Monday Afternoon, June 27, 2022

ALD Applications
Room Van Rysselberghe - Session AA1-MoA

ALD for Catalysis

Moderator: Ashley R. Bielinski, Argonne National Laboratory

1:30pm **AA1-MoA-1 ALD Preparation of TiO_2-MnO_x/SiO_2 Catalyst for Selective Catalytic Reduction of Nitrogen Oxides***, **Saeed Saedy,*** Delft University of Technology, Netherlands*; D. Kazimierz ,* Paul Scherrer Institut, Switzerland*; D. Urbanas,* Vilnius Gediminas Technical University, Lithuania*; D. Ferri,* Paul Scherrer Institut, Switzerland*; J. van Ommen,* Delft University of Technology, Netherlands

The most efficient NO_x abatement process is the selective catalytic reduction using NH_3 (NO_x NH_3-SCR). The commercial V-based NH_3-SCR catalysts have a narrow high-temperature operational window of 350-450°C; this requires installing the catalyst bed before desulfurization and dust removal units, which initiates catalyst deactivation. To avoid this, the SCR unit is currently being placed in the so-called tail-end configuration, which results in exhaust gases temperature below the operational window of the commercial catalysts. Manganese oxide (MnO_x) catalysts show superior NH_3-SCR activity at low temperatures (LT). The various oxidation states (Mn^{2+},Mn^{3+},and Mn^{4+}) of MnO_x, are known to play an essential role in the LT activity of MnO_x catalysts; hence, the existence of multiple oxidation states of Mn is pivotal for its SCR activity. On the other hand, the crystalline MnO_x does not contribute effectively to NH_3-SCR; thus, the dispersion of MnO_x strongly affects SCR activity. The routine catalyst synthesis methods like precipitation impregnation, and sol-gel, are less suitable for preparing MnO_x SCR catalysts since they often require high-temperature post-treatments, which increase the crystallinity of particles and decrease dispersion.

Atomic layer deposition (ALD) offers a reliable LT coating method, with subnanometer control over the process. ALD makes it possible to obtain metal oxide nano-coatings at temperatures significantly lower than conventional methods. In this work, we have employed fluidized bed ALD to deposit highly dispersed MnO_x on SiO_2 for LT NH_3-SCR catalysis. The ultra-fine MnO_x NPs were grown on SiO_2 at 150°C and 1 bar. Additionally, we deposited TiO_2 on ALD prepared MnO_x/SiO_2 to increase the acidity of the catalyst, which is crucial for NH_3 activation during the SCR process. The XPS analysis revealed three oxidation states of Mn^{2+}, Mn^{3+},and Mn^{4+} in these samples, which are essential for NO_x-SCR. Also, powder XRD could not detect any crystalline phases of MnO_x, suggesting that ALD synthesis avoided the crystalline MnO_x; consistently, the MnO_x NPs were scarcely observable using TEM, demonstrating extreme dispersion of MnO_x over SiO_2. NH_3 temperature-programed desorption analysis demonstrated that the acidity of the MnO_x/SiO_2 sample is significantly increased after TiO_2 ALD, increasing the NH_3 activation on TiO_2-MnO_x/SiO_2. The obtained TiO_2-MnO_x/SiO_2 with such characteristics provide a promising catalyst for low-temperature selective catalytic reduction of nitrogen oxides. Accordingly, the catalytic activity evaluation showed~85% NO conversion for the TiO_2-MnO_x/SiO_2 sample, while the MnO_x/SiO_2 sample showed a NO conversion of~30%.

1:45pm **AA1-MoA-2 Unravelling the Mechanism of Electrochemical Activation of ALD Cobalt Phosphate by Digital Control Over Its Chemical Composition***, G. van Straaten, R. Zhang, E. Kessels,* Eindhoven University of Technology, The Netherlands*; R. van de Sanden, M. Tsampas,* Dutch Institute for Fundamental Energy Research, Netherlands*; **Mariadriana Creatore,*** Eindhoven University of Technology, The Netherlands

Storage of electricity into molecules is the most viable answer to the intermittency of renewable sources. In this respect, H_2O splitting to H_2 and O_2 is key to enable the usage of H_2 as fuel for transport, as well as building block together with CO for the electrosynthesis of hydrocarbons. For the O_2 evolution half reaction (OER), cobalt phosphate (CoPi) is interesting because it behaves as bulk electro-catalyst, with electrochemically active Co^{3+} centers. In parallel with others [1], we have demonstrated the synthesis of amorphous CoPi films by ALD [2]. CoPi was prepared by combining ALD of CoO_x from cobaltocene and O_2 plasma, with cycles of trimethyl phosphate and O_2 plasma, according to an ABCD scheme [2,3]. We have also shown that ALD CoPi films are characterized by OER performances beyond those achieved by traditional electro-deposited films [3].

