

## Topical Symposia

### Room Town & Country A - Session TS1-2-MoA

#### Coatings for Energy Storage and Conversion - Batteries and Hydrogen Applications II

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

**2:20pm TS1-2-MoA-3 Influence of Oxygen Content During the Deposition of Scandium Stabilized Zirconia Thin Films by Reactive High Power Impulse Magnetron Sputtering (R-HiPIMS), Isabel Fernandez Romero,** Corporate Sector Research and Advance Engineering- Robert Bosch, Germany; *S. Klein, C. Engel,* Corporate Sector Research and Advance Engineering - Robert Bosch, Germany; *J. Fleig,* Technical University of Vienna, Austria

Hydrogen is one of the key energy carriers in the fight against current climate problems as H<sub>2</sub> can be produced using electrical energy from renewable sources and directly used in production processes, eg steel production or in chemical industry. Solid Oxide Electrolysis Cells (SOEC) transform electricity and water vapor into hydrogen (and oxygen) with the highest energetic efficiency among electrolyzer technologies

The cells of the SOEC require a dense, gas-tight, and thin electrolyte layer which is at the same time ionic conducting and electron blocking. Doped zirconia materials have been broadly used as a suitable material. Over the last years extensive research has been done to investigate the suitability of reactive vacuum techniques for their mass production.

In this work dense Scandium Stabilized Zirconia (ScSZ) layers have been successfully deposited on Gadolinium Doped Ceria (GDC) pellets using reactive High Power Impulse Magnetron Sputtering (r-HiPIMS) technique. The ceria ceramic was as substrate to mimic the microstructural conditions of the SOEC fuel and air electrode surfaces: polycrystalline, rough, and porous

By varying the oxygen content in the chamber (from 1 % to 4 %) the deposition mode can be changed from a non-poisoned (metallic) mode to a poisoned mode, decreasing the discharge voltage as well as the deposition rate but improving the stoichiometry of the ScSZ layers. This process variation modifies the microstructure and crystallinity of the film, which are related to the ionic conductivity and electron blocking ability of the film, thus offering a means to investigate the feasibility of the film as electrolyte material

**2:40pm TS1-2-MoA-4 Comparison of the Impacts of High Entropy Oxide/Alloy Coatings for Lithium-Sulfur Battery Separators, Ming-Roe Wann,** *Y. Lin, S. Chung, J. Ting,* National Cheng Kung University (NCKU), Taiwan

The repeating formation and irreversible diffusion of liquid-state lithium polysulfides (LiPSs) during the discharge and charge of lithium-sulfur batteries (LSBs) represent the major challenge for the development of the high-performance LSB. Therefore, it is essential to alleviate the shuttling of LiPSs that dissolve in the electrolyte and cause the loss of active material. Herein, high entropy oxide (HEO) as an additive in the separator for LiPS trapping is reported. The HEO exhibits single phase spinel structure having a unique core-shell morphology. The HEO is also de-alloyed for enhancing the electrical conductivity. Both the HEO and de-alloyed HEO are subjected to material characterizations, including X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Then, lithium polysulfide adsorption test is done by ultraviolet-visible (UV-vis) test. For electrochemical analysis, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) measurements as well as cycle and rate performance are analyzed. The effect of the alloy percentage in HEO on battery performance is also addressed and discussed.

**Keywords :** High entropy materials, lithium-sulfur battery, lithium polysulfides

**3:00pm TS1-2-MoA-5 BaCeZrYO<sub>3-δ</sub> Coatings Deposited by Solution Precursor Plasma Spray (SPPS) for Sustainable Energy Application, Yen-Yu Chen,** *W. Zeng, C. Liu, G. Yao,* Chinese Culture University, Taiwan  
Perovskite-type proton-conductive ceramic materials have high potentials for the application of sustainable energy fields, such as protonic ceramic fuel cell (PCFC), ammonia fuel synthesis, carbon dioxide conversion, etc. In this study, perovskite-type proton-conductive coatings, BaCeZrYO<sub>3-δ</sub> (BCZY),

were deposited on NiO/BaZrYO<sub>3-δ</sub> (BZY) composite substrates by a solution precursor plasma spray (SPPS) method. The precursors were consisted the BCZY species of the nitrate salts, and dissolved into de-ionic water. The NiO/BZY substrates were prepared by a die-pressing method. Several properties of the coatings were analyzed, including crystal phases by X-ray diffraction (XRD), microstructures by scanning electron microscope (SEM), electrical properties by electrochemical impedance spectroscopy (EIS), etc. The results of XRD show the coatings after post-coating annealing over 600°C are mainly consisted of perovskite phases. The microstructure analysis of the BCZY coatings characterized by SEM show that the coatings are either consisted of overlapped splats of BCZY with a few of surface pores on the surface, or with porous structure by BCZY particle necking. The average thickness of the coating layers are about several microns. The formation mechanism of the BCZY coatings can be purposed as the BCZY precursor droplet breakup, liquid-phase evaporation, thermal pyrolysis of precursors, solid particles melting, and then the melting particles splatted and overlapped on the substrate to form the BCZY coatings. The details electrical property analysis of the BCZY coating samples are as mentioned in the following report.

