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Modeling proton transfer to charged silver electrodes

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ABSTRACT

Density functional theory (DFT) and molecular dynamics (MD) techniques are used to study proton transfer from an aqueous solution to an Ag(1 1 1) surface. DFT is applied to study Ag–water and Ag–hydronium interactions as well as proton transfer for small systems based on the cluster model. The data gained are then used to adjust an empirical Ag–water interaction potential and to reparametrize an empirical valence-bond (EVB) model, which has been successfully applied for the study of proton transfer to a Pt(1 1 1) surface before. Employing these force fields in MD simulations enables dynamic modeling of the electrolyte–metal interface on a scale large enough to give realistic results. Results from a MD trajectory study on Ag(1 1 1) are reported and compared to the analogous study for platinum. Low discharge rates on Ag(1 1 1) are observed, and the potential range for hydrogen evolution can be estimated. The different behavior relative to Pt(1 1 1) can be traced to features of the respective potential energy surfaces and to the different structural properties of the aqueous/metallic interfaces.

1. Introduction

Proton transfer to and discharge on a metal electrode is one of the fundamental processes in electrochemistry. Theoretically, it is less well understood than other ion transfer reactions. This is a consequence of the strong and unique interaction of the proton with water, with which it can form transitory species such as the Eigen complex $H_9O_4^+$ (a solvated hydronium H_3O^+ ion) [1] or the Zundel ion $H_5O_2^+$ (a proton shared by two water molecules) [2]. Consequently, a conceptual distinction between a 'reactive complex' and the 'environment' is not easily possible. Rather, the constitution of the reactive complex fluctuates in time.

In the bulk, besides classical diffusion, the essential mechanism of proton transport is the so-called Grotthuss hopping [3] or structural diffusion mechanism, in which a proton is transferred along the hydrogen bond network from one H_3O^+-like species to a neighbouring water molecule, which is followed by (usually) a transfer of *another proton* of that molecule to the next water molecule, and so on. During the last decade state-of-the-art molecular dynamics (MD) simulations – classical MD simulations on the basis of reactive force fields as well as so-called ab initio MD simulations calculating interactions on the fly from quantum chemistry, usually based on density functional theory – contributed, together with progress in experiment and theory, to the understanding of the detailed nature of these processes [4–14]. The rate determining step was identified as the breaking of a hydrogen bond in the solvation shell of the proton complex [8,12,15]. A view emerged which regards Zundel and Eigen species as limiting forms [16] rather than separate species, and that proton transfer occurs when fluctuatively a configuration is pre-formed such that the barrier for proton transfer is insignificantly small [8,16]. Thus, proton transfer is not determined by quantum-mechanical tunneling but by the (slower, and in better approximation classical) solvent coordinates [8]

A similar view can be adopted for the electrochemical proton discharge reaction. The primary step, the transfer (and discharge) of a proton to the metal electrode, depends on the configuration of the proton-containing complex, the nature of the electrode and the electrode potential. Proton discharge will take place when a suitable configuration occurs. Proton discharge occurs on all metals and – within a certain, metal-specific range – increases exponentially with potential; however, the maximum achievable rates vary by many orders of magnitude. Specifically, it is well known that platinum is a very reactive metal which facilitates proton discharge and in fact forms so-called underpotential deposition (UPD) layers at potentials well positive of the standard hydrogen potential [17]. Silver, on the other hand, is much less reactive than platinum.

It should be stressed from the very beginning that electrochemical hydrogen evolution is a multistep reaction. That is why all steps should be mandatory addressed in a comprehensive model-

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ing of this reaction. As this problem is, however, very complex from the viewpoint of atomistic molecular dynamics simulations, we restrict ourselves to considering the discharge of a hydrated proton (Volmer reaction). Experimental current–voltage curves describing hydrogen evolution from acid solutions on Ag(1 1 1) electrodes [18,19] show Tafel behavior. It was concluded that the Volmer reaction is slow both on the Ag(1 1 1) single crystal surface and on a polycrystalline silver electorde [19,20], and thus rate-controlling. It was shown, on the other hand, by Conway et al. [21] that for hydrogen evolution from acidic solutions on Pt(1 1 1) the surface recombination is about one order of magnitude slower than the proton discharge. Since the Volmer reaction rate does not differ significantly from the rate-controlling recombination step, it is of course also of great importance to study the mechanism of the discharge of the hydrated proton on the Pt(1 1 1) electrode as was done in our previous work [22,23].

One can expect that too many different reaction paths for proton discharge exist, so that individual trajectories of reactive proton-discharge events do not provide statistically meaningful insight. Thus, ab initio MD schemes are currently too expensive to be used on ensembles of reactive or non-reactive trajectories that can model reaction rates for the proton discharge process. Nevertheless several interesting studies of solitary ab initio MD trajectories, at excessively high electric fields, have been performed in the past [24–26]. Using a common approach to describe electrochemical reactions, which makes use of (static, 0 K) DFT calculations of clusters in contact with metal surfaces (e.g. [27–34], is also not adequate since the dynamics of (particularly the aqueous) environment is intrinsic to the process to be studied. Statistical averages over trajectory ensembles is, however, currently feasible when using parametrized force fields.

