

## Topical Symposium on Sustainable Surface Engineering Room Palm 5-6 - Session TS2-2-ThM

### Coatings and Surfaces for Renewable Energy Technology II

**Moderators:** Arnaud le Febvrier, Uppsala University, Sweden, Marcus Hans, RWTH Aachen University, Germany

8:40am **TS2-2-ThM-3 Low-Cost, High-Performance Flexible Supercapacitors Based on Vanadium Oxynitride Reactively Sputtered on Porous Polymeric Substrate for Sustainable Energy Storage Applications, Habeebur Rahman [habeeb.physics10@gmail.com], Davinder Kaur, Indian Institute of Technology Roorkee, India**

This work presents an air bubble method to fabricate a porous polyvinyl alcohol (PVA) substrate for room-temperature (RT) reactively sputtered vanadium oxynitride (VON)-based high-performance, eco-friendly flexible supercapacitor. The air was inserted into the aqueous PVA solution, and controlled stirring was performed to form micron-sized air bubbles, which, upon drying in a mould, formed the porous substrate. Further, vanadium pentoxide ( $V_2O_5$ ) was reactively sputtered at RT on the Ag current collector coated plane and porous substrates. The supercapacitor device fabricated on the porous PVA substrate demonstrated drastically enhanced performance in 1M  $Na_2SO_4$  electrolyte due to remarkably higher surface area. For further improvement, the VON-based supercapacitor was fabricated that exhibited 377 F/g specific capacitance (areal capacitance of 18.9 mF/cm<sup>2</sup> and volumetric capacitance of 196.35 F/cm<sup>3</sup>), 1.2 V potential window, 27.8 Wh/kg energy, and 3.0 kW/kg power density. It demonstrated 100 % capacitance retention after 5,000 charging-discharging cycles. For real applications, five devices connected in series glowed different colored light-emitting diodes (LEDs) for more than 180 seconds, and 10 red LEDs together for 60 seconds. Further, it showed no performance degradation upon bending and twisting, and illustrated fast disposal in normal water and moist soil. The fabricated materials were studied employing various characterising tools.

9:00am **TS2-2-ThM-4 Comparative Electrochemical Performance of  $\alpha$ - $MnO_2$  and  $\delta$ - $MnO_2$  Coatings for High-Performance Supercapacitor Electrodes, Eduardo Estrada Movilla [eduardo.estrada.movilla@uabc.edu.mx], Instituto de Ingeniería, Universidad Autónoma de Baja California, Blvd. Benito Juárez s/n, C.P. 21280, Mexicali, B.C., México., Colombia; Álvaro Ortiz Pérez, Jhonathan Castillo Saenz, Instituto de Ingeniería, Universidad Autónoma de Baja California, Blvd. Benito Juárez s/n, C.P. 21280, Mexicali, B.C., México, Colombia**

Transition-metal-oxide functional coatings have emerged as promising candidates for next-generation electrochemical energy storage systems due to their high theoretical capacitance, chemical stability, and tunable ion-transport pathways. In this work, a comparative evaluation of  $\alpha$ - $MnO_2$  and  $\delta$ - $MnO_2$  phases is reported, focusing on their performance as active electrode coatings. Four  $MnO_2$  variants were synthesized via hydrothermal processing, yielding two  $\alpha$ -type and two  $\delta$ -type compositions with distinct structural and morphological characteristics. The coatings were deposited onto stainless-steel mesh substrates and characterized by XRD, FT-IR, and SEM, confirming phase purity and the formation of hierarchical nanostructures that directly influence electrolyte accessibility.

Electrochemical testing cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy, revealed that  $\delta$ - $MnO_2$  exhibited superior behavior, achieving specific capacitances above 300 F g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and enhanced cycling stability (>90% capacitance retention after 2000 cycles). Nyquist analysis confirmed reduced charge-transfer resistance for  $\delta$ - $MnO_2$ , attributed to improved interlayer ion diffusion and increased electroactive surface area.

These findings highlight  $\delta$ - $MnO_2$  as a high-performance material for supercapacitor applications, and demonstrate its potential integration in scalable metal-mesh-based electrode architectures for energy storage systems.

