Topical Symposia
Room Town & Country A - Session TS1-3-TuM

Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications III

Moderators: Dr. Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany, **Klaus Böbel**, Bosch Manufacturing Solutions, Germany

8:20am **TS1-3-TuM-2 High-Performance Rechargeable Zinc Ion Batteries: From Surface Modification of Zn Anode and Structural Engineered Cathode to Deep Eutectic Solvent (DES)-Based Electrolytes**, ***Yu-Lun Chueh***, National Tsing Hua University, Taiwan

Rechargeable metal ion batteries have been widely studied as efficient energy storage systems for portable devices, such as electric vehicles, which have become the trend in the future. Among these candidates, zinc ion batteries exhibit superior advantages because of the abundance of zinc compared with lithium, while the cost of zinc is lower than that of lithium. Moreover, zinc has been characterized by multivalence in an ionic state, which provides approximately three times higher volumetric capacity than lithium. For Zn ion batteries, the uncontrollable dendrite growth and side reactions existed on the Zn anode seriously restrict the cycle stability of zinc ion batteries. In my talk, different strategies on the design of low dimensional materials on the surface metal anode or cathode for high-performance rechargeable Zn ion batteries will be reported. For example, organic hydrophobic polyvinylidene fluoride and inorganic Santa Barbara Amorphous-15 (PVDF-SBA15) hybrids were designed as a surface modification layer to stabilize the Zn anode, leading to an optimized Zn/electrolyte interface with large-scale feasibility.[1] In addition, an alternative electrolyte system based on the deep eutectic solvent (DES), because of their low cost, high stability, biodegradability, and non-flammability, making them optimal candidates for sustainable batteries, was demonstrated.[2] *Ex-situ* Raman, XPS, and TEM characterization results of the electrodes under different states confirm the reversible alloying conversion and intercalation hybrid mechanism during the discharge and charge cycles for Zn ion batteries. All possible chemical reactions were proposed by the electrochemical curves and characterization.

Reference:

1. Nano Energy 103, 107805, 2022

2. ACS Applied Materials & Interfaces 14, 7814-7825, 2022

8:40am **TS1-3-TuM-3 Electrochemical Performances of LiNi0.8Co0.1Mn0.1O2 Synthesized by Hydroxide Coprecipitation Method**, ***Chia-Hsin Lo***, *J. Huang,* National Cheng Kung University (NCKU), Taiwan; *C. Chang,* National University of Tainan, Taiwan

To meet the rising demand of electric vehicles, cathode materials of rechargeable lithium-ion batteries with high energy density and long cycle life are investigated. Lithium nickel cobalt manganese oxide ($LiNi_xCo_yMn_zO_2$) is a promising candidate to be the next generation cathode materials. A series of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ was successfully prepared by hydroxide coprecipitation method and calcination. The crystal structures and microstructures were characterized by X-ray diffraction and scanning electron microscopy. Charge/discharge cycling were also employed to investigate their electrochemical behaviours. XRD results show that pHvalue have an impressive effect on the crystal structure of the $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powder. Among all the samples, the one prepared at pH=11.5 possessed the lowest degree of Li^+/Ni^{2+} disordering and the . Scanning electron microscopy with element mapping tests reveal that the homogeneous $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ solid solution has been achieved via this synthesis method. The $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powder prepared at pH=11.5 can deliver a high initial discharge capacity of 182.9 mAh/g with coulombic efficiency of 66.0% at 0.5C-rate in the voltage range of 2.8−4.3 V.

9:00am **TS1-3-TuM-4 Pb-Free Halide Perovskite/TiO_2 Heterostructure for Enhanced Solar-Driven PFC**, ***Yong Yu***, *J. Ting,* National Cheng Kung University (NCKU), Taiwan

Photocatalytic fuel cell (PFC) isa promising technology that can simultaneously treat wastewater and generate electricity. Upon solar light irradiation, the photoanode generates electron–hole pairs, the holes degrade organic pollutants by formation of reactive oxidative species and the electrons go through the circuit to the cathode for oxygen reduction reaction (ORR) or hydrogen evolution reaction (HER), depending on the oxygen concentration in solution. Regarding the photoanode, TiO_2 is commonly used due to its low toxicity, low cost, and high stability. However, there are still problems need to be solved, such as low visible light absorption and fast electron-hole recombination rate.

