Topical Symposium on Sustainable Surface Engineering
Room Town & Country B - Session TS1-2-MoA

Coatings for Batteries and Hydrogen Applications II

Moderators: Chen-Hao Wang, National Taiwan University of Science and Technology, Taiwan , **Martin Welters**, KCS Europe GmbH, Germany

1:40pm **TS1-2-MoA-1 The Effect of the Transition Metal Dopant on the Microstructure and Electrochemical Performance of Magnetron Sputtered Electrodes for Solid Oxide Fuel Cells Applications***, **Justyna Kulczyk-Malecka [j.kulczyk-Malecka@mmu.ac.uk]**, Katharina Steier, David Shaw, Kleitos Panagi, Peter Kelly,* Manchester Metropolitan University, UK

The electrolytic energy conversion has become one of the main technologies considered to deliver actions on reducing CO_2 emissions in the energy, heavy-duty transportation and industrial processes sectors. The electrolytic cells (fuel cells and electrolysis cells) can be utilised in energy conversion, generation, and storage, which has been demonstrated at scale in many regions around the world already. Solid oxide cells are typically composed of porous ceramic matrix and Ni metal catalyst fuel electrodes, dense ceramic electrolytes, such as YSZ or GDC, and perovskite air electrodes. These cells operate at relatively high temperatures (typically 600-850°C) and, therefore do not require precious metal group catalysts to drive the reaction forward in both electrolysis (H_2 generation) and fuel cell (energy conversion) modes. Moreover, they are more versatile in terms of required fuel type allowing utilisation of hydrogen as well as alternative fuels, such as methanol, ammonia, or biogas.

In this work, thin (~3 µm) nanostructured cermet anodes consisting of YSZ-Ni and GDC-Ni were doped with transition metals to study their influence on coatings microstructure and electrochemical performance. The anodes were deposited onto commercial YSZ electrolyte support cells using oblique angle pulsed DC reactive magnetron sputtering. The coating microstructure was evaluated using FIB-SEM and TEM and focused on the triple-phase boundary evolution in relation to the amount of the added dopant (0-5 wt.%). The chemical composition of the coatings was assessed using EDX, XPS and XRD analysis. The polarization curves were obtained from SOFC single stack assemblies under hydrogen and air flows for anode and cathode, respectively, at operating temperatures of 850°C to evaluate the electrochemical performance of the deposited films.

2:00pm **TS1-2-MoA-2 Investigation of $Ba_{0.5}Ce_{0.3}Zr_{0.18}Y_{0.01}Yb_{0.01}O_{3-\delta}$ /$Y_{0.2}Ce_{0.8}O_{2-\delta}$ Composite Coatings for the Electrolyte of Solid Oxide Fuel Cell***, **Yen-Yu Chen [yychen@mail.npust.edu.tw]**, Ke-Hsing Wang,* National Pingtung University of Science and Technology, Taiwan

Solid oxide fuel cells (SOFCs) are one of the potential power generation devices for the sources of renewable energy. In this study, the composite coatings consisted of $BaCe_{0.7}Zr_{0.12}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) and $Y_{0.2}Ce_{0.8}O_{2-\delta}$ (YDC) were developed by a colloidal coating process as the electrolyte for SOFC. Both of the powders of BCZYYb and YDC were synthesized by the solid-state reaction methods. The well dispersed suspensions after refined by the planetary ball method were spin coated on the porous $NiO/BaZr_{0.85}Y_{0.15}O_{3-\delta}$ (BZY) substrates, which were prepared by a die pressing method after pre-sintering at 1200°C for 1 h. Several properties were analyzed including microstructures, crystallographic phases, and electrical performance. The BCZYYb/YDC composite coatings still showed duel-phases including perovskite-type BCZYYb and fluorite-type YDC after sintered at 1550oC for 24 h, The coating layer shows high density after sintered. And the thickness of the coating layers are around several µm. The composites show ionic conductive behaviors from the temperature between 500~800°C. The details will be reported in the presentation.

2:20pm **TS1-2-MoA-3 Unveiling the ORR Mechanism on Co Single-Atom Catalysts Using Operando Raman Spectroscopy with Catalyst-Coated Membrane (CCM) Methodology***, **Sun-Tang Chang [suntang925@gmail.com]**, Yi-Qing Chu, Zih-Jhong Huang, Chen-Hao Wang,* National Taiwan University of Science and Technology, Taiwan

In this study, operando Raman spectroscopy was employed to investigate the mechanism of the oxygen reduction reaction (ORR) on a cobalt single-atom catalyst (Co-SAC). The Co-SAC was synthesized and utilized as a cathode catalyst for an alkaline anion exchange membrane fuel cell (AAEMFC). The results demonstrate excellent ORR activity, with an electron transfer number of 3.96 and J_{iming} is 5.5 $mAcm^{-2}$.

