Advanced Microscopy and Spectroscopy to Explore Field-Assisted Chemistry
Room 116 - Session AMS1-WeA

Advanced Microscopy and Spectroscopy to Explore Field-Assisted Chemistry I

Moderators: Sten Lambeets, Pacific Northwest National Laboratory, **Daniel E Perea**, Pacific Northwest National Laboratory

2:15pm **AMS1-WeA-1 Influence of External Electric Fields on Catalytic Reactions: An Insight through Atom Probe Microscopy and Field Ion Microscopy***, **Thierry Visart de Bocarmé**,* Université libre de Bruxelles, Belgium **INVITED**

The study of catalytic reactions under the influence of external electric fields has emerged as a significant area of research in the field of chemistry. This research is driven by the potential to manipulate reaction pathways and enhance catalytic efficiency. This presentation will delve deeper into the role of Atom Probe Microscopy (APM) and Field Ion Microscopy (FIM) in elucidating these effects.

Commercial APM models, with their unique abilities to provide 3D atomic-scale compositional information, enable to probe the catalyst's structure and composition before or after reaction but hardly *during* reaction. Using an isolated counter electrode with a tunable static potential, the static field on the catalyst can be adjusted to the desired value by convenient choices of the respective voltages on the sample and the counter electrode. Short voltage pulses are then superimposed on the static voltage of the counter electrode to raise the electric field at the sample surface to trigger field desorption or field evaporation. This methodology aids in measuring how electric fields modify the catalyst's surface composition during the ongoing reaction, and provides insights on the reaction pathways.

On the other hand, FIM, with its capacity for direct imaging of individual atoms and even surface reactions in real-time, provides an unparalleled view of the instant state of the catalyst surface, i.e. the extremity of a sharp tip the size and shape of which approximate those of one single catalytic grain. This enables to directly visualize how electric fields of some 10 V.nm^{-1} affect the behavior of reactants and products on the catalyst surface, thereby influencing the catalytic reactions.

The presentation will highlight several case studies where APM and FIM have been used in providing insights into the influence of electric fields on catalytic reactions. The hydrogen-oxygen reaction on rhodium surfaces has been monitored by video FIM and probed using voltage pulses. The results show that, on one single catalytic grain, the reaction can proceed simultaneously through Langmuir Hinshelwood and Mars Van Krevelen-type mechanisms.The water-gas shift reaction on gold surfaces at room temperature has been investigated by FIM and APM and shows that the reaction proceeds through the formation of an hydroxyl-type surface intermediate that is reacted off by the presence of CO gas. Eventually, the nitrogen oxide adsorption on platinum surfaces and its field-dependance will be discussed.

2:45pm **AMS1-WeA-3 Charged Surfaces Theory, Atom Probe Microscopy and Other High-Field Techniques Relevant to Electric-Field-Assisted Chemistry***, **Richard Forbes**,* University of Surrey, UK **INVITED**

The action of high electrostatic (ES) fields on chemical reactions is different in solution and in near vacuum, is different depending on whether the chemical entity of interest is in free space or adsorbed onto a substrate surface, and may depend on the nature of the substrate. This talk focuses primarily on the case of adsorption on metals, in a vacuum environment. It seeks to explore/clarify how (and to what extent) high ES-field experimental techniques might be used to investigate the related high-field surface chemistry.

A substantial introduction to necessary background knowledge will include high-level summaries of: (a) charged-surfaces theory at various model-levels, from classical conductor to density-functional theory approaches;(b) basic scientific concepts related to the techniques of interest; (c) the science of how the techniques work, including: field adsorption, field ionization, operating-gas dynamics, field evaporation, field desorption, and basic electrohydrodynamics; and (d) our rather limited knowledge of practical high-ES-field surface chemistry. One possibility is so-called electrocatalysis. Thus, the hypothesis of Lambeetz and colleagues is that the ES field might enhance the rate of a catalytic reaction, in particular hydrogenation of simple carbon-based molecules on a transition-metal substrate.

The techniques of primary interest are field ion microscopy, field desorption mass spectroscopy, and atom-probe tomography (APT), with some emphasis on the last of these. In some respects, APT is the most sensitive of these techniques, but it also seems that for some or many applications there might be signal-level issues and that further technical development of the technique might be needed/helpful.

A question that probably needs a clearer answer is the following:precisely what information about electric-field-assisted chemistry do we wish to get out of the use of these techniques (or precisely what questions do we wish to answer)?And what can we actually hope to achieve in practice?

The talk aims to include references to further information. A copy of the slides and references will be mounted on ResearchGate (search "Richard G Forbes") some weeks after the AVS meeting.

3:15pm **AMS1-WeA-5 Ab-Initio Simulation of Field Evaporation in Atom Probe Tomography***, **Wolfgang Windl**,* The Ohio State University*; J. Qi,* Ohio State University*; E. Marquis,* University of Michigan **INVITED**

Atom probe tomography (APT) is a three-dimensional characterization technique that ideally can resolve both positions and chemical identities of the atoms in a material. Unlike "focused-beam" microscopy techniques which rely on X-rays or electron beams for imaging, in APT, atoms in the sample are imaged by themselves. Individual atoms or molecules are field-evaporated from the surface of a needle-shape specimen under an intense electric field and fly towards a two-dimensional detector where their impact positions and sequence are recorded. From that, along with the chemical identities revealed by a mass spectrometer, a three-dimensional distribution of the atoms in the specimen can be reconstructed. However, since field evaporation is a destructive process, it is impossible to verify reconstruction results and quantify uncertainties in experiments. In this case, atomic-scale forward modeling becomes the only viable way to produce verifiable virtual data to test reconstruction where each single atom is traceable. A number of atomic modeling approaches have been developed during the past 25 years, however, all of them are implicitly based on harmonic transition state theory which can only predict the rate of transition from one state to another but not describe any dynamics between the two states. As an alternative, we propose to simulate field evaporation with full dynamics using molecular dynamics (MD) simulations. For that, we have integrated field evaporation events as part of the MD simulation by combining the electrostatics from the finite element field evaporation code TAPSim with the MD simulator LAMMPS. With full dynamics, atoms in the specimen are evaporated in an "ab-initio" way as a result of the competition between the interatomic forces and the electrostatic forces. To demonstrate our full-dynamics approach, we will show results that explain for the first time the enhanced zone lines in field evaporation maps, "ab-initio" prediction of the evaporation sequence in [001]-oriented γ-TiAl intermetallic compounds explaining the observed artifact of mixed layers, and simulations of GP-zones in Al-Cu alloys that demonstrate the inherent inaccuracies in resolving atomic positions. The overarching goal of this work is to guide APT reconstruction using our "ab-initio" simulation data, gain better interpretations of fundamental processes, and take the quantification capability of the APT technique to the next level.

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