

Renewable Energy and Energy Storage

Room Naupaka Salon 4 - Session RE1-MoM

Electrochemistry and Photocatalysis I

Moderator: Craig Perkins, National Renewable Energy Laboratory

8:40am **RE1-MoM-3 Hot Carrier-Driven Plasmonic Photoelectrochemical Processes, Jeong Young Park**, KAIST, Republic of Korea **INVITED**

The detection of hot electrons and understanding the correlation between hot electron generation and surface phenomena are challenging questions in the surface science and catalysis community. Hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) appears to be correlated with localized surface plasmon resonance. It has been found that the hot electron flux generated under photon absorption and exothermic chemical reaction is the major mediator of energy conversion process [1-3]. In this talk, I introduce the research direction to attempt to detect the surface plasmon driven hot carrier at the nanometer scale by using scanning probe microscopy. To detect and utilize the hot electron flows at the macroscale level, the metal-semiconductor nanodiodes were constructed. At the nanometer scale, we utilized photoconductive atomic force microscopy to observe photoinduced hot electrons on a triangular Au nanoprism on n-type TiO₂ under incident light. This is the direct proof of the intrinsic relation between hot electrons and localized surface plasmon resonance. We observed surface plasmon induced hot hole by using the system of Au nanoprism on p-type GaN [4]. I will discuss the impact of hot carriers in the photocatalytic activity under photoelectrochemical water splitting by using Au-based plasmonic nanostructures [5].

References

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- [2] H. Lee et al. of *Chemical Research* 55, 24, 3727 (2022).
- [3] S. W. Lee et al. *Surface Science Reports* 76 100532 (2021).
- [4] H. Lee et al. *Advanced Science* 7, 2001148 (2020).
- [5] K. Song et al. *ACS Energy Lett.* 6, 4, 1333–1339 (2021).

9:20am **RE1-MoM-5 Next-Generation Electrocatalysts Derived from Metal-Organic Frameworks for Hydrogen Production and Conversion, Di-Jia Liu**, Argonne National Laboratory

Metal-organic frameworks (MOFs) have found their ever growing applications in today's economy and industrial applications. In this presentation, I will discuss some of the recent technological breakthroughs in applying MOFs for green hydrogen applications. I will focus on the discussion on our recent progresses in applying MOFs for a) platinum group metal free (PGM-free) and ultralow platinum metal cathodic catalysts in the proton exchange membrane fuel cell (*Science*, 2018) and b) new application of PGM-free catalyst as the replacement for iridium for hydrogen production operated in proton exchange membrane water electrolyzer (*Science*, 2023). The talk will cover rational catalyst design, electrocatalytic performance, understanding of the catalytic mechanism, and prospects of these emerging technologies in green hydrogen production and application.

9:40am **RE1-MoM-6 Defective Metal Oxides for Electrochemical Ammonia Synthesis, Emma Lovell**, University of New South Wales, Australia

There is a growing and urgent need to decarbonize large-scale industrial process, such as the Haber-Bosch process, used to synthesize ammonia. By using electricity to drive this process and avoiding the requirement for fossil fuel-derived hydrogen, the large scale production of fertilizers can be done sustainably.

Our recent work uncovered an approach to produce ammonia using air and water. By plasma activating air into water, an aqueous solution of NO_x (nitrate and nitrite) can be generated. This solution can then be electrocatalytically reduced to produce ammonia (NO_xRR). This hybrid plasma/electrochemical approach can overcome the limitations of direct nitrogen reduction to ammonia (NRR), such as the relative insolubility and stability of nitrogen [1].

The development of active, selective and stable catalysts for NO_xRR is essential for the application of this hybrid ammonia synthesis approach. In this talk, our recent work on designing metal oxide catalysts for NO_xRR will be discussed [2-4]. By using flame spray pyrolysis (FSP) metal oxides with tunable properties were produced. For example, Ru-doped Co₃O₄ was produced with Ru being shown to be incorporated into the Co₃O₄ lattice.

This doping resulted in an ease in generating oxygen vacancy defects during electrochemical preconditioning which facilitated nitrate adsorption and enhanced Faradaic Efficiency towards ammonia production [3].

