ALD Applications
Room Halla Hall - Session AA1-WeM
Catalyst and Fuel Cell Applications

Moderators: Ji Hwan Ahn, POSTECH, **Hao Van Bui**, Phenikaa University

8:00am **AA1-WeM-1 Atomic Layer Deposition for Highly Durable Hydrogen Fuel Cells: from Catalyst to Cell**, *Xiao Liu, Hang Liu, Yuxin Gao, Jianhua Wu,* ***Rong Chen,*** Huazhong University of Science and Technology, China **INVITED**

The widespread application of hydrogen fuel cells relies heavily on high performance oxygen reduction reaction catalysts. When facing with complex and harsh operational conditions, traditional Pt-based catalysts always surfer from serious electrochemical corrosion or poisoning of sulfonic acid groups at the catalyst or cell level. In this talk, we will present controllable synthetic strategies of advanced catalysts for highly durable hydrogen fuel cells based on atomic layer deposition. A series of highly stable Pt-based alloy catalysts are prepared by ultrathin metal oxide coating and post-annealing process, which could avoid the agglomeration of catalyst particles caused by high ordering temperature. The strategies of sub-surface single atom precise doping and selective passivation of nitrided TiO_2 are developed to prevent the corrosion of low coordination or unsaturated sites on the surface Pt catalysts. At the cell level, spatially confined ultrafine Pt-based alloy in porous carbon support could effectively improve the performance of fuel cells by reducing oxygen transport resistance. Besides, the corrosion resistance of stainless-steel bipolar plate is enhanced by Al_2O_3/TiO_2 nanolaminates composited with niobium-doped amorphous carbon coating. As a very promising thin film technique, ALD has shown its potential to address challenges in hydrogen fuel cell from all aspects.

8:30am **AA1-WeM-3 Interfacial Properties of ALD-Grown In_2S_3 Catalysts in CO_2 Electroreduction**, *Järi Van den Hoek,* University of Antwerp, Belgium*; Femi Mathew, Ruben Blomme,* Ghent University, Belgium*; Lieven Hintjens, Brend De Coen,* University of Antwerp, Belgium*; Eduardo Solano,* ALBA synchrotron, Spain*; Matthias Minjauw,* Ghent University, Belgium*; Nick Daems, Daniel Choukroun,* University of Antwerp, Belgium*; Christophe Detavernier,* Ghent University, Belgium*; Tom Breugelmans,* University of Antwerp, Belgium*;* ***Jolien Dendooven,*** Ghent University, Belgium

Electrochemical reduction of CO_2 is a promising strategy for sustainable production of high-value chemicals like formate, a valuable feedstock in the textiles, food and chemicals industries. In CO_2 electrolysers, selective catalysts that suppress the competing hydrogen evolution reaction (HER) are essential, along with a well-defined triple-phase boundary (TPB) at the gas diffusion electrode (GDE)/catalyst/electrolyte interface to enhance CO_2 mass transfer. Beyond intrinsic catalytic properties, interfacial factors such as surface roughness and hydrophobicity impact the TPB region and performance. To investigate these effects, we employed plasma-enhanced (PE-) and thermal (T-)ALD of In_2S_3 on GDEs, creating model catalysts without ionomers or binders [1].

The ALD processes used $In(acac)_3$ and H_2S (plasma) precursors at a substrate temperature of 180 °C. Saturated growth was confirmed on Si substrate, achieving 0.28 and 0.17 Å/cycle for PE- and T-ALD, respectively. Both films were crystalline, with the PE-In_2S_3 film displaying a tetragonal structure and the T- In_2S_3 film a cubic structure. Next, In_2S_3 films were successfully deposited on GDEs, as confirmed by XPS and XRF mapping. Cross-sectional SEM-EDS revealed the penetration of In and S 100 µm deep inside the GDE, in contrast to superficial deposits by conventional coating methods. The PE-In_2S_3 and T-In_2S_3 electrocatalysts showed a comparable surface roughness and electrochemical active surface area. The hydrophobicity was studied via water contact angle (CA) measurements. Compared to the bare GDE (151.0°), the CA of T-In_2S_3 exhibited a limited decrease to 128.8°, whereas PE-In_2S_3 displayed a significantly diminished value of 76.9°, indicative of plasma-induced modification of the underlying PTFE-rich GDE surface. Thus, the hydrophobicity decreased drastically for PE-In_2S_3.

