ALD Applications
Room Grand Ballroom E-G - Session AA1-TuM

ALD for Catalysts, Electrocatalysts, and Photocatalysts

Moderators: Jeffrey W. Elam, Argonne National Laboratory, Parag Banerjee, University of Central Florida

8:00am **AA1-TuM-1 ALD for Solar Fuels: Rendering Halide Perovskites Acid-Compatible + Precision Cluster Electrocatalysts***, **Alex Martinson**, I Kim, M Pellin,* Argonne National Laboratory **INVITED**

Although solution-processable halide perovskite semiconductors exhibit optoelectronic performance comparable to the best photoabsorbers for solar fuel production, halide perovskites rapidly decompose in the presence of water or even humid air. We show that a hybrid electron transport layer, a $PC_{61}BM + TiO_2$ film (18–40 nm thickness) grown over the sensitive absorber by atomic layer deposition, enables photo-assisted proton reduction without further encapsulation. These semitransparent photocathodes, when paired with a Pt catalyst, display continuous reduction of H^+ to H_2 for hours under illumination, even while in direct contact with a strongly acidic aqueous electrolyte (0.5 M H_2SO_4). More affordable and active catalysts for more challenging solar-to-fuels reactions (e.g. N_2 or CO_2 reduction) will require catalysts with exquisite precision. The bottom-up, selective ALD synthesis of controlled-atom-number clusters will also be discussed as a potentially powerful route to designer solar fuels catalysts.

8:30am **AA1-TuM-3 Plasma-Assisted ALD of Cobalt Phosphate: Process Development and Electro-Catalytic Activity Towards Oxygen Evolution Reaction***, V Di Palma,* Eindhoven University of Technology, Netherlands*; G Zafeiropoulos, R van de Sanden,* Dutch Institute for Fundamental Energy Research*; E Kessels,* Eindhoven University of Technology, Netherlands*; M Tsampas,* Dutch Institute for Fundamental Energy Research*; **Mariadriana Creatore**,* Eindhoven University of Technology, Netherlands

Water splitting is a viable approach to enable storage of renewable energy in the form of fuels. Major issues hampering the development and implementation of this technology, are: the high cost associated with the use of noble-metal-based electro-catalysts; the sluggish kinetics of the oxygen evolution reaction (OER). Cost-effective, transition metal- based electro-catalysts [1], e.g. cobalt phosphate (CoPi), show promising results in terms of performance towards OER. So far, CoPi has been synthesized by electro-deposition with severe limits in the control of layer thickness and chemical composition, the latter being highly influenced by the choice of precursors, electrolyte and pH. Instead, a higher level of control in terms of layer thickness and tunable stoichiometry is expected when adopting ALD.

In the present work we synthesize CoPi thin films by plasma-assisted ALD [2]. The process is based on an ABCD scheme, where A and C are the cobaltocene (CoCp) and trimethylphosphate (TMP) exposure steps. B and D correspond to O_2 plasma steps. CoPi layers, characterized by a stoichiometry of $Co_{3.2}(PO_{4.3})_2$, are deposited at 300˚C with a growth per cycle of 1.1 Å, as determined by *in-situ* spectroscopic ellipsometry. Cyclic voltammetry shows that the ALD CoPi layer exhibits a current density peak of 1.8 mA/cm^2 at 1.8 V vs. Reversible Hydrogen Electrode (RHE). This value is comparable to those reported in literature for electro-deposited CoPi. Since cobalt is recognized in literature as reactive center governing the electrocatalytic activity [3], we also investigate the effect of Co-to-P concentration ratio on the OER. The deposition process is then based on a $(AB)_x(CD)_y$ supercycle. For just 1 extra AB cycle, accompanied by 11 cycles of CoPi (x= 12; y= 11), a Co-rich stoichiometry ($Co_{3.8}(PO_{4.7})_2$) is achieved. The latter leads a higher current density peak (2.9 mA/cm^2 at 1.8 V vs RHE) than the earlier addressed CoPi sample. When comparing the performance of the ALD Co-rich CoPi layer with electro-deposited CoPi [4] in terms of current density, the former exhibits superior OER performance. These results highlight the role that stoichiometry of cobalt phosphate has on its OER activity, suggesting that tuning the Co-to-P ratio can be adopted as approach to design efficient Co-based electro-catalysts for OER.

