ALD Applications
Room Hall 3D - Session AA2-TuA
Energy: Catalysis and Fuel Cells

Moderators: Riikka Puurunen, Aalto University, Finland, **Ruud van Ommen**, Delft University of Technology

4:00pm **AA2-TuA-11 ALD Young Investigator Award Finalist Talk: How Instability Can Be Beneficial for Electrocatalysis: The Case of Nickel Sulfide Oxygen Evolution Reaction Precatalyst***, **Miika Mattinen,*** University of Helsinki, Finland*; J. Schröder, G. D'Acunto, T. Jaramillo,* Stanford University*; M. Burke Stevens,* SLAC National Accelerator Laboratory*; M. Ritala,* University of Helsinki, Finland*; S. Bent,* Stanford University

Water electrolysis is a key technology in building a sustainable world based on renewable energy. Hydrogen gas (H_2) produced by water electrolysis can be used, for example, as a fuel and reactant in diverse industries including chemical and steel manufacturing. Of the two half-reactions occurring inside water electrolyzers, the oxygen evolution reaction (OER) limits the efficiency. Thus, development of highly active, stable, and affordable OER catalysts is critical. Nickel-iron metal alloys, oxides, and hydroxides are among the most active OER catalysts in alkaline electrolytes. Their activity is attributed to oxyhydroxide species formed under OER conditions.[1] Recent studies looking at other promising Ni compounds such as NiS_x have found them, too, to transform to oxyhydroxides. Thus, all the Ni(Fe)-based catalysts listed above may be described as precatalysts to the active oxyhydroxide.[2] However, the effect of the precatalyst material on the activity and structure of the active catalyst as well as the role of electrolyte impurities (e.g. Fe) remain poorly understood.

To answer these questions, we deposited crystalline NiS_x (β-NiS with traces of Ni_9S_8) thin films by ALD using $NiCl_2$(TMPDA) (TMPDA = *N,N,N',N'*-tetramethyl-1,3-propanediamine) and H_2S at 165 °C. The ALD NiS_x films were compared to NiO, $Ni(OH)_2$, and Ni precatalysts deposited on SnO_2:F electrodes by ALD and other methods. Electrochemical measurements in 0.1 M KOH (purified from iron) and X-ray photoelectron spectroscopy revealed that all the precatalysts convert to an oxidized phase ("NiOOH") under OER conditions, yet at substantially different rates ($NiS_x \approx Ni(OH)_2 >> Ni > NiO$). Fast conversion is beneficial for achieving high current densities. We are investigating the structure of the formed oxidized phase using *operando* X-ray absorption spectroscopy.

Iron impurities in the KOH electrolyte incorporate into the (pre)catalysts reaching up to 30 metal-%. This added iron greatly increases the OER activity and stability of the catalysts. Compared to synthesis of multimetal catalysts, incorporating iron from the electrolyte simplifies synthesis and can accelerate the conversion to the active catalyst. The highest iron concentration and best OER performance is found for the fastest converting precatalysts, i.e. NiS_x and $Ni(OH)_2$. Understanding of the structural evolution of OER precatalysts together with the conformality of ALD enables engineering of high-performance electrodes for alkaline electrolyzers.

1 Burke et al., *Chem. Mater.,* 2015, **27**, 7549

2 Kawashima et al., *Chem. Rev.*, 2023, **123**, 12795

4:15pm **AA2-TuA-12 Diffusion–Reaction Modeling for Atomic Layer Deposition on Spheres: Comparison with Experimental Data***, **Niko Heikkinen**,* VTT Technical Research Centre of Finland*; J. Yim, J. Järvilehto,* Aalto University, Finland*; S. Saedy,* Delft University of Technology, Netherlands*; P. Brüner, T. Grehl,* IONTOF GmbH, Netherlands*; E. Haimi, J. Velasco, C. Gonsalves,* Aalto University, Finland*; R. van Ommen,* Delft University of Technology, Netherlands*; J. Lehtonen,* VTT Technical Research Centre of Finland*; R. Puurunen,* Aalto University, Finland

Diffusion–reaction (DR) modeling is a powerful tool to estimate reactant travel and film formation in atomic layer deposition (ALD) in high-aspect-ratio (HAR) features [1]. The modeling work of conformality evolution on (modelling-wise) one-dimensional features (circular pores and channels) has been extended to porous materials described by an average pore size, tortuosity and porosity, still keeping the geometry one-dimensional through considering the slab geometry [2]. While a slab can describe well the case of planar surfaces (e.g. membranes), typically particles used as catalyst supports resemble more spheres or cylinders.