The T-In_2S_3 films achieved a formate Faradaic efficiency of more than 90% at 1 A cm^{-2} in a flow-by electrolyzer. In contrast, PE-In_2S_3 exhibited reduced electrochemical activity and selectivity, attributed to its higher wettability. The increased hydrophilicity caused excessive penetration of the electrolyte into the GDE, resulting in a shift in the TPB, limiting CO_2 diffusion to the catalyst layer and promoting HER over formate production. On the other hand, the conformal coverage provided by T-ALD together with its favourable hydrophobic interfacial properties stabilized the TPB region, allowing for long-term stability of up to 30 h. These findings contribute to the understanding of how catalyst interfacial properties promote activity and stability in CO_2 electroreduction.

[1] Van den Hoek et al. Adv. Energy Mater. 2025, 2404178.

8:45am **AA1-WeM-4 Scaling Up Platinum on Carbon Catalyst Fabrication for Proton Exchange Membrane Water Electrolysis**, ***Peter Michael Piechulla,*** *Mingliang Chen, Sophie van Beusekom,* Delft University of Technology, Netherlands*; Mena-Alexander Kräenbring, Fatih Özcan, Doris Segets,* University of Duisburg-Essen, Germany*; Ruud van Ommen,* Delft University of Technology, Netherlands

Wind and solar have in recent years become the cheapest sources of electricity; however, their intermittency is still an obstacle to further capacity expansion. Hydrogen generation through proton exchange membrane water electrolysis (PEMWE) is a promising solution to this problem but requires scarce platinum group metal catalysts to facilitate the half-reactions at the electrodes, which may soon become a bottleneck for scale-up. Hence, the catalyst is typically deposited sparsely onto a support material (e.g., Pt-loaded carbon, Pt/C), thereby increasing surface area of the catalytically active metal. With incipient wet impregnation as a scalable and thus industrially accepted method, morphology and dispersion of Pt is difficult to control. In contrast, ALD enables Pt/C fabrication at atomic level precision, but is so far only employed in lab scale experiments[1].

In this contribution, we demonstrate the manufacturing of highly active Pt/C catalysts for PEMWE through ALD on particles in a fluidized bed reactor (FBR-ALD), and investigate the upscaling potential of the process[2]. The process is carried out at atmospheric pressure, such that no expensive and difficult to scale vacuum systems are required from the outset. First, we tailor catalysts with a nanometer scale dispersion of Pt on carbon using sub-gram scale batches of catalyst. The catalyst is analyzed for its morphology via TEM imaging and screened for electrochemical performance via cyclic voltammetry measurements to obtain the electrochemically active surface area. Second, to evaluate the performance of the most promising ALD-made Pt/C catalysts under realistic conditions, we manufacture cathode catalyst layers and characterize their performance and durability in a laboratory-scale PEMWE system. Finally, we transfer the FBR-ALD process to a larger scale reactor (>10 g batches of catalyst), where we investigate saturation behavior and utilization of the $MeCpPtMe_3$ precursor through residual gas analysis. In addition to fundamental insights, we thereby gain an indication of economic efficiency of the process. In conclusion, we demonstrate that ALD manufacturing of high performance Pt/C catalyst is a scalable process.

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(2) Grillo, F.; Van Bui, H.; Moulijn, J. A.; Kreutzer, M. T.; van Ommen, J. R.; *J. Phys. Chem. Lett.* **2017**, *8* (5), 975–983. https://doi.org/10.1021/acs.jpclett.6b02978.

9:00am **AA1-WeM-5 Platinum Promoted Cobalt based Fischer-Tropsch Thin-Film Catalysts**, ***Muhammad Hamid Raza,*** *Avela Kunene, Imane El Arrouji,* PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany*; Catalina E. Jiménez,* Department Interface Design, HZB, Berlin, Germany*; Alexander Steigert, Martin Muske, Tobias Köhler, Ali Shan Malik,* PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany*; Marcus Bär,* Department Interface Design, HZB, Berlin, Germany. Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HI ERN), Erlangen, Germany. Dept. Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany*; Nicola Pinna,* Department of Chemistry and The Center for the Science of Materials Berlin, Humboldt-Universität zu Berlin, Berlin, Germany*; Rutger Schlatmann, Daniel Amkreutz,* PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany

