

Monday Morning, July 17, 2017

ALD Applications

Room Plaza E - Session AA+NS-MoM

Energy: Catalysis and Fuel Cells I (8:00-10:00 am)/Nanoparticles and Nanostructures (10:45 am-12:00 pm)

Moderators: Riikka Puurunen, Aalto University, Finland, Necmi Biyikli, Utah State University, Joseph Spencer II, ALD NanoSolutions, Inc.

8:00am AA+NS-MoM-1 Performance of Promoted Rh Catalysts for C₂ Oxygenate Production, *Arun Asundi, N Yang, C MacIsaac, S Bent*, Stanford University

Environmental and economic concerns regarding the rapid consumption of non-renewable energy resources have motivated the development of sustainable methods for fuel and chemical production. The catalytic conversion of biomass-derived syngas (CO + H₂) to ethanol and other higher oxygenates is a promising path towards sustainable energy production. However, a commercial catalyst for this process has not yet been developed due to the many kinetically favorable side reactions that shift selectivity away from the desired products. Experimental and computational studies have shown that rhodium-based catalysts have moderate intrinsic selectivity towards higher oxygenates and that the performance can be improved through the use of metal oxide promoters. However, the performance of Rh-based catalysts can vary greatly depending on a variety of factors, including preparation method and choice of promoter. Fundamental understanding of how these factors affect catalyst performance will allow for more intelligent catalyst design.

Catalysts are commonly prepared using co-impregnation since it is a fast, easy, and scalable method for the deposition of catalyst materials. However, study of the effects of catalyst structure on performance requires a method of catalyst synthesis with atomic-level control not provided by co-impregnation. Atomic layer deposition (ALD) has emerged as a technique for the design of catalysts on the atomic scale, thus allowing for the study of the effects of catalyst structure on performance. In this work, promoted Rh nanoparticles were tested in the conversion of syngas to higher oxygenates. Rh nanoparticles were prepared on porous silica particles using incipient wetness impregnation. By depositing MoO_x on the particles with ALD before and after Rh impregnation, the effects of MoO_x were studied as support and over layers. Promoted Rh catalysts prepared by ALD were compared to those made by conventional wet impregnation.

Rh nanoparticles promoted with MoO_x show a large increase in activity and higher oxygenate selectivity relative to a pure Rh catalyst. As a support layer, ALD MoO_x shows increasing selectivity with higher MoO_x loadings, while an over layer results in equally high selectivity regardless of MoO_x loading. The oxidation states and reducibility of the Rh and MoO_x species prepared by ALD and wet impregnation were studied with temperature-programmed reduction and x-ray photoelectron spectroscopy experiments. Catalysts containing MoO_x show a decrease in CO chemisorption, relative to the pure Rh catalyst. Together, these results demonstrate that MoO_x significantly alters the physical and chemical properties of the Rh catalysts.

8:15am AA+NS-MoM-2 Facile Synthesis of Three-Dimensional Pt-TiO₂ Nano-networks: A Highly Active Catalyst for the Hydrolytic Dehydrogenation of Ammonia-Borane, *Hamit Eren*, Delft University of Technology, Netherlands; *N Biyikli*, Utah State University; *M Guler*, Northwestern University

Three-dimensional (3D) porous metal and metal oxide nanostructures have recently attracted considerable interest because assembly of bulk inorganic materials into 3D nanomaterials possesses extraordinary properties such as low density, high porosity, and high surface area. In this work, we exploited supramolecular self-assembled peptide nanostructures as 3D nanonetwork and sacrificial organic template for the fabrication of 3D Pt@TiO₂ nano-networks. A 3D peptide nanofiber aerogel was conformally coated with TiO₂ via atomic layer deposition (ALD) featuring sub-monolayer thickness precision. The 3D peptide-TiO₂ nano-network was further decorated with highly monodisperse Pt nanoparticles by using ozone-assisted ALD. 3D TiO₂ nanonetwork decorated with Pt nanoparticles shows superior catalytic activity in hydrolysis of ammonia borane generating 3 equivalents of H₂.

