

## Surface Science Division

### Room D136 - Session SS2-MoM

#### Liquid-Solid Interfaces

Moderators: Jan Balajka, TU Wien, Sefik Suzer, Bilkent University, Turkey

#### 10:40am SS2-MoM-8 Local Potential Determinations by XPS Provides the Missing Link about Charge Dynamics of Ionic Liquid Devices, Sefik Suzer, Bilkent University, Chemistry Department, Turkey

Ionic liquid materials show rich dynamic responses on electrified surfaces. A long-standing question is why these materials exhibit very different time responses, ranging from microseconds to several hours, which are attributed to the complex interplay of chemical and physical factors, including steric and molecular interactions. However, experimental observations and theoretical predictions do not always match in IL based devices. Particularly considering the overall electrode capacitance resulting from asymmetric ion size effects, the local voltage levels can show large differences, and drift-diffusion process of ions generally fails to account for them. To clarify this point, we have utilized a combination of electrochemical devices with different chemical make-up, geometry and dynamic XPS analysis and modelling, and were able to probe the spatiotemporal voltage profiles directly from the shifts in the binding energy positions of the ionic core levels, within IL based devices. Results from a number of single and mixed ILs, as well as different device geometries will be presented and discussed.

#### 11:00am SS2-MoM-9 Interactions at the Solid-Liquid Interface of Microcrystalline ZnO and Bacterial Growth Environments, Dustin Johnson, J. Reeks, A. Caron, M. Smit, Texas Christian University; T. McHenry, Texas Christian University; S. McGillivray, Y. Strzemechny, Texas Christian University

Despite the prevalence of traditional antibiotics, new threats are posed by bacterial infections due to the rise of antibiotic resistant strains. As such, development of novel antibacterial agents is a critical area of research. In this regard nano- and microscale ZnO have been found to be particularly promising. ZnO at these scales has been shown to exhibit selective toxicity and growth inhibition for a wide range of both Gram-positive and Gram-negative bacteria as well as for microbial strains resistant to traditional antibiotics. The abundance of constituent elements and inexpensive synthesis methods in combination with the aforementioned antimicrobial properties have led ZnO based antibacterial agents to be implemented in biomedical, water treatment, food storage and various other industries. Refinement of current techniques and development of novel bactericidal applications are limited by incomplete descriptions of the fundamental interactions responsible for the observed antibacterial behaviors. In particular, the role and nature of interactions of ZnO with bacterial growth media is not well understood. Herein, we investigate environmental influences relevant to the antibacterial action of ZnO through the interactions with both bacteria and the bacterial environments on the physicochemical and optoelectronic properties of the free crystalline surface of ZnO microparticles (MPs). We expose hydrothermally grown ZnO MPs to phosphate-buffered saline (PBS) media both with and without the presence of Newman strain *Staphylococcus Aureus* (*S. aureus*) bacteria. Surface electronic structure and charge dynamics are probed via both time- and energy-dependent surface photovoltage (SPV) conducted prior to and following biological assays. We observe significant changes in the characteristic timescales under varying conditions, indicating, among other, a possibility of a significant phosphate adsorption at the free crystalline surface. This is further supported by the suppression of spectral signatures of the oxygen-rich defects after exposure to PBS media.

#### 11:20am SS2-MoM-10 Towards Understanding Interfacial Thermodynamics: Visualizing and Quantifying Competitive Adsorption on Muscovite Mica with AFM, Matteo Ogiati, J. Dziadkowiec, A. Celebi, L. Mears, M. Valtiner, Technische Universität Wien, Austria

Given its peculiar crystal structure and inherent surface charge, the (001) plane of muscovite mica has served as an excellent model system to study the hydration and electric double layer (EDL) forces at solid-liquid interfaces [1]. So far, force spectroscopies, which measure along the direction perpendicular to the surface, as well as molecular dynamics (MD) simulations, have demonstrated a certain ion-specificity towards the strength of hydration forces on mica surfaces [2-5]. These deviations are mainly attributed to the different properties of individual ions (e.g., hydration shell, size, valency, etc.), which ultimately determine their

adsorption character on mica, as well as the interfacial hydration structure [5]. Nevertheless, lateral distribution and arrangement of cations adsorbed on mica was experimentally investigated only to a lesser extent [6], although unravelling the ions' organisation directly at the surface is crucial to elucidate the structure and properties of EDLs.

In the present contribution, we discuss how high-resolution atomic force microscopy (AFM) imaging enables us to visualize the lateral distribution of individual mono- and multi-valent ions on the surface of mica. Thanks to this approach, we are able not only to resolve the crystal structure of mica immersed in aqueous solution, but also to transiently picture the population of adsorbed ions from the salt-rich solutions at different concentrations. By using an automated triangulation algorithm, the ion adsorption coverage as a function of concentration can be quantified in a first order approximation. This methodology highlights the possibility to outline a certain competitive behaviour of charged species at the surface. Understanding such competition as a function of type and concentration of ions allows us to unravel the interfacial thermodynamics directly from AFM data, which has been so far mainly exclusive to MD simulations. To further support our findings, we use surface force apparatus and MD simulations to characterise the structure and mechanical properties of EDLs on mica for different cation species.

#### References

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- [2] T. Baimpos, B. R. Shrestha, S. Raman and M. Valtiner, *Langmuir* **30**, 4322-4332 (2014).
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