The Power-to-Liquids (PtL) approach can produce sustainable fuels by utilizing Fischer-Tropsch (FT) processes to convert green hydrogen and carbon dioxide. While FT is a promising technology for producing sustainable fuels, high-performance catalysts are crucial to its success. Thin film catalysis offers opportunities to tailor the catalysts properties by design that are pre-adapted to specific chemical environment for their targeted application. FT benefits from thin film catalysts by reducing the amount of active materials, streamlining activation phase and enhancing selectivity toward desired end products. We report a cobalt-based thin-film FT catalyst synthesized by a combination of different deposition techniques including atomic layer deposition (ALD), plasma enhanced chemical vapour deposition (PECVD), magnetron sputtering and successive ionic layer adsorption and reaction (SILAR). Mn/MnO$_x$ and Pt are studied as promoters and enhancers toward FT while considering cobalt as the FT active material. The size of platinum particles is controlled by number of ALD cycles. An ultra-low amount of Pt grown by 5ALD cycles is loaded onto the stack of cobalt based heterostructures (Mn-Co-SiO$_x$/Al) to study the effect of platinum as reduction promotor. The reduction behaviour of cobalt in the presence of Mn and Mn-Pt in oxidation-reduction conditions is investigated using *in-situ* synchrotron grazing incident X-ray diffraction. It is revealed that platinum promotes the reduction of cobalt species (spinel-Co$_3$O$_4$ to Co^0) as indicated by a significant lowering of the reduction temperature to 350 °C while the addition of Mn retards the reduction of CoO to Co^0. Temperature-programmed reduction (TPR) studies further confirm the effect of Pt on promoting the reduction of Co$_3$O$_4$ at lower temperatures to the FT active phase. These well-defined Pt-Mn-Co-SiO$_x$/Al hierarchical heterostructures represent a promising thin film FT catalyst system with significantly enhanced FT activity. Clear structure−property correlations required to insight-driven scale up the process, will be presented.

9:15am **AA1-WeM-6 Selectively Located Pt Clusters on Au/CeO$_2$ for Highly Robust Water-Gas Shift Reaction via Atomic Layer Deposition***, Xiao Liu, Yuanting Tang, Bin Shan, Rong Chen,* Huazhong University of Science and Technology, China

CO impurities in hydrogen derived from fossil fuel reforming present a substantial barrier to efficiency and environmental impact. This challenge underscores the importance of the water-gas shift (WGS) reaction, a critical process for purifying hydrogen for fuel cell applications. Au catalysts have shown outstanding low temperature catalytic activity toward WGS reaction, but they are struggling with the durability concerns.We fabricate a depth-controlled TiO$_2$ nanotrap via area-selective atomic layer deposition (ALD) method to balance the activity and anti-sintering properties of Au nanoparticles.[1] It exhibits enhanced sintering resistance while retaining an activity similar to that of pure Au catalyst. The average size of sintered Au (8.4 ± 2.7 nm) is three times smaller than that of pure Au catalyst (21.1 ± 7.1 nm) after calcination in air at 700 ºC. Based on the area-selective ALD method, Pt clusters are selectively located on Au/CeO$_2$ to activate the interfacial active sites poisoned by intermediate species.[2] The selective method effectively avoids the coverage of Au surface sites by Pt atoms and maintains the low temperature catalytic activity of Au/CeO$_2$ catalyst. Durability test indicates that the Pt-activated Au/CeO$_2$ catalyst shows superior durability in WGS atmosphere (200 ºC), which only attenuates 7.9% (from 78.0% to 70.1%) after 150 h. The analysis of surface intermediates and density functional theory calculations reveal that the introduction of Pt ensures the regenerative capacity of Au/CeO$_2$ active sites by facilitating the decomposition of intermediate species and the desorption of CO$_2$.

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[2] Tang, Y. T.; Liu, Z.; Ye, R. L.; Zhao, R.; Dun, Y. H.; Zhao, Y. K.; Liu, X.; Chen, R.; Shan, B. Selectively located Pt clusters on Au/CeO2 for highly robust water-gas shift reaction via atomic layer deposition. Appl. Catal. B: Environ. Energy **2024**, *356*, 124218.

