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Review Article

Frontiers in first principles modelling of electrochemical simulations

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Computer simulations are a useful tool to describe physical and chemical processes. However, the state-of-the-art techniques lack practicality to simulate the dynamical movement of species while accounting for the electron exchange. This is the case of electrochemical processes, i.e. species in solution interact with the surface of the electrode and the solvent molecules arrange at the interface according to the field created by the electrode potential. Here we present the latest innovative methods and frontiers for the treatment of electrochemical simulations including microsolvation protocols implemented in the density functional theory framework. We also suggest alternative electronic structure mixed-force calculations to pioneer a more realistic simulation framework of reactive processes.

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Introduction

The characterisation of the interface between electrodes and electrolytes lies at the heart of the electrochemical processes. However, electrochemical information is commonly derived at a macroscopic level by measuring, for instance, surface tension, work-function and interfacial capacitance [1]. Measurements revealing the atomic structure, such as STM, are not readily performed in aqueous electrolytes, and even if performed will not reveal the structure of the solvent double layer at the interface.

Recent advances in theoretical models, based on classical Poisson–Boltzmann electrostatics from Gouy–Chapmann

and Stern, and the increasing computational power, facilitate the simulation of electrochemical interfaces using density functional theory (DFT) methods [2*]. These have provided approximated insights of the potential-dependence of specific catalytic reactions [3**], [4]. Although first principles simulations seem well suited, the modelling of the electrochemical interface is far from trivial to provide the required fundamental understanding of the structure of the interface. The electrochemical solid–liquid interface represents one of the frontiers in first principles modelling due to the dynamism of the systems, i.e. adsorptions on the electrode of solvent, electrolytes and other species from the interface.

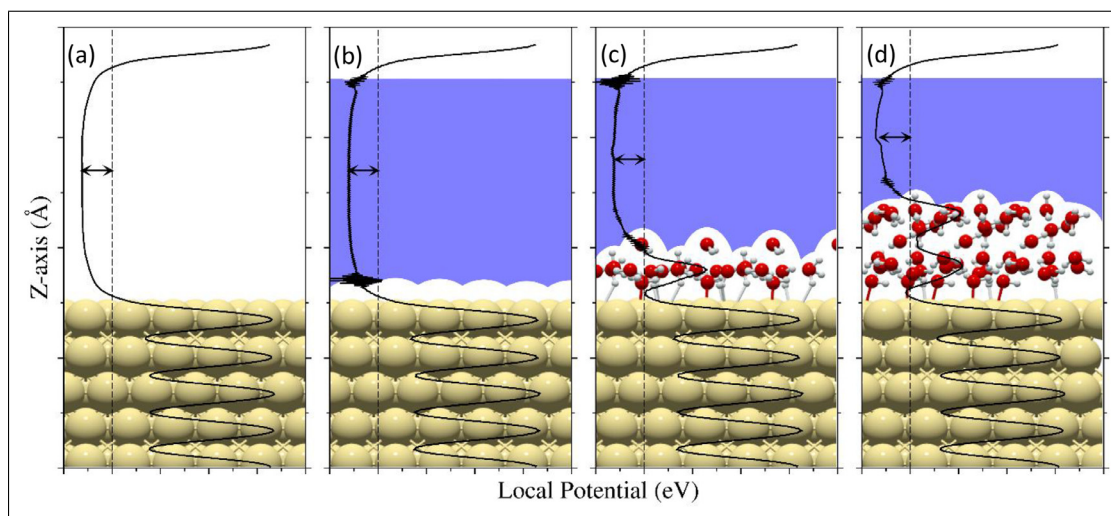
Innovative experimental and theoretical techniques are urgently required to decouple the many-body problem associated with it, where the structure and species on the electrode and in the solution, as well as the potential applied, are key factors. Especial importance has been attributed to the atomic scale computer simulations contributions as they can provide access to the microscopic processes occurring at electrode surfaces and probe the isolated and collective effects of these critical factors on the electrochemical interface [5,6].

Computational approach

DFT enables theoretical elucidation of electron-exchange reaction mechanisms on complex catalyst surfaces [7–9] and nanoparticles [10,11], making it now possible to design efficient catalysts for various industrial applications. The extension of this predictive power to electrochemistry process is highly valuable. However, for a detailed understanding of the electrochemical reaction mechanism, it is of great importance to bridge the gap between the computer models and actual systems exposed to realistic operating conditions. Resolving this issue is not just a matter of adding more atoms to the simulations, but it is a fundamental challenge.