We have recently extended ALD diffusion–reaction modeling to describe spheres and cylinders in addition to slabs [3]. Our study showed for example that the reactant exposure requirement for full saturation increases in the order spheres < cylinders < slabs.

Here, we extend the earlier theoretical work [3] and compare modeling to experimental studies on high-surface-area alumina spheres. Two case examples are presented: zinc on alumina using the recently reported $Zn(acac)_2$ reactant [4] (one reaction step in a fixed-bed reactor, with $Zn(acac)_2$ dose varied), and platinum on alumina using the well-known $MeCpPtMe_3$ reactant (5 cycles with oxygen as counter-reactant, in a fluidized bed reactor, with exposure time varied). Alumina spheres with diameters of 1, 1.8 and 2.5 mm were employed, with a specific surface area on the order of 200 m^2/g. Modelling results are found to agree reasonably well with the experimental data.

[1] V. Cremers, R. L. Puurunen, J. Dendooven, Applied Physics Reviews 6 (2019) 021302. https://doi.org/10.1063/1.5060967

[2] N. Heikkinen, J. Lehtonen, L. Keskiväli, J. Yim, S. Shetty, Y. Ge, M. Reinikainen, M. Putkonen, Physical Chemistry Chemical Physics 24 (2022) 20506-20516. https://doi.org/10.1039/D2CP02491H

[3] N. Heikkinen, J. Lehtonen, R. L. Puurunen, Physical Chemistry Chemical Physics, accepted (2024).

[4] J. Yim, E. Haimi, M. Mäntymäki, V. Kärkäs, R. Bes, A. Arandia Gutierrez, K. Meinander, P. Brüner, T. Grehl, L. Gell, T. Viinikainen, K. Honkala, S. Huotari, R. Karinen, M. Putkonen, R.L. Puurunen, Chemistry of Materials 35 (2023) 7915–7930. https://doi.org/10.1021/acs.chemmater.3c00668

4:30pm **AA2-TuA-13 Highly Durable Pt Based Fuel Cell Catalysts via Atomic Layer Deposition***, **Xiao Liu**, H. Liu, Y. Gao,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China*; B. Shan,* State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, China*; R. Chen,* State Key Laboratory of Intelligent manufacturing Equipment and Technology, School of Mechanical Science and Engineering, Huazhong University of Science and Technology, China

The activity and durability of carbon supported Pt based electrocatalysts (Pt/C) are unchanging goals for the widespread application of hydrogen fuel cells. Under the harsh operation conditions of fuel cell, pure Pt nanoparticles (NPs) suffer from great electrochemical dissolution, leading to serious stability decay. To address this challenge, overcoating Pt NPs with organic capping agent, polymer layers, inorganic carbon-based nanoshell or metal oxide (MO_x), nitride has been recognized as a prospective strategy to prevent the direct exposure of Pt surface. Atomic layer deposition (ALD) is known for its atom-level control accuracy over the film growth on substrates or NPs based on self-limiting chemical half-reactions. Herein, an effective strategy is developed to improve the activity and durability of Pt catalyst for hydrogen fuel cell based on atomically surface and interface modification on Pt nanoparticle, which is a promising scale-up approach via selective atomic layer deposition. Selective ALD of metal oxides such as TiO_2, ZnO, SnO_2 have been performed on Pt/C electrocatalysts by a custom-made fluidized-bed reactor. The behavior of selective deposition is controlled by the reactor temperature, oxygen source and number of ALD cycle. Following post treatments such as nitriding and high temperature reduction are performed to precisely control the surface structure of supported Pt nanoparticles. The activity and durability of Pt based electrocatalysts have been enhanced via selective ALD and following post treatment. N doped TiO_2 (N-TiO_2) is demonstrated to selectively deposit on the low coordination sites of Pt NPs and expose (111) facet without changing their size distribution and wasting the electrochemical active surface area. The selective decoration of N-TiO_2 could effectively inhibit the intrinsic degradation of Pt NPs and prevent the electrochemical sintering during accelerated durability tests. Besides, the intrinsic activity of Pt NPs is also enhanced based on ultra-thin ZnO coating. The prepared uniform PtZn intermetallic nanocrystals with the size of 2.50 ± 0.65 nm achieve outstanding single-cell performance with the mass activity of 0.48 A $mgPt^{-1}$ at 0.9 V and 10.42% loss of mass activity after 30000 voltage cycles, which is superior to commercial Pt/C. The enhanced activity and durability is attributed to the decreased binding energy of Pt-oxygen intermediates for weakly polarized surface Pt atoms and suppressed electrochemical Ostwald ripening.