**3:20pm TS1-2-MoA-6 Aluminum-Doped Non-Stoichiometric Titanium Oxide (Al-TiO<sub>x</sub>) for Anode in Lithium-Ion Batteries, Guan-Bo Liao,** National Cheng Kung University (NCKU), Taiwan; *Y. Shen,* Hierarchical Green-Energy Materials (Hi-GEM) Research Center, Taiwan; *J. Huang,* National Cheng Kung University (NCKU), Taiwan

Lithium-ion batteries (LIBs) are regarded as the most promising recyclable energy storage system nowadays. Among those anodes, TiO<sub>2</sub> is a candidate due to its excellent safety and cycling performance. Moreover, a recent report suggested that non-stoichiometric titanium oxide (TiO<sub>x</sub>) has the high-rate capability as the non-stoichiometry creates more oxygen vacancies creating voids for ion transportation thereby facilitating lithium-ion diffusion. The report exhibits the fast-charging potential of TiO<sub>x</sub>. Nevertheless, the low capacity is still a problem. In this study, an aluminum-doped non-stoichiometric titanium oxide (Al-TiO<sub>x</sub>) was used as an anode in LIBs. Here, we used the sol-gel method followed by annealing to synthesize Al-TiO<sub>x</sub>. First, the Aluminum precursor was incorporated into titanium-based sol to form Al-TiO<sub>2</sub> gel. After evaporation and grinding, the Al-TiO<sub>2</sub> powder was formed. Second, the Al-TiO<sub>2</sub> powder was annealed in a reduced atmosphere to synthesize Al-TiO<sub>x</sub> to increase the capacity and the rate capability further. The TEM and XRD results (shown as supplementary file) showed that aluminum was successfully doped in TiO<sub>2</sub> lattice. The best electrochemical results showed that the first cycle capacities were 480 and 350 mAh/g for Al-TiO<sub>x</sub> and TiO<sub>x</sub> respectively, which both exceeded the theoretical capacity of pristine TiO<sub>2</sub> (335 mAh/g). The cycling test also shows a good performance. Both Al-TiO<sub>x</sub> and pure TiO<sub>x</sub> remain stable for more than 200 cycles. Al-TiO<sub>x</sub> also showed better rate capability than pure-TiO<sub>x</sub>. The Al-TiO<sub>x</sub> specific capacities are 131, 125, 115, 86, 70, 40, 25 mAhg<sup>-1</sup> while TiO<sub>x</sub> showed 137, 120, 80, 62, 27, 7, 3 mAhg<sup>-1</sup> for 0.1, 0.2, 0.5, 1, 2, 5, 10C respectively. EIS and GITT will be used to measure the diffusivity of Lithium-ion later.

After this study, we had a preliminary understanding of the anode performance of Al-TiO<sub>x</sub>. Recently, we are preparing in-operando measurements (e.g., **in-situ XRD, in-situ Raman...etc.**). We will observe the crystal structure change during charging-discharging using in-situ XRD and the defect analysis by in-situ Raman, especially focusing on the normal speed and fast-charging behavior.

**3:40pm TS1-2-MoA-7 Unveiling Capacitive and Diffusion-Limited Li-Ion Storage in Semiconducting 2d-MoS<sub>2</sub> Composed with Aluminium Nitride Nanoflowers for Flexible Electrodes of Supercapacitors, D. Kaur, Gagan Kumar Sharma,** Indian Institute of Technology Roorkee, India

A flexible supercapacitor electrode can be realised by combining the exclusive characteristics of two-dimensional MoS<sub>2</sub> layered material with a conventional key material, aluminium nitride (AlN). We present a bendable electrode that is straightforwardly grown on stainless-steel foil via a binder-free sputtering route. The inherent merits of good conductive pathways among MoS<sub>2</sub> nanolayers and enriched pseudocapacitive and dielectric activity from AlN nanoflowers enable synergism of intermixed porous structure. This unique surface morphology facilitates sulfur and nitrogen edges to make insertion/de-insertion of Li-ions more feasible to store electrochemical energy. The MoS<sub>2</sub>-AlN@SS hybrid working electrode achieves a gravimetric capacitance of 372.35 F/g at a 5 mV/s scan rate with a wide potential window of 2 V in 1 M Li<sub>2</sub>SO<sub>4</sub> electrolytic aqueous solution. The composite thin film of better adhesion with the current collector exhibits a remarkably high specific power of 28.05 W h/kg at a specific

power of 0.26 kW/kg, simultaneously an advanced cycling lifespan of 91% over 5,000 charge-discharge cycles. The capacity of the hybrid electrode is almost unperturbed under bending from 0° to 175°, while only ~5% degradation in capacitance was noticed at a flexing angle of 175°. These distinctive features of this electrode material elucidate the practical applicability and recommend it as a promising candidate in wearable bendable supercapacitors.

