

Topical Symposium on Sustainable Surface Engineering Room Town & Country B - Session TS1-1-MoM

Coatings for Batteries and Hydrogen Applications I

Moderator: Nazlim Bagcivan, Schaeffler Technologies GmbH & Co. KG, Germany

10:00am **TS1-1-MoM-1 New Coating Methods for New Electrolyzer Technologies for PEM Electrolyzer and AEM Electrolyzer, Thomas Kolbusch (tkolbusch@coatema.de), Coatema, Germany** **INVITED**

The author describes in his talk the scale up process for PEM electrolyzers regarding coating technologies. The first part of the talk shows the need for scale up in the green hydrogen market due to the huge amount of green hydrogen which has to be produced till 2030 and 2050 to reach net zero targets. For this industrial standardization of coating processes are needed as soon as possible. Here the upscale process of reproducible and reliable roll 2 roll equipment are shown and getting over the limiting factors like dimension instability of membrane materials and multi-layer coating applications of rare materials like iridium.

The second part describes the boundaries of today's coating methods describing the parameters needed to be optimized. The background on one of the standard methods today, slot die coating is described here in detail with some theoretical background on slot die coating technology and an overview on developments for intermittent slot die coatings. The third part of the talk describes a new digital fabrication method for electrolyzers and shows the opportunity for the overall green hydrogen market using digital fabrication methods, reducing the carbon footprint of coating equipment for PEM electrolyzer.

10:40am **TS1-1-MoM-3 Dual Doped Two-dimensional Carbon Supported Single Atomic Iron for Oxygen Reduction Reaction in Alkaline-Exchange Membrane Fuel Cells, Afandi Yusuf (afandi2102@gmail.com), F. T. D. Wijaya, H. Hsin-Chih, C. Wang, National Taiwan University of Science and Technology, Taiwan**

Single atom catalysts (SAC) represent an intriguing option due to their ability to unlock the latent catalytic potential in oxygen reduction reaction (ORR). Nevertheless, the endurance of individual atomic entities is confronted by numerous impediments, encompassing the dissolution of metallic species, metal agglomeration, and the deactivation of catalytically active sites. A crucial factor in enhancing stability lies in the judicious selection of a compatible support catalyst capable of fostering strong metal-support interaction (MSI).

Carbon is widely utilized as a catalyst support material owing to its favorable electron conductivity and the ability assume diverse dimensional configurations, ranging from 0D to 3D. Additionally, the carbon support facilitates additional customization, such as the introduction of Chalcogen or Pnictogen atom groups through doping, leading to enhanced catalytic activity.

In this work, we successfully fabricated a two-dimensional porous nanosheet electrocatalyst designed to enhance the Oxygen Reduction Reaction (ORR) in Anion-Exchange Membrane Fuel Cells (AEMFCs). This catalyst featured single atomic active sites of Iron supported by a Nitrogen-Phosphorus co-doped Carbon material, aimed at reducing catalyst cost and thereby increasing the accessibility of the fuel cell for commercial applications. The electrochemical performance of the material was exemplified by the MDP-4-Fe-800 sample, demonstrating an onset potential of 0.97 V, an $E_{1/2}$ of 0.86 V, and a $J_{limiting}$ of 5.5 mA/cm² under alkaline conditions, surpassing that of commercial Pt/C under the same conditions. Moreover, the material exhibited notable stability after 30,000 cycles, experiencing only a marginal 0.39 mA/cm² in $J_{limiting}$ and 30 mV decrease in both onset and $E_{1/2}$. While MDP-4-Fe-800 did not outperform the single-cell performance of commercial Pt/C, it displayed commendable activity, generating a power density of 244.8 mW/cm².

11:00am **TS1-1-MoM-4 CO₂ Laser Processed Nickel Catalyzed Graphene Coating for Electrocatalytic Water Splitting and Energy Storage Applications, Suparna Saha (suparna.saha@tcgcrest.org), TCG CREST (RISE), India; S. Hiwase, IISER PUNE, India; S. Ogale, IISER PUNE, TCG-CREST (RISE), India**