In the present study, we use all-inorganic lead (Pb)-free halide perovskite to form a heterostructure with TiO_2 to tackle the above issues. The heterostructure increases the absorption of visible light, reduces the recombination of electron–hole pairs, and improves the efficiency of PFC. Halide perovskite is chosen due to the easy synthesis, narrow energy gap, and high carrier mobility. The Pb is replaced by bismuth. The photodegradation performance is investigated using tetracycline antibiotic as organic pollutant and reported.

9:20am **TS1-3-TuM-5 Inline PVD Coating of Bipolar Plates for Electrochemical Energy Converters**, *K. Böbel, M. Mueller,* Bosch Manufacturing Solutions, Germany; *D. Beisenherz, S. Huebner,* Singulus Technologies AG, Germany; *J. Jiao, S. Wetzel,* Bosch Automotive Products (Suzhou) Co., Ltd., Germany; ***Rafael Gryga***, Matthias Mueller, Bosch Manufacturing Solutions, Germany

Electrochemical energy converters are key components for a broad establishment of green hydrogen economy. The relevant technologies have been applied for decades in several niche applications. Recently many countries and companies pursue the mass production of fuel cells and electrolyzers. Hence, great efforts are made towards cost efficient systems, components and fabrication methods.

In practice single fuel cells and electrolyzer cells are stacked to a powerful system consisting of up to several hundred cells. The single cells are separated and electrically connected via bipolar plates. Those plates must withstand different electrochemical and temperature conditions without significant deterioration of their performance. Widely applied performance indicators are interfacial contact resistance and corrosion current. Those properties can be perfectly controlled by means of noble metal coatings applied onto steel or other bipolar plate materials. In order to replace this expensive solution, many coating systems and a wide variety of coating techniques have been suggested so far.

The paper reports on the optimization of both, bipolar plate properties as well as production efficiency based on PVD coating technology. Different coating designs have been tested and promising candidates have been optimized in terms of process parameters and coating thickness. The coating process has been transferred from batch to inline systems with a cycle time of a few seconds. This results in a competitive solution for the mass production of cost efficient bipolar plate coatings.

9:40am **TS1-3-TuM-6 Studies on the TiO_2 Thin Film on the Silicon Nanowire Arrays using Taguchi - Grey Method for Heterojunction Solar Cell**, *A. Chiou, H. Liao,* ***Jun-Luo Wei***, National Formosa University, Taiwan

In recent years, the problem of energy has become more and more serious, and renewable energy is the most important.Among the renewable energy sources, solar energy is the best developed. Many different materials have been applied to solar cells by scholars. One way to produce large-area, easy-to-process thin films is to use radio frequency magnetron sputtering. In this study, P-layer silicon nanowire arrays were prepared by electroless etching method to replace the previous multilayer films. TiO_2-SiNW Arrays heterojunctions were formed by preparing TiO_2 as N layer by magnetron sputtering method. In this paper, the Grey-Taguchi method was used to analyze and optimize PN heterojunctions with TiO_2 films. The effects of sputtering process parameters (RF power, process pressure, deposition temperature and deposition time) on surface morphology, material structure, photoelectric conversion efficiency and reflectivity were investigated.An AZO window layer is then added and annealed.

The gray correlation analysis shows that the reflectivity is reduced from 8.02225% to 7.72081%, and the photoelectric conversion efficiency is increased from 0.01915% to 0.082%. In the confirmation runs, the TiO_2 film was amorphous and wound around an array of silicon nanowires.After adding the AZO window layer, the reflectivity increased to 18.04712%, and the photoelectric conversion efficiency increased to 0.124%.Confirmation runs show that the AZO film is polymorphic. The experimental results demonstrate the effectiveness of the RF magnetron sputtering method, which provides good reflectivity and photoelectric conversion efficiency.

