Topical Symposium on Sustainable Surface Engineering
Room Golden State Ballroom - Session TS1-ThP

Coatings for Batteries and Hydrogen Applications Poster Session

TS1-ThP-2 Y-doped $Li_7La_3Zr_2O_{12}$(Y-LLZO) Based all Solid-State Lithium Ion Battery Prepared by Colloidal Coating Processes*, **Yen-Yu Chen [yychen@mail.npust.edu.tw]***, Guang-Yi Yao,* National Pingtung University of Science and Technology, Taiwan

All solid-state lithium ion batteries (ASSLIBs) were widely investigated due to safety issue and higher electrical performance. In this study, Y-doped $Li_7La_3Zr_2O_{12}$ (Y-LLZO)-based solid electrolyte coatings on the $LiCoO_2$ (LCO)-based cathode substrate with C/Si anode printed on the coatings were prepared. The Y-LLZO powders were synthesized by a solid-state reaction method. Several properties were analyzed including microstructures by scanning electron microscopy (SEM) and transmission electron microscopy, crystal phases by the X-ray diffraction (XRD) method, electrical performance by electrochemical impedance spectroscopy (EIS) and battery testing system. The Y-LLZO coatings after sintered at 1100°C for 12 h show highly dense configuration on the LCO-based cathode substrate. The thicknesses of the coating layers are around several to ten more micrometers. Only a few of pores can be found in the coating layers. The crystal phases after sintering were including the major LLZO garnet and a rare of $La_2Zr_2O_7$ phases. The interface between Y-LLZO and LCO grains shows slightly inter-diffusion behavior. The electrical conductivity of Y-LLZO is around 10^{-4}~10^{-5} $S\cdot cm^{-1}$. The more details will be reported in the presentation.

TS1-ThP-5 PVD-Coated Interconnects for Solid Oxide Electrolysers*, **Giuseppe Sanzone [giuseppe.sanzone@teercoatings.co.uk]***,* Teer Coatings Ltd, UK*; Kun Zhang,* University of Birmingham, UK*; Susan Field, Hailin Sun,* Teer Coatings Ltd, UK*; Jangwoo Seo, Hyo Ki Hwang, In-sung Lee,* E&KOA Co., Republic of Korea*; Parnia Navabpour,* Teer Coatings Ltd, UK

Achieving net-zero emissions by 2050 continues to be a significant challenge for the global energy sector. Hydrogen, and specifically green hydrogen can play a key role in decarbonisation, as it has the potential to be used as fuel for power and transportation. Green hydrogen can be produced in several ways using renewable energy sources like solar, wind or nuclear, through high- and low-temperature electrolysis, various thermochemical and photochemical processes. Water electrolysis is the most effective technique which is capturing the market's attention.

Amongst the electrolyser technologies, solid oxide electrolysers (SOE) are the most energy efficient. However, there are challenges related to their performance, lifetime, durability and cost, along with the scale-up from kW to MW level. The interconnect plays an important role as a current collector and a physical barrier that separates the electrodes between cells. It has to meet technical requirements such as matching thermal expansion coefficient to other (ceramic) layers, high thermal and electrical conductivities, formation of a dense low-resistive oxide layer in redox atmospheres, and high thermomechanical strength at elevated temperatures (600 to 900 °C). The metallic interconnects employed in the SOC stack operated usually suffer high temperature corrosion and Cr-evaporation in the steam-rich environment at high temperature, leading to material failure of interconnects and degradation electrolysis stack. There is a need to control the chromium (VI) diffusion from the metallic interconnects and its poisoning of the air electrode to achieve increased electrolyser durability and performance.

This work presents conducting, protective spinel oxide coatings deposited by PVD method in order to reduce chromium evaporation from the interconnects. These coatings benefit from a dense structure as well as scalability, allowing high performance and making them suitable for commercialisation. The effect of coating thickness and composition on high temperature stability and chromium evaporation rate from ferritic stainless steel has been investigated.

TS1-ThP-6 Porous $BiVO_4$ Thin Films Deposited by Radiofrequency Co-Sputtering as Photoanode for H_2 Production by Water Splitting*, Mathias Goutte,* ***Angélique Bousquet [angelique.bousquet@uca.fr]****, Eric Tomasella,* Institut de Chimie de Clermont-Ferrand, France*; Guillaume Monier,* Institut Pascal, France*; Thierry Sauvage,* CEMHTI, France

H_2 is consider as a potential new fuel which will participate to decarbonate the mobility sector. Unfortunately, this molecule is nowadays mainly formed from fossil gases, and so, does not meet criteria for the sustainable development. Efforts are then engaged to developp new clean H_2 synthesis technologies such as water photo(-electro)lysis. However, this latter method still suffers from low global efficiency because of limited properties of photoanode. Thanks to its band gap in the visible range (near 2.4 eV) and its low valence band, Bismuth vanadate $BiVO_4$ is one of the most promising candidate for this application.