Development of efficient, cost-effective, and environmentally friendly processes for the realization of high-quality graphene on metallic substrates is highly desirable for multiple energy applications as well as next-generation graphene-based green electronics. Several polymers including

those derived from natural sources represent a rich source of carbons that can be converted into graphitic carbons by energy inputs in different forms. Lasers represent a form of energy input that is direct-write type and does not need the whole substrate to be heated at high temperatures for carbonization. Herein, we examine carbonization of natural product-derived polymer(s) into graphitic (few layers graphene) carbon using CO₂ laser-assisted direct-write process. Such a process is generally termed as Laser-Induced Graphene (LIG). In particular, we demonstrate the key and interesting role played by nickel in enhancing the degree of graphitization (Ni-LIG). Indeed, the unique advantage of this nickel-catalyzed scanning laser-induced transient pyrolysis process implemented under ambient conditions is that we are able to uniformly graphitize the thermoset polymer coating that would otherwise yield hard carbons or a mixture of ordered/disordered carbon in a furnace-based pyrolysis process. It was observed that upon optimized laser processing condition, the Ni-(CH₃COO)₂·4H₂O salt added to the polymer gets reduced to Ni (111), which in turn catalyzes the nucleation process. We note the appearance of disordered carbon chains initially, which upon interacting precisely with the nickel surface lowers the activation barrier for graphene formation by annealing the defects. Moreover, due to the very low lattice mismatch between Ni (111) and graphene, a strong interphase is formed, facilitating efficient contact and charge transfer. As the surface coating is decorated with a mixture of Ni/NiO (as confirmed by XRD and XPS), water dissociation as well as adsorption of water oxidation intermediates is promoted, leading to an impressive value of overpotential for oxygen evolution reaction (OER) at 10 mA/cm² of only 330 mV in 1M KOH. We also examined the case of urea-incorporated material to induce N-doping so as to enhance the conductivity via the incorporation of the π -conjugated system. However, the incorporated pyrrolic N defects in the carbon layer were noted to hinder the nucleation of graphitization at the Ni atom, resulting in a low I_a/I_b ratio. This material was therefore studied for charge storage property by cyclic voltammetry and galvanostatic charge-discharge (GC) measurement. It was found that N-doped Ni-Ni-LIG has a higher specific capacitance compared to Ni-LIG.

11:20am **TS1-1-MoM-5 Bimetal Phosphide (NiCoP)/Graphitic Carbon Nitride(g-C₃N₄) Composites for Hydrogen Evolution Reaction in Alkaline Electrolyte, Yu-Hsuan Kao (hsuan890411@gmail.com), National Cheng Kung University, Taiwan; S. Wang, Southern Taiwan University of Science and Technology, Taiwan; J. Huang, National Cheng Kung University, Taiwan; Y. Shen, Hierarchical Green-Energy Material (Hi-GEM) Research Center, Taiwan**

In order to address the growing energy crisis and environmental concerns, the development of hydrogen energy through electrochemical water splitting into hydrogen represents a viable solution. The hydrogen evolution reaction (HER) during water splitting is multi-electron transfer process that requires catalysts to proceed at appreciable rates. Noble metals have been widely used for water splitting due to their low Gibbs free energy; however, their high cost limits their availability and hinders commercialization. To address this challenge, we conducted a study on HER in alkaline electrolytes with the aim of developing highly efficient and durable electrocatalysts. The efficiency of HER in an alkaline environment is determined by a delicate balance among three crucial factors: the energy required to dissociate water molecules, hydrogen adsorption (H_{ad}) on the catalyst's surface, and the prevention of hydroxyl adsorption (OH_{ad}), often referred to as the poisoning of active sites.

Graphitic carbon nitride (g-C₃N₄) has been extensively studied due to its two-dimensional layered structure and high nitrogen content. However, its poor conductivity limits its application in the field of HER. Therefore, we modified transition metal phosphide on g-C₃N₄ to enhance its conductivity and increase the number of active sites. Additionally, it has been mentioned in previous studies that nickel and cobalt atoms can promote the reaction kinetics of HER in the first and second steps, respectively, thus improving the efficiency of HER in an alkaline electrolyte. Therefore, we synthesized NiCoP/g-C₃N₄ composites in different weight percent to replace the platinum electrode in a 1.0 M KOH electrolyte.