[1] Sun et al., (2021) *Energy & Environmental Science* 14 (2), 865-872

[2] Bui et al., (2023) *Advanced Materials* 35 (28), 2205814

[3] Lim et al., (2024) *Small*, 2401333

[4] Rahman et al., (2021) *Energy & Environmental Science* 14 (6), 3588-3598

Renewable Energy and Energy Storage

Room Naupaka Salon 4 - Session RE2-MoM

Surfaces and Interfaces in Photovoltaics

Moderator: Elisa Miller, National Renewable Energy Laboratory

10:20am **RE2-MoM-8 Multifunctional Coating for Solar Module Glass, Ning Song**, UNSW, Australia **INVITED**

Currently, single-layer antireflection coated (SLARC) solar glass has a dominant market share of 95% compared to glass with other coatings or no coating, for Si PV modules. This antireflection coating (ARC) results in an efficiency gain of 2-3%. However, there are issues with these SLARCs:

(1) Solar cell warming due to increased sub-bandgap light absorption (by +0.4~1.2 K), counteracting the cell current gain and accelerating the aging of the solar panels.

(2) Poor durability due to the coating's porous structure (typically lasting ≤5 years).

This paper aims to develop a non-porous multilayer coating (MLC) that is more durable and will act as a spectrally selective filter for solar modules. Studies have been conducted on MLCs in terms of optical, microstructure, mechanical, and durability properties compared with commercial single-layer AR coatings. The MLCs showed superior performance in durability and benefit in reducing parasitic heat absorption in the non-usable wavelength range. Also, a techno-economic analysis model based on the multifunctional coating specifically to evaluate economic benefits has been developed.

11:00am **RE2-MoM-10 Low Dos Tails Dominate Band Alignments in State-of-the-Art Cd(Se,Te) Solar Cells, Craig Perkins**, National Renewable Energy Laboratory

As the efficiency of single junction CdTe-based solar cells approaches the thermodynamic limit, further device improvements depend heavily on identifying the limiting aspects of cell architectures. Device modeling is the main tool for apportionment of efficiency losses and for guiding research into which aspects of cell designs need improvement. State-of-the-art device models though require numerous input parameters related to both bulk and interfacial properties, many of which are not known. Detailed characterization of an interface in any completed thin film solar cell presents a challenge but is particularly difficult in CdTe-based solar cells where the heterojunction is formed first, evolves during subsequent processing, and ultimately gets buried between mm-thick glass and microns of other materials. In this contribution, we show how an unusual sample preparation method coupled with electron spectroscopic methods was used to tease out details of the front interface of new record efficiency CdTe solar cells. A combination of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy inverse photoemission spectroscopy (LEIPS), and Auger electron spectroscopy (AES) was used to probe the electronic and structural properties of the front oxide-Cd(Se,Te) interface in fully completed solar cells. Prior to our destructive analysis of the front interface, operating cells were fully characterized by transport measurements, which when modeled, allowed independent assessment of band positions measured by surface analytical techniques. Band alignments based mainly on X-ray excited valence band spectra do not agree with alignments estimated from device modeling, whereas measurements using UPS-derived band edges do agree. A major conclusion from this is that low density of states (DOS) tails can be missed by X-ray excited valence band measurements, even when XPS data are used in conjunction with theoretical total DOS. The low DOS tails detected directly by UPS are found to be present in several different materials and structures found in modern CdTe solar cell designs, including SnO₂, a material used widely in other solar cell designs as well as in gas sensors and other electronic devices. It is believed that the low DOS band edges critical to this work are present in many other electronic materials. For that reason, our work has important implications for the use of electron spectroscopy in

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understanding and improvement of a wide variety of semiconducting devices.

Renewable Energy and Energy Storage Room Naupaka Salon 4 - Session RE1-TuM

Electrochemistry and Photocatalysis II

Moderator: Craig Perkins, National Renewable Energy Laboratory

9:00am RE1-TuM-4 Tuning Optoelectronic Properties of 2D Transition Metal Dichalcogenides and p-Conjugated Polymers, *Elisa Miller*, National Renewable Energy Laboratory

INVITED

This talk will review recent research tuning optoelectronic properties of 2D transition metal dichalcogenides (TMDCs) and p-conjugated polymers to ultimately control energy conversion processes. First, a major roadblock to the commercial deployment of TMDC monolayers for next generation electronic devices has been the inability to controllably dope these materials at wafer scale as can be done with traditional semiconductors. We demonstrate dedoping with high spatial fidelity in wafer-scale monolayer MoS₂ upon illumination with a mechanistic understanding. Second, the p-conjugated polymer n-type N2200 and P90 polymers (alternating naphthalene dicarboximide (NDI) acceptor and bithiophene (T2) donor units, where NDI units in P90 alternately feature methyl end-capped heptaethylene glycol (90%) and 2-octyl dodecyl (10%) side chains) are studied to understand how electrolyte cation insertion influences the polymer electronic behavior, which is necessary for energy conversion applications.