[1]M.W. Kanan, D.G. Nocera, *Science* 321, 1072 (2008)

[2] V. di Palma *et al*., Electrochemistry Communications 98, 73 (2019)

[3] J. Surendranath *et al*., *J. Am. Chem. Soc*., 132, 13692 (2010)

[4] K. Klingan *et al*., ChemSusChem 7, 1301 (2014)

8:45am **AA1-TuM-4 Improved Electrochemical Activity of Pt Catalyst Fabricated by Vertical Forced-Flow Atomic Layer Deposition***, **Tzu-Kang Chin**, T Perng,* National Tsing Hua University, Republic of China

Currently, carbon black is the most commonly used support material for depositing platinum (Pt) nanoparticle catalyst by wet chemical reduction of Pt salts in aqueous solution. However,oxidation of carbon black occurs under highly humid atmosphere and corrosive operating condition of proton exchange membrane fuel cell (PEMFC), which results in agglomeration of Pt nanoparticles, leading to degradation of catalytic performance. In addition, Pt nanoparticles fabricated by wet chemical reduction require additional steps to purify, such as removing the residual capping agent, and post-treatment to increase the crystallinity of Pt. Consequently, it is urgent to develop a novel support material with high electrical conductivity and electrochemical stability and a more facile fabrication method for Pt catalyst. Titanium oxynitride (TiO_xN_{1-x}) is an intermediate phase which is regarded as a solid solution of titanium nitride (TiN) and the cubic titanium oxide (TiO). It has been reported that the Pt deposited on TiO_xN_{1-x} results in significant enhancements of specific activity, mass activity, and corrosion resistance compared to that deposited onto carbonous support material. Atomic layer deposition (ALD) is a dry process that is able to deposit materials without contamination from capping ligands and residual organic compounds. Pt catalyst prepared by ALD has advantages of high activity and precise particle size control. However, the uniformity and conformity of the coating by conventional ALD equipment on high aspect-ratio or porous substrate is still a great challenge to overcome. To solve this problem, a novel forced-flow configuration was designed recently by our group, i.e., vertical forced-flow ALD. In this study, conductive TiO_xN_{1-x} nanoparticles were fabricated and investigated for the potential application in PEMFC as a catalyst support material. Vertical forced-flow ALD was utilized to deposit Pt nanoparticles with very small particle size uniformly on TiO_xN_{1-x}. The electrochemical activities were examined by cyclic voltammetry and oxygen reduction reaction. The Pt nanoparticles deposited on TiO_xN_{1-x} with 30 cycles show 2-3 times higher electrochemical surface area and also larger half-wave potential of oxygen reduction reaction than those of Pt prepared by conventional wet chemical reduction and commercial E-tek electrocatalyst.

9:00am **AA1-TuM-5 Improved Catalyst Selectivity and Longevity using Atomic Layer Deposition***, C Marshall,* Argonne National Laboratory*; A Dameron, R Tracy,* Forge Nano*; C Nicholas, L Abrams, P Barger,* Honeywell UOP*; T Li, **Lu Zheng***, Argonne National Laboratory

Introduction

Many important industrial scale chemical reactions rely on catalysts and require high temperatures to achieve commercially viable product yields. However, catalysts deactivate over time and lose surface area due to thermal degradation (sintering), fouling, and poisoning. Decreased catalytic activity results in lower selectivity and higher yields of unwanted byproducts. In many cases, the remedy for sintering of metals is to raise the reactor temperature and thus increase energy consumption, or to remove and replace the spent catalyst, which is expensive and leads to loss in productivity.

This project is overcoming catalyst degradation issues via an ALD overcoating technology that deposits protective layers around the active metal, preserving catalyst integrity under reaction conditions. The ALD overcoating technique applies one or more protective layers to the catalyst to inhibit metal sintering. Channels introduced into the ALD layers provide reactants with access to the catalyst's active metal and improve reaction selectivity. This project is applying the overcoating technology to extruded platinum-based catalysts used in the propane dehydrogenation (PDH) to propylene. Improvements in both the efficiency and selectivity reduce the energy required for the process.

