

Electrochemical Impedance Spectroscopy of a LiFePO₄/Li Half-Cell

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Abstract: This study demonstrates that a multiphysical model of a LiFePO₄/Li half-cell can be applied to simulate the impedance results from an EIS. 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 0.1 to 200 kHz. The methodology used to adjust the three key parameters used to fit the experimental data is described. However, this work is still in progress, so we do not know exactly yet what is actually responsible of the slope observed at lower frequencies. There might be a missing phenomenon somewhere in our model or some parameter values still to be adjusted.

Keywords: Lithium-ion batteries, LFP/Li coin cell, Electrochemical Impedance Spectroscopy.

1. Introduction

Li-ion battery models designed with Comsol Multiphysics are usually intended for simulating the battery behavior during a period of time going from few minutes to many hours. However, most of Li-ion battery models designed today are based on equivalent circuit models. These models are composed of electrical components (resistances, inductances, capacitances...) whose values are identified when the battery is at equilibrium by an experimental method called "Electrochemical Impedance Spectroscopy" (EIS). Therefore, we tried to simulate a model of a LiFePO₄/Li half-cell, for which we had EIS experimental data, in order to see if our model was also able to simulate the battery behavior for frequencies going from 100 mHz to 200 kHz.

2. Model of the LiFePO₄/Li half-cell

A schematic of the LiFePO₄/Li half-cell studied in this work is presented in Fig. 1. The lithium foil used as the counter electrode is also the reference electrode.

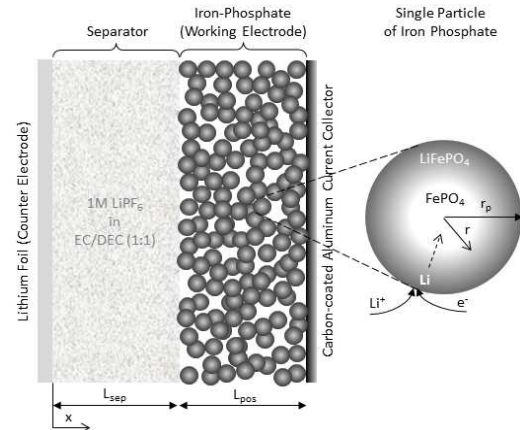
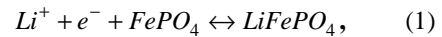
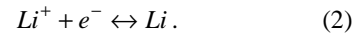


Figure 1. Schematic of the LiFePO₄/Li half-cell

The model used to simulate the half-cell is based on the most recent publications [1-5]. The reaction (1) occurs at the working electrode (iron phosphate)



and the reaction (2) occurs at the counter electrode (lithium foil)



Our 1D macroscopic model of the half-cell is made up of two domains. The first one is the separator and the second one is the positive electrode (iron phosphate). The negative electrode (lithium foil) is the first boundary on the left. The second boundary is the interface between the separator and the positive electrode. The third boundary is the interface between the positive electrode and the carbon-coated aluminum current collector.

Our 1D microscopic model of the iron phosphate spherical secondary particle is made up of one domain and two boundaries, respectively for the surface and the center of the particle.

3. Governing equations

The model is composed of four equations and two dimensions depending of the scale considered. The dimension x represents the distance to the lithium foil and the dimension r the distance from the center of the particle.

The first equation is the Ohm's law (current conservation) for the electronically conducting solid phase (denoted subscript 1)

$$\nabla \cdot \left(-\frac{\kappa_1^{eff}}{L_i} \nabla \phi_1 \right) = -i_{loc} S_i L_i, \quad (3)$$

where the differentiation operator is with respect to a dimensionless distance variable x/L_i .

