Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM1-2-TuA

Spatially-resolved and in situ Characterization of Thin Films, Coating and Engineered Surfaces I

Moderators: Damien Faurie, Université Sorbonne Paris Nord, France, **Naureen Ghafoor**, Linköping University, Sweden, **Aparna Saksena**, Max Planck Institute for Sustainable Materials, Germany

1:40pm **CM1-2-TuA-1 Advancements in XPS Depth Profiling using Femtosecond Laser Ablation (fs-LA) for Thin Film and Metal Oxide Surfaces***, **James Lallo [james.lallo@thermofisher.com]**,* Thermo Fisher Scientific, USA*; Tim Nunney, Robin Simposn,* Thermo Fisher Scientific, UK*; Mark Baker, Charlie Chandler,* University of Surrey, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers by using argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. We have introduced a novel XPS system, Hypulse, that employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (several 10s microns) and is much faster than traditional ion beam sputter depth profiling. fs-LA XPS depth profile results will be shown for selected thin films, coatings, multilayers and oxidized surfaces and the outlook for this new technique discussed.

2:00pm **CM1-2-TuA-2 Improving the Low-Temperature and Fast-Charging Properties of MoOx@TiO$_2$-Based Li-Ion Battery Anodes***, **Xian-Jun Zeng [dres641861@gmail.com]**, Horng-Hwa Lu,* National Chin-Yi University of Technology, Taiwan*; Sheng-Chang Wang,* Southern Taiwan University of Science and Technology, Taiwan*; Ching-Huan Lee,* National Chin-Yi University of Technology, Taiwan*; Yu-Min Shen,* National Cheng Kung University (NCKU), Taiwan

Titanium dioxide (TiO$_2$) is considered a promising anode material for lithium-ion batteries due to its excellent chemical stability, safety, and environmental friendliness. However, its intrinsically low electronic conductivity and sluggish lithium-ion diffusion kinetics lead to significant capacity degradation under low-temperature conditions. To overcome these limitations, this study introduces the transition metal molybdenum (Mo) in oxide or suboxide form (MoOx), deposited or doped into the TiO$_2$ lattice and surface. The incorporation of MoOx is expected to generate oxygen vacancies and locally reduced Ti^{3+} species, thereby improving electronic conductivity and Li$^+$ diffusion capability.

In this work, TiO$_2$ precursors were synthesized via a hydrothermal process, followed by the addition of a molybdenum source ($(NH_4)_6Mo_7O_{24}$). The resulting powders were dried and then subjected to short-term (3 h) heat treatment at 700°C and 750°C under a reducing atmosphere (H$_2$/Ar) to control the reduction degree and oxygen vacancy concentration. The structural and electronic states were characterized mainly by X-ray photoelectron spectroscopy (XPS) to quantify the Ti^{4+}/Ti^{3+} ratio, oxygen vacancy level, and Mo oxidation states (Mo^{6+}/Mo^{5+}/Mo^{4+}), while TEM/SAED analyses were performed to observe crystal structure and possible secondary phases. Electrochemical performance was evaluated at low (−20°C), ambient (25°C), and elevated (60°C) temperatures through galvanostatic charge–discharge cycling (rate 0.2, 0.5, 1, 2, 5, and 10 C, 5 cycles each), long-term cycling tests (0.2 C, 1 C, 5 C, ≥500 cycles), and electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) analyses. The results showed that MoOx@TiO$_2$ annealed at 750°C exhibited a first-cycle discharge capacity of 910 mAh g^{-1}, maintaining 880 mAh g^{-1} after five cycles with only 3.3% capacity decay, along with stable charge–discharge voltage plateaus.

Overall, moderate reduction under H$_2$/Ar atmosphere effectively enhanced the low-temperature discharge capacity, reduced charge-transfer resistance (EIS), and improved the reversibility observed in CV and rate-performance tests. These findings establish a clear correlation between the structural defects and electrochemical behavior of MoOx@TiO$_2$, providing a valuable guideline for designing high-stability anode materials capable of operating over a wide temperature range.

2:20pm **CM1-2-TuA-3 Sample Charging During X-Ray Photoelectron Spectroscopy Analyses of Thin Film Insulators: From Understanding to Solution***, **Grzegorz (Greg) Greczynski [grzegorz.greczynski@liu.se]**,* Linkoping University, Sweden **INVITED**

Sample charging during X-ray photoelectron spectroscopy (XPS) analyses of electrically insulating samples is a widely recognized challenge of this essential technique. If the electron loss caused by the photoelectric effect is not compensated due to specimens' poor electrical conductivity, the positive charge building up in the surface region results in an uncontrolled shift of detected core level peaks to higher binding energy (BE). This seriously complicates chemical bonding assignment, which is based on measured peak positions, and accounts for a large spread in reported core level BE values. In this talk a new method for charging elimination is presented. The solution is based on the *ex-situ* capping of insulating samples with a few nm thick metallic layers that have low affinity to oxygen. The application examples include several industry-relevant oxides. The versatility of the charging elimination is demonstrated for different oxides/cap combinations and air exposure times. Results of the follow-up study aiming at a better understanding of physics behind charging and its elimination are also discussed. Although these studies are based on thin films, the conclusions give insights into critical factors that govern charging phenomena in any other type of insulating samples.

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