4:45pm **AA2-TuA-14 Catalyst on Top? Importance of the Final Layer of an ALD Deposited Catalyst. Ni-Fe Catalysts Deposited by ALD***, **Ruben Blomme,*** Ghent University, Belgium*; R. Ramesh,* Ghent University, Belgium, India*; L. Henderick, M. Minjauw, P. Vereecke, M. Adriaens, C. Detavernier, J. Dendoven,* Ghent University, Belgium

H2 is considered a crucial energy carrier in the transition to a more sustainable future. It serves as an essential feedstock for many industries and can also be used as an alternative, low-emission fuel for keyindustrial processes, such as steel production. However, the renewable method to produce H2, viawater electrolysis, is currently uncompetitive compared to the fossil fuel-based alternative.

One aspect in which the efficiency of water electrolysis can be improved is through the development of effective catalyst materials. Currently, noble metal-based catalysts are utilized for H2 production, but this approach is not sustainable in producing the required amount of H2 due to the high cost and scarcity of these metals.

To address this, alternative catalysts are under development, with some of the more promising materials being transition metal oxides and phosphates. The use of Atomic Layer Deposition (ALD) allows for the precise control during the catalyst production process, including conformal layer-by-layer control and compositional tailoring. Previous works on ALD development of metal phosphate materials, such as iron[1], nickel[2], and cobalt[1,3], have demonstrated their viability and effectiveness as Oxygen Evolution Reaction (OER) catalysts.

In this study, a series of Ni-Fe mixed phosphate materials were deposited via a supercycle approach and quantified for their electrochemical performance. Notably, during the deposition process, there was a preferential incorporation of Ni over Fe across all measured samples (Fig. 1). According to X-ray fluorescence (XRF) measurements, the effectiveness of one NiPO ALD cycle in a NiPO – 4 FePO process is twice that of the same ALDcycle in a pure NiPO deposition.

The order of the ALD processes in the supercycle recipe and the overall film thickness had significant impact on the performance as a catalyst material. The most noteworthy effect of customizing the ALD sequence was observed when the cycle sequence in the supercycle was reversed to ensure FePO was deposited as the final layer (Fig. 2). This resulted in an overall potential gain of 20 mV (at 10 mA/cm^2) for materials with identical composition.

By increasing the thickness of the deposited layer, additional gains could be achieved. These findings align with previous reportsthat observed the restructuring of cobalt phosphate materials to oxides/hydroxides with a significantly increased electrochemical active surface area[4].

[1] Nanoscale Adv., **1**, 4166-4172., (2019)

[2] Dalton Trans., **51**, 2059, (2022)

[3] J. Vac. Sci. Technol. A **38**, 022416 (2020)

[4] ACS Catal., **11**, 5, 2774–2785, (2021)

5:00pm **AA2-TuA-15 Enhanced Oxygen Evolution Reaction Catalysts by PE-ALD: Atomically Dispersed Co_1 and Fe_1 Supported on Ultra-thin Films of Doped NiO_x***, **Ina Oestroem,*** University of New South Wales, Australia*; M. Favaro,* Helmholtz Zentrum Berlin, Germany*; P. Burr, B. Hoex,* University of New South Wales, Australia

