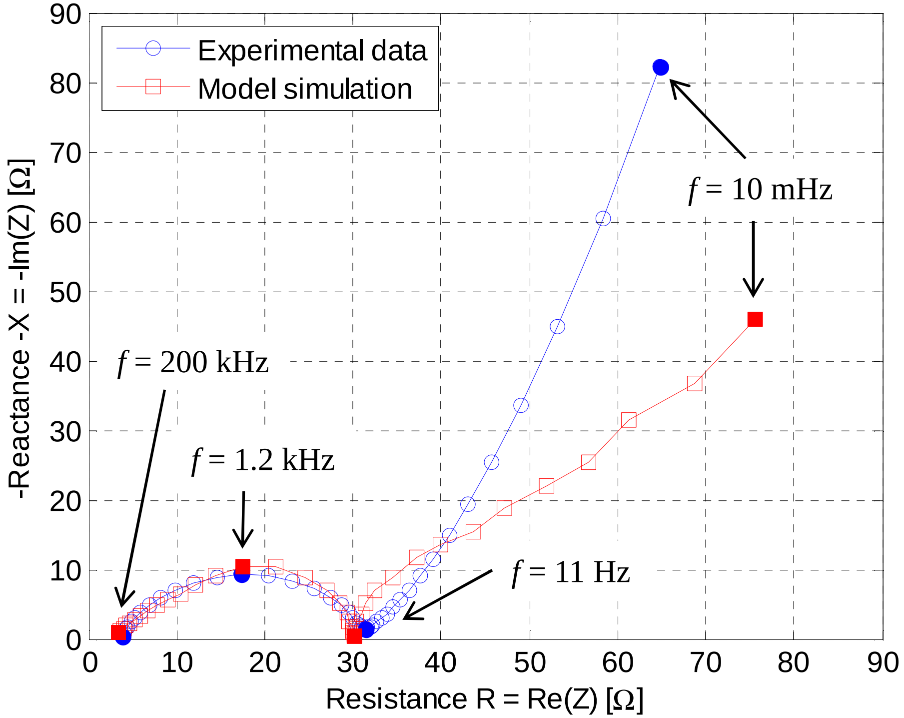
- ☐ Taking into account the EDL is necessary to simulate the real behavior of the half-cell on the frequencies ranging from 10 Hz to 200 kHz





OPTIMIZATION OF THE KEY PARAMETERS

- **At 200 kHz,** the half-cell is almost purely resistive. Since the positive electrode is composed of iron phosphate, the key parameter is the electronic conductivity of the positive active material. The optimized value of κ_1 is **38 mS.m^{-1}**.
- **At 11 Hz,** the half-cell is again almost purely resistive. The key parameter is the charge transfer resistance defined by the rate coefficient. Assuming a transfer coefficient α = 0.5, the optimized value of k_{pos} is **200 nA.m$^{2.5}$.mol$^{-1.5}$**.
- **At 1.2 kHz,** the half-cell impedance phase is very sensitive to the specific double layer capacitance of the positive active material. A good match between experience and simulation is achieved for $C_{dl,pos}$ = **200 µF.m^{-2}**.
- **At low frequencies,** the half-cell impedance is mainly defined by the diffusivity of lithium ions in the positive active material, which leads to an optimized value of the diffusion coefficient $D_{1,pos}$ equals to **50 nm^2.s^{-1}**.



CONCLUSIONS AND PERSPECTIVES

CONCLUSIONS & PERSPECTIVES

- This study demonstrates that a multiphysical model of a $LiFePO_4$/Li half-cell can be applied to simulate the impedance from an EIS at 100 % SOC
- However, it implies that the double layer capacitance has to be taken into account, since it is responsible of the semi-circle in the impedance spectrum
- A 15 min simulation allows getting a complete spectrum of the half-cell impedance from 10 mHz to 200 kHz
- The methodology used to adjust the four key parameters in order to fit the experimental data is described
- This work is still in progress to extend the model capability to other SOC values and various temperatures, and to try other excitation voltage magnitudes

Thank you for your attention!

Do you have any questions?

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