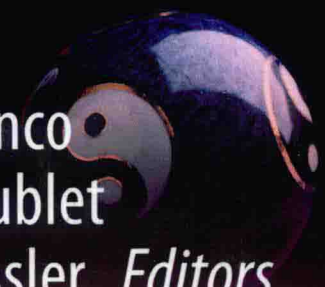
Green Energy and Technology



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Physical Multiscale Modeling and Numerical Simulation of Electrochemical Devices for Energy Conversion and Storage

From Theory to Engineering to Practice

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Preface

World-scale challenges such as climate change, depletion of fossil resources, and the fast increasing energy demand has significantly boosted the R&D on alternative devices for energy conversion and storage. In this context, emerging technologies such as fuel cells and batteries are called to play an important role in any sustainable scenario. However, the successful large-scale implementation of these devices in realistic applications is subjected to numerous constraints in terms of cost, efficiency, durability, safety and impact on the environment. Precise design of cells and stacks is then required, and production cost constraints drive more and more the R&D to go beyond trial-error approaches: the use of numerical simulation and mathematical modeling arises as a natural approach to deal with the design optimization problem.

Since almost 60 years numerous mathematical models of fuel cells and batteries have been reported showing powerful capabilities for *in silico* studies of a large diversity of mechanisms and processes. These models are generally devoted to link the chemical and microstructural properties of materials and components with their macroscopic efficiency. In combination with dedicated experiments, they can potentially provide tremendous progress in designing and optimizing the next-generation cells. The available spectrum of approaches already available is wide: quantum mechanics, nonequilibrium thermodynamics, Monte Carlo and molecular dynamics methods, continuum modeling, and more recently, multiscale and/or multiparadigm models connecting multiple simulation techniques and describing the interplay of mechanisms at multiple spatiotemporal scales.

Through several comprehensive chapters written by recognized scientists in the field, we aim at reviewing the latest progresses in the development and deploy of innovative physical modeling methods and numerical simulations to better understand, rationalize, and predict the electrochemical mechanisms involved in electrochemical devices for energy storage and conversion. Concepts, methodologies, and approaches connecting *ab initio* with micro, meso, and macroscale modeling

of the components and cells are revisited, jointly with appropriate illustrations and application examples. Major remaining scientific challenges are also discussed. We hope this book will provide an interesting support to students, researchers and engineers from the industry and academic communities.

Alejandro A. Franco
Marie Liesse Doublet
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Atomistic Modeling of Electrode Materials for Li-Ion Batteries: From Bulk to Interfaces

Matthieu Saubanère, Jean-Sébastien Filhol and Marie-Liesse Doublet

Abstract In the field of energy materials, the computational modeling of electrochemical devices such as fuel cells, rechargeable batteries, photovoltaic cells, or photo-batteries that combine energy conversion and storage represent a great challenge for theoreticians. Given the wide variety of issues related to the modeling of each of these devices, this chapter is restricted to the study of rechargeable batteries (accumulators) and, more particularly, Li-ion batteries. The aim of this chapter is to emphasize some of the key problems related to the theoretical and computational treatment of these complex systems and to present some of the state-of-the-art computational techniques and methodologies being developed in this area to meet one of the greatest challenges of our century in terms of energy storage.

1 Introduction

Despite the apparent simplicity of the operation of a Li-ion battery, the electrochemical mechanisms involved at the bulk scale and at the interfaces between the electrodes and the electrolyte often rely on complex physical and chemical processes. These processes may occur at different time- and length scales involving static (electromotive force, resistances) and dynamic (charge transfer, mass transport) variables. Addressing these mechanisms simultaneously is intractable at the highest atomistic level of theory, i.e., the ab initio level. Continuum models exist to address battery operation as a whole and under operating conditions of pressure and temperature that rely on phenomenological approaches, e.g., equivalent circuit models [1] or electrochemical kinetic models [2]. Based on the Butler–Volmer equation with varying degrees of sophistication depending on the number of physicochemical effects described, these methods represent a class of "top–down" approaches. They have already benefited the optimization of battery performances

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[3–6] but are not strictly predictive. In particular, they do not correlate the performance of a battery to the intrinsic properties of electrode materials as no data specific to the chemical/electronic nature of these materials are included.