We recently ventured into this direction by developing a reactive force field for proton discharge from aqueous solutions on Pt(1 1 1) electrodes [22,23]. Platinum was chosen as model system because it is experimentally known to be very reactive for this reaction. The approach utilizes so-called empirical valence bond (EVB) force fields, which were pioneered by Warshel and coworkers [35–37] and later adopted for proton transfer in water [9–11,14,16,38–40]. In an EVB model the state of a reactive complex is described by a superposition of zeroth order states. Each state is characterized by a particular bonding pattern and described by a classical force field. These states interact via coordinate-dependent coupling functions to form an adiabatic ground state, which describes the trajectory of the reactive system in phase space. In the bulk, this approach has led to insightful models of proton transfer [8,12,13,41]. The proton discharge model of Ref. [22] goes beyond an EVB model in the bulk by choosing additional zeroth order states. In the bulk, the different zeroth order states of the model correspond to those states where the excess proton is bonded to a specific water molecule to form a H_3O^+ ion. In a proton discharge model additional states that describe the interaction of the (discharged) hydrogen atom with the metal atoms are included.

The key result of our trajectory study on Pt(1 1 1) was an exponential Tafel like dependence of the discharge rate on the electrode potential at moderately negative surface charges and a transport limitation at very negatively charged electrodes. In the present manuscript we extend our approach to study proton discharge on the unreactive Ag(1 1 1) surface. To study this system, a suitable force field needs to be developped, since not many relevant data can be found in the published literature. DFT calculations of the interaction of silver with isolated water molecules were performed by Patrito and co-workers [42] using the cluster approach and by Sanchez [43] and Ranea et al. [44] using the slab approach. Izvekov and Voth [45] reported a short ab initio MD study of water in contact with a silver slab. Adsorption energies of the isolated water molecule in the on-top position (see also Table A.1) were obtained in the range of 0.2–0.53 eV. The different energies reflect the different quantum chemical techniques and chosen DFT functionals. Furthermore the interactions of an isolated hydronium ion with silver [42,46] were studied and an optimum adsorption energy of 2.46 eV in the fcc hollow site (and little surface corrugation) was reported. The only mechanistic study of interest in the present context is the Monte Carlo (MC) study by Pecina and Schmickler [47,48]. These authors investigated the role of reorientation in the first and second layer for proton transfer, whereas the actual bond breaking step was assumed to be fast and not considered explicitly. Since none of the published theoretical work provides enough data to construct a reactive EVB model, we decided to develop a comprehensive model which is able to describe all stages of the reaction. In the next section we briefly discuss the main ideas behind the reactive EVB model for proton discharge on Ag(1 1 1) surfaces; all technical details are collected in Appendix A. In Section 3 we investigate the equilibrium properties of the charged and uncharged water/Ag(1 1 1) interface. Section 4 provides the central results concerning the reactive trajectory calculations. In agreement with experiment, we observe significantly reduced discharge rates on silver in comparison with platinum, which will be discussed in the final section.

Before presenting our own work, we would like to mention the model for hydrogen evolution developed by Santos et al. [49] and Santos and Schmickler [50]. This work focuses on the role of the electrode metal, and treats the solvent in a summary way through the energy of reorganization; it thus complements our present work which emphasizes solvent dynamics.

2. An empirical valence bond model for proton transfer to Ag(1 1 1)

Empirical valence bond models have been introduced originally by Warshel and coworkers [35–37] to describe proton transfer reactions in condensed matter. Starting in the 1990s extended versions of such models were further developped by several groups with the intent to model proton mobility in bulk water and later applied to study proton transfer in a variety of inhomogeneous systems of biological relevance such as proteins and of technological relevance such as polymer electrolyte membranes (e.g., Refs. [12,51]).

We recently extended the EVB methodology to study the electrochemical proton discharge reaction on a Pt(1 1 1) surface [22,23]. We were able to perform statistical averages over reactive trajectories to calculate discharge rates and to gain atomistic insight into the reaction mechanism, all for different surface charge densities on the electrode. In the present work we followed the same approach to study the corresponding discharge reaction on the – less reactive – Ag(1 1 1) surface. By and large the approach in the present work is the same as the one used for the Pt(1 1 1) surface (see Refs. [22,23] for a detailed presentation), although a few technically mandated differences exist. These and all relevant information including the functional form and the fit parameters of the force field will be presented in Appendix A. Here we briefly summarize the main steps.

In the original quantum valence bond (VB) method the electronic ground state $|\psi\rangle$ of a molecular system is written as a superposition ('resonance hybrid') of several zeroth order ('resonance') structures $|i\rangle$ according to

$$|\psi\rangle = \sum_i c_i |i\rangle. \tag{1}$$

The coefficient vector $c = (c_i)$ is obtained by solving a generalized eigenvalue problem

$$Hc = ScE, \tag{2}$$