Pt particle size and loadings were tuned by altering the number of Pt ALD cycles. The Pt₂₅@TiO₂ with ca. 2.4 nm particle size showed superior catalytic activity in H₂ generation from AB with a TOF value of 311/min at room temperature. Moreover, Pt leaching was fairly low from 3D Pt@TiO₂ nano-networks. Combination of supramolecular peptide nanofiber 3D templates with ALD technique allows facile, straightforward, and highly

reproducible preparation of metal, metal oxide, and semiconductor 3D nanomaterials as next-generation nanocatalysts with light weight, highsurface-area and porosity.

8:30am AA+NS-MoM-3 Cobalt/Alumina Interactions in ALD Synthesized Catalysts for Fischer-Tropsch Synthesis, *Jacob Clary, S Van Norman, H Funke, J Falconer, C Musgrave, A Weimer*, University of Colorado - Boulder
Cobalt metal was deposited onto an alumina (Al₂O₃) support using atomic layer deposition (ALD) to create dispersed catalysts for Fischer-Tropsch Synthesis (FTS). These catalysts are highly active for the FTS reaction, exhibiting triple the cobalt mass activity of standard incipient wetness catalysts at similar reaction conditions. HRTEM imaging shows that cobalt has simultaneously deposited during ALD in both crystalline plane and nanoparticle regimes, regardless of the number of ALD cycles. However, it was found that the number of ALD cycles alters the activity of these catalysts, with 4 and 8 cycle catalysts being much more active than the 1 cycle catalyst. The known structure sensitivity of FTS indicates that the crystalline cobalt regions are the active regions for FTS. The ALD process allows deposition of metallic cobalt onto Al₂O₃ with protective organic capping ligands, preventing cobalt oxidation and reconstruction in air prior to reaction. Additional ALD experiments on different phases of Al₂O₃ followed by FTS testing proves the influence of support structure on the cobalt deposition regime and consequently FTS activity. Finally, density functional theory (DFT) calculations were done to understand the metal/support properties responsible for planar vs. nanoparticle growth during ALD and explain the high activity shown by these catalysts.

8:45am AA+NS-MoM-4 ALD of Platinum on Metal Organic Framework Nodes: Toward Single Site Synthesis and Sinter-Resistant Catalysts, *I Kim*, Argonne National Laboratory, USA; *Alex Martinson*, Argonne National Laboratory

The connectivity of NU-1000, a metal-organic framework (MOF), gives rise to Zr₆ nodes with hydroxyl-containing functional groups pointing into the large 1D mesoporous hexagonal channels of the framework. These free and exposed -OH groups are ideal grafting sites for atomic layer deposition (ALD). Through ALD in MOFs (AIM), we demonstrate the ability to form monodisperse Pt clusters with atomic precision without significantly changing the overall structure of the framework. An experimentally and computationally informed mechanism for the low temperature surface reaction of MeCpPtMe₃ will be presented. The resulting platinum clusters on Zr₆ nodes also provide a unique opportunity to test the ability of MOF node "islands" to inhibit Pt atom migration under catalytic conditions. Computational, synchrotron, and in situ and operando analytical methods including FTIR and extended X-ray absorption fine structure (EXAFS) are brought to bear on this uniquely active ethylene hydrogenation catalyst.

9:00am AA+NS-MoM-5 Particle Atomic Layer Deposition for Stabilization of Pt/C Fuel Cell Catalysts, *William McNeary, A Lubers, M Maguire*, University of Colorado - Boulder; *S van Rooij*, Ecole Polytechnique Fédérale de Lausanne, Switzerland; *S Bull, A Weimer*, University of Colorado - Boulder

As a highly efficient, portable, non-greenhouse gas emitting source of electrical power, the proton exchange membrane (PEM) fuel cell holds great potential as a replacement for the internal combustion engine. One of the most significant development challenges in the commercialization of the PEM fuel cell is the long-term durability of the catalyst material. Cathode potential cycling—resulting from the variable voltage loads imposed during vehicular operation—is known to promote agglomeration and growth of the Pt nanoparticle catalyst, which in turn degrades the power output of the fuel cell. In this work, atomic layer deposition (ALD) was used to deposit protective TiO₂ films onto commercial Pt/C catalyst in order to increase its electrochemical durability. Deposition half-reactions during fluidized bed particle ALD were observed via in-situ mass spectrometry, and chemisorption analysis was used to quantify changes in Pt surface area following TiO₂ deposition. Rotating disk electrode analysis indicated that although electrochemical surface area (ECSA) was slightly depressed by the addition of TiO₂ ALD layers, catalyst activity of the coated samples was improved, likely due to beneficial interactions between the metal oxide and Pt. Activity retention during electrochemical durability testing was greatly improved, with TiO₂-coated catalysts retaining upwards of 70% of their initial activity. Examination of catalysts before and after testing also showed that TiO₂ ALD layers were effective at preventing Pt agglomeration under fuel cell operating conditions.