We used Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) to determine the structure of NiCoP/g-C₃N₄. In addition, Linear Sweep Voltammetry (LSV) and Tafel slope were employed to confirm the electrochemical performance of NiCoP/g-C₃N₄ in HER. The results demonstrate that we successfully synthesized g-C₃N₄ and NiCoP/g-C₃N₄ electrocatalysts using a wet chemical method and calcination. Furthermore, the electrochemical results indicate that the addition of 10 wt% NiCoP to g-C₃N₄ significantly improves and exhibits excellent performance in HER in an

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alkaline electrolyte, reducing the overpotential from 560.7 mV to 338.9 mV and decreasing the Tafel slope from 197.2 mV/dec to 89.6 mV/dec. Then we will use in-situ TEM and in-situ Raman analysis to confirm the contribution and role of the NiCoP alloy on $g\text{-C}_3\text{N}_4$ in the hydrogen evolution reaction.

11:40am **TS1-1-MoM-6 Hybrid Inorganic-Organic Nanolayered Thin Films Based on ZnS-Ethylenediamine for the Photocatalytic Production of Hydrogen**, *L. Cerezo*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México; *K. Valencia*, Instituto de Ingeniería, Universidad Nacional Autónoma de México; *M. Bizarro*, **Sandra E. Rodil** (srodil@unam.mx), *A. Hernández-Gordillo*, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México

Hybrid ZnS-ethylenediamine nanomaterials ($\text{ZnS}(\text{en})_{0.5}$) were produced in a mixed solvent of water, butanol, and ethylenediamine by solvothermal and precipitation methods. The effect of different molar ratios $\text{H}_2\text{O}/\text{Zn}^{2+}$ between 15 and 91 have been investigated by diverse techniques; TG-DSC analysis, X-ray Diffraction, Scanning Electron Microscopy, Infrared, and Diffuse Reflectance spectroscopy. The material was then exfoliated using a combined sonication-illumination process to obtain stacked 2D ZnS nanolayers intercalated with the organic material. After optimization, the as-prepared and exfoliated $\text{ZnS}(\text{en})_{0.5}$ nanosheets were prepared as films by spin coating to evaluate the photocatalytic H_2 production reaction. The H_2 evolution reaction was performed in a homemade glass photoreactor containing 30 mL of ethanol-water solution (50:50 vol. %). Eight films were fixed around the internal walls of the glass reactor. The solution was magnetically stirred (at 600 rpm), irradiated with UV light provided by a Hg lamp Pen-ray (of $\lambda=254$ nm and $I_0 = 4.4$ mWcm $^{-2}$), and placed in the center of the solution into the quartz tube. The system was bubbled with N_2 (to reduce the O_2 pressure), then it was sealed, and the lamp was turned on. The quantity of H_2 was measured using a Shimadzu GC-2014 gas chromatograph and N_2 as the carrier gas. The photocatalytic activity of all the as-prepared and sonicated-irradiated $\text{ZnS}(\text{en})_{0.5}$ samples was evaluated by 6 h and 6 cycles. The results showed an enhancement of 7 to 22 times in the H_2 production rate as a function of the synthesis and exfoliation conditions. Intrinsic hydrogen evolution rates up to 76 mmol $g^{-1}h^{-1}$ were achieved using the optimized exfoliated $\text{ZnS}(\text{en})_{0.5}$ hybrid material. This value constitutes a record in the community, which is more significant when the lamp's low power is considered. The increased photoactivity was correlated to the degree of exfoliation and the number of stacked ZnS layers in the structure.

12:00pm **TS1-1-MoM-7 One-pot Synthesis of NiFeCo(OH) $_x$ @FeOOH@(NiFeCo) S_x Electrocatalyst for Urea Oxidation Reaction**, *Thi Xuyen Nguyen* (nguyenxuyen1511@gmail.com), *Z. Wei, J. Ting*, National Cheng Kung University, Taiwan

Urea oxidation reaction (UOR) is a promising energy-saving avenue for sustainable hydrogen production. However, the 6-electron transfer reaction lead the sluggish kinetic. In this work, an ultrafast, one-step method has been used to synthesize novel NiFeCo(OH) $_x$ @FeOOH@(NiFeCo) S_x heterostructure supported on Ni foam as electrocatalyst toward UOR. We demonstrate that the NiFeCo(OH) $_x$ @FeOOH@(NiFeCo) S_x exhibits outstanding UOR performance with a low potential of 1.36 V versus reversible hydrogen electrode at a current density of 100 mA cm $^{-2}$. The catalyst also shows great durability for 50 hours at 10 mA cm $^{-2}$. The outstanding electrochemical performance is attributed to the high surface area, the faster electron transfer, free of binder, and the synergistic effects of among metallic components.

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