ALD Applications

Room On Demand - Session AA1

Energy: Catalysis and Fuel Cells

AA1-1 High-crystalline RuO$_2$based on Atomic Layer Deposition for Oxygen Evolution Catalyst*, Jaehyeok Kim*, *D. Kim, J. Park, H. Kim,* Yonsei University, Korea

To alternate carbon-based energy source to protect the nature, hydrogen is widely researched worldwide. Electrochemical water splitting is the promising method that produces no pollutant, only H$_2$and O$_2$. However, Oxygen Evolution Reaction (OER) is sluggish, which determines the overall efficiency of electrocatalyst, so that water splitting is limited in industrial field.

RuO$_2$has been researched as efficient catalyst for oxygen evolution. The crystallinity of the RuO$_2$affects the efficiency. Therefore, synthesis of high-crystalline RuO$_2$is important. To enhance the efficiency of RuO$_2$, large surface-to-volume ratio and controllability of the crystallinity are the key factors in synthesis method.

Atomic Layer Deposition (ALD) has advantages of excellent conformality, large-area uniformity, and precise controllability of the thickness. For efficient catalyst, large surface area is helpful because it is directly related to the reaction sites. ALD is suitable fabrication process for electrocatalyst.

In this report, RuO$_2$film was synthesized based on ALD on Carbon Fiber Paper (CFP) at different growth temperature, which has large surface-to-volume ratio with high conductivity. It can be directly used for OER catalyst with enlarged active sites of OER. For the analysis, material properties of ALD RuO$_2$ such as X-ray photoelectron spectroscopy, X-ray diffraction, scanning electron microscopy, SiO$_2$substrate was prepared as reference. Electrochemical properties was measured in 3-electrode system consists of working electrode, reference electrode, and counter electrode. It showed low overpotential and Tafel slope, which imposes promising candidate for OER catalyst.

References

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AA1-2 Atomic Layer Deposition of Pt@Pd Core-Shell Structure Electrocatalyst for Carbon Dioxide Reduction*, Ming Li,* Delft University of Technology, China*; R. Kortlever, R. van Ommen,* Delft University of Technology, Netherlands

Using electrocatalysts to convert CO$_2$ into chemicals or fuels through electrochemical reactions is an attractive approach to reduce CO2 emissions and decrease the greenhouse effect. However, existing electrocatalysts have several technological limitations, such as low selectivity, poor stability, low conversion rates of the feedstock, and high overpotential which will lead to energy losses. Most of the electrocatalyst improvement strategies focus on catalyst structure and composition optimization such as nanostructuring, doping and alloying, etc. However, the widely used catalyst fabrication methods, like impregnation, colloidal, ion-exchange methods are tough to tailor the morphology of the catalyst down to the atomic scale, let alone other delicate structures like nano-sized core-shell particles. One promising solution is to use the atomic layer deposition method to fabricate electrocatalysts with well-defined nanostructure. It is reported that Pd-Pt bimetallic catalyst can reduce CO$_2$ toward formic acid and achieve a high faradic efficiency at room temperature and atmospheric pressure. We investigate whether the performance of this catalyst could be further improved by tuning the nanostructure of the catalyst with ALD. We studied how to use fluidized bed ALD to synthesize core-shell structure bimetallic electrocatalysts, and synthesized the Pd-Pt bimetallic catalyst with core-shell structure on carbon black substrate in this work. The metal loading of the catalyst is precisely controlled. TEM, XPS, XRD, SEM, and ICP-OES were used to characterize the catalyst structure and metal loading. Electrochemical measurements were carried out in a custom-made H-cell using a three-electrode assembly at room temperature. This gives us a better understanding of the effect of the catalyst structure on carbon dioxide reduction, helping us to come to an optimized structure and the corresponding ALD strategy to make it.

AA1-3 Understanding Metal-Support Interactions in Model Pd/ALD-Al$_2$O$_3$/SiO$_2$ Catalysts*, Arun Asundi*, *E. Goodman,* Stanford University*; A. Hoffman,* SLAC National Accelerator Laboratory*; K. Bustillo,* Lawrence Berkeley Lab, University of California, Berkeley*; J. Stebbins,* Stanford University*; S. Bare,* SLAC National Accelerator Laboratory*; S. Bent, M. Cargnello,* Stanford University

The synergy between coexisting metal and metal oxide phases is critical in determining the reactivity of many supported heterogeneous catalysts. The interaction between the active metal and the support is one example of this synergy and can be controlled to modulate catalyst performance. ALD offers a unique opportunity to study metal-support interactions by enabling support modification one atomic layer at a time. Metal-support interactions are readily apparent in Pd methane combustion catalysts, where support properties can affect reaction rate by several orders of magnitude. Previous work has shown that the methane combustion rate is significantly higher for Pd/Al$_2$O$_3$ than Pd/SiO$_2$, but the nature of the metal-support interaction that determines this reaction rate is not well-understood. In this work, we study the effects of support chemical properties and morphology on the methane combustion reactivity of Pd supported on ALD Al$_2$O$_3$-modified SiO$_2$.