9:15am **AA+NS-MoM-6 ALD CeO₂ to Improve Catalytic Activity and Thermal Stability of Low Temperature SOFC Electrodes**, *J Yu, S Oh*, Seoul National University of Science and Technology, Republic of Korea; *W Noh*, Air Liquide Laboratories Korea; *Jihwan An*, Seoul National University of Science and Technology, Republic of Korea

Solid oxide fuel cell(SOFC) is an energy conversion device which can convert chemical energy into electrical energy. SOFC is known to have several advantages over other types of energy devices: high efficiency, environmental cleanliness, and so on. SOFCs usually operate at high temperature(800-1000C), which, however, poses practical issues such as thermal degradation and material selection. Low-temperature SOFC(LT-SOFC, operating temperature <500C) is therefore attracting lots of attention from researchers.

Cathodic activation loss is the dominant loss in the operation of LT-SOFCs due to sluggish oxygen reduction reaction(ORR). Also the thermal degradation of metallic cathodes decreases the performance of LT-SOFCs, causing the practical issues in long-term operation. In this paper, we demonstrate that CeO₂ thin films deposited by atomic layer deposition(ALD) can significantly improve the reaction kinetics as well as the thermal stability of the Pt cathode in LT-SOFC. ALD CeO₂ layer can be employed as an interlayer between electrode and electrolyte, or an overlayer on top of electrode. In both ways, ALD CeO₂ helped to improve the oxygen reduction kinetics by up to a factor of 3, and the performance stability at long-term operation(>10hrs, 450C) by approximately one order of magnitude. ALD CeO₂ layer may be also applied to other energy conversion devices for simultaneous enhancement of performance and long-term stability.

9:30am **AA+NS-MoM-7 Atomic Layer Deposition of Metal Oxide Thin Films and Metal Nanoparticles for Improving the Electrode Performance in Photoelectrochemical Applications**, *Valerio Di Palma, M Verheijen*, Eindhoven University of Technology, Netherlands; *R Sinha, G Zafeiropoulos, A Bieberle, M Tsampas*, DIFFER, Dutch Institute for Fundamental Energy Research; *W Kessels, M Creatore*, Eindhoven University of Technology, Netherlands

Photoelectrochemical water splitting is considered a viable route to store solar energy into hydrogen. However, it presents several technical issues that hinder its development, such as low conversion efficiency and high overpotential, which is required to promote products' evolution. In this contribution we investigate selected ALD layers and their effect on the electrode performance, specifically in terms of current density and electrode stability in aqueous environment. Particularly, we address three case studies:

1) Hematite is known to be a suitable photoanode for photoelectrochemical water splitting. Charge recombination is, however, a limiting factor toward high current densities. ALD ZnO and TiO₂ were adopted as interlayer to prevent charge recombination at the interface between glass/fluorine doped tin oxide (FTO) and hematite. Cyclic voltammetry (CV) was used to compare the samples with and without ALD interlayer. It was shown that a 2 nm thick ZnO interlayer resulted in 25% increase in photocurrent density at 1.5 V_{RHE} along with a 200 mV cathodic shift in the onset potential, with respect to plain hematite thin film. Interestingly, a 1 nm thick TiO₂ interlayer deposited by plasma-assisted ALD showed better electrode performance (67% higher photocurrent at 1.5 V_{RHE}), compared to the thermally grown TiO₂.

2) 3D microstructured Ti₂/WO₃/BiVO₄ photoelectrodes necessitate protective layers to limit the photo-corrosion of BiVO₄ under high pH conditions. 2 nm thick thermal ALD TiO₂ was shown to lead to an increase by 25% of the photocurrent density peak in linear sweep voltammetry measurements, when compared to the pristine device.