Hydrogen production through water splitting is hindered by the anodic oxygen evolution reaction (OER), which has a complex, sluggish mechanism leading to a high overpotential.Nickel oxide-based catalysts (NiO_x) are a highly active, cheaper alternative to the precious metal catalysts of IrO_2 and RuO_2. Plasma-enhanced atomic layer deposition (PE-ALD) is a powerful tool for optimising thin films to increase OER activity. This work employs PE-ALD, using O_2 and H_2 plasma, to atomically disperse Co_1, Fe_1, and Fe_1Co_1 at the surface of thin films of $SnNiO_x$. The films were conditioned by 600 cycles of cyclic voltammetry (CV) at 20 mV/s, testing their stability and formation of the catalyst OER-active structure. Electrochemical Impedance Spectroscopy (EIS) was employed (0.1 – 10^4 Hz and 1.5 – 1.7 *vs* RHE), after 20 cycles, and at the end of the 600 cycles, to investigate the changes in double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}). The apparent activity was studied with linear sweep voltammetry (LSV) at 1 mV/s, and the durability by chronopotentiometry (CP) at 10 mA/cm^2 for 12 hrs. The 12 hr CP tests were followed by rest and another CP for 1 hr, showing further improvements in activity after a recovery period. The turn-over frequency (TOF) at different potentials was obtained through redox peak integration and C_{dl}. Our results show that atomically dispersed Co_1 and Fe_1 produced via H_2 plasma, in contrast to an O_2 plasma, further improved the OER activity of thin films of $SnNiO_x$. The best OER catalyst is $Fe_1Co_1/SnNiO_x$ with 284 mV of overpotential at 10 mA/cm^2 on FTO, compared to 320 mV for Ru on glassy carbon (GC) in 1M NaOH, with remarkable stability and durability after prolonged CP test. Tafel analysis and EIS suggest the improved performance is due to a lower R_{ct}. All-electron hybrid Density functional theory (PEB0/pob-TZVP) provided insights into the thermodynamics of the OER mechanism and electronic properties of the catalysts. X-ray diffraction, X-ray photoelectron spectroscopy, and soft X-ray absorption characterised the atomic structure, active sites oxidation state and coordination environment. The morphology and conformality were analysed with atomic force microscopy (AFM), scanning tunnelling electron microscopy (STEM), and spectroscopic ellipsometry (SE). This work shows that the OER activity of $SnNiO_x$ can be improved by atomically dispersed Fe_1Co_1 by PE-ALD and that the catalysts are stable after prolonged CP tests. Our study highlights PE-ALD as a promising technology for optimising low-cost catalysts with high atom economy and atomic-level precision.

5:15pm **AA2-TuA-16 Optimization of Photocurrent Response of Atomic Layer Deposited $Ti_xFe_{2-x}O_3$ Photoanodes***, **Anjan Deb**, A. Vihervaara, G. Popov, M. Chundak, M. Heikkilä, M. Kemell, M. Ritala, M. Putkonen,* University of Helsinki, Finland

Hematite (α-Fe_2O_3) has attractive properties, such as a low band gap energy (1.9-2.2 eV), abundant availability and high chemical stability, for photoelectrocatalytic applications such as water splitting and organic micropollutant decomposition (Liu, et al., 2023). However, it has also several limitations, including low optical absorption coefficient and a short minority carrier diffusion length ranging from 2-4 nm. To address this intrinsic problem of hematite, researchers are exploring the use of nanoscale fabrication techniques and doping with aliovalent cations, such as Ti^{4+}, as a potential solution. Atomic layer deposition (ALD) is a promising technique that enables the deposition of pinhole free thin films with precise atomic-level composition and thickness control over an extensive surface area and high aspect ratio surfaces (Leskelä & Ritala, 2002).

In this study, we employed response surface methodology (RSM) based face-centred central composite design (FC-CCD) for modelling and optimization of photocurrent response of $Ti_xFe_{2-x}O_3$ thin film photoanodes grown by ALD. Two ALD process, $FeCp_2$ + O3 and $Ti(OMe)_4$+H_2O, were combined to grow the $Ti_xFe_{2-x}O_3$ thin film photoanodes. Deposition parameters such as total number of ALD cycles (film thickness), cycle ratio of TiO_x to FeO_x (the dopant concentration) and deposition temperature were chosen as the independent factors while the photocurrent densities (PCD) at 1.23V and 1.70V vs RHE were considered as response. Thin film depositions were carried out according to the FC-CCD design matrix (Figure 1-a) based on the level of experimental factors presented in Table 1. After deposition, all the films were subjected to annealing at 500°C for 1 hour in air and evaluated for photocurrent response using a photoelectrochemical cell under standard illumination of AM 1.5G, 100 mW/cm^2. Linear sweep voltammetry (LSV) method was used to record the photocurrent responses at 1.23 and 1.70V vs RHE (Figure 1-b) at water oxidation conditions ($pH \approx 13.2$).

After fitting the experimental data to the second-order polynomial equation, a mathematical model was developed that correlates the experimental variables with the response. The analysis of model parameters indicates that film thickness and dopant concentration are the most important elements that govern the PCD of $Ti_xFe_{2-x}O_3$ photoanode. The predicted PCD values using the model equations agreed well with the experimental data (R^2=0.95 for PCD@1.23V and R^2=0.98 for PCD@1.7V vs RHE) as shown in Figure 2. This study demonstrated the effectiveness of RSM based modelling to predict the photocurrent response of photoelectrode materials.

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