In the present contribution we focus on the mechanism behind the enhancement of the catalytic activity of ALD CoPi when tuning the Co-to-P ratio in the film. We show that CoPi films progressively undergo activation under alkaline conditions (ph=8-14) with increasing number of cyclic voltammetry (CV) cycles. During this activation process induced by the infiltration of the electrolyte in the bulk of the film, the current density increases in parallel with the leaching of phosphorus out of the electro-catalyst and the shift of the oxidation state of cobalt from Co^{2+} to Co^{3+} [4]. In parallel, the film undergoes a change in morphology upon activation. CV analysis and Rutherford backscattering measurements indicate that after activation, as much as 22% of all cobalt content in the film becomes accessible to the electrolyte and is activated. The electrochemical surface area (ECSA), i.e. the surface area accessible to promote H_2O splitting, increases up to a factor of 30, accompanied by a current density of 5 mA/cm^2. The increase in ECSA is strongly dependent on the composition of the pristine CoPi films: while the above-mentioned 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 4. We find that for all investigated Co-to-P ratios, the electrochemical activity scales linearly with ECSA upon activation. It can be concluded that the digital control over the chemical composition of CoPi offers a novel merit to ALD: unravelling the mechanism behind CoPi electrochemical activation.

[1] J. Ronge et al., Nanoscale Adv. 1, 4166 (2019)

[2]V. Di Palma et al., Electrochem. Commun. 98, 73 (2019)

[3] V. Di Palma et al., J. Vac. Sci. Technol. 38, 022416 (2020)

[4] R. Zhang et al., ACS Catal.11, 2774 (2021)

2:00pm **AA1-MoA-3 Increasing ALD Complexity: How to Transform Ternary Oxide Films Into Tunable Bimetallic Thin Films and Nanoparticles***, J. Feng, **Matthias Filez**, M. Minjauw, E. Solano, C. Detavernier, J. Dendooven,* Ghent University, Belgium

ALD of ternary compounds ($A_mB_nC_o$) typically combines two binary ALD processes, each consisting of a metal precursor source and a co-reactant. Recently, however, we have demonstrated that ternary compounds, in casu $MRuO_x$ (M = Al, Pt), can be deposited using a single binary ALD process, thus reducing deposition complexity.[1] During such process, metal-organic precursors ($MeCpPtMe_3$ and TMA) are combined with RuO_4, the latter functioning both as metal source and co-reactant which combusts organic ligands. Yet, such multi-constituent co-reactant limits deposition to ternary compounds, such as $MRuO_x$, while often metallic MRu films or nanoparticles (NPs) are desired. Herein, we show that by increasing the complexity of the original $MRuO_x$ process by adding extra 'functionalities', such as reduction or even etching steps, bimetallic films and NPs can be deposited with full thickness and compositional control. This approach therefore significantly extends the applicability of the original process toward bimetallic compounds.

We first show that ALD of bimetallic PdRu films can be achieved by inserting a RuO_4 step in the $Pd(hfac)_2$ / H_2-plasma (H_2*) process, leading to a three-step $Pd(hfac)_2$ / RuO_4 / H_2* process with a high growth per cycle of 0.19 nm/cycle.[1, 2] Herein, RuO_4 acts both as an oxidizing agent and a Ru source, while H_2* reduces the surface. Thin films resulting from this process are Ru-rich, and we show that the Pd content can be increased by not including the RuO_4 step in every cycle, thus decreasing the incidence rate of the RuO_4 step in the ALD process (Fig. 1).