Materials and Methods

Alumina extrudates were synthesized by peptizing Versal-251 and extruding it into 1/16" cylinders. The dried extrudates are calcined at temperatures ranging from 500ºC to 1185ºC to generate Al_2O_3 bases with varying surface area and porosity. Pt is impregnated via standard incipient wetness techniques.

ALD is performed in fixed bed reactors typically at 200 °C during all depositions. Precursors for Al_2O_3 were TMA and H_2O, while for TiO_2 they were $TiCl_4$ and H_2O. Depositions are monitored in situ by measuring the reaction composition downstream of the reactor with a quadrupole mass spectrometer.

Results and Discussion

The project team applied overcoatings with different shell thicknesses and compositions. Initial investigations were carried out with $TiCl_4$ to distinguish overcoated layers from the catalyst base. The growth rate of TiO_2 measured by ellipsometry is 0.4Å/cycle, which is similar to previously reported studies. The $TiCl_4$ dose and soak time were then increased simultaneously until the Ti loading reached saturation on 1/16" Al_2O_3 extrudates. We report that loading of Ti after one cycle is 4.5%. No crystalline TiO_2 phase is visible in XRD.

We investigated, and report on, the effect of these overcoated layers on the propane dehydrogenation reaction rate, selectivity and catalyst deactivation.

9:15am **AA1-TuM-6 Enhancing Co_2C Activity for C_{2+} Oxygenate Production from Syngas using ALD Promoters***, **Sindhu Nathan**, J Singh, A Asundi, S Bent,* Stanford University

Residential, transportation, and industrial needs have led to a reliance on nonrenewable energy sources, which has contributed to the rising greenhouse gas concentration in the atmosphere and a subsequent rise in global temperature.The scarcity of nonrenewable fossil fuels and the continually growing demand for energy necessitates the search for renewable and carbon neutral energy sources. One promising pathway is to catalytically convert molecules like CO and H_2 (syngas), which can be generated renewably, to fuels like ethanol or other higher oxygenates which produce fewer emissions than traditional fossil fuels.

Modified cobalt nanoparticle catalysts are of interest for this reaction. Cobalt, a prevalent Fischer-Tropsch catalyst, readily converts syngas to linear hydrocarbons. Much work has been done to direct the selectivity of cobalt towards higher oxygenate production, but there has been little success in engineering a practically useful catalyst. Nanoparticle catalyst activity and selectivity are influenced by interaction with the support and any other metal or metal oxide promoters that interact with the metal surface. Atomic layer deposition (ALD) offers the capability of depositing precise amounts of modifying material on catalyst nanoparticles, allowing atomic-level control over surface composition, which in turn enables better understanding of the catalyst surface.

Prior work has shown that modifying Co with ZnO ALD (using diethylzinc and water) causes restructuring of metallic Co to Co_2C on SiO_2-supported catalysts, and further modifies the carbide, resulting in enhanced oxygenate selectivity but significantly lowered activity [1]. In this work, we investigated whether Co/Co_2C activity towards higher oxygenates could be enhanced by varying the support of ZnO-modified Co. The modified Co on most of the tested supports also showed restructuring to Co_2C. However, these alternate support materials did not enhance the oxygenate activity compared to the ZnO-modified Co/SiO_2. In contrast to the other materials, we found that ZnO-modified Co/Al_2O_3 did not carburize, but that the activity of the catalyst was much greater than Co/SiO_2. To combine this activity improvement with the selectivity of Co_2C, Al_2O_3 ALD (using trimethylaluminum and water) was applied to ZnO-modified Co/SiO_2. The additional Al_2O_3 ALD enhanced the activity of the Co/Co_2C catalysts, and an Al_2O_3 ALD support modifier improved the turnover frequency of ZnO-modified Co/SiO_2 by four times. By using ALD modifying layers, the activity of Co/Co_2C catalysts towards higher oxygenates can be improved while retaining enhanced selectivity.

[1] J. A. Singh et al., *ChemCatChem*. **2018**, 10, 799.