The second equation is the Ohm's law (current conservation) for the ionically conducting liquid phase (denoted by subscript 2)

$$\nabla \cdot \left(-\frac{\kappa_2^{eff}}{L_i} \left(\nabla \phi_2 - \frac{K_{junc}}{c_2} \nabla c_2 \right) \right) = i_{loc} S_i L_i. \quad (4)$$

The third equation is the material balance on the salt LiPF_6 dissolved in the liquid phase

$$\varepsilon_{2,i} L_i \frac{\partial c_2}{\partial t} + \nabla \cdot \left(-\frac{D_2^{eff}}{L_i} \nabla c_2 \right) = i_{loc} S_i L_i \frac{1-t_+}{F}. \quad (5)$$

In the fourth equation we define a dimensionless distance variable $y = r/r_p$, scaled by the particle radius in the electrode. In terms of y , Fick's law in spherical coordinates can be written as

$$y^2 r_p \frac{\partial c_1}{\partial t} + \nabla \cdot (-\mathbf{D}_1 \nabla c_1) = 0, \quad (6)$$

where \mathbf{D}_1 is a tensor that characterizes solid-state diffusion of the reduced-lithium species within (in the y direction), but not between particles (in the x direction of the electrode)

$$\mathbf{D}_1 = \begin{pmatrix} \frac{y^2 D_{1,0} \times 10^{-6}}{r_p} & 0 \\ 0 & \frac{y^2 D_{1,0}}{r_p} \end{pmatrix}. \quad (7)$$

This assumption is appropriate for electrodes with relatively low particle packing density. The matrix is meant to characterize anisotropic diffusion in a two-dimensional system with components xx , xy , yx , and yy , reading left to right. The 10^{-6} factor in the xx component reflects the suppression of particle-to-particle diffusion.

4. Boundary conditions

At the boundaries, the default condition is zero flux. In order to simulate a Potentiostatic Electrochemical Impedance Spectroscopy (PEIS), a sinusoidal excitation signal has to be applied to the half-cell by means of a Dirichlet

boundary condition on the potential in solid phase ϕ_1 , at the interface between the positive electrode and the current collector

$$\phi_1|_{x=L_{sep}+L_{pos}} = E_{pos} + V_a \sin(2\pi ft). \quad (8)$$

Another Dirichlet boundary condition is applied to the potential in liquid phase ϕ_2 , at the interface between the separator and the negative electrode, the latter being the reference electrode

$$\phi_2|_{x=0} = 0. \quad (9)$$

The flux of liquid species at the same interface is described by a Neumann boundary condition:

$$-\mathbf{n} \cdot \left(-\frac{D_2^{eff}}{L_{sep}} \nabla c_2 \right) \Big|_{x=0} = -I \frac{1-t_+}{F}, \quad (10)$$

where I is the cell current density based on the cell surface A_{cell}

$$I = \frac{\kappa_1^{eff}}{L_i} \nabla \phi_1 \Big|_{x=L_{sep}+L_{pos}}. \quad (11)$$

The two distance dimensions are linked by the constraint that the flux of lithium at $y = 1$ is determined by i_{loc}

$$-\mathbf{n} \cdot (-\mathbf{D}_1 \nabla c_1) \Big|_{x=0} = -\frac{i_{loc}}{F}. \quad (12)$$

The symmetry (insulating) condition on the flux of reduced-lithium species applies at the centers of the particles ($y = 0$).

5. Functions of the dependent variables

Some quantities are functions of one or more of the four dependent variables ϕ_1 , ϕ_2 , c_1 , and c_2 in Eqs. (3)–(6). These quantities are i_{loc} , E_{pos} , K_{junc} , κ_2 , and D_2 . The solid diffusion coefficient $D_{1,0}$ could also be assigned a functional dependence on c_1 in the same manner. The reader interested to get more details about those functions should refer to [2-5].

