ALD Applications
Room Grand Ballroom H-K - Session AA1-TuA

Energy: Catalysis and Fuel Cells

Moderator: Dr. Chang-Yong Nam, Brookhaven National Laboratory

1:30pm **AA1-TuA-1 Surface Texture Design of Pt/C Catalyst to Enhance Oxygen Reduction Reaction by FBR-ALD***, J. Baek, M. Jung, S. Lee, S. Kwon,* ***MinJi Kim,*** Pusan National University, Republic of Korea

Proton exchange membrane fuel cell (PEMFC) is an efficient electrochemical energy conversion device that directly generates electricity from the chemical energy of fuels without the emission of greenhouse gases. The most reliable catalyst in PEMFC is Platinum (Pt) metal nanoparticles (NPs) that exhibit excellent electrochemical activity and stability compared to other catalysts. However, using of Pt catalyst is limited due to its very high cost and low abundance on Earth. Therefore, it is important to use Pt catalyst efficiently for making the PEMFC economically viable. In this regard, several synthesis techniques have been developed to reduce the loading and uniform distribution of Pt NPs on carbon support with high electrochemically active surface area (ECSA).One of the most efficient techniques to uniformly deposit Pt NPs with a controllable size on carbon support is to use a fluidized bed reactor (FBR) atomic layer deposition (ALD). Our group recently demonstrated that FBR-ALD Pt/C catalysts can exhibit high fuel cell performance and high endurance even with low Pt NPs loading by optimizing the surface of carbon supports combined with proper ALD process parameters [1]. However, it is still challenging to further improve the fuel cell performance by rational designing the Pt NPs surfaces in order to make FBR-ALD into a viable commercial production.

In this study, a unique way to improve the fuel cell performance was suggested to design and optimize atomic scale surface textures of Pt NPs. During the FBR-ALD of Pt NPs, in-situ surface modulation of Pt NPs was applied via a proper protective oxide deposition and etching. A careful surface studies was performed to analyze the surface morphology, distribution and uniformity of Pt NPs. Electrochemical performances were evaluated and optimized by measuring cyclic voltammetry (CV) and oxygen reduction reaction (ORR).

References

1. W.-J. Lee, S. Bera, H.-C. Shin, W.-P. Hong, S.-J. Oh, Z. wan, S.-H. Kwon, *Adv. Mater. Interfaces* 6, 1901210 (2019).

1:45pm **AA1-TuA-2 Stabilization of ALD-grown Iridium Species for the OER Activity***,* ***Muhammad Hamid Raza,*** Humboldt-Universität zu Berlin, 2-Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), Germany*; M. Frisch, R. Kraehnert,* Department of Chemistry, Technische Universität Berlin, Germany*; N. Pinna,* Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Water-splitting electrocatalysts are vital because of the growing demand for renewable energy and the concurrent depletion of fossil fuels. Different types of catalytically active oxides are used as electrode materials for electrochemical water splitting. The catalytic performance of those materials depends on the surface composition and morphology of the active species. Increasing the number of potentially active sites on electrode surfaces leads to enhancing the catalytic efficiency of such electrodes. Iridium (Ir) / iridium oxides (IrO_x) are currently one of the most promising candidates for competent oxygen evolution reaction (OER) in acidic media. So far, the very high costs for Ir impede the large-scale production of hydrogen (H_2). Atomic layer deposition (ALD) has been researched to maximize the utilization of Ir-based electrocatalysts. However, the stability of the system with an ultra-thin film of electrocatalytically active species is challenging especially in acidic media. We report an electrode coating concept with template-controlled mesoporosity surfaces modified with Ir species. A temperature-controlled ALD process of Ir/IrO_x films grown has been studied and the resulting films have been examined structurally and in terms of their electrocatalytic activities. Ir/ IrO_x films are successfully grown using 1-Ethylcyclopentadienyl-1,3-cyclohexadieneiridium(I) and ozone between 160 and 120 °C. Metallic Iridium can be deposited at higher temperatures. However, a pseudo amorphous Iridium oxide film is deposited at a lower temperature that not only provides a remarkable catalytic performance but also stabilizes the overall system by conformally covering the carrier's surfaces. With our ALD process at low temperatures, we can achieve an outstanding mass-specific OER activity of the order of 3000mA mg_{Ir}^{-1} at 1.60 V vs. RHE at 25°C and 0.5 m H_2SO_4. This shows great promise for the development of highly efficient (electro-)catalysts. The peculiarities of ALD not only make this a technique of choice to synthesize optimized electrocatalysts, but also provide the possibility to verify fundamental theories and develop a clear structure−property relationship will be discussed.