Next, by replacing part of the RuO_4 units in the three-step process by O_2*, the morphology of the PdRu is transformed from thin films to bimetallic nanoparticles (BMNPs, Fig. 2). This change of morphology is attributed to the etching of the deposited Ru as volatile RuO_4 during the O_2* steps. In situ grazing-incidence small-angle X-ray scattering and X-ray fluorescence revealed that the composition and size of the BMNPs can be adjusted independently by changing the proportion of RuO_4 versus O_2* pulses in the sequence, and the total number of ALD cycles, respectively. Finally, grazing-incidence wide-angle X-ray scattering and electron energy loss spectroscopy revealed that the RuPd BMNPs are crystalline, and Ru and Pd intimately mixed, suggesting the formation of solid-solution RuPd nanoalloys.

[1]Minjauw, M. M. et al. (2022).*Dalt. Trans.* Advance Article (DOI: 10.1039/D1DT03543F)

[2]Feng, J. Y. et al. (2020).*Phys. Chem. Chem. Phys.*, **22**, 9124–9136.

2:15pm **AA1-MoA-4 Tunable TiO_2-BN-Pd Nanofibers by Combining Electrospinning and Atomic Layer Deposition to Enhance Photodegradation of Acetaminophen***, **Syreina Alsayegh,*** Institut Européen des Memabranes, France*; M. Bechelany,* Institut Européen des Membranes, France*; F. TANOS,* Institut Européen des membranes, France*; A. NADA, G. LESAGE, F. Zaviska,* Institut Européen des Membranes, France*; M. Weber,* Laboratoire des Matériaux et du Génie Physique LMGP , France

The demand for fresh and clean water sources increases globally, and there is a need to develop novel routes to eliminate micropollutants and other harmful species from water. Photocatalysis is a promising alternative green technology that has shown great performance in the degradation of persistent pollutants. Titanium dioxide is the most used catalyst owing to his attractive physico-chemical properties, but this semiconductor presents limitations in the photocatalysis process due to the high band gap and the fast recombination of the photogenerated carriers. Herein, a novel photocatalyst has been developed, based on titanium dioxide nanofibers (TiO_2 NFs) synthesized by electrospinning. The TiO_2 NFs were coated by atomic layer deposition (ALD) to grow boron nitride (BN) and palladium (Pd) on their surface. The UV-Vis spectroscopy measurements confirmed the increase of the band gap and the extension of the spectral response to the visible range. The obtained TiO_2/BN/Pd nanofibers were then tested for photocatalysis, and showed a drastic increase of acetaminophen (ACT) degradation (>90%), compared to only 20% degradation obtained with pure TiO_2 after 4h of visible light irradiation. The high photocatalytic activity was attributed to the good dispersion of Pd NPs on TiO_2-BN nanofibers, leading to a higher transfer of photoexcited charges carriers and a decrease of photogenerated electron-holes recombination. To confirm their reusability, recycling tests on the hybrid photocatalyst TiO_2/BN/Pd have been performed, showing a good stability over 5 cycles under UV and Visible light. Moreover, toxicity testsas well as quenching tests were carried out to check the toxicity in the formation of byproductsand to determine active species responsible for the degradation. The results presented in this work demonstrate the potential of TiO_2/BN/Pd nanomaterials, and open new prospects for the preparation of tunable photocatalysts.

Keywords: TiO_2-BN-Pd nanocomposites; nanofibers, electrospinning; atomic layer deposition; photocatalysis; acetaminophen

2:30pm **AA1-MoA-5 Ultra-Low Dimensional Ir-Ru Thin-Film by Atomic Layer Deposition on Porous Titanium Felt Substrate for Electrochemical Water Splitting Application***, **Rahul Ramesh**, N. Park, T. Cheon,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)*; M. Byeon, T. Hong,* Busan Center, Korea Basic Science Institute, Korea (Republic of)*; S. Kim,* School of Materials Science and Engineering, Yeungnam University, Korea (Republic of)