3) ALD Pt nanoparticles (NPs) serve as electrocatalyst on 3D Ti and TiO₂ substrates. CV measurements show that an increase in the number of ALD cycles from 50 to 100 lead to an increase in electrochemical surface area by a factor of 8. Therefore, ALD prepared Pt NPs result to be highly dispersed and electrochemically active and can be employed in the production of hydrogen or oxygen evolution reaction on cost effective (photo)electrodes.

In conclusion, we showed that ALD is a powerful tool to design and fabricate interlayers, protective layers and metal NPs, with different morphologies (2D and 3D) to improve the photoelectrode performance in photoelectrochemical water splitting.

9:45am **AA+NS-MoM-8 Carbon-templated Nb:TiO₂ Nanostructures as Oxygen Evolution Catalyst Supports for PEM Electrolyzers**, *Alexander Hufnagel, D Böhm, S Häringer, D Fattakhova-Rohlfing, T Bein*, University of Munich (LMU), Germany

The generation of hydrogen via electrochemical water splitting in proton exchange membrane (PEM) electrolyzers is an appealing means of storing energy from fluctuating renewable generators (e.g. solar and wind). To improve efficiency and to decrease production cost, nanostructured conductive supports for the noble metal oxide oxygen evolution catalyst at the anode are required. Conductive oxides are inherently stable towards oxidation at the high anodic potentials. We used thermal ALD to conformally coat nanostructured carbon (soot) templates with mixed TiO₂/Nb₂O₅ films using alkoxides and water as precursors. The carbon stabilizes the nanostructure during annealing, yielding crystalline materials from which the carbon can be removed without structural collapse. This effectively results in the replication of the carbon nanostructure by the conductive oxide. The conductivity of the oxide material reaches up to 400 S cm⁻¹. This carrier material can be used flexibly as either a pre-formed film for transfer during membrane-electrode assembly (MEA) manufacture or as a powder for ink coating. The carrier was loaded with an OER catalyst developed in our group, consisting of ultrasmall Ru₂O_x nanoparticles and the OER performance and stability under operation were investigated.

References

- [1] J.-P. Niemelä, M. Karppinen *et al.*, *Thin Solid Films* **2014**, 551, 19–22.
- [2] P. Heikkilä, M. Vähä-Nissi *et al.* ALD2016, 24-27 July 2016, Dublin, Ireland
- [3] V. Pore, M. Järn *et al.*, *Cryst. Growth Des.* **2009**, 9, 2974–2978.

10:45am **AA+NS-MoM-12 Atomic Layer Deposition Route to Tailor Nanoalloys of Noble and Non-Noble Metals**, *Ranjith Karuparambil Ramachandran, J Dendooven, M Filez, V Galvita, H Poelman, E Solano, M Minjauw, K Devloo-Casier*, Ghent University, Belgium; *E Fonda*, Synchrotron SOLEIL, SAMBA Beamline, France; *D Hermida-Merino*, Netherlands Organisation for Scientific Research, DUBBLE@ESRF, France; *W Bras*, Netherlands Organisation for Scientific Research, DUBBLE@ESRF; *G Marin, C Detavernier*, Ghent University, Belgium

Bimetallic nanoparticles (BMNPs) play a pivotal role in optical, magnetic and electronic applications, and are true workhorses during the catalytic transformation of chemicals. In particular, supported Pt nanoparticles alloyed with In, Ga or Sn are highly selective catalysts for the dehydrogenation of propane to propylene. It is well established that the size and composition of the nanoparticles strongly impact the catalytic properties and performance. Yet, conventional synthesis strategies lack proper control over the nanoparticle morphology and composition. ALD has proven its potential for the size and composition controlled synthesis of supported BMNPs, but has to date only been applied for the synthesis of binary noble metal nanoparticles like Pt-Pd, Pt-Ru and Pd-Ru BMNPs. Extension of this approach to BMNPs containing non-noble metals has so far been hampered by unfavorable ALD chemistries to deposit non-noble metals in their elemental state. As a consequence, a strong need has arisen to develop alternative ALD-strategies which can deal with non-noble metals also.