2:00pm **AA1-TuA-3 Atomic Layer Deposited Nickel Sulfide as a (Pre)Catalyst for Oxygen Evolution Reaction***,* ***Miika Mattinen,*** *T. Hatanpää, K. Mizohata,* University of Helsinki, Finland*; S. Bent,* Stanford University*; M. Ritala,* University of Helsinki, Finland

Hydrogen gas (H_2) is currently one of the most important feedstocks of the chemical industry. In the future, H_2 is foreseen to play a major role in decarbonizing society, for example by acting as a clean fuel and replacing carbon in steelmaking. These uses require replacement of the current fossil fuel based H_2 production with cleaner alternatives, such as electrochemical water splitting. Of its two simultaneously occurring half-reactions, the oxygen evolution reaction (OER) is limiting the efficiency of water splitting. Thus, development of highly active, stable, and affordable OER catalysts is critical.

Nickel sulfides (NiS_x) have been identified as highly active OER electrocatalysts. It has been shown that at least the surface of NiS_x may transform to oxyhydroxide under the highly oxidizing OER conditions.[1] Therefore, NiS_x electrocatalysts may best be described as precatalysts for the actual catalyst. However, factors such as the extent and rate of the catalyst transformation process and ultimately the catalytically active species remain poorly understood. Well-defined thin films catalysts prepared by ALD are ideal for obtaining such insights.

We began by developing a new ALD process for NiS_x using a low-cost, easily synthesized $NiCl_2$(TMPDA) precursor[2] (TMPDA = *N,N,N′,N′*-tetramethyl-1,3-propanediamine) with H_2S. The process exhibits saturating growth behavior and deposits highly conducting films on a range of different substrates at 165–225 °C. The deposited films are highly pure (<3% total H, C, N, O, and Cl impurities) and consist of a mixture of β-NiS and Ni_9S_8 phases.

For the OER electrocatalysts, we deposited NiS_x films on SnO_2:F coated glass and studied them under alkaline conditions. X-ray photoelectron spectroscopy measurements indicate that the NiS_x films lose the vast majority of S under the OER conditions and transform to (oxy)hydroxide-like material. Electrochemical measurements and electron microscopy show that this transformation is accompanied by an increase in surface area due to the films becoming porous. We propose that the porosity enables the nickel atoms inside the films to participate in OER, thus increasing the electrocatalyst activity. Additional studies examine the transformation process in more detail as well as the long-term stability of catalysts formed from NiS_x. In order to tailor the porosity and surface area of nickel-based electrocatalysts, we are also working on expanding the family of thiolate hybrid materials[3] to nickel.

1 Wygant et al., *ACS Energy Lett.*, 2018, **3**, 2956

2 Väyrynen, Ritala et al., *Adv. Mater. Interfaces*, 2018, **3**, 1801291

3 Shi, Bent et al., *JVSTA*, 2022, **40**, 012402

2:15pm **AA1-TuA-4 Novel Phosphite Doping into ALD SiO_2 to Improve H^+ and H_2 Permeability in Water Electrolyzers***,* ***Sara Harris,*** *M. Weimer,* Forge Nano*; K. Yim, L. Cohen, D. Esposito,* Colombia University*; A. Dameron,* Forge Nano

H2 is a carbon-free and versatile energy carrier, anticipated to be an integral part of the clean energy future. Hydrogen fuel has significant relevance today; currently comprising roughly 1.5% of global energy use. Unfortunately, over 95% of H2 production comes from highly polluting, oil and coal, or grey (methane) sources. Currently, the cost of green H2 from electrolysis is not competitive with fossil fuel sources.[i] One pathway to drive down cost is by increasing the efficiency of polymer electrolyte membrane (PEM) electrolyzes by reducing the ohmic overpotential required by the cell. In this work, the path to ohmic overpotential reduction, which is partially dictated by the membrane thickness [ii] and the H^+ conductivity, will be explored by replacing Nafion with an ultra-thin proton-conducting oxide membrane (POM) deposited by ALD. Specifically, an SiO2 ALD film deposited with a unique catalytic process has been explored over a range of temperatures and thickness to measure the H^+ conductivity and gas permeation (H2). To address the inherently low H^+ permeability of baseline SiO2 films, phosphorous-based dopants were explored to increase H^+ permeability without sacrificing other requirements. Phosphate, $PO4^{-3}$ species were doped into an SiO2 ALD film using two novel ALD precursors.[iii] Both precursors were found to incorporate into the growing SiO2 film, as measured by X-ray photoemission spectroscopy (XPS), but not grow a P2O3 or P2O5 monolith with H2O, O2 or O3. The largest PO4^{-3} percent incorporation was observed in an ABC-type ALD sequence, where the PO4^{-3} precursor did not see a separate oxidant, shown in Figure 1 below. All POx:SiO2 films also showed a decrease in refractive index. Critically, H^{+} permeability improved with PO4^{-3} addition. An ABC-type ALD processes showed the largest improvement of ~8.5x in acidic solution with a rotating disk electrode. Unexpectedly, the addition of PO4^{-3} also decreased H2 gas permeability across all samples by up to 12x. Importantly, ALD POM films have the potential to directly coat membranes onto high surface area porous transport or gas diffusion layers for integration into current PEM electrolyzer cells, further improving efficiency. This work is the first step in building full electrolyzers that employ a novel ultra-thin ceramic membrane with the potential to enable a competitive green H2 market.