9:30am **AA1-WeM-7 Fluorine-Free and Freestanding Bipolar Membranes Based on Metal-Oxide Ald-Coated Electrospun Nanofibers for Water Electrolysis and Fuel Cells***, Arnaud Demore, Damien Voiry,* IEM - CNRS, France*; Philippe Miele,* IEM - ENSCM, France*; Mikhael Bechelany,* IEM - CNRS, France

As the demand for green hydrogen production grows, processes such as water electrolysis are among the most promising technologies. However, several limitations remain unresolved yet, Proton Exchange Membrane Water Electrolysis (PEMWE) relies on noble metal (IrO$_2$ for OER in acidic conditions) and Anion Exchange Membrane Water Electrolysis (AEMWE) can use earth-abundant metals for the OER in alkaline conditions, but HER is limited by to the lack of available protons at the cathode. In this context, simultaneously achieving a high-pH OER and a low-pH HER is desirable and this is precisely one of the opportunities offered by bipolar membranes (BPM). When operated in reverse bias, BPMs can maintain a pH gradient across the electrochemical cell by dissociating water into protons and hydroxide ions. This allows for optimized reaction conditions at both anode and cathode, reducing catalyst costs. A BPM consists of two ion exchange layers of opposite polarity, separated by a catalytic layer. Water dissociation (WD) occurs at the interface of those two ion exchange layers known as bipolar junction. Water dissociation efficiency directly impacts energy consumption and overall cell performance. Additionally, while some catalysts have shown the ability to dissociate water effectively, the current deposition processes often produce a thick catalytic layer that can lead to delamination, catalyst leakage, further affecting long-term stability and performance. Therefore, our objective is to implement an efficient catalytic layer for WD, as thin as possible, in order to minimize catalyst usage while maintaining a strong bond to the polymer. A combination of Atomic layer deposition (ALD) and Electrospinning (ES) methods appears well suited to achieve this goal. ALD is a low temperature process that allows a precise control of thickness, conformity and uniformity of deposited layer, providing a chemically strong bonded layer even on polymer surfaces. ES is a cost effective method for producing high-surface-area, tunable, fluorine-free polymer nanofibers. By using quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (Q-PPO) and sulfonated polyether ether ketone (S-PEEK), two ion exchange polymers of opposite polarity, TiO$_2$ ALD-coated nanofibers were produced and further processed to obtain a fully dense bipolar membrane. Bipolar membranes are tested in two compartment H-cell with a four probe electrode set-up, and in electrolysis cells. WD is studied threw Current-Voltage (j-V) measurements to investigate the nature, thickness and distribution of the catalyst to obtain optimal WD performances in the BPM as well as to ensure long-term stability and strong catalyst bonding.

9:45am **AA1-WeM-8 Efficient Alkaline Hydrogen Evolution Reaction with Iridium Nanostructures synthesized by Atomic Layer Deposition*****, Jhonatan Rodriguez Pereira****, Raul Zazpe, Jan Macak,* University of Pardubice, Czechia

The outstanding performance of noble metals such as Pt, Ru, Pd, Ir, etc., for different catalytic applications has been widely demonstrated.[1,2] However, due to their scarcity, efforts have been made to reduce or substitute these noble metals. Atomic Layer Deposition (ALD) is one of the best technique to facilitate loading mass reduction on a support of interest.[3,4] Moreover, ALD is the most suitable technology to decorate with noble metal nanoparticles, high aspect ratio and high surface area substrate architectures.[5]

Surface energy variations between the noble metals and the support surfaces cause the ALD growth to initiate as single atoms, then nanoclusters and as the number of ALD cycles increases nanoparticles (NPs), the agglomeration between NPs dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. These surface energy variations considerably increase the nucleation delay of noble metals. In this sense, our efforts focused on improving the functionality with pretreatments on carbonaceous supports that showed promise in reducing the nucleation delay of Ir deposited by ALD.[6]

It is highly important to choose the right substrates for electrocatalytic applications. Among the available substrates, TiO$_2$ nanotube (TNT) layers and carbon papers (CP) are the best options considering their physiochemical properties, availability, extensive literature and the low costs incurred when using them as support substrates in electrocatalysis. Variations in the morphological aspects of TNT layers and several surface modifications for CPs have received great attention from applied fields due to their enhanced surface area, conductivity and stability.[7–12]

The presentation will introduce and describe the synthesis of Iridium nanostructures by ALD on TNT layers and CP substrates, including the corresponding physico-chemical and electrochemical characterization and the encouraging results obtained for alkaline Hydrogen Evolution Reaction (HER).

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