**Keywords:**  $MnO_2$  coatings, energy-storage electrodes, hydrothermal synthesis, supercapacitors.

9:20am **TS2-2-ThM-5 Thermal Treatment Effects on the Structural and Optoelectronic Properties of  $Nb_2O_5$  Thin Films Deposited by DC Magnetron Sputtering, Rodrigo Prado Medeiros Leite da Silva, Natali da Silva Barbosa, Bianca Sartori, Instituto Federal de Educação, Ciência e Tecnologia de São Paulo, Brazil; Lucas Diniz Araujo, Aeronautics Institute of Technology (ITA), Brazil; Carlos Eduardo Gomes, Instituto Federal de Educação, Ciência e Tecnologia de São Paulo, Brazil; Filipe Caldato Dalan, André Luis de Jesus Pereira, Argemiro Soares da Silva Sobrinho [argemiro@ita.br], Aeronautics Institute of Technology (ITA), Brazil**

The development of efficient semiconductor oxides for solar-driven energy conversion is a key step toward achieving a sustainable hydrogen economy. Transition-metal oxides such as  $TiO_2$ ,  $WO_3$ , and  $Nb_2O_5$  have emerged as promising photoactive materials due to their chemical stability and suitable band-edge alignment for photoelectrochemical (PEC) water splitting. Among them, niobium pentoxide ( $Nb_2O_5$ ) is particularly attractive for its abundance, low toxicity, and tunable optoelectronic properties associated with oxygen-vacancy engineering. Understanding how deposition and post-treatment conditions affect its structure and charge-transport characteristics is therefore essential for optimizing its functional performance. In this work,  $Nb_2O_5$  thin films were deposited by DC magnetron sputtering onto Si, glass, and FTO substrates and subsequently annealed at 300 °C, 400 °C, 500 °C, and 600 °C for eight hours under two controlled atmospheres: air at atmospheric pressure and vacuum ( $\sim 10^{-2}$  Torr). The films were characterized by X-ray diffraction, Raman spectroscopy, UV-Vis transmittance, and electrochemical techniques to evaluate the influence of temperature and ambient on crystallization, defect formation, and electronic behavior. Structural analyses revealed a transition from amorphous to orthorhombic (Pbam)  $Nb_2O_5$  above 500 °C, while vacuum-treated samples exhibited more pronounced oxygen-vacancy-related Raman features and a narrower optical band gap. Electrical impedance and cyclic-voltammetry results indicated reduced charge-transfer resistance for oxygen-deficient films, evidencing the beneficial role of substoichiometry in enhancing carrier mobility. These results demonstrate that both annealing temperature and atmosphere strongly modulate the structural and optoelectronic properties of sputtered  $Nb_2O_5$ , providing valuable guidelines for tailoring its performance in PEC and photocatalytic applications.

9:40am **TS2-2-ThM-6 Optimization of Tunable Interfacial Engineering in  $WO_x/\alpha$ - $Fe_2O_3$  Heterostructures via Dc Magnetron Sputtering for Enhanced PEC Activity and Carrier Transport Efficiency, Carlos Gomes [c.e.gomes@ifsp.edu.br], Mariane Murase Murase, Matheus Torres, Douglas Leite, Rodrigo Pessoa, Argemiro Sobrinho, André Pereira, Instituto Tecnológico de Aeronáutica, Brazil**

Transition metal oxide heterostructures are crucial for advancing sustainable energy technologies, demanding precise control over interfacial charge dynamics and long-term chemical stability. This work presents a systematic study on the fabrication and optimization of an Iron Oxide ( $\alpha$ - $Fe_2O_3$ ) a visible-light absorber heterojunction with a Tungsten Oxide ( $WO_x$ ) as an electron-transport layer, serving as a band alignment at the interface. Junction formation is a powerful strategy to overcome intrinsic limitations like poor charge transport and high surface recombination in semiconductors [1]. The staggered band alignment creates an internal electric field that promotes efficient separation of photogenerated electron( $e^-$ )/hole( $h^+$ ) pairs and facilitates electron extraction, significantly reducing surface charge recombination [1,2].

The structures were fabricated using scalable DC Magnetron Sputtering, depositing the  $\alpha$ - $Fe_2O_3$  layer over FTO glass ( $SnO_2/F$ ) followed by the  $WO_x$  transport layer. The study investigates tunable surface engineering by systematically varying the  $WO_x$  deposition time to precisely control the layer's thickness and potentially its stoichiometry ( $WO_{3-x}$ ), thereby modulating the electronic band alignment and transport efficacy.