Iridium (Ir) and ruthenium (Ru) are crucial ingredient in various applications, and their proper utilization is essential due to the extreme rarity of those elements. For example, in the case of electrocatalysis, only the surface participate in the reaction, and whatever lies beneath (within the nanoparticle or thin film) are un-utilized. Therefore, fabrication of Ir/Ru thin-film with high uniformity and conformality onto high surface area porous substrate is beneficial to reduce the metal content and increase its utilization. Atomic layer deposition (ALD) can be used to deposit uniform and conformal films with precise thickness control. In this study, we report the fabrication of ultra-low dimension (~5 nm) Ir-Ru thin film on to porous Ti felt substrate using a sequential approach with two precious metal ALD processes. The nano-secondary ion mass spectrometer depth-profiling (Nano-SIMS) results confirm the homogeneous, conformal and uniform growth of Ir-Ru thin film as predicted from the ideal ALD growth characteristic and XTEM on Si substrate. The electrochemical performance of Ir-Ru nanolayer electrode towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are evaluated in an acid electrolyte (0.5 M H_2SO_4). The Ru film shows the highest onset for HER (-112 mV), the Ir (5 nm) and Ir-Ru (5 nm) has an HER onset potential of ~-50 mV. In the case of the OER voltammogram, all the electrodes with precious metal films show the current due to OER. Contrary to the HER, here Ru shows the highest activity both in terms of OER onset potential and the overpotential at a specific current density; noteworthy the slightly better activity of 5 nm Ir film is attributed to the Ru nucleation layer (~2 nm) deposited on to the Ti substrate for uniform deposition of Ir, since, there is a huge nucleation delay for Ir ALD on Ti-based substrate. The stability of the film is characterized by chrono-potentiometric stability analysis for 24 hours at an OER current density of 10 mA cm^{-2}. As expected the Ru film is very unstable during OER and complete dissolution of 5 nm film happens at around ~4 hour of operation. However, the Ir-Ru (5 nm) display enhanced stability and is attributed to the inclusion of Ir. In conclusion, ALD can be used as an efficient technique to coat ultra-low dimension Ir-Ru thin film/nano-materials on to porous substrate with precise thickness control and high conformality, which is beneficial in terms of utilization and cost-effectiveness of electrocatalyst.

Acknowledgements

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2:45pm **AA1-MoA-6 Influence of Co/Ni Ratio on OER-catalytic Performance of Atomic Layer Deposited Nickel Cobalt Oxide***, **Renee van Limpt,*** Eindhoven University of Technology, Netherlands*; M. Lavorenti, M. Tsampas,* Dutch Institute for Fundamental Energy Research, Netherlands*; A. Creatore,* Eindhoven University of Technology, Netherlands

A promising approach to answer the challenge of intermittency of renewable sources such as wind and solar energy, is to store green electricity into H_2 via H_2O electrolysis. Sustainable electrolysis can be achieved, for example, under alkaline conditions, with the sluggish oxygen evolution reaction (OER) representing the main limitation. Mixed oxides of the earth-abundant cobalt and nickel are considered promising OER electrocatalysts. Cobalt nickel oxide ($Co_xNi_{1-x}O_y$) can adopt both the Co_3O_4 spinel and the NiO rock-salt structure depending on the cobalt concentration. The present study aims at exploring the effect of cobalt concentration in $Co_xNi_{1-x}O_y$ on the OER catalytic activity to expand on previous literature studies which are either limited to single phase structures[1, 2] or disregard the effect of bulk (film thickness >5 nm) effects[3].

Atomic layer deposition (ALD) offers the opportunity to tune the stoichiometry and therefore the structure of $Co_xNi_{1-x}O_y$. This work therefore employs plasma-enhanced ALD by combining a cobalt cyclopentadienyl ($Co(Cp)_2$)[4] based process for CoO_x with a nickel methylcyclopentadienyl ($Ni(MeCp)_2$) process[5] for NiO_x. Energy Dispersive X-ray mapping shows no variation in elemental composition, indicating that nickel intermixes with cobalt to form an alloy. X-ray spectroscopy (XPS) furthermore reveals the presence of mixed Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{3+} valence states, with an increase in the Ni^{3+}-to-Ni^{2+} ratio for increasing cobalt concentrations. Preliminary x-ray diffraction measurements furthermore suggest a transition from rock-salt to spinel phase with increasing cobalt concentration, indicating that nickel occupies the octahedral sites in the spinel structure at high cobalt concentrations. The OER activity of $Co_xNi_{1-x}O_y$ films (~30 nm) is determined by cyclic voltammetry (CV) in 1M KOH. The current density at 1.8 V vs RHE increases whilst the onset potential decreases, with a decrease in cobalt concentration in the film. An increased number of CV cycles leads to an increase in the current density, suggesting the activation of the bulk of the electrocatalyst. After CV, XPS reveals a dominant Ni^{3+} oxidation state in the film and an increase in oxygen concentration and hydroxide phase. These results indicate that the rock-salt phase is favourable for OER, implying that further research should focus on low cobalt- content $Co_xNi_{1-x}O_y$.

