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# Some challenges in the first-principles modeling of structures and processes in electrochemical energy storage and transfer

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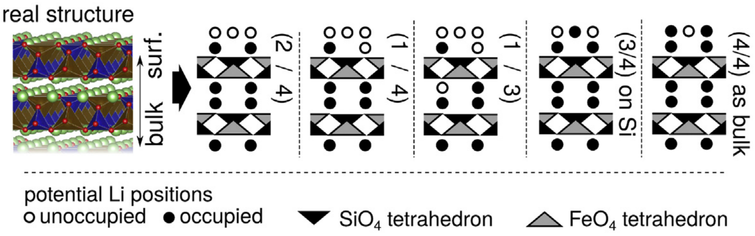
## HIGHLIGHTS

- Problems in the theoretical modeling of electrochemical interfaces are identified.
- Adsorbate structures at electrode/electrolyte interfaces are determined.
- Basic properties of Li and Mg relevant for dendrite growth are discussed.
- The weak interaction of ionic liquids with electrodes is addressed.
- A multiscale approach for modeling bulk volume changes is sketched.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In spite of the strong relevance of electrochemical energy conversion and storage, the atomistic modeling of structures and processes in electrochemical systems from first principles is hampered by severe problems. Among others, these problems are associated with the theoretical description of the electrode potential, the characterization of interfaces, the proper treatment of liquid electrolytes, changes in the bulk structure of battery electrodes, and limitations of the functionals used in first-principles electronic structure calculations. We will illustrate these obstacles, but also indicate strategies to overcome them.

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## 1. Introduction

In spite of its technological relevance in the electrochemical energy conversion and storage, our knowledge about the microscopic structure of devices, in particular at electrode/electrolyte interfaces, is still limited [1]. This is among others caused by the fact that the experimental determination of bulk and interface structures is not trivial. Here simulations on the microscopic level together with a multi-scale modeling approach could be rather helpful.

However, the atomistic theoretical description of these structures is hampered by several facts. i) Electrochemical interfaces, in particular in batteries, are often very poorly characterized since experimental tools with atomic resolution often do not work at these interfaces. This makes the theoretical structure

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determination difficult as hardly any experimental information can be used as input. ii) Liquid electrolytes require to determine free energies instead of just total energies. This means that computationally expensive statistical averages have to be performed [2,3]. iii) In electrochemistry, structures and properties of the electrode–electrolyte interfaces are governed by the electrode potential which adds considerable complexity to the theoretical treatment since charged interfaces need to be considered [4,5,6,7,8]. iv) Upon charging and discharging, significant structural changes can occur in the electrodes, realized as volume changes or phase transitions [9]. These cannot be properly handled by atomistic techniques alone, but require the combination of atomistic modeling with a continuum description. v) As far as first-principles approaches are concerned, electronic structure methods based on density functional theory (DFT) combine numerical efficiency with satisfactory accuracy for a wide class of systems and materials [10]. However, this is not true for all materials used as electrodes or electrolytes in electrochemical energy storage and conversion.

It is fair to say that despite these obstacles, significant progress has already been made in the atomistic modeling of devices in electrochemical energy storage and conversion [11]. It is furthermore evident that nowadays computational modeling is an integral part of research and development in materials and interface sciences [10,12]. Still, in this contribution we will illustrate some of the challenges in the atomistic modeling of electrochemical storage and conversion devices, but also indicate possible strategies to handle these obstacles. We will mainly concentrate on interface issues at the electrochemical boundary between electrode and electrolyte, in particular with respect to the structure and composition of these interfaces, but we will also discuss issues associated with the volume change upon charging and discharging in batteries.

## 2. Computational details

The periodic density functional theory calculations presented in this paper have been performed using the Vienna ab initio simulation package (VASP) [13]. Electron–core interactions were accounted for by the projector augmented wave method [14,15]. Typically the functional of Perdew, Burke, and Ernzerhof (PBE) [16] was employed in the Generalized Gradient Approximation (GGA) in order to describe the exchange-correlation effects. The electronic one-particle wave functions were expanded in a plane-wave basis set up using a sufficiently high energy cutoff of at least 400 eV. The convergence of the results with respect to the *k*-point set was carefully monitored. In the surface calculations, at least the uppermost two layers were allowed to relax.