Comprehensive characterization, including XRD, SEM, EIS, and CV, was employed to correlate layer thickness with interfacial structure. Analysis confirmed  $WO_x$  crystallization at 550°C, showing a direct relationship between peak intensity and deposition time. Deposition of an optimal  $WO_x$  layer enhanced  $Fe_2O_3$  optical modulation, resulting in a 15% lower visible transmittance minimum (at  $\approx$  600 nm).

Functional performance such as stability and charge transfer dynamics was assessed, revealing that the  $WO_x$  (180s) sample's highest carrier number and lowest flat band voltage directly correlate with superior electrochemical performance (Specific Power under light and Specific Energy in the dark), suggesting that the improved electronic structure drives enhanced charge storage and transfer capabilities.

This research presents valuable insights into controlled thin film deposition and advanced surface engineering of robust oxide structures. These findings support the development of next-generation photoelectrochemical cells (PEC) for water splitting.

**Keywords:** WO<sub>x</sub>/α-Fe<sub>2</sub>O<sub>3</sub>, Heterojunction, DC Magnetron Sputtering, Thin Film Deposition, Advanced Surface Engineering.

[1] N. Al-Aisae et al., *Solar Energy Materials and Solar Cells*, 263 (2023).

[2] B. Liu et al., (Review article on heterojunctions and charge separation mechanisms) (2025).

10:20am **TS2-2-ThM-8 Interface-Driven Evolution and Electrochemical Behavior of CuO/WO<sub>x</sub> Heterostructures Deposited by Magnetron Sputtering**, *Rafael Leal, Giovana Fazenda, Helen Barros, David Graves, Filipe Dalan, Mariane Murase, Marcilene Gomes*, Aeronautics Institute of Technology (ITA), Brazil; *Douglas Leite*, Aeronautics Institute of Technology, Brazil; *Argemiro Silva-Sobrinho, André Pereira [andrejp@ita.br]*, Aeronautics Institute of Technology (ITA), Brazil

Heterostructures composed of copper and tungsten oxides have drawn increasing attention for solar-driven photoelectrochemical (PEC) hydrogen generation due to their complementary optical and electronic properties [1]. The interface between p-type CuO and n-type WO<sub>x</sub> plays a critical role in charge separation and carrier transport; however, its efficiency strongly depends on the structural order and chemical composition of the WO<sub>x</sub> layer [1,2]. In this work, CuO/WO<sub>x</sub> heterostructures were fabricated entirely by DC magnetron sputtering. CuO films were first deposited onto FTO substrates and annealed at 450 °C for 2 h to promote crystallization and improve adhesion. WO<sub>x</sub> overlayers were then deposited for 1, 5, and 10 min, followed by post-annealing at 450 °C for 2 h to obtain crystalline layers; as-deposited samples were kept amorphous. The WO<sub>x</sub> layer thickness, determined by profilometry and ellipsometric modeling, increased linearly with deposition time (~15 nm min<sup>-1</sup>), while the refractive index was slightly higher for crystalline samples, indicating greater density and lower porosity. Structural and vibrational analyses revealed distinct interface behaviors. For crystalline WO<sub>x</sub> layers, Raman and XRD showed that samples with 5 and 10 min deposition underwent interdiffusion at the interface, forming CuWO<sub>4</sub>, whereas the 1 min sample exhibited a substoichiometric WO<sub>x</sub> layer. In contrast, amorphous WO<sub>x</sub> overlayers preserved only CuO peaks. Electrochemical measurements confirmed the correlation between structure and functionality. Cyclic voltammetry and impedance spectroscopy revealed that crystalline samples containing CuWO<sub>4</sub> exhibit lower charge-transfer resistance and higher photocurrent under illumination, while amorphous heterostructures display slower carrier dynamics and greater capacitive behavior. The electrochemically active surface area (ECSA), estimated from non-faradaic capacitive current, was significantly larger for crystalline samples, particularly those with CuWO<sub>4</sub>, indicating an increased density of electroactive sites and enhanced charge accumulation capability. Overall, the controlled formation of CuWO<sub>4</sub> or substoichiometric WO<sub>x</sub> interlayers offers a promising strategy to improve PEC efficiency and long-term stability of CuO-based photoelectrodes for sustainable hydrogen generation.