To build more predictive multiscale models, it is essential to assess quantitative parameters that take into account not only the structural and electronic properties of the electrode materials, but also their reactivity versus lithium (activity, distribution, etc.). At the most local scale (microscopic), first-principles computational methods provide valuable quantitative data, either thermodynamic (electrochemical potentials and equilibrium structures of the electrode material) or kinetic (ion diffusion barriers, interface migration) that can be used as input parameters in models of higher time- and length scales. Among them, Kinetic Monte Carlo simulations, [7] nonequilibrium thermodynamic models [8, 9], or phase-field models [10] intend to simulate time evolution of some elementary processes—whose rates have been previously investigated at the ab initio level (atomic scale)—in order to determine their respective impact on the structure of the electrodes at the nanoscopic scale. These approaches are the so-called bottom–up approaches. They have already proven to be powerful in the field of fuel cells [11] and are currently under development in the field of Li-ion batteries [12, 13]. They represent a holy grail for theoreticians involved in this field, not only to ensure the transferability of parameters from one scale to another but also to solve the nonlinearly coupled equations of ion and electron transport which govern the macroscopic behavior and lifetime of electrochemical cells.

Pending this ultimate method, it can be useful to combine the "bottom–up" and "top–down" approaches to study the electrochemical battery performance by taking advantage of (i) the limited computational cost of phenomenological approaches and (ii) the accurate description of materials and interfaces provided by atomistic quantum methods. These approaches are promising but still very limited in the field of Li-ion batteries, not only due to the large number of parameters to be extracted but also to the methodological and numerical locks associated with ab initio methods for extracting these parameters. Thus, in this area, the vast majority of computational scientists focus their studies on one element of the battery (electrode or electrolyte) in order to optimize their performance with respect to strict industrial specifications. Focusing on battery materials, the candidates have to be safe, cheap, and environmentally friendly and must meet several criteria such as high-energy density, good rate capability, and long-term cycling life. Besides the economic and ecologic aspects on which chemists can act to meet the industrial specifications, fundamental chemistry can also be used to improve the electrochemical performance of electrode materials. To that aim, first-principles quantum methods may provide solid-state chemists with a powerful tool to reproduce, understand, or predict material properties. On the one hand, they give access to thermodynamic or kinetic quantities such as equilibrium structures and energies or energy barriers that are further used to interpret the microscopic parameters influencing the structural and electronic behavior of a material. In that sense, they are useful to decide whether or not a given material is suitable for the application of interest and whether or not chemical functionalizations or appropriate engineering could

improve the material performance. On the other hand, these studies aim at parameterizing multiscale models with quantitative thermodynamic and kinetic inputs which are sometimes inaccessible from experiments. In this way, computational chemists invested in this area contribute—even unconsciously—to feeding the virtual database of input parameters required for the next generation of multiscale "bottom–up" models.

In this chapter, we will give a non-exhaustive review of what first-principles calculations can bring to the understanding of material performance and to the extraction of quantitative thermodynamic and kinetic parameters, with a special focus on the methodological and numerical remaining locks. Basic thermodynamics are first used to describe the energetics of electrochemical reactions underlying the battery operation. Then, a brief review of first-principles approaches to condensed matter is given, along with technical aspects/locks associated with the computation of the thermodynamic quantities of interest. The last section is devoted to the perspectives.

2 Macroscopic Picture of an Electrochemical Reaction

The **voltage** delivered by a rechargeable Li-ion battery is a key parameter to qualify the device as promising for future applications. It is a thermodynamic quantity that is directly linked to the difference in the electric potentials of the two electrodes constituting the Li-ion cell. During the discharge, two simultaneous redox reactions occur at both electrodes when Li^+ ions and electrons are transferred from the negative electrode (low-potential vs. Li^+/Li^0) to the positive electrode (high-potential vs. Li^+/Li^0). At each step of the reaction x, the equilibrium battery voltage, $V(x)$, is directly linked to the reaction Gibbs energy $\Delta_r G(x)$ through the Nernst equation:

$$\Delta_r G(x) = -nFV(x) \tag{1}$$

where F is the Faraday constant and n is the number of charge transported through the electrolyte by the exchanged (Li) ions. In order to specifically check the performance of a given electrode material, hereafter denoted $\mathcal{H}$, chemists usually build half-cells in which the Li-metal reference electrode is used at the negative electrode of the cell. In this way, the battery voltage directly gives the material potential with respect to the Li^+/Li^0 reference potential (−3.04 V vs. NHE). During operation, the electrochemical reactions occurring at both electrodes are

$$\begin{array}{r} \mathrm{Li} \rightleftarrows \mathrm{Li}^+ + \mathrm{e}^- \\ \frac{1}{\varepsilon}\mathrm{Li}_x\mathcal{H} + \mathrm{Li}^+ + \mathrm{e}^- \rightleftarrows \frac{1}{\varepsilon}\mathrm{Li}_{x+\epsilon}\mathcal{H} \\ \hline \frac{1}{\varepsilon}\mathrm{Li}_x\mathcal{H} + \mathrm{Li} \rightleftarrows \frac{1}{\varepsilon}\mathrm{Li}_{x+\epsilon}\mathcal{H} \end{array} \tag{R1}$$