Theoretical methods have made exciting progress in modelling and understanding electrochemical phenomena. Methods such as Canonical Monte Carlo [12], Wertheim–Lovett–Mou–Buff integral equation [13], modified Poisson–Boltzmann [14] and molecular dynamics [15] have been successfully implemented. The solid–liquid interface can now be approached with quantum mechanics approaches. Similar to heterogeneous phase reactions, the energy landscapes of electrochemical reactions are influenced by the atomic structure of

Figure 1



Schematic representation of an *fcc* metal electrode in (a) vacuum, (b) implicit solvent, (c) and (d) one and two layers of explicit H₂O molecules and implicit solvation model. The solid lines indicate the local potential along the Z-axis. The dashed lines correspond to the Fermi energy, and the arrows point the difference $\Phi_{ref} - \Phi_{Fermi}$ related to the point of zero charges of the electrode surface.

the electrodes and the presence of surrounding species – (co-)adsorbates, promoters, poisons and solvents. In addition, electrochemical processes are highly dependent on variations of the electric potential applied to the electrode, which also may alter the stability of reactants, intermediates and products on surface reactions. Specific mechanisms and pathways may be preferred or mitigated by tuning the electrode potential [16^{••}]. However, it requires considering the complexities of an electrolyte in solution and potential reference for an accurate description of the process.

The advancement of electrochemical simulations accuracy should involve a reliable method to model the electrode/solution interface considering the operating conditions, such as concentration of species, pH and applied potential, and provide the relevant information of atomic structure at the electrode surface and interface with the solution, the charge, and the number of electrolytes on the slab species.

Importance of the solvation model

The constraint of treating liquids, including their electronic behaviour, requires intensive computational power to sample the thermodynamic variables of atomic configurations. Empirical models for describing bulk liquids [17[•]] suitable for solid–liquid interfaces have been implemented with the DFT [18]. These models, represented in Figure 1a and b, have made important advances towards the reliable yet efficient treatment of electrochemical systems.

The continuum solvation model presents the advantages to neutralise the charge electrode-ions, essential for periodic calculations [19], and to define a meaningful absolute reference value for potentials [20[•]]. These imply well-defined calculations with a net charge per unit cell in the solute and the electron chemical potential referenced to zero at infinity. Despite accurate representation of molecular solvation energies [21], these homogeneous solvation models cannot represent directional interactions such as hydrogen bonds, crucial to describe the stabilisation of adsorbed species. An alternative is to consider a metal–solution interface explicitly, actually including the solvent [22]. The resulting effect is a change in the Fermi energy directly influenced by local changes in the solvent and (co-)adsorbates electronic structure. This model enables the band structure alignment between different surfaces with the same solution level (i.e. the potential zero defined far from the surface or between periodic slabs). More importantly, it corrects the DFT energy with the long-range electrostatic interaction due to solvation. While ab-initio molecular dynamics are a viable solution [23^{••}], they remain generally unaffordable. Static DFT calculations, however, require a statistical average over a large number of atomic configurations to integrate over meaningful thermodynamics observables, i.e. interaction energies and electronic structure properties for the predominant molecular arrangements under reaction conditions (concentrations and temperature) [22,24]. Besides, it also needs a large simulation cell, and a number of molecules explicitly described to minimise finite size errors – artificial electron work-function values and molecular arrangements due to size constraints [25]. These factors

make the simulations prohibitively expensive computationally with the addition to being difficult to set up and analyse.

The combination of implicit and explicit solvation models, i.e. microsolvation as shown in Figure 1c and d, minimise the computational requirements as it accounts with, at least, an explicit solvation layer in addition to continuum solvation in the rest of space that defines the solution bulk and the reference potential. This is a more affordable solution and combines benefits from previous solvating models to describe the interface [16**].

Treatment of the applied potential

External potentials play the central role in electrochemistry as it influences (co-)adsorption, reaction and desorption of species on the electrode [26]. Several computational techniques implemented within DFT models provide an approach accounting for electric potential, e.g. for calculating capacitance in metal–insulator–metal [27,28] and carbon nanotube systems [29], and for field emission from metal surfaces [30]. These allow calculating the Helmholtz free energy and electrochemical potential of specific microscopic configurations of the double layer and adsorbates on the electrode surfaces [31,32].

However, self-consistent DFT calculation involves a fixed number of electrons and therefore additional frameworks, such as canonical-ensemble, are required to integrate the electron fluctuations within the simulation and derive, for instance, reaction rates [33,34]. The combination of DFT fixed electron chemical-potential within a canonical treatment of electrons is based on charged slab models (by homogenous background charge [3**], explicit protons in the electrolyte [35*], compensating plane of charge [36] and others methods [20*,37]). Canonical approaches implement the flux of electrons and mimic the experimental condition on a surface [38,39]. For instance, an external potentiostat can be included in molecular dynamics simulations to allow the exchange of electrons and drive the process towards a chemical potential [6].

A different strategy is to perform constant charge electronic structure calculations and relate the slab potential to its work-function as outlined by Trasatti [40,41**]. The main idea is to vary the dipole of the interface and measure the corresponding change in the electron work-function (an increase in the Fermi level), which corresponds to a change in electrode potential [22]. The reference to the simulated potential is typically the standard hydrogen electrode (SHE), which absolute position is relative to the vacuum level. The SHE can be measured computationally from zero charge calculation of solvated electrodes [42]. Although this method minimises systematic errors, experimental values are also a good approximation.