We report a new ALD based procedure for the tailored synthesis of BMNPs containing a non-noble metal next to a noble metal (*ACS Nano*, 2016, **10**, 8770–8777), here exemplified for nanoalloys containing In as non-noble and Pt as noble metal. **Figure 1a** schematically describes the steps involved in the fabrication process of the Pt-In BMNPs. Thin layers of In₂O₃ and Pt are sequentially deposited by ALD, yielding a Pt/In₂O₃ bilayer structure. These bilayers are then subjected to a temperature programmed reduction (TPR) in hydrogen to induce the formation of Pt-In nanoalloys. The BMNP formation during TPR was followed by *in situ* XRD measurements (**Figure 1b**) and was further confirmed by *ex situ* XAS (**Figure 1c**) and SEM measurements. The composition of the formed bimetallic alloys can be tuned by controlling the ratio of the deposited thickness of Pt to the thickness of In₂O₃. **Figure 2a** presents the relation between the as-deposited Pt/(Pt+In) atomic ratio and the alloy phase(s) obtained after TPR. In addition, our method enables tuning of the particle size with high precision in a range from 1 to 30 nm by changing the total thickness of the ALD-grown Pt/In₂O₃ bilayer (**Figure 2b**). Tuning of the particle size while keeping the composition the same can thus be achieved by scaling the layer thicknesses of the Pt and In₂O₃ layers while keeping the Pt/(Pt+In) atomic ratio constant.

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Finally, successful BMNP synthesis was achieved on mesoporous silica, resulting in high surface area nanocatalysts which showed promising high activity for propane dehydrogenation (Figure 3).

11:00am **AA+NS-MoM-13 Aggregative Growth of Noble-Metal Nanoparticles in Atomic Layer Deposition: Effect of Temperature, Partial Pressure, Exposure Time, Coreactant, and Substrate**, *Fabio Grillo, H Van Bui, J Moulijn, M Kreutzer, J van Ommen*, Delft University of Technology, Netherlands

Already an established technique for the growth of conformal thin films, atomic layer deposition (ALD) is now emerging as an attractive route for the controlled growth of NPs. Compared to conventional synthesis routes, ALD boasts a number of advantages: atomic-level control over the amount of material being deposited, conformality, scalability to high-surface-area substrates, and its being solvent-free. Yet, bringing the unparalleled precision of ALD of thin films to ALD of NPs is not straightforward. The precision of ALD relies, in fact, on cyclic repetitions of self-saturating surface reactions that lead to the deposition of less than a monolayer per cycle. Hence, if the growth proceeds in a layer-by-layer fashion, as is the case with ALD of thin films, varying the number of cycles translates into tuning the film thickness with atomic-level precision. However, if the as-deposited atoms form into NPs upon deposition, a growth per cycle of less than a monolayer does not necessarily enable atomic-level control over the NP size. This is because the NP morphology (e.g., size, shape and number density) is dictated by atomistic processes other than "ALD reactions" such as surface diffusion and aggregation of atoms and NPs, and atom attachment to and from NPs. Understanding the role of such kinetic processes during the ALD of NPs is therefore crucial to the development of ALD routes for the synthesis of NPs with a well-defined morphology and thus functionality.

Here, we present an atomistic understanding of thermal ALD of Pt and Pd NPs on nanostructured oxides (TiO_2 , CeO_2 , ZnO , Al_2O_3 , SiO_2 , V_2O_5) and graphene nanoplatelets. In particular, we study the effect of temperature, number of cycles, coreactant (i.e., O_2 or H_2), and coreactant partial pressure and exposure time on the evolution of the NP size distribution and metal loading. Atomistic modelling of our experiments shows that the NPs grow mostly due to Smoluchowski aggregation, that is, NP diffusion and coalescence, rather than through single atom processes such as precursor chemisorption, single atom diffusion and attachment, and Ostwald ripening. While the metal loading can be precisely controlled over a wide range of temperatures, atomic-level precision over the NP size is retained only at low deposition temperatures ($T \leq 100^\circ\text{C}$) when growth by atom attachment/deposition becomes relevant. Furthermore, we show that the coreactant partial pressure and exposure time are far more important parameters for the NP size than the number of cycles. Crucially, high coreactant partial pressures significantly reduce the temperature window at a given exposure time.