## References

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4:00pm **TS1-2-MoA-8 Lithium Passive Diffusion and Surface Oxidation on Battery Materials at Room Temperature**, *Jozef Ociepa*, OCI Vacuum Microengineering Inc., Canada

Passive Li diffusion is defined as the process of Li atom/ions migration under a concentration gradient and activated by thermal energy from atomic vibrations of the host structure at room temperature. This process of passive Li diffusion is important for a better understanding of the active diffusion processes that are happening in lithium-ion batteries (LIBs), where external energy component such as electrical potential is applied. It is expected that materials that exhibit good “natural” Li diffusion properties will perform much better under the external electrical potential. This approach offers a unique opportunity to observe the free movement of lithium atoms/ions into the solid structure and simplify the understanding of diffusion processes especially if single-crystal structures are used. The single-crystal structures are free from grain boundaries and the lithium diffusion process is limited to lattice diffusions such as interstitial, vacancies, and dislocations. This approach allows for categorizing materials that are attractive to lithium diffusion based on the pure lattice component. The characterizing techniques are Auger electron spectroscopy (AES) for tracing Lithium concentration on the surface (Li-KVV peak at 52eV) and Low Energy Electron Diffraction (LEED) for surface crystallography changes. The lithium concentration gradient is created on the surface of the host material by the evaporation of a thin film of lithium with an effective thickness from 5 Angstroms to 250 Angstroms under ultra-high vacuum conditions. The data obtained from these experiments are showing different lithium diffusion behavior on the selected materials and there is an indication of three categories of the characterized materials. 1-Rapid lattice diffusion of Li into HOPG and no change in the surface crystalline structure. 2-Moderate lattice diffusion of Li into CVD Diamond, SiC-6H, SiO<sub>2</sub>/Si(001), LiNbO<sub>3</sub>, and TiO<sub>2</sub> and some changes in the surface crystalline structure. 3-No lattice diffusion of Li into Si single crystals, Ga<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub>, and no long-range order in the surface crystalline structure. Comparison of the Li diffusion on SiC single crystals and polycrystalline structure shows faster Li diffusion on single-crystal. The exposure of lithiated SiC to an oxygen gas environment at 5x 10<sup>-6</sup> Torr at room temperature indicates a Li diffusion toward the surface. This method simplifies the understanding of diffusion processes and limitations such as oxidation, plating, and the role of grain boundaries.

4:20pm **TS1-2-MoA-9 Development of Carbon-based PVD Coatings for Stainless Steel PEMFC's Bipolar Plates**, *Michaël Ougier*, *M. Leroy*, IREIS/HEF group, France; *A. Chavanne*, HEF group, France; *H. Christophe*, IREIS/HEF Group, France

Proton Exchange Membrane Fuel Cells (PEMFC), employing dihydrogen as fuel, are promising energy sources (for their high energy conversion and near-zero emission), particularly for the automotive sector. In these electrochemical systems, bipolar plates (BPP) enable to electrically connect the cells and represent 20-30% of the total cost of the system, for about 70% of its mass and volume.

Stainless steel bipolar plates are widely used in fuel cell because of its combination of a good corrosion resistance and manufacturability. However, due to a native oxide layer they exhibit a high interfacial contact resistance. Additionally, in certain conditions, the harsh environment in a fuel cell is able to corrode stainless steel. By the deposition of coating onto the BPP surface, the electrical conductivity and the corrosion resistance can be greatly enhanced. Finally, the main objectives of coating are:

1. to ensure an efficient protection against corrosion, avoiding electrolytic membrane contamination with metallic corrosion products.
2. to minimize the electrical contact between the plate and the gas diffusion layer, guarantying low electrical losses.

A high-performance coating is therefore key to the durability and efficiency of the bipolar plates and of the fuel cell stack itself.

Among all deposition techniques, Physical Vapor Deposition (PVD) methods like magnetron sputtering and cathodic arc evaporation are able to deposit highly adherent, conductive and corrosion resistant coatings. PVD gold coatings have long been the reference solution to fulfill the above-mentioned requirements, and nowadays in heavy duty vehicles. However, treatment price is a sticking point for large volume commercialization and cost-effective alternative materials are now developed.

In this present work, we review the deposition methods and present experimental results on the performance of various PVD coatings such as gold, ceramic, and carbon-based coatings, with and without interlayer. Coupons of coated stainless steel are investigated both in simulated aggressive PEMFC environment (80°C, H<sub>2</sub>SO<sub>4</sub> pH 3). Beyond these basic tests, accelerated corrosion stress tests are also developed to simulate in a few hours the more detrimental conditions that can be encountered in the 7000 hours lifetime of the electrochemical system. Coating degradations mechanisms are evidenced by post-mortem coupons and plates analysis. Complementary to these corrosion tests, electrical contact resistance of the coated surface is also evaluated before and after corrosion tests.

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