In open-circuit conditions (OCV), the total Gibbs energy of the electrochemical system at any given temperature (T) and pressure (p) conditions is

$$G_{\{n_i\},T,p}(x) = \sum_i n_i \mu_i = n_{\mathcal{H}} \mu_{\mathrm{Li}_x\mathcal{H}} + (n_{\mathrm{Li}} - x.n_{\mathcal{H}})\mu_{\mathrm{Li}} \tag{2}$$

where μ_i are the chemical potentials of species i, $n_{\mathcal{H}}$ and n_{Li} the total number of mole of $\mathcal{H}$ and Li and $x \cdot n_{\mathcal{H}}$ the reaction extent. The molar free energy of reaction R1 is

$$\Delta_r G = \frac{1}{n_{\mathcal{H}}} \frac{\partial G(x)}{\partial x} = \frac{\partial \mu_{\mathrm{Li}_x\mathcal{H}}}{\partial x} - \mu_{\mathrm{Li}} \tag{3}$$

Using the Nernst relation, the electrode potential $V(x)$ with respect to the $\mathrm{Li}^+/\mathrm{Li}^0$ reference is then

$$V(x) = -\frac{1}{F}\left\{\frac{\partial \mu_{\mathrm{Li}_x\mathcal{H}}}{\partial x} - \mu_{\mathrm{Li}}\right\} = -\frac{1}{n_{\mathcal{H}}F}\frac{\partial G(x)}{\partial x} \tag{4}$$

From this equation, it is possible to extract the potential variation with lithiation

$$\frac{\partial V(x)}{\partial x} = -\frac{1}{F}\frac{\partial^2 \mu_{\mathrm{Li}_x\mathcal{H}}}{\partial x^2} = -\frac{1}{n_{\mathcal{H}}F}\frac{\partial^2 G(x)}{\partial x^2} \tag{5}$$

At equilibrium, the free energy function of the electrochemical system $G(x)$ must be a convex function of the reaction extent since the electrode achieved at each given composition is assumed to be the most thermodynamically stable electrode. This does not preclude multiphasic electrodes as we will see below. The second derivative of $G(x)$ with respect to x is then positive (or nil), whatever the reaction mechanism (i.e., single- or two-phase process). This implies that the equilibrium material potential $V(x)$ with respect to $\mathrm{Li}^+/\mathrm{Li}^0$ decreases (or remains constant) upon lithiation

$$\frac{\partial V(x)}{\partial x} \leq 0 \tag{6}$$

The Gibbs function of the $\{\mathrm{Li}_x\mathcal{H} + (n_{\mathrm{Li}} - x)\mathrm{Li}^0\}$ system, hereafter denoted as $G(\mathrm{Li}_x\mathcal{H}/\mathrm{Li})$ is represented in Fig. 1 for $n_{\mathcal{H}} = 1$ as a function of the Li content x inserted in $\mathrm{Li}_x\mathcal{H}$ (green line). When $G(\mathrm{Li}_x\mathcal{H}/\mathrm{Li})$ shows a concave shape, i.e., in the composition range $x_1 \leq x \leq x_2$, the electrode is metastable and disproportionates into $\{\mathrm{Li}_{x_1}\mathcal{H} + \mathrm{Li}_{x_2}\mathcal{H}\}$ to maintain the convexity of $G(x)$ (red line). In that case, the electrochemical mechanism corresponds to a *two-phase process* along which the electrode is a proportional mixture of two single phases of distinct Li compositions. For all other compositions ranges where $G(\mathrm{Li}_x\mathcal{H}/\mathrm{Li})$ shows a convex shape, the electrochemical mechanism corresponds to a *single-phase process* along which the electrode is a solid solution in Li composition. The shape of $G(x)$ thus sets the