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[2]A. Asho etl al., *Int. J. Hydrogen Energy*, 2019.

[3]L. Trotochaud et al., *J. Am. Chem. Soc.*, 2012.

[4]M. E. Donders et al. *J. Electrochem. Soc.*, 2011.

[5]D. Koushik *et al.*, *J. Mater. Chem. C*, 2019.

3:00pm **AA1-MoA-7 Fundamental Studies of s-ALD Grown Iridium Thin Films on Planar Substrates for Acidic Water Splitting***, J. Shen ,* TNO-Holst Centre, Netherlands*; P. Shirvanian,* TNO-STIP, Netherlands*; E. Balder,* TNO-Holst Centre, Netherlands*; B. van Dijk,* TNO-STIP, Netherlands*; N. Huijssen, A. Bronneberg, P. Poodt, **Mahmoud Ameen,*** TNO-Holst Centre, Netherlands

One of our greatest challenges for the upcoming decades is the transition to a sustainable way of generating, storing, and converting energy. Green hydrogen produced by PEM Water Electrolyzers (PEMWE's) is part of the solution, but still faces several challenges. Among the major challenges towards widespread adoption and commercialization of PEMWE's are the cost, performance, and durability of iridium (Ir) material as used to catalyze the oxygen evolution reaction (OER) [1]. Sluggish OER kinetics and ensuing large overpotential above the thermodynamic equilibrium level required to drive the reaction will inevitably result in PEMWE inefficiency along with high catalyst loadings. It has previously been demonstrated that atomic layer deposition (ALD) can be used to deposit high quality and stable electrocatalyst layers with a low Ir loading [2], but the low deposition rate of ALD limits up-scaling for mass production. Spatial atomic layer deposition (sALD) has emerged as a viable tool for the atomically precise design and synthesis of materials with high deposition rates on both large substrates (square meters) and roll-to-roll [3].

Herein, we present an atmospheric-pressure spatial ALD process of Ir/IrO_x ultra-thin films on flat substrates. We investigate the temperature window of the ALD process down to 80 degrees. We study the growth characteristics as well as the thin film properties using ellipsometry, inductively coupled plasma mass spectrometry (ICP-MS), X-ray photoelectron spectroscopy (XPS) and grazing incidence X-ray diffraction (GIXRD). Furthermore, we evaluate the OER catalytic behaviour and durability using rotating disc electrode (RDE). Our study sheds light on structure, thickness, and morphology of Ir deposits and corresponding OER catalytic properties. The findings will pave the way towards identifying optimal catalytic system with the promise of ultra-low Ir loading at high OER performances.

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3:15pm **AA1-MoA-8 Functionalization of MoS_2 With Noble Metal by Atomic Layer Deposition for Hydrogen Evolution Reaction**

JungYub Lee*, J. Kim, I. Sohn, S. Chung, H. Kim,* School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)

Hydrogen is a good, sustainable alternative energy that can replace fossil fuels that cause air pollution and global warming. To produce hydrogen, electrochemical water splitting is the promising sustainable method without producing carbon containing pollutant.[1]

Platinum has been widely used for hydrogen evolution reaction(HER) for its high performance compared to other materials. However, platinum faces the problem in commercial use because of its low cost efficiency. In order to replace platinum, Transition Metal DichalCogenides(TMDCs) have been actively researched, which have a high surface-to-volume ratio and provide a sufficient number of active sites.[2] To further enhance the HER performance of TMDCs, many research has focused on the structure of TMDCs, defect engineering and heterojunction with graphene. However, this research will highlight the signficance of Pt and its better performance than those methods. To prove, this study will funtionalize TMDCs with the very small amount of noble metals, including Pt and Ru. Atomic Layer Deposition(ALD) will be a key technique to control the amount of noble metals and synthesize the uniform, conformal TMDCs on graphite foil.

Here we prepared catalyst using the noble metal functionalized MoS_2 synthesized on graphite foil by ALD. Various experimental methods were performed to analyze film growth characteristics including X-ray photoelectron spectroscopy (XPS) , Raman spectroscopy, Scanning Electron Microscope (SEM), X-ray diffraction and etc. The electrochemical properties of HER catalyst show high exchange current density and low Tafel slope compared with ALD MoS_2 film.

References

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Author Index

Bold page numbers indicate presenter