The quantity of interest for this study is the current density localized at the particle-surface/liquid interface i_{loc} , which includes not only the Butler-Volmer equation for the electrode kinetics, but also the electrical double-layer

$$\begin{aligned}
i_{loc} = & k_{pos} (c_1^{\max} - c_1)^{\alpha_{pos}} c_1^{1-\alpha_{pos}} c_2^{\alpha_{pos}} \\
& \times \left[\exp\left(\frac{\alpha_{pos} F}{RT} (\phi_1 - \phi_2 - E_{pos})\right) \right. \\
& \left. - \exp\left(-\frac{(1-\alpha_{pos}) F}{RT} (\phi_1 - \phi_2 - E_{pos})\right) \right] \cdot (13) \\
& + C_{dl,pos} \left(\frac{\partial \phi_1}{\partial t} - \frac{\partial \phi_2}{\partial t} \right)
\end{aligned}$$

The double layer is usually not taken into account in the Li-ion battery mathematical models, mostly because it does not have a big impact on the simulation results during complete charges or discharges.

6. Model simulations

The model is intended to simulate the impedance of the half-cell as if it was virtually plugged to an EIS device. It is not possible to derive this impedance directly from the equations mentioned above, since they are all time-dependent. Thus, the model has to be run for each frequency with the sinusoidal excitation signal used to get the experimental data. The latter have been obtained by applying the PEIS technique of the BioLogic® WMP3® battery tester to the half-cell we made in our lab. For this experiment, the half-cell is completely charged (SOC = 100 %), which means that the positive electrode is almost completely delithiated. The amplitude of the sinusoidal excitation signal is 7.1 mV around the equilibrium potential and is made up of three periods per frequency. The frequencies range from 0.1 Hz to 200 kHz and six frequencies are tested by decade.

First, we were wondering if we should simulate the excitation signal including all frequencies in a single run, as it was actually applied to the half-cell by the battery tester. In fact, we did not know if the previous frequency tested was going to have an impact on the next one. However, by doing so the computation time was extremely long (few hours).

Hopefully, the results obtained with a single run or a run for each frequency are actually the same. By decreasing the number of points per period to 30, the model is able to simulate a frequency in less than a minute with an Intel® Xeon® W3520 @ 2.67 GHz (8 cores) and 16 Gb of RAM.

After resetting the history of the original COMSOL model mph-file, it is saved as a model m-file readable by MATLAB®. The LiveLink for MATLAB®, which is an additional COMSOL product, is used here to run our model for each frequency and then process the result in order to get the full impedance spectrum of the half-cell. With a total of 44 frequencies, it takes between 10 and 15 minutes to complete the spectrum.

The input of our model m-file is the sinusoidal excitation signal defined in Eq. (8). The output is the resulting current derived from Eq. (11)

$$I_{cell} = A_{cell} \times I. \quad (14)$$

Since we are not running all the frequencies in a single run, we cannot calculate the mean of the three amplitudes and phases measured at each period of the signal, as the battery tester manufacturer does to get reliable values. If we do that, our result is going to be influenced by the transient period at the beginning of each new frequency, which does not represent the steady state of the half-cell. To ensure that the result is reliable, we analyze only the last period of the output signal.

Fig. 2 shows the simulation results obtained with the model described above. First of all, if the double layer capacitance were not taken into account, then all the red squares ranging from 200 kHz to 11 Hz would be superposed on the one corresponding to 11 Hz. In that case, the charge transfer would be equal to a simple resistance and no semi-circle would appear in the impedance spectrum.

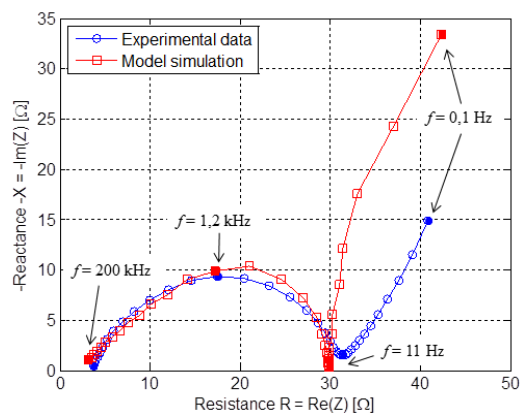


Figure 2. Impedance spectra of the LiFePO₄/Li half-cell from the experimental data (red square) and the model simulation (blue circle)

The first step to get a match with the experimental data is to simulate the model at the highest frequency, here at 200 kHz. At this frequency the half-cell is almost purely resistive. Since the positive electrode is composed of iron phosphate, the parameter having the biggest impact on the overall half-cell resistance is the electronic conductivity of the positive active material κ_1 . A good fit can thus be achieved by adjusting the value of κ_1 to $0.038 \text{ S}\cdot\text{m}^{-1}$, which is consistent with [2].

