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1 Introduction

Lithium-ion batteries are a type of rechargeable battery, current in portable electronics, automotive and aerospace applications because of their high energy-to-weight ratios and slow self-discharge when not in use. In a Lithium-Ion Battery (LIB), lithium ions move from the anode electrode to the cathode electrode through a polymer electrolyte during discharge and from the cathode to the anode during charge. The anode materials are usually metal oxides or graphite. The cathode is generally made of oxides (e.g. lithium cobalt oxides, lithium manganese oxides) or polyaniions (e.g. lithium iron phosphates). It is experimentally known that depending on the materials choice for the anode, cathode, and electrolyte, the performance (voltage, charge capacity), durability (materials degradation), and safety of a LIB can change dramatically. In this context intensive researches have been devoted to the search for new electrode materials or electrolytes in order to enhance performances and increase lifetime. On the other hand, understanding the degradations, chemical and electrochemical phenomena at the micro- and nanoscale is nowadays are crucial steps for the design of new systems and engineering strategies.

Direct interpretation of experimental observations is made difficult by the strong couplings between physicochemical phenomena. An analysis through physical modelling becomes thus crucial to elucidate the mechanisms such as degradation and failure, and to help improving both electrochemical performance and durability of the devices. The development of theoretical tools is now essential to predict electrochemical properties of various materials at multiple material and component scales in a diversity of operating conditions for both industries and the scientific community.

Mathematical models could contribute to this development in very different ways. Indeed these approaches could help to adapt the geometrical parameters of a battery such as the size of the electrodes, the porosity, and the dimensions of active material particles. Models could also allow predicting the influence of new components and/or experimental conditions (e.g. scan regime, temperature) on the behaviour of the cell, to identify the process of aging and to estimate the durability.

The methods of quantum chemistry can bring a valuable help, in particular to rationalize the nanoscopic electronic phenomena at the origin of the energy storage. Some works have been already reported on the calculation of the electrode materials properties (e.g. related to the insertion of Lithium ions in the covalent matrices used as an electrode), based on first principles calculations. However, until now there is a lack on scaling up these atomistic data into elementary kinetic models that could allow predicting the battery electrochemical behaviour. This is explained by the difficulty of treating the electrode/electrolyte interfacial phenomena electric field during the electrochemical reactions.

In this deliverable we report our first attempts on proposing a methodology to scale up atomistic data into elementary kinetic models of LIBs, allowing predicting the behaviour of experimental observables (e.g. voltage as function of charge). This approach is supported on a general framework previously developed by Franco et al. The framework consists on a comprehensive description of the electrochemical interfaces, based on non-equilibrium thermo-dynamics physicochemical concepts at the nanoscale, and it is adapted for LIBs (Section 3). Description of the physiochemical properties of LIB was originally planned to be reported in deliverable D12.1. In drafting this deliverable we realized that the relevant physiochemical properties are best described after the full model has been introduced. Deliverable D12.1 is therefore reported as Section 3 of this document.

Development and optimization of LIB remains highly relevant point to open interesting technological challenge, in particular concerning issues problems of electrochemical performance and safety. The
modelling results here are compared with dedicated experimental data (Section 4) and remaining challenges and perspectives are indicated (Section 5).

2 MEMEPhys: a multiscale model for the simulation of electrochemical systems

The multiscale simulation package MEMEPhys is being developed by Franco et al. since more than 10 years, and describes the detailed physicochemical processes at multiple scales in electrochemical devices for electric power generation, such as Polymer Electrolyte Membrane Fuel Cells [1, 2]. Such a model is a multiscale one in the sense that it is made of a set of interconnected sub-models describing the phenomena occurring at different scales in the PEMFC. MEMEPhys is a N * 1D model resulting from the coupling of different geometrical scales: e.g. reactants and charge 1-D mesoscale description across the membrane/separatorder-electrodes assembly and the interfacial nanoscale mechanisms at the vicinity of the electrochemically active materials including both elementary kinetics (with ab initio calculated activation barriers) and electrochemical double layer effects. For the PEMFC application, the model includes novel continuum descriptions of coupled electrochemical aging processes. The model numerically describes “on the fly” the feedback between the instantaneous performance and the intrinsic material aging processes, thus the individual components and cell durability can be predicted. The approach provides new insights on the interplaying between the different aging phenomena and analyses the cell response sensitivity to operating conditions, initial materials composition and structure and temporal evolution of the electrochemical activity.