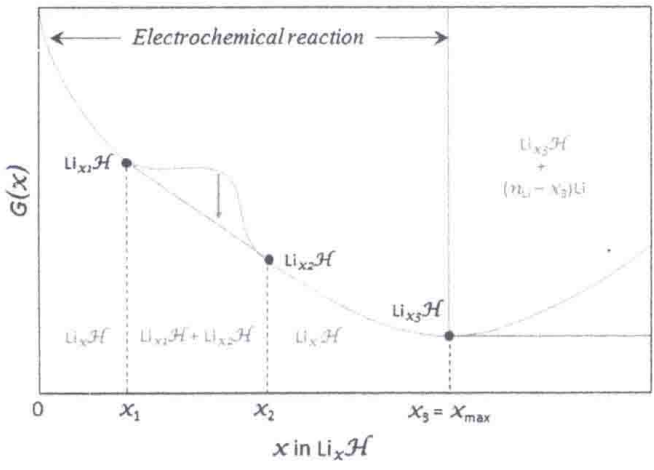

Fig. 1 Evolution of the electrode free energy $G(x)$ along the electrochemical reaction with Li. The *green line* stands for the Gibbs function of the $\{Li_x\mathcal{H} + (n_{Li} - x)Li^0\}$ system in which the $Li_x\mathcal{H}$ phase is a single-phase of composition x. The *red line* indicates the convex hull of $G(x)$, i.e., the pathway followed by the electrode to minimize its free energy. The *gray rectangle* indicates the domain in composition where the electrochemical reaction is energetically no longer achievable (Color figure online)

thermodynamic electrochemical mechanism of the total reaction as well as the intermediate phase compositions which are expected to be stabilized, and therefore observed upon lithium insertion/de-insertion.

The slope of the $G(x)$ function is directly proportional to the potential that must continuously decrease with lithiation. Thus, the composition x_{max} for which the electrochemical potential vanishes sets the end of the electrochemical reaction and therefore the theoretical **capacity** of the electrode material. This quantity is important for an electrode material as it corresponds to the maximal number of Li the material is able to accommodate or release during a cycle of discharge/charge. It is related to the amount of energy stored by the material per mass or volume unit and contributes to the total **energy density** ($\mathcal{E}$) of the material through

$$\mathcal{E} = \frac{F}{\mathcal{M}} \int_{x_{min}}^{x_{max}} V(x)\mathrm{d}x \tag{7}$$

where $\mathcal{M}$ is the molar mass of the material.

2.1 Microscopic Picture of an Electrochemical Reaction

As shown in the previous section, the overall reaction corresponds to a variation in the Li chemical composition of the intercalation material, $\mathcal{H}$. The distribution of the added charges (Li^+ ions and electrons) into the host material obviously differs from

that of the reference metallic electrode (Li^0) and depends on the electronic structure of the host material, that is, whether the electrons are localized or delocalized in the system. The spatial localization of the added electron (ρ_{e^-}) defines the *redox active center* of the host material, hereafter denoted RAC. High-potential cathode materials are generally strongly ionic systems, e.g., transition metal oxides, phosphates, or sulfates in which the added electron mainly localizes on the transition metal. In contrast, low-potential anode materials are covalent systems, e.g., Li-intercalated graphite, in which the added electron delocalizes on the system. Based on a qualitative approach, Goodenough [14] introduced in 1997 the so-called inductive effect to link the potential variations of a wide variety of transition-metal based electrode materials to the RAC electron affinity. More recently, we used a first-order perturbative approach to show that the ionic contribution to the reaction free energy may also be significant [15]. Given the general electrochemical Reaction R1 we rewrote Eq. (3) as an expansion of the host matrix energy with the added charges

$$\begin{aligned}\Delta_r G &= \Delta E_{Li^+/\mathcal{H}} + \Delta E_{e^-/\mathcal{H}} \\ &= q_{Li^+} V_{\mathcal{H}}(r_A) + \left(\mu^0_{RAC} + 2\eta_{RAC} + \int_{RAC} \rho_{e^-}(r) V_{\mathcal{H}}(r) dr \right)\end{aligned} \tag{8}$$

In this expression, $V_{\mathcal{H}}(r_A)$ and $V_{\mathcal{H}}(r)$ are the electrostatic fields exerted by the ions of the host matrix at the Li and RAC sites, μ^0_{RAC} is the chemical potential of the RAC which can be assimilated to the Fermi level of the host material and η_{RAC} is the RAC chemical hardness. The reaction free energy and therefore the voltage amplitude are governed by the electronic reduction of the RAC which is directly linked to its chemical nature (short-range effects) and by the electrostatic modulations associated with the addition of two separated charges (e^- and Li^+) which is directly linked to the crystal structure and polymorphism (long-range effects). Including both the electronic and ionic contributions to the reaction free energy, this approach not only generalizes the qualitative approach of Goodenough [14] but also allows rapid and quantitative assessment of materials potential.