11:15am **AA+NS-MoM-14 In situ Grazing Incidence Small Angle X-ray Scattering Study of the ALD Growth and Thermal Stability of Pt Nanoparticles**, *Jolien Dendooven, E Solano, R Ramachandran, M Minjauw*, Ghent University, Belgium; *A Coati*, Synchrotron SOLEIL, France; *D Hermida-Merino*, ESRF, France; *C Detavernier*, Ghent University, Belgium

Supported noble metal nanoparticles (NPs) are widely used in heterogeneous catalysis because of their high resistance against chemical poisoning. ALD can be used to synthesize noble metal NPs on different high surface area supports, and offers sub-monolayer control over the metal loading (atoms per cm^2 of support) [Lu et al., Surf. Sci. Rep. 71, 410, 2016]. However, an improved understanding of how the deposition parameters influence the formation and growth of noble metal NPs is required to fully exploit the tuning potential of ALD. In addition, it is important that the synthesized NPs remain stable at the elevated temperatures typically required to carry out the catalytic reactions. Particle coarsening, leading to a loss of active surface area, is the main cause for a diminishing activity and/or selectivity of NP catalysts.

We developed a synchrotron-compatible high-vacuum setup that enables *in situ* monitoring during ALD growth as well as during thermal treatments [Dendooven et al., Rev. Sci. Instrum. 87, 113905, 2016]. Using this setup, we investigated how the choice of reactant affects the island growth during ALD of Pt with the MeCpPtMe_3 precursor at 300°C . The Pt loading on planar SiO_2 supports was determined by means of X-ray fluorescence (XRF). Grazing incidence small-angle X-ray scattering (GISAXS) provided information on the evolution in Pt cluster shape, size and spacing. Surprisingly, a fundamentally different growth mechanism was found for Pt ALD using N_2 plasma as reactant [Longrie et al., ECS J. Solid State Sci.

Technol. 6, Q123, 2012] compared to the more conventional O_2 gas-based ALD process (Figure 1). While surface diffusion of atoms and/or clusters plays an important role during the latter process, a static growth mode is observed for the N_2 plasma-based process. This insight provided the ground for the development of a tuning strategy that is based on combining the O_2 -based and N_2 plasma-based ALD processes and offers independent control over NP size and coverage.

Secondly, *in situ* GISAXS was used to investigate the morphological evolution of these supported Pt NPs during annealing under different O_2 partial pressures, providing a nearly continuous set of data on the evolution of average particle size during the annealing (Figure 2). A systematic study revealed that the as-deposited morphology and O_2 concentration largely influence the onset temperature for Pt coarsening: bigger and more widely spaced NPs as well as larger O_2 concentrations entail a higher onset temperature for coarsening. This knowledge is vital towards an improved understanding of the mechanisms that govern Pt NP coarsening.

11:30am **AA+NS-MoM-15 High-Precision Growth of Metal Oxide Nanoparticles on Carbon Composites for Energy Related Applications**, *F Yang, Mato Knez*, CIC nanoGUNE, Spain

Transition metal oxides show great potential for numerous energy-related applications, including batteries or supercapacitors, due to their excellent catalytic activity or electrochemical properties. Zero-dimensional nanomaterials made of metal oxides, often used as active components in composites for electrode materials, promise great improvement of the performance upon integration into devices. ALD is a thin film deposition technology and therefore commonly used for growing 2D films on various substrates. However, it also offers the possibility to controllably fabricate nanoparticles if the substrate is appropriately chosen and its surface chemistry can be controlled. For example, given the chemical inertness of reduced graphene oxide (rGO) or carbon nanotubes (CNTs), metal oxides (like RuO_2 or Co_3O_4) will grow specifically on defect sites, which can be native or intentionally created. The density of the defect sites and in consequence the nanoparticles after ALD growth can be controlled by initial treatment of the substrate, while the size of the nanoparticles can be controlled with high accuracy by altering the number of applied processing cycles. After the nanoparticle growth, the fabricated rGO/ RuO_2 system exhibits improved capacitive performance with great promise for a use in supercapacitors, while the Co_3O_4 /CNT system shows excellent oxygen reduction reaction (ORR) activity with exceptional stability/durability upon further stabilization with a thin carbon shell. This presentation will give insight into the fabrication of the composites as well as the characterization of the electrochemical and catalytic performance of the materials.