The description of the mechanisms in MEMEPhys remains macroscopic in the sense that it is based on irreversible thermodynamic concepts as they are extensively used in chemical engineering: use of conservation laws coupled to closure equations (flux expressions, chemical rate models, and thermodynamic models). A good way to derive such a model is to use the Bond Graph approach: this approach allows building the model as a collection of interconnected and reusable sub-models through the concept of port power-conjugate variables. Such an approach allows to easily modify the sub-models and to test new assumptions.

MEMEPhys is currently used to carry out intensive multiscale numerical simulations for PEMFC and PEM Water Electrolyzer applications, to calculate the relative impact weight of the different mechanisms on the global cell performance and durability as function of the chemical and structural properties of the materials and components, and of the operation conditions. This model at the single cell level, accounts for the coupling between self-consistent physical-based mechanistic descriptions of the cell phenomena (e.g. reactants, water and charge transport and detailed electrochemistry) and different materials aging mechanisms. On a physical basis, the model describes the feedback between the instantaneous performance and the intrinsic material aging processes, and already provides for PEMFCs:

- simulated experimental observables time-evolution under realistic stationary operating conditions (e.g. time evolution of polarization curves, linear and non-linear impedance spectra, current interrupt, cyclic voltammetry…) as function of initial material compositions (e.g. initial active material loadings and volumetric distributions within the electrodes…);
- a cartography of the relative synergies and competitions between different physicochemical phenomena, in particular between different aging processes as function of the operation conditions;
- predictions of local materials efficiency and durability as function of the operation conditions;
● suggestions of operating protocols and materials structure to mitigate the cell degradation at the local scale.

The objective within this WP in MMM@HPC project is to adapt MEMEPhys for the simulation of LIBs. As a first application example, our work is focused on describing the lithium transport and intercalation mechanisms in a cell constituted by a graphite anode and an Iron-Phosphate cathode.

3 Physiochemical Properties

Adaptation of MEMEPhys for Li-Ion Batteries

Figure 1 shows the most relevant scales that should be described in MEMEPhys for the accurate and robust simulation of ideal LIBs based on intercalation materials. In analogy to the other available MEMEPhys applications (e.g. PEMFCs), the model should describe:

● Li transport across the electrode (anode and cathode) and separator thickness;
● Li transport across the electrochemical double layer formed between the active material and the bulk electrolyte;
● Li intercalation mechanisms and transport within the intercalation material.

Figure 1: The different scales that should be described in a multiscale model of LIBs. Here the case of a LiFePO4/Graphite battery is represented. a) The model should take into account of both positive and negative electrode b) including description of transport phenomena of the lithium ions at the mesoscale level between the active particles, c) and a description of the double layer formation around an active particle and the transport of lithium within the intercalation material.

At the present stage of development the model for LIBs considers:
• a 0D static (pure resistive) description of lithium transport across the separator
• a 1D static description of lithium transport across the diffuse layer
• a 0D description of the intercalation mechanism from the electrolyte within the compact layer, including a formulation of the kinetics as function of ab initio calculated data,

i.e. the model neglects the transport of lithium across the electrode thicknesses and inside the intercalation materials. These are important mechanisms that should be included in the model in further developments, once dedicated ab initio studies provide deeper insights on the phenomena involved. Input to the model consists of the physiochemical properties of the battery components, which are discussed in detail in the remainder of this section.