In this paper, we studied the deposition of $BiVO_4$ thin films by radiofrequency magnetron co-sputtering of Bi and V targets into Ar/O_2 atmospheres. By tailoring the target powers, we were able to deposite coatings with various V/Bi ratios (determined by Rutherford Backscattering Spectroscopy). Since these as-deposited films are amorphous, thermal post-treatments were used to crystallize them. Interestingly, this treatment leads also to the developpement of porosity into the films thickness (observed by SEM), which will be beneficial to increase contact surface aera with water. After 2 hours at 450°C in air, XRD analysis shows that $BiVO_4$ in monoclinic phase is mainly formed. This phase could be associated to Bismuth or Vanadium oxides ones for non-stoechiometric films. The XPS also confirms these heterojunctions formation following the shift of binding energy positions. Analysis by ellipsometry and UV-visible spectroscopy shows, that the films exhibit direct band gaps between 2.4 and 2.6 eV, while flat band voltages from -0.05 to -0.13 V (vs RHE) are deduced from the Mott-Schottky technique. Hence, diagram with band positions can be drawn for each thin films, indicating that their valance band positions are convenient for O_2 production. Stoechimetric film, that exhibits the lower valence band, also presents the higher photo-current density of 0.05 mA/cm^2 at 1.3 V vs RHE and this current density remains high under irradiation for more than one hour, while significant drop of 75% has usually been reported for electrodes made from powder.

To go further, Bismuth metallic nanoparticles were added on the top surface of $BiVO_4$ thin film by sputtering the Bismuth target in pure Argon during very short times. The presence of metallic nanoparticles, thanks to heterojunction and plasmonic effect, highly enhances the measured photocurrent, keeping a good stability in time.

TS1-ThP-7 HiPIMS Deposition of Ti_xN Coatings for Oxygen Evolution Reaction Catalysts*, **Yi-Cho Tsai [ljesskoghjk@gmail.com]***,* National United University, Taiwan*; Ying-Hsiang Lin,* National United University, Taiwan*; Siang-Yun Li, Thi Xuyen Nguyen, Chia Ying Su, Ruei Chi Lin, Jyh-Ming Ting,* National Cheng Kung University, Taiwan*; Wan-Yu Wu,* National United University, Taiwan

Electrochemical reactions, particularly hydrogen and oxygen evolution reactions (HER/OER), are crucial for advancing clean energy technologies. However, current OER catalysts primarily rely on noble metals like Ir and Ru, which are expensive and less durable. Transition metal nitrides (e.g., Ti, Fe, Co, Ni) have gained attention due to their high conductivity and cost-efficiency. TiN, specifically, shows metal-like conductivity (3.34×10^{-7} $\Omega\cdot cm$), strong resistance to acids/alkalis, oxidation, and chemical inertness, making it ideal for OER.In this study, High Power Impulse Magnetron Sputtering (HiPIMS) was used to deposit TixN films on Ni foam, chosen for its high porosity (98%) and conductivity, to enhance the active surface area. HiPIMS, with its high plasma density and strong film adhesion, is superior to traditional DC sputtering, particularly for complex substrate structures. The TixN film with 63.1 at.% Ti content showed an overpotential of 377 mV at 50 mA/cm^2 (η10), a Tafel slope of 121.4 mV/dec, and a charge transfer resistance (Rct) of 3.05 Ω, outperforming commercial RuO_2 (421 mV). Further optimization of the Ti/N ratio revealed that a film with 52.6 at.% Ti and 47.4 at.% N had the best performance, achieving an overpotential of 333 mV, a Tafel slope of 97.8 mV/dec, and Rct of 1.95 Ω. This demonstrates that a near 1:1 stoichiometric ratio in TiN significantly enhances conductivity and electron transfer, thus improving OER efficiency.Preliminary analyses using EDX, XPS, XRD, TEM, and SEM suggest that adjusting the Ti/N ratio may impact the catalytic activity of the films. Based on the current test results, the optimized TixN films show promising potential in 1 M KOH electrolyte, indicating their prospective application as cost-effective and durable OER catalysts.