The second step is to simulate the model at the second frequency at which the half-cell does behave again almost like a pure resistance, here at 11 Hz. At this frequency, what is important to adjust is the charge transfer resistance. The latter is almost entirely defined by the charge transfer rate coefficient k_{pos} . With the transfer coefficient $\alpha = 0.5$, the adjusted value of k_{pos} is $2 \times 10^{-7} \text{ A}\cdot\text{m}^{2.5}\cdot\text{mol}^{-1.5}$.

The third step is to simulate the model at the frequency corresponding to the top of the semi-circle, here at 1.2 kHz. At this frequency, the parameter to adjust is the specific double layer capacitance $C_{dl,pos}$. The shape of the semi-circle is definitely described by this parameter, as previously discussed. A good fit can be achieved with a value of $2 \times 10^{-4} \text{ F}\cdot\text{m}^{-2}$.

The shape of the simulated semi-circle is a little bit distorted compared to the measured one, but the fit presented at the Fig. 2 is quite good.

Another way of presenting the results is the Bode plot. It consists of two graphs presenting separately the magnitude and the phase of the impedance with respect to the frequency, as shown in Fig. 3. The Bode plot seems to show that our half-cell behaves like a low-pass filter with a cutoff frequency of around 200 Hz. However, the slope is not 20 dB/decade, as in a first-order filter, but around 10 dB/decade at best.

The Bode plot can be used to fit the experimental data the same way the impedance spectrum was used. It is just a representation useful for people who want to understand the cell behavior as any other system. It is also possible to couple a battery with another electrical component and simulate what will be the behavior of the complete system. Then, we could define the control to apply in order to get the most out of this system.

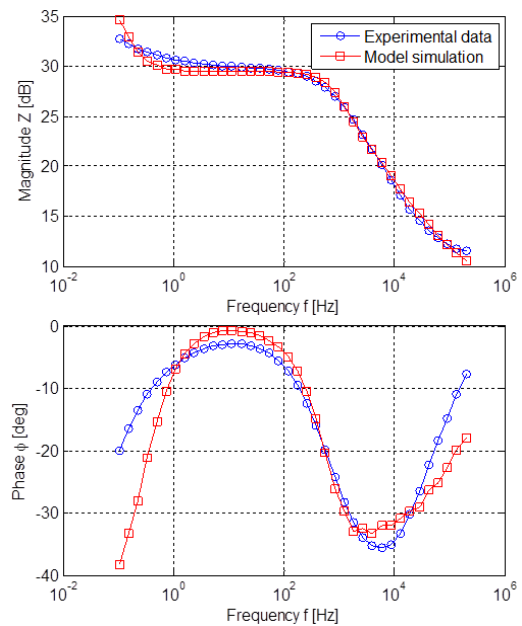


Figure 3. Bode plot of the $\text{LiFePO}_4/\text{Li}$ half-cell impedance from the experimental data (red square) and the model simulation (blue circle)

This work is still in progress, so we do not know exactly yet what is actually responsible of the slope observed at lower frequencies. There might be a missing phenomenon somewhere in our model or some parameter values still to be adjusted. We hope to be able to come up at the conference with the answer to that question.

7. Conclusions

This study demonstrates that a multiphysical model of a $\text{LiFePO}_4/\text{Li}$ half-cell can be applied to simulate the impedance results from an EIS. 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 0.1 to 200 kHz. The methodology used to adjust the three key parameters used to fit the experimental data is described. However, this work is still in progress, so we do not know exactly yet what is actually responsible of the slope observed at lower frequencies. There might be a missing phenomenon somewhere in our model or some parameter values still to be adjusted.

8. References

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