Ab initio data

Within an ongoing collaboration with the Institut Charles Gerhardt of Montpellier (group of Dr. Marie Liesse Doublet), we have performed DFT+U calculations [3] for the LiFePO$_4$ material in order to estimate the Li$^+$ insertion energy into the FePO$_4$. We have used VASP software with a PBE functional, with U=4.5 eV. In particular, by considering the following chemical reaction

$$\text{LiFePO}_4 \leftrightarrow \text{FePO}_4 + \text{Li}^+ + e^-$$ (1)

we can write the associated equilibrium potential as

$$U_{eq} \sim -\Delta G/F$$ (2)

where $\Delta G$ is the Gibbs free energy for the reaction and $F$ is the Faraday constant. If we neglect as a first approximation the changes in volume and entropy and approximate $\Delta G$ by the internal energy $\Delta E$, given by the difference in total energies between LiFePO$_4$ and the addition of FePO$_4$ and metallic lithium, we have

$$\Delta E = E_{total}[\text{LiFePO}_4] - E_{total}[\text{FePO}_4] - E_{total}[\text{Li}]$$ (3)

where $E_{total}[\text{LiFePO}_4]$ and $E_{total}[\text{FePO}_4]$ are the total energies per formula unit of LiFePO$_4$ and FePO$_4$, respectively, $E_{total}[\text{Li}]$ is the total energies of metallic lithium. Based on this simple approach, we have estimated the Li$^+$ insertion energy into the FePO$_4$ structure to 3.23 V. However further contributions can enter into the estimation of the total intercalation energy. In fact, when a lithium ion enters the FePO$_4$ crystal a geometry transformation and a deformation of the network are created (the so–called domino-cascade process [4]). The simulation of these phenomena at the atomistic level is still challenging: still in collaboration with the group of Dr. Marie Liesse Doublet, we have started to perform preliminary ab initio calculations on FePO$_4$ and LiFePO$_4$ networks to reveal the possible changes in the intercalation energy due to the mechanical stress changes. In particular, by considering lithium arrival from the 010 direction in the crystal, the intercalation of Li follows two directions: 100 and 001 through $a$ and $c$–axial. However, we know that during the formation of LiFePO$_4$ there is a strain applied on FePO$_4$, and vice–versa applied on the former during the delithiation. For the strain process, we have imposed the lattice constants of FePO$_4$ on LiFePO$_4$ for all the calculated intercalation potential, e.g. $a(e)$ lattice parameters of FP on $a'(e')$ of the LiFePO$_4$ geometry. The $a$ and $c$ lattice constants they are following the (100) and (001) direction, respectively. Figure 2 shows that at the beginning of the discharge (i.e. starting of the lithium intercalation in the FePO$_4$), $V_{strain}$ is 3.19 V by applying a strain through the $a$ parameter, and however, the $V_{strain}$ is equal to 3.11 V following the $c$ parameter. At
the end of the discharge (intercalation) process, we have estimated an increase of the $V_{\text{strain}}$ in both 100 and 001 directions to 3.32 and 3.27 V, respectively. It is however still unclear if one of the both directions will be predominant in real LIB operation during discharge and charge: understanding this is crucial for further implementation of this atomistic data into MEMEPhys.

![Figure 2: Intercalation potential of strain effect of charge/discharge Li–FePO4, the simulations were done following lithium growth through [100] and [001] directions.](image)

The lithium intercalation energies in the graphite electrode are estimated from experimental fitting.

**Electrochemical Double Layer: general formulation**

Following the previous approach by Franco et al. (see Section 2 and Figure 1), the electrochemical double layer formed at the interface between the active material and the electrolyte is described here as constituted by a diffuse layer (where the charge and electrostatic potential distribution is spatially heterogeneous) and a compact layer (surface of the active material in contact with the electrolyte).

The diffuse layer model describes transport by the diffusion and electro-migration (at nanometers length from the active particles) of the lithium ions coupled with the electric field generated by the resulting charge distribution. In order to describe the transport of lithium in the diffuse layer, as a first approach the following equation is used

\[
0 = \frac{dC_{H^+}}{dt} = -\nabla \left[ -D_{H^+} \frac{\partial C_{H^+}}{\partial x} - \frac{F}{RT} D_{H^+} C_{H^+} \frac{\partial \phi}{\partial x} \right]
\]  

(4)
which gives the steady state solution of the Nernst-Planck equation in Cartesian coordinates (perpendicular direction to the active material), where the electrostatic potential is given by

$$\phi(x) = \frac{E}{4L^3} x^4 + \phi(x = 0) \quad (5)$$

which is resulting from a numerical fitting from the full 1D calculated potential profile issued from the Poisson’s equation.