## Acknowledgments

We acknowledge the financial support from FAPESP (Grant No. 2022/02994-2) and CNPq (Grant No. 302823/2025-5).

[1] X. Wen et al., *ACS Appl. Nano Mater.* 7 (2024) 14936–14945. DOI: 10.1021/acsanm.4c00769.

[2] M. Castaneda Mendoza et al., *Materials* 18 (2025) 2896. DOI: 10.3390/ma18122896.

10:40am **TS2-2-ThM-9 Unlocking the Potential of Medium-Entropy Prussian Blue for Superior Electro-Fenton Oxidation**, *Sheng-Wei Lin [alec97622964@gmail.com]*, *Jyh-Ming Ting*, National Cheng Kung University (NCKU), Taiwan

Electro-assisted advanced oxidation processes, such as the electro-Fenton (EF) process, are gaining intensive attention recently. This work investigates the application of a medium-entropy Prussian blue analogue (designated as 3M-PBA) as a heterogeneous EF catalyst for the removal of organic pollutants from water. EF process can overcome the drawbacks of conventional Fenton process, such as the limited pH range and poor reusability. In this work, the 3M-PBA catalyst further enhances the EF performance by providing multiple redox-active sites, which accelerate electron transfer and improve structural stability during operation.

The phase, morphology, oxidation state, charge-transfer behaviour, hydroxyl-radical generation efficiency, and EF degradation performance were characterized using several techniques. UV-Vis spectroscopy analysis

shows a continuous decrease in the characteristic TC absorption peak at 357 nm with time, confirming the molecular breakdown. The 3M-PBA catalyst achieves a high TC removal within a short time under an applied potential (0.6 V vs. Ag/AgCl). Iron leaching remains below 0.4 ppm throughout the five cycles, indicating strong structural integrity and environmental safety.

**Keywords:** electro-Fenton, high-entropy PBA, charge transfer, catalyst stability, wastewater treatment

11:00am **TS2-2-ThM-10 Hierarchical Heterostructure of Co<sub>3</sub>O<sub>4</sub>/NiCoB for Enhanced Bifunctional Electrolysis: Towards Green and Sustainable Energy Solution**, *Krishna Modi [modi.krishna079@gmail.com]*, *Anand Joshi*, Micro-Nano Research & Development Center, Parul University, Vadodra, 391760, Gujarat, India

The production of hydrogen is a viable path for achieving the Sustainable Development Goals (SDGs). However, classical hydrogen production techniques require high energy and are not financially feasible, emphasizing the urgent need to develop cost-effective and efficient electrocatalysts. Herein, cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) nanoflowers were initially fabricated on Ni foam using hydrothermal synthesis techniques. After that, NiCoB nanosheets were uniformly deposited on Co<sub>3</sub>O<sub>4</sub> using the dip-coating chemical reduction reaction technique. This hierarchical nano-heterostructure demonstrates the excellent electrocatalytic activity towards both the hydrogen evolution reaction and the methanol oxidation reaction. In contrast to the oxygen evolution reaction (OER), the active nano-heterostructure exhibits a low overpotential of 1.3V to reach the current density of 100 mA/cm<sup>2</sup>. Moreover, the Co<sub>3</sub>O<sub>4</sub>/NiCoB nano-heterostructure exhibits excellent stability, sustaining the methanol oxidation reaction for over 50 hours. In addition, compared to combined HER||OER systems, the nano-heterostructure in coupled HER||MOR requires a sufficiently low overpotential. Economically, the coupled HER||MOR not only enhance the energy efficiency but also generates formic acid as a byproduct, which significantly increases the net profit in the hydrogen generation as compared to coupled HER||OER systems. These results provide the groundwork for the SDGs aligned with green and sustainable energy applications.