9:40am RE1-TuM-6 Transition Metal Doped NiOx Faceted Nanosheets for Electrocatalytic Water Oxidation, *K. Ruecker*, German Aerospace Center Oldenburg, Germany; *D. Taffa*, Carl von Ossietzky University of Oldenburg, Germany; *E. Brim*, D. Hayes, Colorado School of Mines, USA; *J. Lorenz*, German Aerospace Center Oldenburg, Germany; *S. Alia*, B. Pivovar, National Renewable Energy Laboratory; *M. Risch*, Hemholtz Center Berlin, Germany; *C. Harms*, German Aerospace Center Oldenburg, Germany; *M. Wark*, Carl von Ossietzky University of Oldenburg, Germany; **Ryan Richards**, Colorado School of Mines, USA

The ability to manipulate earth abundant metal oxides presents an important potential technology to develop sustainable materials with novel properties. These materials are of interest due to the coordination environments that can be achieved and to the high degree of control over properties that can result from tailoring the exposed facets of metal oxides. Here, recent highlights regarding nanostructured metal oxides and their applications in electrocatalysis will be presented. Water electrolysis enables the production of green hydrogen as part of the energy transition. Moving to alkaline media using an anion exchange membrane (AEM) enables the usage of non-precious metal electrocatalysts and thereby limitations in the availability and the cost of catalyst materials required for proton exchange membrane water electrolysis. The oxygen evolution reaction (OER) at the anode involves multiple electron and proton transfer steps and thus suffers from a higher overpotential than the hydrogen evolution reaction at the cathode, making catalyst development for the OER critical for water electrolysis. Transition metal oxide (TMO) catalysts are promising as efficient electrocatalysts for the OER in alkaline media, since they are relatively active and the material is comparably inexpensive. It has been shown, that the electrocatalytic activity of nickel-based catalysts is strongly influenced by the morphology, by the crystallographic orientation of the material and by the combination of different transition metals into the nickel oxide host structure.

In this study, NiO nanosheets predominantly oriented in the (111) crystallographic planes were synthesized by either hydrothermal (HT) or microwave-assisted (MW) routes, to investigate the influences of faceting as well as the enhancements by doping with transition metals (Fe, Mn, Co), where especially doping with small amounts of Fe (e.g. 5 mole %) enhanced the OER activity. Furthermore, the syntheses were adopted to produce Fe, Mn and Co doped NiO (111) nanosheets with various dopant concentrations. The Fe and Co doped NiO (111) nanosheets outperformed the pure NiOx materials during the testing, whereas the Mn doping decreased the electrocatalytic activity of the materials. Structural characterization by synchrotron-based X-ray absorption spectroscopy and X-ray photoelectron spectroscopy before and after electrochemical testing were used to elucidate underlying processes like phase transformation and oxidation state changes.

Renewable Energy and Energy Storage Room Naupaka Salon 4 - Session RE2-TuM

Materials for Energy Conversion

Moderator: Ryan Richards, Colorado School of Mines

10:20am RE2-TuM-8 Physical Properties Control of Metal-Hydride Thin Films and Application of Autonomous Synthesis Systems, *Ryota Shimizu*, The University of Tokyo, Japan

INVITED

Hydrogen-containing compounds have been attracting considerable attention. Until now, extensive research has focused on hydrogen energy applications such as hydrogen storage systems and fuel cells. However, recent research has diversified into various fields. For example, among various hydride materials, the ionic conductivity of Li⁺ and Na⁺[1] ions and hydride (H⁻) ions[2] has been reported, with potential applications in electrochemical devices. Furthermore, discoveries of optoelectronic properties in rare-earth oxyhydrides[3] and high-temperature superconductivity under ultrahigh pressure[4] have opened new directions in solid-state physics and solid-state chemistry.

One unique characteristic of hydrogen is its flexible charge state. Hydrogen has an intermediate electronegativity among all elements, allowing it to exist as H⁺ (proton), H (atomic), or H⁻ (hydride) depending on the surrounding environment. Therefore, if this charge state can be controlled by external fields, it is possible to develop devices with dramatically altered physical properties.

