

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

Coatings for Batteries and Hydrogen Applications Poster Session

TS1-ThP-1 Room Temperature DC Sputtered V₂O₅-Based Flexible Robust and Transparent Electrode Over Polymeric PVA Substrate for Green Supercapacitor Applications, *Habeebur Rahman*

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This work presents a flexible, robust, and transparent electrode for green supercapacitor device. For biodegradability, a polymeric polyvinyl alcohol (PVA) substrate was utilized for the supercapacitor electrode development. To ensure a robust electrical connection, partially embedded copper contact was made during the substrate development. The vanadium pentoxide active layer was sputter coated at room temperature for the supercapacitor transparent electrode formation. In particular, the active element was fabricated in two different layers possessing an interface in between that assisted in the current collection. The sputtered components were systematically studied using various materials characterization tools. The two similar electrodes were then assembled with an aqueous Na₂SO₄ electrolyte-soaked glassy fiber separator to form the supercapacitor device. The two electrode mode electrochemical measurements demonstrated a wide 1.3 V voltage window with a remarkable 178.7 F/g specific capacitance at 10 mV/s scan rate. It delivered 9.6 kW/kg power density at 3.5 Wh/kg energy density. It retains the 82 %, and 67.3 % capacitance after 10,000, and 18,000 charging-discharging cycles respectively. Further, the device exhibited negligible performance loss upon bending, twisting, and stretching and showed excellent stability with device-to-device variation. In addition, the biodegradability of the electrode was tested in water and moist soil, which illustrated quick degradation. The transparency of the electrode was determined by UV Vis spectroscopy that demonstrated 70 % transmittance in the visible region. Therefore, the biodegradable PVA substrate, environment-friendly Na⁺ ion charge storage, and non-toxic V₂O₅ active layer combined together to procure a green energy storage device. The excellent mechanical flexibility of the device and the transparent nature of the electrode make it suitable for modern-day advanced energy storage technology.

TS1-ThP-2 Y-doped Li₇La₃Zr₂O₁₂(Y-LLZO) Based all Solid-State Lithium Ion Battery Prepared by Colloidal Coating Processes, *Yen-Yu Chen*

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All solid-state lithium ion batteries (ASSLIBs) were widely investigated due to safety issue and higher electrical performance. In this study, Y-doped Li₇La₃Zr₂O₁₂ (Y-LLZO)-based solid electrolyte coatings on the LiCoO₂ (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 La₂Zr₂O₇ 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·cm⁻¹. The more details will be reported in the presentation.

TS1-ThP-3 MXene Based Thin Film Nonstructural Composite for Oxygen Evolution Electrocatalysis, *Md Zaved Hossain Khan*

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There is a continuous high demand for an effective electrocatalytic-oxygen evolution reaction (OER) to mitigate energy crises by offering renewable energy sources. Metal oxide and metal carbide are well regarded electrocatalysts for water splitting; however, they produce sluggish reaction kinetics and further require higher energy to launch OER reaction. The transitional metal carbide MXene coupled with earth abundant metal oxide show good catalytic performance overcoming potential barrier by enhancing reaction kinetics. Therefore, MXene (Ti₃C₂T_x) coupled earth-

abundant metal oxide nanocomposite (Zn_{0.92}Cu_{0.04}Ni_{0.02}O₂) based electrocatalyst for OER is presented in this work for the first time. Ti₃C₂T_x enhances electroconductivity, offers large surface area, increases the number of active sides of the electrocatalyst and enhances the electrocatalytic performances. A simple hydrothermal method was used for the fabrication of the electrocatalyst Zn_{0.92}Cu_{0.04}Ni_{0.02}O₂@MXene. The proposed electrocatalyst exhibits an extremely low overpotential of 169.5 mV at 10mAcm⁻² and long-term stability (higher than 10 hours) in an acidic condition in 1M H₂SO₄ solution. This work demonstrates a facile and an effective strategy to boost up the electrocatalytic performance of OER in an acidic medium aiming for the design of efficient and cost effective electrocatalyst.

TS1-ThP-4 Pseudocapacitive Kinetics in Synergistically Coupled MoS₂-Mo₂N Nanowires with Enhanced Interfaces towards All-Solid-State Flexible Supercapacitors, *Bhanu Ranjan*

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Pseudocapacitive kinetics in rationally engineered nanostructures can deliver higher energy and power densities simultaneously. The present report reveals a high-performance all-solid-state Flexible symmetric supercapacitor (FSSC) based on MoS₂-Mo₂N nanowires deposited directly on stainless-steel mesh (MoS₂-Mo₂N/SSM) employing Direct current (DC) Reactive Magnetron Co-sputtering technology. The abundance of synergistically coupled interfaces and junctions between MoS₂ nanosheets and Mo₂N nanostructures across the nanocomposites results in greater porosity, increased ionic conductivity, and superior electrical conductivity. Consequently, the FSSC device utilizing Polyvinyl alcohol-sodium sulfate (PVA-Na₂SO₄) hydrogel electrolyte renders an outstanding cell capacitance of 252.09 F.g⁻¹ (44.12 mF.cm⁻²) at 0.25 mA.cm⁻² and high rate performance within a wide 1.3 V window. Dunn's and b-value analysis reveals significant energy storage by surface-controlled capacitive and pseudocapacitive mechanisms. Remarkably, the symmetric device boosts tremendous energy density ~10.36 μWh.cm⁻² (59.17 Wh.kg⁻¹), superb power density ~6.5 mW.cm⁻² (37.14 kW.kg⁻¹), ultrastable long cyclability (~93.7% after 10,000 Galvanostatic charge-discharge (GCD) cycles) and impressive mechanical flexibility at 60°, 90°, and 120° bending angles.

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TS1-ThP-5 PVD-Coated Interconnects for Solid Oxide Electrolysers, *Giuseppe Sanzone*

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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 BiVO₄ Thin Films Deposited by Radiofrequency Co-Sputtering as Photoanode for H₂ 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*

H₂ is considered 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 develop new clean H₂ 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 BiVO₄ is one of the most promising candidate for this application.

In this paper, we studied the deposition of BiVO₄ thin films by radiofrequency magnetron co-sputtering of Bi and V targets into Ar/O₂ atmospheres. By tailoring the target powers, we were able to deposit 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 development of porosity into the films thickness (observed by SEM), which will be beneficial to increase contact surface area with water. After 2 hours at 450°C in air, XRD analysis shows that BiVO₄ in monoclinic phase is mainly formed. This phase could be associated to Bismuth or Vanadium oxides ones for non-stoichiometric 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 valence band positions are convenient for O₂ production. Stoichiometric film, that exhibits the lower valence band, also presents the higher photo-current density of 0.05 mA/cm² 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 BiVO₄ 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 [ijesskoghjk@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 ($3.34 \times 10^{-7} \Omega\text{-cm}$), 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 Ti_xN 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 Ti_xN film with 63.1 at.% Ti content showed an overpotential of 377 mV at 50 mA/cm² (η_{10}), a Tafel slope of 121.4 mV/dec, and a charge transfer resistance (R_{ct}) of 3.05 Ω , outperforming commercial RuO₂ (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 R_{ct} 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 Ti_xN films show promising potential in 1 M KOH electrolyte, indicating their prospective application as cost-effective and durable OER catalysts.

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