Catalysts were prepared through a combined ALD and colloidal synthesis method. Uniform SiO$_2$ nanospheres were modified with different thicknesses of Al$_2$O$_3$ films deposited by ALD. Colloidal Pd nanocrystals were then deposited on the ALD-Al-$_2$O$_{3--}$/SiO$_2$ supports. This synthesis method enabled independent control over the Pd nanocrystal size, Pd loading, and chemical nature of the support. The transition of the support properties from SiO$_2$ to Al$_2$O$_3$ results in two regimes of improved reactivity as a function of Al$_2$O$_3$ ALD cycle number: the reaction rate increases rapidly at low Al$_2$O$_3$ coverage and increases gradually at high Al$_2$O$_3$ loading. The two stages of promotion show that both surface and bulk properties of Al$_2$O$_3$ are important factors in controlling the reaction rate. At sub-monolayer alumina coverage, the reaction rate is determined by the number of Pd/Al interface sites. Through infrared spectroscopy we show that a monolayer of Al$_2$O$_3$ is deposited during the first three ALD cycles, leading to a linear increase in reaction rate as a function of ALD cycle number as the support surface transitions from SiO$_2$ to Al$_2$O$_3$. At high Al$_2$O$_3$ loadings, bulk properties of Al$_2$O$_3$ such as purity and crystallinity also affect reaction rate. ^{27}Al nuclear magnetic resonance spectroscopy reveals intermixing between Si and Al and crystallization of the Al$_2$O$_3$ for sufficiently thick coatings, both of which modulate the methane combustion rate. This work demonstrates the many support characteristics that influence catalyst reactivity through metal-support interactions. The controlled ALD-colloidal synthesis method used in this work can be applied to fundamental studies of metal-metal oxide interactions in many catalyst systems.

AA1-4 Size Control of Gold Nanoparticles Using Sequential Atomic Layer Deposition of Gold and Titanium Dioxide*, Saeed Saedy*, *R. Baaijens,* Delft University of Technology, Netherlands*; E. Goodwin, M. Griffiths, S. T. Barry,* Carleton University, Canada*; J. van Ommen,* Delft University of Technology, Netherlands

Gold nanoparticles (AuNPs) supported on metal oxides exhibit exceptional catalytic activities in several processes, especially oxidation reactions. The performance of AuNPs strongly depends on size. Large gold particles do not show notable catalytic activity; the lack of efficient synthesis and stabilization methods of AuNPs resulted in gold being considered a catalytically inactive metal for decades. Additionally, due to weak interaction with the supports, the supported GNPs usually are not stable enough and tend to agglomerate, again resulting in activity loss.

This strong dependency of catalytic activity imposes a significant obstacle in developing supported AuNPs as catalysts, especially when the AuNPs with an average size smaller than 5 nm are desired. This challenge becomes more significant when the preparation of large amounts of supported AuNPs is the final goal, which is the prerequisite of practical applications. For such applications, the supported AuNP synthesis method needs to be capable of controlling the AuNPs size, scaling to large-scale production, and reproducibility. The conventional AuNP syntheses are a variety of liquid phase methods, which have been widely studied for decades; however, they still suffer from poor size control, contamination of the final product with residual solvents/co-reactants, reproducibility issues, and high sensitivity to operating conditions.

Atomic layer deposition (ALD) has proven successful for the synthesis of supported metal NPs for various applications, especially as catalysts. ALD makes it possible to synthesize supported NPs with controlled size, shape, and morphology. Recently we reported ALD synthesis of supported AuNPs on TiO-$_2$ in a fluidized bed reactor, with the minimum average particle size of 4 nm. In this work, we report a modification to our previous synthesis, enabling us to attain Au/TiO_2 with an average particle size of 2.8 nm. In this method, a sequential ALD of metallic gold (using trimethylphosphinotrimethylgold(III)), TiO_2 (using isopropoxytitanium (IV)), and ozone (as an oxidizer) at 105°C were used to confine the ALD deposited AuNPs with a TiO_2 over-coat. Different TiO_2:Au pulse ratios from 1 to 4 were used. An analysis by inductively coupled plasma optical emission spectrometry of the resulting samples showed a gold loading of about 0.8% in samples. Transmission electron micrographs indicated a decrease of AuNP average size from 3.7 nm to 2.8 nm. Interestingly, the particle size distribution became narrower with increasing the TiO_2:Au pulse ratio. The standard deviation of AuNP size decreased from 1.4 nm to 0.8 nm.