TS1-ThP-8 Enzyme-Catalyzed Thin-Film Coatings for Bipolar Plates*, Chiara Nenninger **[c.nenninger@biotec.rwth-aachen.de]**, Marisa Sárria Pereira de Passos,* Institute of Biotechnology, RWTH Aachen University, Aachen, Germany*; Philipp Niemietz,* Manufacturing Technology Institute (MTI), RWTH Aachen University, Aachen, Germany*; Thomas Bergs,* Manufacturing Technology Institute (MTI), RWTH Aachen University, Aachen, Germany; Fraunhofer Institute for Production Technology (IPT), Aachen, Germany*; Ulrich Schwaneberg,* Institute of Biotechnology, RWTH Aachen University, Aachen, Germany; DWI-Leibniz Institute for Interactive Materials e.V., Aachen, Germany

Thin-film coatings are applied to almost all material surfaces to enhance their physical and chemical properties, as corrosion resistance and conductivity. Protection of metal materials used in batteries and bipolar plates from highly corrosive environments using functional coatings can extend their lifetime and improve performance. Despite advances in coating technologies, challenges remain in achieving uniform surface functionalization, broad material compatibility, control over film thickness, scalability and sustainability.

Within this work, a biological method for the surface-confined polymerization of thin-film coatings using immobilized enzymes was developed. A fusion protein consisting of an enzyme, a linker and an adhesion-promoting peptide (AP) [1] was immobilized via dip- or spray-coating from an aqueous solution at room temperature and atmospheric pressure. The enzyme catalyzes the polymerization reaction, that “automatically” stops at approximately 30 nm. The self-termination of the polymerization reaction occurs when the immobilized enzyme becomes encapsulated by the coating, thereby controlling the film thickness.

The scalability of this method was demonstrated by coating a stainless-steel plate measuring 30 × 100 × 0.02 cm. The performance of the bio-based coatings was assessed on different metal alloys used in bipolar plates for hydrogen fuel cells through an alternating corrosion test, including climate storage and salt spray test, an acid resistance test, a pencil hardness test and a pull-off adhesion test. The coatings exhibited sheet resistance values within the range of 109 – 8250 kΩ sq^{-1}.

This work presents a novel enzymatic coating approach for materials used in bipolar plates and battery applications that need protection from highly corrosive environments. The coating method is resource- and energy-efficient due to the use of enzymes as catalysts in aqueous environment, at room temperature and atmospheric pressure. The method has the potential to be transferred to other materials and coatings by engineering or exchanging the AP, the enzyme, or by selecting alternative monomers.

Reference

[1] M. Mao, L. Ahrens, J. Luka, F. Contreras, T. Kurkina, M. Bienstein, M. Sárria Pereira De Passos, G. Schirinzi, D. Mehn, A. Valsesia, C. Desmet, M.-A.S. Beltrán, D. Gilliland, U. Schwaneberg, Material-specific binding peptides empower sustainable innovations in plant health, biocatalysis, medicine and microplastic quantification, Chem. Soc. Rev. (2024) 10.1039.D2CS00991A. https://doi.org/10.1039/D2CS00991A.

TS1-ThP-12 Collaboration between Atomic Clusters of Co, Sn, Ni Hydroxides, Pt Atoms in Pd Nanoparticle Surface Boosts Outstanding Oxygen Reduction Reaction Performance*, Jia-Yu Tsai **[ym1015139@gmail.com]**, Po-Chun Chen,* National Taipei University of Technology, Taiwan

The rational design and synthesis of heterogeneous interfaces with tailored structural and functional properties are highly sought to realize green energy technologies. In the present study, quaternary metallic heterogeneous nanocatalysts (NCs) consisting of Pt-cluster decorated CoOx-SnOy-NiOz-Pd hierarchical structures (namely CSNPP) are proposed with improved heteroatomic interactions for an oxygen reduction reaction (ORR) in alkaline medium (0.1 M KOH). The CSNPP NCs have been synthesized with different Pt contents (0.334, 0.836, and 1.672 wt%) by using a wet chemical reduction method on an active carbon (AC) support with simultaneous heterogeneous and homogeneous nucleation. Of special relevance, the mass activity (MA) of CSNPP- 0025 (0.836 wt% Pt) and CSNPP-005 (1.672 wt% Pt) NCs is 23826.48 mA mg -1 and 11099.71 mA mg -1, which is 355.619 and 165.667-fold increased, respectively, as compared to that of the commercial J.M.-Pt/C catalyst (20 wt% Pt) at 0.85 V vs. RHE. Through intensive analysis of microscopy and spectroscopy results, we demonstrated that such enhanced ORR activities for the ultra-low dosage of Pt are mainly dominated by incorporation of Pt atoms into the defect sites of the Co–Sn-Ni–Pd surface.These Pt-atoms lower the adsorption strength for oxygenated species via electron confinement from adjacent sites, resulting in enhanced splitting and relocation kinetics of subsequent oxygen molecules on the NC surface and thus ORR performance.

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