[i] https://hub.globalccsinstitute.com/ and https://www.mckinsey.com/industries/oil-and-gas/our-insights/global-energy-perspective-2022

[ii] Han, et al., Int. J. Hydrogen Energy, 40, 2015

[iii] Henderick, L., et al., Appl. Phys. Rev. 9, 011310, 2022

2:30pm **AA1-TuA-5 Atomic Layer Deposition of Copper Catalysts for Electrochemical Recycling of Carbon Dioxide***, J. Lenef, S. Lee, K. Fuelling, K. Rivera Cruz,* University of Michigan, Ann Arbor*; A. Prajapati, C. Hahn,* Lawrence Livermore National Laboratory*; C. McCrory, **Neil P. Dasgupta**,* University of Michigan, Ann Arbor

Electrochemical recycling of carbon dioxide into value-added products is a promising strategy to mitigate climate change as the CO_2 reduction reaction (CO_2RR) can be driven using renewable electricity (i.e. wind, solar). So far, copper metal is the only known single element catalyst to form multi-carbon products, such as ethylene and ethanol, from CO_2RR. Numerous synthesis strategies have been employed to deposit copper-based catalysts including sputtering, evaporation, electrodeposition, and solution processing; however, they do not enable atomically precise control of film thickness and particle size and have limited conformality on 3D substrates such as carbon gas diffusion electrodes. To address this knowledge gap, we fabricate Cu catalysts using plasma-enhanced atomic layer deposition (PE-ALD) with varied PE-ALD cycle numbers on 3D carbon electrodes to achieve precise control of catalyst loading. A polycrystalline Cu metal layer was confirmed by grazing incidence X-ray diffraction. The catalyst surface morphology was probed by scanning electron microscopy and atomic force microscopy, highlighting the island-growth mode of the metal catalyst.

We demonstrate that Cu surfaces prepared by PE-ALD can reduce CO_2, forming value-added products such as carbon monoxide, methane, and ethylene. Parasitic hydrogen evolution was minimized to Faradaic efficiencies of ~10%, as quantified using *in situ* gas chromatography measurements. We further demonstrate a selectivity over 40% Faradaic efficiency for ethylene production, which is among the highest values reported to date in an H-cell geometry. Compared to evaporated Cu catalysts, we show significant methane suppression for the PE-ALD Cu. Finally, we demonstrated stability for up to 15 h for CO_2 reduction products with minimum loss in the ethylene production rate. In summary, we demonstrate CO_2RR using PE-ALD of Cu catalysts with high selectivity and stability, which provides a pathway to conformal deposition on 3D substrates with precise control of particle size and catalyst loading.

2:45pm **AA1-TuA-6 Stability of Molecular Layer Deposited (MLD) Alucone in Acetonitrile for Photoelectrochemical CO_2 Reduction Applications***, **Hyuenwoo Yang**,* North Carolina State University, Republic of Korea*; H. Margavio, L. Keller, G. Parsons,* North Carolina State University

In this work, we study an organic-inorganic hybrid metalcone material deposited by molecular layer deposition (MLD) for applications in solar-energy driven CO_2 reduction to liquid fuel.In the field of photoelectrochemical CO_2 reduction reaction (CO_2RR), controlling the selective absorption of CO_2 on silicon-bound molecular catalysts for photo-electron driven reduction ischallenging to avoid the hydrogen evolution reaction (HER) that proceeds during the competitive reduction of available protons.Recently, researchers have shown that for some geometries, organic encapsulation layers can improve the stability of the catalysts and at the same time increase the selectivity of CO_2 conversion.To date, however, organic layers formed by MLD have not been significantly studied for this application. Advantages of metalcones have great potential as an encapsulation layer for inducing selective catalytic reactions. Here, we demonstrate photoelectrochemical compatibility of alucone thin films on Si photoelectrode in acetonitrile electrolyte. Alucone layer was deposited with trimethylaluminum (TMA) and ethylene glycol (EG) in low temperature (< 100°C). Alucone showed outstanding stability in acetonitrile (0.1 M Tetrabutylammonium hexafluorophosphate, $TBAPF_6$) electrolytes under 1 sun illumination and applied potential of -1.8 to 0.7 V versus Ag/$AgNO_3$ reference electrode. In contrast, the thickness of alucone shrank by 94% within an hour in water based electrolyte (0.1 M potassium chloride, KCl) under -1.5 to 0 V versus Ag/AgCl reference electrode. This result matches with the previous research that vapor absorption changes the thickness of metalcone. This results supports the photoelectrochemical stability of alucone to acetonitrile which has high solubility of CO_2.