X-ray absorption spectroscopy (XAS) revealed that the Co-SAC features a Co-N5 coordination structure, with cobalt in the +3 oxidation state. Furthermore, wavelet transform (WT) analysis confirmed the presence of isolated cobalt single atoms.

To minimize interference from the electrolyte during Raman laser measurements, the catalyst-coated membrane (CCM) method was adopted. This approach effectively prevents direct interaction between the laser and the electrolyte while ensuring efficient OH^- group transfer to the catalyst. Additionally, in the operando setup, electrochemical impedance spectroscopy (EIS) was integrated with Raman spectroscopy. This combination enabled a detailed observation of the ORR mechanism and the evolution of surface phenomena under different applied biases.

This study represents a significant breakthrough in unveiling the ORR mechanism, particularly for Co-based single-atom catalysts.

2:40pm **TS1-2-MoA-4 Study on Mo_xN Thin Films Deposited by HiPIMS and RF Sputtering with Heteroatom Doping for Hydrogen Evolution Reaction Catalysts***, **Hung-I Wu [a8794191@gmail.com]**,* National Yunlin University of Science and Technology, Taiwan*; Ying-Hsiang Lin,* National United University, Taiwan*; Shih-Hung Lin,* National Yunlin University of Science and Technology, Taiwan*; Fan-Bean Wu, Chi-Yueh Chang,* National United University, Taiwan*; Thi Xuyen Nguyen, Chia-Ying Su, Ruei-Chi Lin, Jyh-Ming Ting,* National Cheng Kung University (NCKU), Taiwan*; Wan-Yu Wu,* National United University, Taiwan

In recent years, materials such as transition metal oxides and nitrides have been popular in catalyst research. Compared to scarce noble metals, molybdenum-based materials not only have more abundant resources but also exhibit excellent activity[1], making them highly suitable to replace the costly noble metal catalysts (Ru, Ir, RuO_2, IrO_2). Molybdenum nitride (MoN) possesses outstanding corrosion resistance and electronic conductivity[2], allowing it to perform the hydrogen evolution reaction (HER) in acidic media. If different elements like Ti, Co, Ni, and V are doped into Mo_xN as a substrate, a synergistic effect is expected to further enhance HER performance. Additionally, when attaching catalysts to electrodes, one must consider the uniformity of surface coverage and adhesion on electrodes of various shapes. As is well known, sputtering offers advantages such as uniform coating, easy control of film thickness, and excellent adhesion. Therefore, using this method to prepare catalyst thin films on electrodes is the optimal choice.

In this study, we employed RF sputtering and High Power Impulse Magnetron Sputtering (HiPIMS) techniques to deposit Mo_xN thin films for comparison. Initially, we deposited Mo_xN thin films using HiPIMS and found in preliminary results that the HiPIMS-deposited Mo_xN thin films exhibited an overpotential of 415 mV at $\eta=10$ during hydrogen evolution reaction (HER) tests in 0.5M H_2SO_4. Energy-dispersive X-ray spectroscopy (EDS) analysis revealed that the Mo and N contents in the Mo_xN thin films were 60 at.% and 40 at.%, respectively. Grazing-incidence X-ray diffraction (GIXRD) results indicated that the thin films have a face-centered cubic (FCC) structure similar to Mo_3N_2. Building on these Mo_xN results, we will further explore the impact of varying the N/Mo ratio on HER performance. Additionally, we plan to attempt doping other elements into Mo_xN to observe the changes induced by doping.

3:00pm **TS1-2-MoA-5 Ternary FeCoNi / Graphene Composites as Electrocatalysts for Highly Efficient Hydrogen Evolution Reaction***, **Yu Tsung Lin [asd881228@gmail.com]**, Jow Lay Huang, Sheng Chang Wang, Yu Min Shen,* National Cheng Kung University (NCKU), Taiwan

As a consequence of the depletion of fossil fuels, the escalating energy crisis has driven researchers to explore innovative energy. To address this problem, exploring hydrogen energy generation via water splitting emerges as a promising solution. This process involves the hydrogen evolution reaction (HER), a multi-electron transfer process necessitating catalysts to facilitate efficient rates. Despite noble metals have conventionally served this purpose due to their favorable Gibbs free energy, their prohibitive costs pose challenges for widespread adoption and commercialization. In response, our investigation focuses on HER within alkaline electrolytes, aiming to engineer alternative electrocatalysts that are both cost-effective and efficient.