The compact layer corresponds to the thin layer on the surface of the active particle (around 0.1 nm thick). In our model, an interfacial potential due to the surface dipolar moment due to the electronic spillover and solvent adsorption on the active material governs the development of the intercalation reaction on the active particles with an electronic density $\sigma(t)$. This potential, known as the “surface potential” $\eta(t)$, is given by

$$\eta(t) = \psi(t) - \phi^{DL}(t) \quad (6)$$

where, $\phi^{DL}(t)$ is the interfacial electrostatic potential in the electrolyte and $\psi(t)$ is the potential in the active material phase. $\psi(t)$ is calculated as the sum of the potential $\phi^{DL}(t)$ and of $\eta(t)$. In a first approximation the expression of this surface potential is simpler than in the case of fuel cells where we have to take account of the contribution of the water absorption.

According to gauss’s theorem $\sigma(t)$ can be expressed as a function of $-\frac{\partial \phi}{\partial x}(x, t)$ the electric field at the particle/electrolyte interface. For anodic and cathodic reactions $\psi(t) - \phi(L, t) > 0$ and $\psi(t) - \phi(t) < 0$, respectively, and due to the small thickness of the compact layer (d), the potential drop can be approximated to:

$$\eta(t) \approx -\frac{\sigma(t)}{\varepsilon_{CL}} d > 0 \text{ (anodic); } \eta(t) \approx -\frac{\sigma(t)}{\varepsilon_{CL}} d < 0 \text{ (cathodic);} \quad (7)$$

with $\varepsilon_{CL}$ refers to the permittivity of the compact layer. We have to notice that this expression may be easily adapted if solvent adsorption is considered. $\sigma(r, t)$ is calculated from the law of conservation of charge at the active material/electrolyte interface. This means that during a discharge process we have

$$J(t) - J_{Far}(t) = -\frac{\partial \sigma(t)}{\partial t} \text{ (anode)} \quad (8)$$

$$J(t) - J_{Far}(t) = \frac{\partial \sigma(t)}{\partial t} \text{ (cathode)} \quad (9)$$

where $J_{Far}(t)$ is the faradic current densities given by the electrochemical reaction rates (see next). $J(t)$ is the surface current density calculated from the initial current applied on the battery, following
\[ f(t) = I(t)/S_{active} \]  \hspace{1cm} (10)

where \( I(t) \) refers to the total current entering the cell and \( S_{active} \) refers to the surface of active material in contact with the electrolyte.

In the following part of our model description, we assume that lithium ions arriving on the active particles surfaces enter immediately in the crystal if the transport processes allowed it). Thus we do not consider the possibility of the creation of a chemical bond between the ions and the surface (no chemisorption, only insertion into the particle). However it is necessary to calculate the flux rate of the lithium going inside or outside the particle. For the case of a discharge of the positive electrode we have

\[ v_s = k \theta_s C_{Li}^{CL} e^f(v) - k_{-} \theta_{Li} e^{f(v)} \]  \hspace{1cm} (11)

This rate depends on the coverage \( \theta_s \) and \( \theta_{Li} \) which are respectively the fractions of free and lithium occupied sites in the intercalation material. \( C_{Li}^{CL} \) is the lithium concentration in this compact layer (boundary condition for the diffuse layer concentration). This equation which also depends on the surface potential \( \eta(t) \) should be adapted to the considered electrode and to the desired battery process (charge or discharge).

The faradic current can be deduced from equation (11). Still in the case of a positive electrode discharge we have

\[ j_{Li}^{CL} = -v_s = -\frac{j_{Far}(r,t)}{F} \]  \hspace{1cm} (12)

Where \( j_{Li}^{CL} \) is the ionic density flux of lithium and \( F \) is the Faraday constant.