Reaction energies at a fixed potential can be obtained by plotting the energies as a function of the work-function for initial and final states of structures with varying interface dipoles. It is related to the fact that during redox processes, the dipole at the interface changes locally, which may have a significant effect on small simulation cells [39]. An alternative approach is to employ increasingly larger simulation cells and then extrapolate the result to the limit of the infinite area as the dipole variation is inversely proportional to the size of the electrode simulated [43]. To retain the link between work-function and energy, the solvent structure should remain practically constant as the structural arrangement of polar solvents, e.g. water, leads to dipole and work-function variations but not necessarily to the energy. Besides considering the energy—work-function relationship one-to-one, the main backward of fixed potential simulations is that the pH also determines the interface's structure and the driving force. The restricted relaxation of the double layer is also related to the pH, what constitutes additional complexity for simulating electrochemical processes.

The proton potential is related to the electrochemical environment, and it gets more significant as pH increases because the protons are more stable at high pH (higher configurational entropy). To facilitate its treatment, the proton potential is often connected to the electron, $\mu(\text{H}^+ + \text{e}^-)$, see Equation (1). Nevertheless, recent methods treat the combined proton–electron potential and the electron potential (from the electrode) individually [44*].

$$U = \phi - \phi_{SHE} + \frac{RT}{F} \ln(10) \cdot pH \quad (1)$$

Scope for development

The methods outlined above provide approximations of electrochemical experiments although it remains unclear whether it is possible to treat the static properties of the electrode/electrolyte interface and the dynamism of species in electrochemical reactions in a unified, realistic and practical simulation framework. Using standard DFT calculation means keeping fixed the electrochemical potential and the pH during the electronic structure calculation, and the need of exploring several sizes of the simulation cell and solvent arrangements leads to an unfeasible protocol. The microsolvation of the surface and ionic species speed this process by decreasing the number of explicit molecules considered during the simulation, though an average of atomic configurations is still required to sample the energy landscape.

Instead of assuming attributes for the interface structure and then calculating the working conditions, the combination of DFT with canonical ensemble allows to include the variation of applied potential and other observables

[45,46]. For instance, a grand canonical ensemble would correct energies derived from DFT by integrating the electrostatic potential within the working volume over the applied charge.

$$G_{(T=0)} = E_{DFT} + \int_0^q \langle \bar{V} \rangle dQ + \mu q \quad (2)$$

A canonical mean-field microkinetic treatment of the DFT results can incorporate an accurate description of the molecular interactions (adsorption and desorption) to the surface of heterogeneous electrodes, where the local potentials may differ from the average potential over the exposed surface [47].

The reaction dynamism can be accounted by molecular dynamics providing a fair sample of most of the thermodynamic constraints imposed on the interface structure by the electrochemical environment. However, fully ab-initio molecular dynamics implies considerable computational costs. Pioneering techniques to achieve reliable simulations are being developed. For instance, it is now possible to account electrons and the movements of solvent and solvated species during a reaction by combining, in a single hessian matrix, accurate DFT and parametrised dynamic simulations [48–50*]. This setup initially evaluates the system using precise static DFT, i.e. electronic structure and interatomic forces. It proceeds to solve the equations of motion with standard algorithms, which trajectories are corrected by the accurate initial description. Hence, it allows coarsening the intervals at which high precise forces are calculated, with the advantage of efficiency and enhanced sampling resolution [51,52]. Upon reaching the required threshold between interatomic forces, the last step is a precise DFT providing accurate electronic structure, i.e. the work-function over an equilibrated electrode-solution interface. Furthermore, while parametrised potentials are constructed commonly employing physical models of atomic interactions, innovative integration of adaptive potentials have paved a novel way to construct them. These potentials improve their accuracy within the self-consistent calculation following schemes such as artificial neural networks [53], non-linear regression models [54] and others [48,54,55]. Hence, the size of the cell can be large enough to consider negligible variation the dipole and constrictions in the solvent and solvated species.

Conclusion

The development of computational techniques led to methods to predict physical and chemical processes. Nevertheless, a realistic simulation of electrochemical reactions remains a grand challenge. It marks a frontier where the accuracy, efficiency and affordability of computer models are compromised. Previous methods have framed the importance of (i) including an explicit solvent

in the simulations, integrating the polarisability, (ii) the long-range stabilisation of species within the dynamic environment of reaction processes, and (iii) the exchange of electrons at the electrode-solvent interface.

Along with the microsolvation and integration of static DFT in canonical frameworks, we propose the assimilation of dynamic and precise static calculations within a single mixed-forces scheme. This is more efficient than ab initio molecular mechanics while conserving the DFT accuracy describing electronic structures.

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