Transition metals from the first row are active centers for the HER due to their 3d orbital, exhibiting excellent activity. Among them, nickel (Ni) and cobalt (Co) shows the most promising potential because the hydrogen adsorption energy of them approaches that of Pt. Furthermore, recent studies have indicated that the incorporation of third transition metals, such as iron (Fe), can further enhance the HER activity. This is attributed to the synergistic effect among the three metals. Additionally, it can be observed that a large number of studies use two-dimensional carbon materials as supports. Graphene, a highly conductive 2D material, serves as an excellent supporting matrix due to its high surface area, facilitating efficient electron transfer during HER. Consequently, we synthezised ternary FeCoNi-LDH/graphene composite by hydrothermal method and measured the HER performance in 1.0 M KOH electrolyte.We used X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) to determine the crystal structure and morphology of the composite. The results demostrate that we successfully synthesized FeCoNi-LDH/graphene. In addition, Linear Sweep Voltammetry (LSV) were employed to confirm the HER performance. The overpotential and Tafel slope is -386.6 mV and 85.8 mV/dec, respectfully.

4:00pm **TS1-2-MoA-8 One Step Fabrication of Highly Ordered Binder Free Vanadium Oxide Thin Film Cathode for Next Generation Micro Batteries***, **Ananya Bansal [ananya_b@ic.iitr.ac.in]**,* Indian Institute of technology Roorkee, India*; Ramesh Chandra,* Indian Institute of Technology Roorkee, India

The increasing demand for microelectronics has significantly driven the advancement of thin film energy storage devices, specifically batteries. Till now, a range of materials have been investigated for lithium-ion batteries, with vanadium oxide emerging as a promising material. Vanadium oxides are known for multiple oxidation-reduction states during electrochemical reaction, hence, can promote multiple diffusion of Lithium ions resulting in high energy and power density. In this work, binder-free Vanadium oxide (V_2O_5) has been synthesized by reactive DC magnetron sputtering on aluminium foil substrate. Vanadium target (99.99% pure) is bombarded with high-energy Ar^+ ions which dislodge atoms from the vanadium surface. These ejected atoms then react with oxygen ions to form highly pure V_2O_5 and deposit onto a substrate, forming a thin film. The deposited layers were analyzed for their structural and surface morphology using XRD and SEM techniques. Highly ordered brick like nanostructures were observed during SEM analysis. X-ray photoelectron spectroscopy measurements were carried out to understand the chemical bonding of the cathode. The surface of vanadium oxide obtained from this binder-free approach helps us to create a high-quality cathode-electrolyte interface with high wettability (33.3^o). Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) cycling, and electrochemical impedance measurements were used to investigate the capacity and cycling stability of the V_2O_5 cathode in 1 M lithium hexa-flouro-phosphate. As a result, it can be interpreted that this binder-free technology can be used to fabricate efficient lithium free cathode for new generation thin film batteries.

4:20pm **TS1-2-MoA-9 Research Coating Conductive Material on SiO_x@rGO Composite Materials as Anode Material in Lithium-Ion Batteries***, **Yi-Ling Chen [n56124155@gs.ncku.edu.tw]**,* National Cheng Kung University (NCKU), Taiwan

With the advancement of technology, lithium-ion batteries have emerged as a future energy storage technology with the gradual development of electric vehicles. Silicon-based materials, due to their high theoretical capacity, energy density (~4200mAh/g), and natural abundance, are considered as candidates for negative electrode materials in lithium-ion batteries.

In this study, our research team successfully prepared reduced graphene oxide (rGO) using the Hummer method and incorporated commercial SiO_x micron-sized powder to synthesize SiO_x@rGO composite material as an anode for lithium-ion batteries. The initial charge capacity was measured at 1487 mAh/g, with a discharge capacity of 1060 mAh/g, yielding an initial coulombic efficiency of 71%. After 40 cycles, the capacity retention remained at 91%. However, there are currently no theoretical studies addressing the lithiation process and lithium ion insertion/extraction mechanisms in SiOx materials.

Therefore, in our study, we not only explore the use of SiO_x@rGO composite material as an anode to improve the theoretical capacity and energy density of lithium-ion batteries but also aim to enhance the electrical conductivity and electrochemical performance of the battery. Conductive materials such as copper, gold, and platinum will be deposited on the prepared SiO_x@rGO anode material. These conductive coatings will provide additional electrons, creating a driving force for lithium ion diffusion into the anode material during discharge to achieve charge conservation. This process is expected to enhance the capacity and cycling stability of lithium-ion batteries. We will characterize the materials using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and transmission electron microscopy (TEM). Furthermore, charge-discharge and cycling performance tests will be conducted on the lithium-ion batteries to investigate the effect of the conductive materials on their performance. Cyclic voltammetry will be employed to observe the electrochemical reactions during charge and discharge cycles.

This study conducts a theoretical analysis of SiO_x@rGO composite material as an anode for lithium-ion batteries by coating it with conductive materials, aiming to provide valuable reference data for both commercial and academic purposes.

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