The lithium coverage rate is obtained by

\[ \frac{n^{max} \theta_{Li}}{N_A \theta_s} \frac{d \theta_{Li}}{dt} = v_s \]  \hspace{1cm} (13)

with \( n^{max} \) the total number of available sites on the active particle surface and \( N_A \) the Avogadro constant. It is then obvious to obtain free site rate with the condition

\[ \theta_s + \theta_{Li} = 1 \]  \hspace{1cm} (14)

Equation (11) is also function of the kinetic constants \( k_{+} \) and \( k_{-} \) that depend on the activation energies related to the formation or the suppression of the chemical bond. These activation energies are related to the calculated DFT insertion energies. As a first approach within the Transition State Theory (TST), the kinetic parameters can be estimated by the Eyring equations:
where $\Delta G_\pm$ are the energies as calculated from DFT, $k_B$ and $\hbar$ Boltzmann and Planck constants and $T$ the temperature. The remaining theoretical challenge for further theoretical studies is now to estimate $\Delta G_\pm$ as function of the fraction of occupied sites in the intercalation material, and this report, for the purpose of simplicity, only the energy estimated from equation (2) is used for the FePO₄.

### Degradation phenomena

#### Graphite exfoliation

In order to demonstrate the flexibility of our approach for the simulation of degradation processes, graphite exfoliation in the negative electrode has been considered [5]. During the intercalation of solvated lithium in graphite, it removes graphene sheets, decreasing the number of available sites for lithium intercalation during the cycles. As this degradation mechanism should be dependent on the interfacial graphite/electrolyte lithium concentration, we write the temporal evolution of the graphite Intercalation sites

$$\frac{dn_{\text{max}}}{dt} = k_{\text{exfol}} C_{Li^+}^{CL_i}$$

(16)

where $k_{\text{exfol}}$ is a kinetic parameter of the graphite exfoliation and $C_{Li^+}$ the lithium concentration in the compact layer. $k_{\text{exfol}}$ is obtained from a fit of experimental potential curves obtained by Liu et al.

#### Iron dissolution

Iron dissolution in the cathode could be responsible of cell capacity loss under cycling. Amine et al. [6] showed that the global diminution of the performances of these types of batteries could be relied to the presence of small quantities of iron ions (Fe²⁺) within the electrolyte.
Figure 3: Iron dissolution mechanism and possible impact on the graphite intercalation properties.

For our simulations we proposed to add the description of the iron dissolution in the active material of the positive electrode by implementing two different chemical mechanisms. The first describes the effect of small quantities of water on the creation of fluorhydric acid (HF) and the influence of this acid on the bond between iron and the active material crystal. The second mechanism supposes that the dissolution is related to the effects of the different solvents (carbonates) composing the electrolyte. In this case, we assume that an important quantity of solvent on the electrode/electrolyte interface could be able to break the iron bond. Both of these processes are described by implementing a kinetic equation related to the corresponding chemical reaction. The kinetic coefficients could be fitted on experimental results. Furthermore, we have combined these phenomena with the loss of available sites for lithium insertion and thus a diminution of the positive electrode capacity.

However, it has been showed [1,7] that the main effect of these phenomena on the performances of the cell is the impact of the iron on the negative electrode (graphite). So we add the description of the transport of the iron ions trough the electrolyte phase and the influence of these ions on the electrochemical double layer of the graphite electrode by reducing the number of available sites for lithium insertion.

4 Preliminary simulation results

The equations described in Section 3 have been programmed within the MEMEPHys framework, by combining C and Simulink languages. Calculations have been performed with standard Simulink numerical solvers in a standard desk computer.

A preliminary calculation result of a charge-discharge curve is shown in Figure 4, without and with the consideration of the evolution of the intercalation energy with the number of occupied sites. These results are still preliminary because as discussed in Section 3, it is still unclear how different intercalation directions will compete in real operation of the battery, and because the transport of lithium inside the material is neglected in the model. The later aspect could in particular strongly impact the energy variation with the number of occupied sites.
The experimentally fitted variation of the anode electrode potential with the fraction of occupied sites is provided in Figure 5, showing the experimentally known “stage-behaviour”. The energies have been fitted from equation (15) and estimating them from DFT calculations is also still a challenge.