10:00am **TS1-3-TuM-7 Impacts of Mutual Phase Interactions on Crystal Polarity and Photocatalytic Hydrogen Evolution Reactions**, ***Jrjeng Ruan***, National Cheng Kung University (NCKU), Taiwan

The secondary molecular interactions are well known able to influence the organization behaviors and electrooptical responses of dispersed molecules. Whereas, for dispersed phase domains of organic and inorganic components, including amorphous and crystalline phases, mutual

polarization/interactions are much less recognized. In general, the interactions among phases, especially crystalline phases, have not been envisaged yet as a factor of crystal engineering and the electrooptical features of phase domains.

Upon the coalescence and mutual drawing behaviors, arrayed stacking of PVDF-TrFE ferroelectric lamellar crystals has been achieved, and, with activated mutual polarization, the dielectric constants of a monolayer of oriented lamellar crystal are able to be enhanced above 80 at room temperature. As the roughness of FTO substrate is tailorable upon the deposition of PMMA molecules, various degrees of coalescence and thus thickening of PVDF-TrFE lamellar crystals are achievable. Following this result, crystal surface potentials and piezoelectric responses of lamellar crystals were found critically dependent on reached lamellar thickness, exhibiting the relationship between crystal dimension and crystal polarity for the first time. Surprisingly, simply with the spread of P3HT-wrapped MoS2 or graphene quantum dots on PVDF-TrFE ferroelectric lamellar crystals, the piezoelectricity of stacked ferroelectric polymer crystals has been dramatically enhanced. These results have been viewed to unveil mutual interactions between the ferroelectric lamellar crystals and deposited 2D materials. Furthermore, depending on reached crystal polarity/surface potentials of underneath ferroelectric polymer crystals, the capability of P3HT-wrapped MoS2 in catalyzing hydrogen evolution upon water splitting under the irradiation of visible light is able to be activated and enhanced. The mutual polarization between dispersed ZnO nanorods crystals and nearby polymer ferroelectric lamellar crystals has been identified also, which causes one order of magnitude increases of piezoelectric responses, and dielectric constants of hybrid thin films. The antiparallel interactions of crystal dipole have been realized able to serve as a new type of phase interactions, which gradually decay with the increase of separation distance between interacting crystals.

The impacts of phase evolution and dispersion on phase interactions have been investigated in this research, which are expected to indicate a new direction for the preparation of hybrid crystalline materials capable to overcome the current bottlenecks of materials applications.

10:20am **TS1-3-TuM-8 Systematic Investigation of the Piezocatalysis–Adsorption Duality of Polymorphic Mos_2 Nanoflowers***, Hsun Yen Lin,* National Tsing Hua University, Taiwan

This study theoretically and experimentally investigates the piezocatalytic and adsorption effects of different phases of polymorphic MoS_2 NFs. To verify whether the polymorphic MoS_2 NFs would exhibit adsorption or piezocatalytic effects, the electrostatic surface charge of these NFs and the RhB solution is varied using sodium hydroxide and nitric acid solutions. The cationic dye is adsorbed on the surfaces of the 1T MoS_2 NFs; however, the few-layer 2H MoS_2 NFs generate a considerable quantity of hydroxyl species for degrading RhB molecules through the mechanical-force-induces piezopotential. This study discovers that the polymorphicMoS_2 NFs exhibit a piezocatalysis–adsorption duality.

10:40am **TS1-3-TuM-9 Improving Urea Oxidation Reaction Performance by Enhancing Gas Releasing***, Ming Feng Tsai, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Urea electrolysis, or urea oxidation reaction (UOR) on nickel is considered to be one of the high overpotential routes for water splitting. However, the rate determining step (RDS) during the reaction is related to the release of gas molecule from the active site. In this study, we aim to directly release the creamy gas at the anode via investigating a group of metal organic framework (MOF) electrocatalysts based on nickel.We demonstrate an Ni-based MOF electrocatalyst having a current density of 1 $A \cdot cm^{-2}$ at 1.48 eV (vs. RHE), which is comparable to that of the commonly used noble metal catalyst like Rh and Pt. A mechanism is proposed to explain the excellent performance of the Ni-based MOF electrocatalyst.

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