2.2 *Beyond the Thermodynamic Equilibrium*

Besides the thermodynamic quantities that define whether or not a material is suitable for application, kinetic quantities related to the electrochemical reaction rates are also of great importance for battery performance. In particular, the ionic and electron transport into the host matrix and/or at the interfaces between the active material and the electrolyte (Li^+ transport) or the current collector (electron transport) may lead to kinetic limitations, which in turn alter the electrochemical mechanisms. These limitations generally induce electrode polarization effects (gradient of Li composition and/or local electric fields) that directly translate into

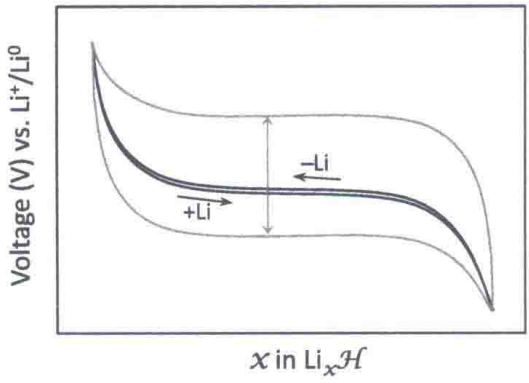

Fig. 2 Effect of electrode polarization (*red*) on the voltage profile of a $Li_x\mathcal{H}/Li$ half-cell in operating charge (−Li) and discharge (+Li) conditions with respect to the thermodynamic equilibrium (*black*) (Color figure online)

different working voltages between the charge and the discharge. As shown in Fig. 2, the electrode follows a kinetically activated pathway that is no longer dictated by the convex $G(x)$ function and is associated with different potentials in charge (delithiation) and discharge (lithiation). Such kinetic limitations obviously affect the efficiency of the device as the energy required to recharge the battery is higher than the energy delivered in discharge. To overcome this issue, chemists often play with appropriate engineering of the electrode (particle size, carbon additives, and binders) to increase the electric contacts and ionic diffusion rates inside the particles and at grain boundaries. Often beneficial to the battery performance, the impact of these formulations is, however, not trivial. Indeed, the decrease in the particle size may promote some interfacial electrochemical effects that are not well understood, yet are crucial in the prediction and understanding of the overall reaction mechanism. It is therefore important to account for these phenomena when studying the electrochemical properties of battery materials. This supposes the development of new methodologies to capture and include these effects in the response property of electrode material under electrochemical conditions.

2.3 *First-Principles Approach to Condensed Matter*

The first-principles approach to condensed matter consists in starting from what we know about a material, i.e., its chemical composition and to calculate its energy and properties. The interactions between atoms, such as chemical bonding, are determined by the interactions of their constituent nuclei and electrons. In the Born–Oppenheimer approximation, the electrons are the particles setting the many-body problem and their behavior is governed by basic quantum mechanics. What makes first-principles calculations difficult is mainly the size of the problem in terms of a

numerical formulation, in particular to describe the complex issue of electron repulsions. The development of accurate and efficient theoretical methods and computational techniques for dealing with so many particles is therefore central to the ongoing research in this field. Among the theoretical methods available to solve the many-body problem, the Density Functional Theory (DFT) [16] is the most widely used formalism in condensed matter as it combines numerical efficiency with acceptable accuracy and reliability. It is regarded as the main computational tool to perform electronic structure calculations for periodic systems with a realistic complexity. Within the framework of Kohn–Sham DFT (KS DFT), [17] the intractable many-body problem of interacting electrons moving in a static external potential is reduced to a tractable problem of noninteracting electrons moving in an effective potential:

$$\left\{-\frac{\hbar^2}{2m}+v_{\text{eff}}(\mathbf{r})\right\}\phi_i(\mathbf{r})=\varepsilon_i\phi_i(\mathbf{r}) \tag{9}$$

The effective potential $v_{\text{eff}}(\mathbf{r})$ includes the electrostatic external potential set by the atomic coordinates (nuclei) and the Coulomb interactions between electrons modulated by many-body effects:

$$v_{\text{eff}}(\mathbf{r})=v_{\text{ext}}(\mathbf{r})+e^2\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}'+\frac{\partial E_{\text{xc}}[\rho]}{\partial\rho(\mathbf{r})} \tag{10}$$