Figure 4: Simulated and experimental charge/discharge potential curve function of the time for a LiFePO4//Graphite battery, for a constant intercalation energy as given by Equation (2) (left) and for an assumed linear variation of the intercalation energy following the red dashed evolution in Figure 2.

The experimentally fitted variation of the anode electrode potential with the fraction of occupied sites is provided in Figure 5, showing the experimentally known “stage-behaviour”. The energies have been fitted from equation (15) and estimating them from DFT calculations is also still a challenge.

Figure 5: variation of the anode electrode potential with the fraction of occupied sites.

Figure 6 shows 600 charge/discharge simulated cycles for the model accounting for Graphite exfoliation. The results show a coherent decrease of the electrode capacity coupled with an augmentation of the voltage in agreement with the experimental data reported by Liu et al.
Figure 6: Calculation of the graphite electrode potential during 600 hundred charge/discharge cycles and representation of the degradation process simulated by reducing the total number of available sites for lithium insertion.

Some preliminary results for the case of the model when the iron dissolution process is taken into account are presented in Figure 7. Our first results showed that we can be able to simulate the proportion of dissolved iron and the decrease of the total capacity during cycling and with specific conditions of temperature and current (312 K and C/10). Ongoing experiments at CEA will help us to validate these results.

Figure 7: Calculated percentage of dissolved iron and associated impact on the capacity.

5 Challenges and perspectives

In this report, the MEMEPHys multiscale framework, originally developed by Franco et al. for the simulation of electrochemical systems, has been firstly presented. For the case of PEMFCs, this multiscale modelling approach allows resolving simultaneously multiple physicochemical phenomena (e.g. materials aging, contamination reactions, water transport, transport, charge transport, detailed electrochemical reactions...) occurring at multiple spatiotemporal scales and allows predicting the
instantaneous performance and durability of the electrochemical devices. The model is supported on ab initio–extracted kinetic databases and structural data representing important prerequisites for engineering practice to understand the synergies and interactions between the aging phenomena, to interpret the electrochemical cell behaviour under realistic operating conditions, to predict the components (e.g. electrodes, separator) degradation and durability as a function of the initial nanomaterials composition and nano/microstructure. The capabilities of this model to propose several experimentally-validated innovative procedures (operation strategies and electrodes formulation) to enhance the performance, durability have been illustrated through numerous practical examples in the case of PEMFCs.

In this report we have presented our first efforts on adapting this model for the case of LIBs. Probably the major challenges on this are related to the calculation from first principles of the activation energies of the intercalation and transport of lithium in the intercalation materials. Some preliminary kinetic results have been presented for the case of a graphite/FePO$_4$ cell, including descriptions of some experimentally observed degradation phenomena (graphite exfoliation, iron dissolution). Another important challenge is the scaling up of the ab initio data into the elementary kinetic model, especially on the aspects related to the mechanical stresses changes during the intercalation process. Further theoretical and methodological efforts within this sense are still necessary. Once this achieved, the model would have interesting capabilities to predict the impact of the chemistry of the active material on the experimental observables (if the associated DFT database of activation energies are available). Probably the best strategy to build up these types of multiscale models will consist first on the estimation from DFT of the activation barriers that will serve as initial numerical guess for MEMEPhys (Figure 8). Then a sensitivity study to the parameters values in MEMEPhys will allow re-adjust the domain (e.g. type of reaction to be deeply analyzed) where the DFT should be done to then re-inject in MEMEPhys for more accurate calculations. Automating these iterations between ab intio and MEMEPhys calculations will be one of the purposes of our contribution in MMM@HPC project.

![Figure 8: e-infrastructure for the iterative enhancement of the MEMEPhys calculation accuracy from ab intio data.](image)

6 References