Our study opened the new possibility of applying MLD metalcone thin films to CO_2RR fields through its excellent transparency, molecular permeability and CO_2 selectivity. MLD alucone layer is expected to be feasible as an encapsulation layer for Si photoelectrodes and surface modification layer to form favorable CO_2 microenvironment with its permeability, transparency and hydrophobicity.

3:00pm **AA1-TuA-7 Enhanced Green Hydrogen Production Using ALD-based Catalysts for Ammonia Decomposition***, **Yu-Jin Lee**, H. Sohn, H. Jeong, S. Nam,* Korea Institute of Science and Technology (KIST), Republic of Korea*; J. Park,* Seoul National University, Republic of Korea*; Y. Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

Ammonia-based hydrogen value chains are emerging as one of the most promising ways for achieving a carbon-neutral hydrogen economy. In order to expedite the development, it is essential to develop highly efficient and scalable catalysts for ammonia decomposition. In this study, we demonstrate the use of atomic layer deposition (ALD) to fabricate highly efficient Ru/TiO_2-ALD/γ-Al_2O_3 bead catalysts for ammonia decomposition. By utilizing the ALD technique to introduce an ultrathin TiO_2 layer between Ru nanoparticles and the γ-Al_2O_3, followed by high-temperature alloying, we were able tochange the electronic structure of the Ru and shift the nitrogen binding energy to lower, resulting in an enhancement of catalytic activity. One of the most intriguing aspects of this study is the use of ALD technology to overcome the limitations of reducible oxides in high-temperature reducing atmospheres, such as particle encapsulation or consolidation that can diminish the catalytic activity of nanoparticles. Compared to state-of-the-art Ru-based catalysts with rare-earth metal oxides such as Y_2O_3 and La_2O_3, the Ru/ALD-TiO_2/γ-Al_2O_3 catalysts developed in this study demonstrated superior catalytic performance as well as cost competitiveness due to minimized utilization of functional oxide. The promising results of this study indicate that the use of ALD technology catalysts has the potential to significantly advance the establishment of ammonia-based hydrogen value chains, leading to enhanced efficiency in the hydrogen reconversion process and ultimately reducing the levelized cost of hydrogen.

3:15pm **AA1-TuA-8 Atomic Layer Depositied Silver Catalysts for Anion Exchange Membrane Fuel Cells***, **Gwon Deok Han**, H. Han, F. Prinz,* Stanford University*; J. Shim,* Korea University, Republic of Korea

In the automotive industry, the paradigm shift from internal combustion engine vehicle to electric vehicle is accelerating to respond to the global climate crisis. Fuel cell electric vehicles (FCEVs) powered by hydrogen are one of the zero-emission means of transportation, and its advantages are long mileage and fast charging time. However, proton exchange membrane fuel cell (PEMFC), which is the propulsion system of FCEVs, requires the use of precious metal catalysts such as Pt. This is a decisive factor hindering the popularization of FCEVs in terms of economic feasibility. Anion exchange membrane fuel cell (AEMFC) is receiving considerable attention as a next-generation technology due to its unique advantage of operating in an alkaline environment that allows the use of Pt-free catalysts. In this study, a high-performance AEMFC cathode containing carbon nanotubes surface-modified with Ag particulates was fabricated using plasma-enhanced atomic layer deposition (PEALD). HEMFC cathode coated with ALD Ag particulates delivers a maximum power density of 2,154 $mW\cdot mg_{Ag}^{-1}$ in an alkaline environment. The AEMFC cathode decorated with ALD Ag contributed to reducing the polarization energy loss by improving the cathodic oxygen reduction reaction. Through the application of PEALD, it was successfully demonstrated that an optimized microstructure design is possible while minimizing the load of the Ag catalyst at the cathode. This study is significant in that it successfully demonstrated the potential applicability of ALD in the manufacture of high-performance AEMFC cathodes.

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