AA1-7 Atomic Layer Deposition for Improved Biomass Conversion Catalysts*, **Wilson McNeary**, S. Tacey, G. Lahti, D. Conklin,* National Renewable Energy Laboratory*; K. Unocic,* Oak Ridge Natinal Laboratory*; E. Tan,* National Renewable Energy Laboratory*; E. Wegener,* Argonne National Laboratory*; T. Eralp Erden,* Johnson Matthey, UK*; S. Moulton, C. Gump, J. Burger,* Forge Nano*; M. Griffin, C. Farberow,* National Renewable Energy Laboratory*; M. Watson, L. Tuxworth,* Johnson Matthey, UK*; K. van Allsburg,* National Renewable Energy Laboratory*; A. Dameron, K. Buechler,* Forge Nano*; D. Vardon,* National Renewable Energy Laboratory

Heterogeneous catalysts are a key enabler of the transition towards a sustainable, bio-based economy for fuels and chemicals. However, the harsh conditions in many biomass conversion processes lead to nanoparticle sintering, support collapse, and metal leaching in conventional PGM catalysts. Next-generation catalysts must be developed to address these stability challenges. This presentation will discuss ongoing work between the Catalytic Carbon Transformation and Scale-Up Center at NREL and various industrial partners to develop scalable and cost-effective atomic layer deposition (ALD) coatings for improving the performance of biomass conversion catalysts.

The substantial focus will be devoted to the benefits of TiO_2 ALD coatings on supported Pd hydrogenation catalysts. Ten cycles of TiO_2 ALD were found to dramatically improve the activity of a conventional Pd/Al_2O_3 catalyst towards aromatic hydrogenation, despite partial coverage of the Pd sites by the ALD layer. Subsequent advanced characterization and atomic-scale computational modeling revealed that the ALD coating weakened the adsorption strength of hydrogenation surface intermediates, leading to higher reaction rates. Reaction testing after exposure to sulfur impurities, high temperature oxidation, and hydrothermal treatment demonstrated the improved stability of the ALD-coated catalyst. Additionally, the ALD synthesis process was found to be scalable over two orders of magnitude with minimal deviation in synthesized catalyst properties. These results were contextualized with cost models of industrial ALD coating and aromatic hydrogenation processes to further refine the value proposition of ALD coatings. Given the demonstrated improvements in hydrogenation, TiO_2 ALD coatings have also been applied to supported Pt catalysts for use in other biomass conversion reactions, such as hydrodeoxygenation for the production of sustainable aviation fuel (SAF) and the oxidation of glucose to bio-derived gluconic acid. Recent findings from these experimental campaigns will also be shared. ALD technology holds great potential in the development of next-generation catalysts for biofuels and bioproducts, and this work constitutes an important examination of the impact of ALD coatings in a variety of reaction environments.

AA1-10 Electrochemical Activation of Atomic Layer Deposited Cobalt Phosphate Electrocatalysts for Water Oxidation*, **Gerben van Straaten**, R. Zhang, V. DiPalma,* Eindhoven University of Technology, Netherlands*; G. Zafeiropoulos,* Dutch Institute For Fundamental Energy Research, Netherlands*; E. Kessels,* Eindhoven University of Technology, Netherlands*; R. van de Sanden, M. Tsampas,* Dutch Institute For Fundamental Energy Research, Netherlands*; A. Creatore,* Eindhoven University of Technology, Netherlands

Storage of electricity into chemicals is the most viable answer to the intermittency of renewable sources and the most investigated example this is water splitting. For the O_2 evolution half reaction (OER), cobalt phosphate-based electrocatalysts (CoPi) are interesting as they are made of earth-abundant elements and their catalytic activity scales with film thickness. In parallel with others[1], we have demonstrated synthesis of amorphous CoPi films by ALD [2]. CoPi is prepared by combining ALD of CoO_x from cobaltocene ($CoCp_2$) and O_2 plasma, with cycles of TMP ($(CH_3O)_3PO$) and O_2 plasma, according to an ABCD recipe scheme [2,3]. We have also shown that tuning the Co-to-P ratio, by combining this recipe with extra cycles of CoO_x, enhances the OER performance [3], beyond that achieved by traditional electro-deposited films.

In the present contribution we focus on the mechanism behind the enhancement of the catalytic activity of CoPi when tuning the Co-to-P ratio. We show that ALD CoPi thin films undergo activation with increasing number of cyclic voltammetry (CV) cycles. During this activation process, the current density increases in parallel with a progressive leaching of phosphorous out of the electrocatalyst and the shift of the oxidation state of Co from Co^{2+} to a mixture of Co^{2+} and Co^{3+} [4]. This induce structural changes in the electrocatalyst: CV combined with Rutherford backscattering indicate that after activation, for the best performing CoPi film, as much as 22% of all Co atoms become accessible to the electrolyte. Measurements of the electrochemical surface area (ECSA) reveal that during activation, the ECSA of this film increases by a factor 30. However, this increase in ECSA is strongly dependent on the initial composition of the CoPi films. While the aforementioned increase holds for CoPi films with a Co-to-P ratio of 1.6, for films with a Co-to-P ratio of 1.9 the ECSA only increases by a factor 3.6. We find that for all investigated Co-to-P ratios, after activation the electrochemical activity scales linearly with ECSA. Thus, the initial composition affects the activity of the catalyst indirectly by guiding the restructuring of the catalyst during potential cycling and the ECSA is a critical parameter in determining the activity of CoPi-based and related electrocatalysts. Thus, next to the well-established control over film properties ALD of CoPi enables to disclose the mechanisms behind its electrochemical activation.

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