Our aim is to create epitaxial thin films of these intriguing metal hydrides and explore their applications in material property research and electronic devices. To date, we have successfully achieved the epitaxial growth of metal hydrides such as TiH₂, NbH, MgH₂ (hydrogen storage materials), YH₂ (smart mirrors), and EuH₂ (ferromagnetic semiconductors)[5] using reactive sputtering techniques. We have also succeeded in the epitaxial growth of yttrium oxyhydrides (YO_xH_y)[6] and calcium nitride hydrides (Ca₂NH)[7] through anion complexation with reactive gases like O₂ and N₂. We will present these deposition techniques and discuss the intriguing physical properties associated with hydride thin films involving electrons and ions.

Furthermore, aiming to accelerate the rapid discovery of such novel thin film materials, we have developed an autonomous synthesis system that integrates AI and robotics. In this talk, I will discuss future perspectives regarding a materials exploration system integrated with various measurement instruments.

References:

[1]: Unemoto *et al.*, Adv. Funct. Mater. **24**, 2267 (2014), [2]: Kobayashi *et al.*, Science **351**, 1314 (2016), [3]: Mongstad *et al.*, Sol. Energy Mater. Sol. Cells **95**, 3596 (2011), [4]: Drozdov *et al.*, Nature **525**, 73 (2015), [5]: Shimizu *et al.*, J. Phys. Soc. Jpn. **89**, 051012 (2020), [6]: Komatsu, Shimizu *et al.*, Chem. Mater. **34**, 3616 (2022), [7]: Chon, Shimizu *et al.*, J. Phys. Chem. Lett. **13**, 10169 (2022).

11:00am RE2-TuM-10 Non-Precious Metal Electrocatalysts for Anion Exchange Membrane Fuel Cells, *Jin-Song Hu*, Institute of Chemistry Chinese Academy of Sciences, China

Under the carbon neutrality scenarios, the demand for fuel cell electric vehicles (FCEVs) is rapidly growing. According to the IEA report, the transportation section will demand more than 15,000 thousands of FCEVs by 2030. Besides continuing to improve the fuel cell performances, the fuel cells cost and FCEVs running cost come into attention. Anion exchange membrane fuel cells (AEMFCs) offer the opportunities for using non-precious metal based electrocatalysts for both anodic and cathodic reactions to reduce the fuel cell cost and relieve the concerns on the Pt scarcity.

This presentation will be focused on our recent efforts on the development of non-precious metal based electrocatalysts for alkaline oxygen reduction reaction (ORR) and the CO-tolerant electrocatalysts for hydrogen oxidation reaction (HOR). A couple of new strategies will be introduced to develop the efficient electrocatalysts, including a molecular-based cascade anchoring strategy for general mass production of high-density metal-nitrogen single-atomic catalysts, metastable rocksalt oxide mediated synthesis of high-density well-armed transition metal nanoparticle electrocatalysts, and interface assembly strategy for achieving high-density binary single-atomic catalysts with much improved active site utilization. Moreover, the binary active sites electrocatalysts will be introduced to synergistically boost the elementary reactions of the alkaline HOR. These

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results may provide new insights for the rational design and bottom-up synthesis of cost-effective and high-performance electrocatalysts for AEMFCs.

References:

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[5] Zhao, L.; Zhang, Y.; Huang, L.-B.; Liu, X.-Z.; Zhang, Q.-H.; He, C.; Wu, Z.-Y.; Zhang, L.-J.; Wu, J.; Yang, W.; Gu, L.; Hu, J.-S.; Wan, L.-J. *Nat. Commun.* **2019**, *10* (1), 1278.

11:20am **RE2-TuM-11 Elucidating Early-Stage Lithium Growth and Dendrite Suppression Strategies in Lithium Metal Batteries, Seung-Yong Lee**, Hanyang University, Korea
INVITED

Lithium metal batteries (LMBs) offer significant advantages over traditional lithium-ion batteries due to their high theoretical capacity and energy density. However, their practical application is hindered by the formation of lithium dendrites during charging, which leads to poor performance, reduced lifespan, and severe safety risks. Current research aims to understand and mitigate these challenges to unlock LMBs' full potential, but a comprehensive understanding of the fundamental mechanisms driving lithium dendrite formation remains elusive.

In this study, we employed various air-free techniques, including cryo-transmission electron microscopy (cryo-TEM), to investigate the early-stage growth behaviors of lithium metal. By enabling direct lithium deposition on copper TEM mesh grids within coin cell batteries, we examined lithium growth without additional sampling processes that could introduce artifacts and damage. Preliminary experiments showed that the stepped edges of certain TEM mesh grids served as preferential nucleation sites, guiding lithium growth within confined spaces. This finding highlights the potential of TEM mesh grids as effective 3D hosts for lithium metal anodes and underscores the need for caution in interpreting lithium growth kinetics using this method.