The $E_{\text{xc}}[\rho]$ term is the so-called exchange-correlation energy term. It includes corrections to the kinetic and Coulomb energies but its exact expression is unknown. Various flavors of energy functionals were developed so far to reach an accurate description of this energy functional, among which the most popular are the Local Density Approximation (LDA) [18] and the Generalized Gradient Approximation (GGA) [19, 20]. Although very powerful in describing the ground-state structure, energy and properties of a wide variety of materials ranging from metals to large-gap semiconductors, these functionals are unable to capture the physics of strongly correlated electrons or weak interactions. In particular, transition metal oxides such as those known as Mott–Hubbard insulators (NiO) are predicted to be metallic in the LDA or GGA approximations due to the so-called self-interaction error (SIE), which tends to over-delocalize the electrons along the chemical bonds. In these cases, more sophisticated functionals, e.g., hybrid (DFT/HF) [21–23], range-separated (HSE0) [24], or Hubbard-corrected (DFT+U) [25–27] functionals are required to properly describe the energetics and electronic structure of these materials. As we will see in the following, these functionals rely on adjustable parameters whose reliability needs to be evaluated before use. The DFT/HF functionals incorporate a portion of the exact Hartree–Fock exchange energy in the E_{xc} term to balance the overestimated DFT exchange energy. In condensed matter, the most popular hybrid functional is

the PBE0 (Perdew–Burke–Ernzerhof) [23] which mixes the Hartree–Fock and DFT exchange energies in a 1:3 ratio:

$$E_{xc}^{\mathrm{PBE0}} = \frac{1}{4}E_x^{\mathrm{HF}} + \frac{3}{4}E_x^{\mathrm{PBE0}} + E_c^{\mathrm{PBE0}} \tag{11}$$

The HSE0 (Heyd–Scuseria–Ernzerhof) formalism introduces another adjustable parameter λ to discriminate the regions in space where the HF/DFT mixing is needed:

$$E_{xc}^{\lambda\mathrm{PBE0}} = aE_x^{\mathrm{HF,SR}}(\lambda) + (1-a)E_x^{\mathrm{PBE0,SR}}(\lambda) + E_x^{\mathrm{PBE0,LR}}(\lambda) + E_c^{\mathrm{PBE0}} \tag{12}$$

where the mixing parameter a is 1/4 for the HSE06 functional and SR and LR stand for short- and long-range interaction regions. The idea behind the DFT+U formalism is physically different from that of hybrids or range-separated functionals. It consists in describing the strongly correlated (localized) electronic states of the system with a Hubbard-like model, and to treat the rest of valence electrons with standard DFT functionals. Practically, an effective on-site Coulomb U_{eff} (also adjustable) is added to the subset of strongly correlated orbitals i (e.g., d- or f-orbitals) in order to penalize their partial occupation. The simplest expression of the DFT+U energy functional is the rotationally invariant approximation of Dudarev et al. [27] and is given by

$$E^{\mathrm{DFT}+U}[\rho, \{n^{\sigma}\}] = E^{\mathrm{DFT}}[\rho] + \left\{E^{\mathrm{Hub}}[n^{i\sigma}] - E_{\mathrm{dc}}[n^{i\sigma}]\right\} \tag{13}$$

where ρ is the total density and $n^{i\sigma}$ the spin occupation matrix of the strongly correlated orbitals i. While the U_{eff} parameter can be extracted from a self-consistent procedure based on a linear-response approach [28], it is most widely used as an adjustable parameter.

How efficient are first-principles calculations to investigate the electrochemical properties of complex electrode materials? A literature survey is sufficient to realize that the pioneer work of Ceder and coworkers in 1997 on first-principles predictions of electrode potential [29] has opened a tremendous field of investigation for theoreticians. Ever since, the number of computational studies devoted to the electrochemical properties of electrode materials keeps on increasing every year. Besides, new methodologies emerge to (i) improve the accuracy of the calculations, (ii) describe more finely the electrochemical mechanisms, and (iii) introduce experimental reality such as particle size, pressure and temperature conditions, and so on. In the following, we give a non-exhaustive review of the methodologies used to link the thermodynamic equations of Sect. 2 to first-principles calculations. We distinguish systems for which the electrochemical properties are governed by the bulk phase (Sect. 3) from those for which interface electrochemistry is dominant (Sect. 4).