9:30am **AA1-TuM-7 Atomic Layer Deposition of Bismuth Vanadate Core-Shell Nanowire Photoanodes***, **Ashley Bielinski**, S Lee, J Brancho, S Esarey, A Gayle, E Kazyak, K Sun, B Bartlett, N Dasgupta,* University of Michigan

Photoelectrochemical (PEC) water splitting is a direct route for capturing solar energy and storing it in the form chemical bonds. Bismuth vanadate (BVO) is one of the most promising photoanode materials for water oxidation. It has a bandgap of 2.4 eV, which enables visible light absorption and its bands are favorably positioned for water oxidation. BVO has demonstrated potential for high anodic photocurrents, but it is limited by electron-hole separation, charge transport, and water oxidation kinetics. The development of an ALD process for BVO enables core-shell architectures that help address the charge transport and carrier separation challenges by decoupling carrier diffusion and light absorption lengths.

In this study we demonstrate the deposition of ALD BVO using $Bi(OCMe_2{}^iPr)_3$ as the bismuth source, vanadium(V) oxytriisopropoxide as the vanadium source, and water as the oxidant [1]. The choice of this Bi precursor provides full control of Bi:V stoichiometry. The BVO films were deposited as a nanolaminate of binary bismuth and vanadium oxides and then post-annealed to achieve the photoactive monoclinic $BiVO_4$ phase. Film composition and photocurrent were investigated as a function of deposition pulse ratio and film thickness. Additionally, we demonstrate 3D nanostructured BVO photoanodes by depositing the BVO on ZnO nanowires with an ALD SnO_2 interlayer.

The photoactivity of the ALD BVO photoanodes was measured in a three-electrode cell under simulated AM1.5G illumination. A planar photoanode of 42 nm thick BVO produced a photocurrent density of 2.24 mA/cm^2 at 1.23 V vs. RHE (reversible hydrogen electrode) and the application of a ZnO nanowire substrate provided a 54% increase in photocurrent to 3.45 mA/cm^2 at 1.23 V vs. RHE. These values are the highest reported to date for any photoanode using an ALD film as the primary light absorber.

[1] A. R. Bielinski, S. Lee, J. Brancho, S. L. Esarey, A. J. Gayle, E. Kazyak, K. Sun, B. M. Bartlett, N. P. Dasgupta *Submitted*

9:45am **AA1-TuM-8 Improved Photocatalytic Efficiency by Depositing Pt and SiO_2 on TiO_2 (P25) using Atomic Layer Deposition in a Fluidized Bed***, **Dominik Benz**, H Nugteren, H Hintzen, M Kreutzer, R van Ommen,* Delft University of Technology, Netherlands

Photocatalysts for water cleaning typically lack efficiency for practical and economical applications. Here we present a new material that was developed using knowledge of working mechanisms of catalysts and the abilities of Atomic Layer Deposition (ALD). The deposition of ultrathin SiO_2 layers on TiO_2 nanoparticles, applying ALD in a fluidized bed reactor, showed in earlier studies in our group their beneficial effects for the photocatalytic degradation of organic pollutants. There we assume that due to the surface modification with SiO_2 the surface becomes more acidic which benefits the hydroxyl radical generation. Furthermore, we have investigated the role of Pt on P25 as an improved photocatalyst. There we found the main reason for the catalytic improvement is adsorbed oxygen on the Pt particles, which is an important reactant in the photocatalytic degradation process of organic pollutants. Having recognized, that the two independent materials, SiO_2:P25 and Pt:P25, have different mechanisms improving the photocatalytic activity gave us the opportunity to combine these two materials into a new material, where we deposited SiO_2 onto P25 followed by deposition of nanoclusters of Pt. Indeed, this new material exceeded the performance of the individual SiO_2:P25 and Pt:P25 catalysts. This unconventional approach shows that by understanding the individual materials' behavior and using ALD as an appropriate deposition technique, new materials can be developed, further improving the (photo-)catalytic activity and moving one step closer to implementation. We will demonstrate that ALD is an attractive technology to produce the catalysts developed by this approach in a precise and scalable way.

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