11:45am **AA+NS-MoM-16 Tuning the Isoelectric Point of Conical Nanochannel Surfaces by Atomic Layer Deposition of Al_2O_3 , TiO_2 , and SiO_2 to Tailor Selective Ion Transport**, *Nils Ulrich, A Spende*, GSI Helmholtz Center, Germany; *N Sobel*, TU Darmstadt, Germany; *M Toimil-Molares, C Trautmann*, GSI Helmholtz Center, Germany

Solid state nanopores and in particular ion-track etched channels exhibit unique ion transport properties and functionalities including ion selectivity, ion current rectification, and responsive behavior to external stimuli such as pH-value, temperature or concentration of a specific ion. [1, 2]

The ion conductivity of a nanochannel is described by nanofluidic models exhibiting the surface charge as a determining parameter. [3]

Here, we apply atomic layer deposition of Al_2O_3 , TiO_2 and SiO_2 to conformally modify the surface of polymer track-etched membranes, fabricated by swift heavy ion irradiation and chemical etching. [4] The different isoelectric points of these oxides ($\text{Al}_2\text{O}_3 \sim \text{pH } 9$, $\text{TiO}_2 \sim \text{pH } 5$, $\text{SiO}_2 \sim \text{pH } 2$ [5]) allow us to tailor the surface charge of the nanochannels. The resulting inorganic and well-defined nanochannels constitute excellent model systems to study ion-transport characteristics.

We will present current-voltage measurements on single conical Al_2O_3 , TiO_2 and SiO_2 ALD-coated nanopores exhibiting tip diameters of approx. 100 nm. The dependency of current rectification as a function of surface material and electrolyte pH will be discussed. In all cases, ALD coating improved the stability of the channels exhibiting more reproducible ion conductivity than their uncoated counterparts, and enhanced long term stability.

The ion conductivity data are complemented by a detailed characterization of the channel morphology. For this, a supporting electrode is electrodeposited on the base side of the conical nanopore, the

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polycarbonate membrane is dissolved in an organic solvent, and the single freestanding cone is imaged by scanning electron microscopy. Complementary measurements on multi-channel membranes reveal a homogeneous deposition of the oxides inside all nanochannels as well as smooth inner and outer surfaces. EDX results prove the absence of contamination in the ALD layers. Moreover, the mechanical stability of the free-standing conical nanotubes reflects the expected behavior.

[1] Perez-Mitta G.; Albesa A.G.; Trautmann C.; Toimil-Molares M.E.; Azzaroni A. *Chem. Sci.* **2017**, *8*, 890-913

[2] Siwy Z.; Gu Y.; Spohr H.A.; Baur D.; Wolf-Reber A.; Spohr R.; Apel P.; Korchev Y.E. *Europhys. Lett. EPL* **2002**, *60* (3), 349-355

[3] Schoch R.; Han J.; Renaud P. *Rev. Mod. Phys.* **2008**, *80* (3), 839-883

[4] Cornelius T.W.; Apel P.Y.; Schiedt B.; Trautmann C.; Toimil-Molares M.E.; Karim S.; Neumann R. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **2007**, *265* (2), 553-557

[5] Barry Carter C.; Grant Norton M. *Ceramic Materials: Science and Engineering*; Springer Science, New York, **2007**

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Tsampas, M: AA+NS-MoM-7, **2**

— U —

Ulrich, N: AA+NS-MoM-16, **3**

— V —

Van Bui, H: AA+NS-MoM-13, **3**
Van Norman, S: AA+NS-MoM-3, **1**
van Ommen, J: AA+NS-MoM-13, **3**
van Rooij, S: AA+NS-MoM-5, **1**
Verheijen, M: AA+NS-MoM-7, **2**

— W —

Weimer, A: AA+NS-MoM-3, **1**; AA+NS-MoM-5, **1**

— Y —

Yang, F: AA+NS-MoM-15, **3**

Yang, N: AA+NS-MoM-1, **1**

Yu, J: AA+NS-MoM-6, **2**

— Z —

Zafeiropoulos, G: AA+NS-MoM-7, **2**