11:20am **TS2-2-ThM-11 Defect-Engineered Copper-Based Materials for Electrocatalytic Nitrate Reduction**, *Ting-Chun Hung [jim8965976@gmail.com]*, *Jyh-Ming Ting*, National Cheng Kung University (NCKU), Taiwan

Electrochemical nitrate reduction reaction (NO<sub>3</sub>RR) has emerged as a promising strategy for simultaneously addressing nitrate pollution and producing valuable ammonia via a carbon-free process. Ammonia is an important chemical feedstock, widely used in fertilizer production, and offers advantages such as an alternative energy source for replacing hydrogen due to its ease of storage and transport.

For NO<sub>3</sub>RR, copper-based materials are known to be highly active catalysts by facilitating the conversion of nitrate (NO<sub>3</sub><sup>-</sup>) to nitrite (NO<sub>2</sub><sup>-</sup>), which is the rate-determining step. In this study, novel Cu-based heterostructure nanosheets rich in oxygen vacancies (Ov) were investigated as an effective electrocatalyst for NO<sub>3</sub>RR. The catalyst was synthesized via a hydrothermal method, followed by chemical reduction for controlled creation of Ov. The catalyst exhibits excellent NO<sub>3</sub>RR performance, achieving a Faradaic efficiency of ~95% at -0.2 V vs. RHE, a high ammonia yield rate of 0.92 mmol h<sup>-1</sup> cm<sup>-2</sup>, and outstanding stability over 1000 hours, demonstrating both superior activity and long-term durability. Density functional theory calculation was performed to support the experimental data.

**Keyword:** Electrochemical nitrate reduction, heterostructures, oxygen vacancy, high ammonia yield rate

11:40am **TS2-2-ThM-12 Plasma-Driven Surface Activation of Mo-Based Chalcogenides for Energy Storage Performance**, *Poonam Lakhiwal [poonamlakhiwal00@gmail.com]*, *SANTOSH KUMAR MAHAPATRA*, Central University of Punjab, India

Molybdenum-based chalcogenides such as MoS<sub>2</sub>, MoSe<sub>2</sub>, and MoS<sub>2</sub>Se were synthesized and subsequently treated using an Electron Cyclotron Resonance (ECR) argon plasma to induce surface activation. The structural, morphological, and electrochemical modifications induced by the plasma treatment were characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), Raman spectroscopy, Brunauer-Emmett-Teller (BET) surface area analysis, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The plasma-treated samples exhibited distinct changes in surface morphology and electronic structure, confirming successful surface activation. Electrochemical analyses

performed prior to and following plasma-driven evidenced significant variation in charge storage characteristics, including specific capacitance, charge transfer resistance, cycling stability, as well as energy and power density. These differences are attributed to the surface modification induced by ECR plasma, which, combined with optimized morphology and altered surface chemistry with variation of electroactive sites, redox activity, and ion diffusion. The results show that ECR plasma treatment is an efficient strategy to tune the electrical and physicochemical properties of Mo-based chalcogenides for energy storage systems.

12:00pm **TS2-2-ThM-13 Non-Precious Metal Phosphide/Sulfide Heterostructure Electrocatalyst for SOR, JIAN-AN WU [tommy77222@gmail.com], Jyh-Ming Ting, National Cheng Kung University (NCKU), Taiwan**

With the increasing discharge of wastewater containing sulfur compounds from various industries, the need for efficient sulfur removal and recovery is becoming more urgent. The Sulfion Oxidation Reaction (SOR), which converts sulfide ions ( $S^{2-}$ ) into elemental sulfur ( $S_8$ ), which is common for industrial use. Unlike the conventional oxygen evolution reaction (OER), which is thermodynamically challenging and energy-consuming, SOR operates at a much lower potential (-0.48 V vs. RHE), making it a more energy-efficient alternative for sulfur oxidation. Furthermore, the added economic value makes SOR an attractive option for wastewater treatment, as it reduces the need for costly disposal methods while turning a pollutant into a resource.

Herein, we have synthesized a non-precious metal phosphide/sulfide heterostructure catalyst with conductive backbone and abundant active site on the surface. The catalyst demonstrates an exceptional SOR performance in 1M KOH with 1M  $Na_2S$ , achieving a low potential of 0.278V at 100 mA  $cm^{-2}$  and 0.368V at 300 mA  $cm^{-2}$ , and a lower onset potential.

Keywords: Sulfion Oxidation Reaction (SOR), transition-metal based catalyst, heterostructure

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