## 3. Structure of interfaces in electrochemical storage and conversion devices

### 3.1. Thermodynamic approach to model the presence of electrolytes at interfaces

As far as the interfaces between electrodes and electrolytes are concerned, it is important to note that the presence of the electrolyte has a significant influence on the surface structure of the electrode. Now in particular in batteries these interfaces can be rather complex. The classical example is the solid electrolyte interphase (SEI) that forms at negative battery electrodes (see Fig. 1).

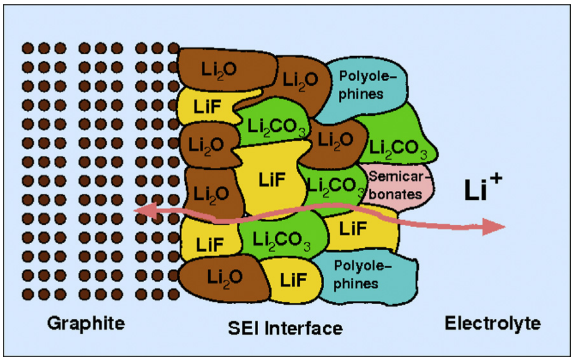

**Fig. 1.** Schematic structure of the solid liquid interphase forming at negative battery electrodes.

Modeling the SEI atomistically represents a significant challenge. Because of its complexity, first-principles studies are limited to the initial stages of SEI formation [17,18,19,20] which are assumed to be due to the decomposition of the electrolyte such as ethylene carbonate (EC) [21]. Ion transport through the SEI can hardly be modeled on a first-principles basis, but it can be addressed on a force-field level [22]. For example, MD simulations of the $Li^+$ transport through the dilithium ethylene dicarbonate ($Li_2$EDC) component of the SEI yielded activation energies for $Li^+$ diffusion and conductivity in good agreement with experiment [23].

Still, it is desirable to address electrode properties by electronic structure calculations inspired by the applicability of traditional surface science approaches for electrochemistry surfaces [7,24]. The complexity of realistic half cells with electrode, active particles, conducting carbons, binders, solvent, electrolyte and additives necessitates to introduce appropriate approximations and simplifications. According to one of these simplified approaches, the electrolyte can just be regarded as a thermodynamic reservoir which supplies particles that are characterized by their chemical potential [25,26]. In thermal equilibrium, the appropriate thermodynamical potential describing the electrode consisting of different particles $i$ is the Gibbs free energy $G(T,p,\{N_i\})$. The most stable electrode surface structure is given by the minimum of the surface free energy that can be expressed [27] as

$$\Delta\gamma(T,p) = \frac{1}{A_s}\left(G(T,p,\{N_i\}) - \sum_i N_i\mu_i(T,p)\right) \tag{1}$$

$$\Delta\gamma(T,p) \approx \frac{1}{A_s}\left(E_{\text{ads}} - \sum_i N_i\Delta\mu_i(T,p)\right), \tag{2}$$

where $A_s$ is the surface area. In the last line (Eq. (2)), we have separated the pressure and temperature-dependent components from the chemical potential. The adsorption energy $E_{\text{ads}}$ with respect to the most stable species in the reservoir in the limit of zero temperature and pressure can be derived from DFT calculations. Note that the values of $E_{\text{ads}}$, $A_s$, and $N_i$ are assumed to be taken with respect to a chosen surface unit cell. Any change in entropy and zero-point energies upon adsorption can be taken into account, but in fact it is often neglected in theoretical surface studies as these contributions are typically small [27].

For electrochemical systems in the presence of an electrode potential $U$, the chemical potential $\mu$ has to be replaced by the electrochemical potential

$$\tilde{\mu} = \mu + neU, \tag{3}$$

where $n$ is the charge of the particle. Still the problem remains that the reservoir is given by the electrolyte which requires to derive the solvation energy of the species as the proper reference. The

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