

O 44: Focus Session: Structure, Chemistry, and Ion Solvation at Solid-Liquid Interfaces III

Time: Wednesday 10:30–11:30

Location: HE 101

O 44.1 Wed 10:30 HE 101

AFM investigation of charge distribution and ion adsorption at solid-liquid interfaces — •FRIEDER MUGELE¹, IGOR SIRETANU¹, CUNLU ZHAN¹, DIRK VAN DEN ENDE¹, and DANIEL EBELING^{1,2} — ¹University of Twente, MESA institute for Nanotechnology; Physics of Complex Fluids, Enschede, The Netherlands — ²Universität Giessen, Giessen, Germany

Solid surfaces immersed in water almost invariably assume a finite surface charge typically due to either (de)protonation of functional groups on the surface or adsorption of ions from the solution. While the resulting electrostatic interaction forces are crucial for many phenomena in science and technology, such as colloid science, biophysics, foodtechnology, and enhanced oil recovery, important aspects of charge distribution and spatial arrangement of adsorbed ions in the Stern layer are poorly understood. Here, high resolution dynamic atomic force spectroscopy and microscopy experiments in ambient liquid will be described that provide detailed insight into the organization of ions in the Stern layer at various mineral-electrolyte interfaces. The experiments highlight the preferential adsorption of divalent cations (Mg²⁺, Ca²⁺) as compared to monovalent ones (Na⁺, K⁺), including the incorporation of Cl⁻ co-ions at higher concentrations. Complementary Density Functional Theory calculations demonstrate the role of hydration water upon adsorption.

Topical Talk

O 44.2 Wed 10:45 HE 101

Electronic spectroscopy at the solid-liquid interface: a window to electrochemistry and solvation phenomena — •MIQUEL SALMERON — Lawrence Berkeley National Laboratory. Berkeley, CA 94720. USA

Basic phenomena in electrochemistry, and environmental science occur at solid-liquid interfaces. To obtain information on the atomic structure, composition, electronic levels of surface and adsorbed molecules optical (IR, SFG), structural (STM, AFM, GIXS), and x-ray spectroscopy techniques (XAS-XES) can be used.

In fluorescence yield mode, XAS provides information on the elec-

tronic structure of sample materials within the escape/penetration depth of x-rays, which for soft x-rays is about 100-1000 nm. In my laboratory we use a well-known variant known as electron yield mode (EY-XAS), by measuring the electrode current which is the balance between emission and capture of secondary electrons.

We applied EY-XAS to study electrode interfaces in aqueous electrolytes. In the case of graphene we studied reactions leading to the oxidation. In the case of gold we determined the orientation of water molecules near the interface, due to interaction with gold and as a function of applied bias. In the case of Platinum we studied oxidation-reduction reactions in acid electrolytes.

Because XAS spectra are dependent on x-ray absorption rules and transition probabilities in the presence of core holes, interpretation of the spectra is not trivial and requires theoretical calculations for interpretation.

O 44.3 Wed 11:15 HE 101

Formation energy of ions in water: an ab-initio molecular dynamics study — •ANOOP KISHORE VATTI, MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf, Germany

Water is the most complex and ubiquitous liquid. Understanding the structure and properties of ions in liquid water is a key feature needed to describe and understand the properties and processes occurring in biological and electro-chemical systems. Using ab-initio molecular dynamics we study charged ions in water using various exchange-correlation functionals. We will discuss the geometric and electronic structure of the studied ions, as well as their formation energies and compare our findings to experimental observations. Evaluating the formation energy of the investigated ions, we find, e.g. that the Zn²⁺-Ion is the dominant defect over the extent of the theoretical band-gap. Aligning the calculated and measured water band-edges on an absolute scale [1] allows us to compare our calculated formation energy for the Zn²⁺-Ion with experimental ones, revealing an excellent agreement.

[1] M. Todorova and J. Neugebauer, Phys. Rev. Applied 1, 014001 (2014).