Further investigations using this approach revealed mechanisms behind lithium dendrite suppression with a lithium nitrate electrolyte additive. Air-free cryo-TEM experiments, including energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), along with air-free X-ray photoelectron spectroscopy (XPS), identified the predominant phases of the solid-electrolyte interphase (SEI) formed with the electrolyte additive. These analyses indicated that an inorganic SEI layer significantly suppresses dendritic growth, transforming lithium deposition into a more spherical morphology. Additional controlled experiments confirmed the influence of the inorganic SEI layer on lithium morphology.

Our research advances battery technology by providing in-depth mechanistic insights and practical strategies to overcome the limitations of LMBs. By addressing the fundamental challenges of lithium dendrite formation, we pave the way for developing safer, high-performance energy storage solutions essential for future technological advancements.

Renewable Energy and Energy Storage Room Naupaka Salon 1-3 - Session RE-TuP

Renewable Energy and Energy Storage Poster Session

RE-TuP-1 Graphene-Based Solar Cell Energy Harvester Intermittently Recharges a Battery-Powered Temperature Sensor System, Paul Thibado, J. Mangum, T. Amin, S. Rahman, R. Kabir, A. Ashaduzzaman, University of Arkansas; G. Carichner, H. Do, D. Blaauw, University of Michigan, Ann Arbor

Transparent, flexible, and electrically conductive graphene membranes hold great promise for multimodal energy harvesting. These sources include solar and ambient radiation, thermal, acoustic, and kinetic power. This poster reviews several graphene energy-harvesting avenues, then focuses specifically on the fabrication of graphene-based solar cells using mainstream semiconductor manufacturing methods. Our two-write maskless laser lithography process creates an array of graphene-based solar cells on a commercially available 100-mm silicon wafer topped with a 2-micron thick wet thermal oxide layer on top. The first pattern marks the wafer locations for etching the silicon dioxide down to the bare silicon substrate. The second pattern marks the wafer for gold traces and bonding pads. Once completed, the exposed silicon and graphene bonding pad are covered using a large-area graphene transfer method. The samples are then characterized using atomic force microscopy, optical microscopy, and photovoltaic measurements. We also used our energy harvester to charge a 3-volt rechargeable battery, which is simultaneously driving an ultralow power consuming custom temperature sensor system. This work was financially supported, in part, by a grant from the WoodNext Foundation, which is administered by the Greater Houston Community Foundation.

RE-TuP-2 A Study on Robust VO₂ Protection Layer and Defect Inactivation in BiVO₄ Photoelectrodes through Photoelectrochemically Transition-Metal Engineering, H. Cho, Kun Woong Lee, School of Advanced Materials Science & Engineering, Sungkyunkwan University (SKKU), Republic of Korea

Photoelectrochemical (PEC) cells for water splitting have garnered significant attention as a promising technology for solar-to-hydrogen energy conversion. Bismuth vanadate (BiVO₄), serving as the photoanode among photoelectrodes, stands out as a representative ternary oxide-semiconductor with several advantages. However, BiVO₄ photoanodes face controversial issues such as surface defects, performance limitations, and susceptibility to photo-corrosion instability. To address these challenges, we propose a groundbreaking protection layer. Based on deep understanding of the photo-corrosion mechanism regarding the dissolution of V⁵⁺ ions on BiVO₄ surface, we introduce a surface photoelectrochemical oxidation approach. By strategically introducing V⁵⁺ ions and H₂O₂ into the electrochemical electrolyte, we artificially modify photo-corrosion into advanced photo-oxidation. This induces a surface phase transition, leading to the formation of a novel vanadium oxide (VO₂) photoelectrochemical protection layer by transitioning the V⁵⁺ ions to the electrochemically favorable V⁴⁺ state. This layer is both conductive and ultrathin (~ 5 nm), while offering atomic-level controllability.

Characterizations of the BiVO₄/VO₂ photoanodes reveal enhanced carrier dynamics, with faster transport of interfacial charges (86%) and efficient transfer of photogenerated carriers through the VO₂ protection layer (95%). This innovative approach enables near-ideal performance, contributing to high stability and remarkable durability. Consequently, the BiVO₄/VO₂/CoFeO_x photoanodes exhibit an impressive photocurrent density of 6.2 mA/cm² and an onset potential of 0.25 V_{RHE}. Additionally, they demonstrate an applied bias photon-to-current efficiency of 2.4% at 0.62 V_{RHE} and stable operation without serious performance degradation for 100 hours, showcasing vigorous active oxygen evolution.

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