## ALD Applications
## Room 104-106 - Session AA2-WeA

### Catalytic Application

**Moderators:** Yongbeom Kim, Hanyang University, Min Hwan Lee, University of California Merced

1:30pm **AA2-WeA-1 Surface Treatment of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition***, **Min Hwan Lee**,* University of California Merced **INVITED**

The high operating temperature of solid oxide fuel cells (SOFCs) has limited their lifetime, cost competitiveness, start-up/shut-down speed and applicability to small-scale devices. Reduction of operating temperature, however, results in a dramatic loss of kinetics in both ionic transport and electrode reaction. In particular, sluggish electrode kinetics of oxygen reduction reaction (ORR) at the cathode side has been the main issue to resolve for a decent performance. As ORR of conventional intermediate-temperature SOFCs is often limited by dissociative adsorption and/or transport of electroactive species, an enlargement of catalytically active surface area while minimizing the transport distance is expected to improve the overall ORR kinetics significantly. For this end, a well-dispersed coating of nanoparticle-like catalysts on a cathodic backbone is achieved by e.g. infiltration of proper nitrate solution. The choice of infiltrated material can be mostly based upon catalytic activity and chemical inertness in the given environment, not limited by other criteria such as thermal expansion matching with underlying electrolyte and charge conductivity, which makes the material choice quite flexible. However, the merits of these high surface area structures come with susceptibility to thermal instability caused by particle agglomeration (by ripening and coarsening) during high-temperature operation. In this talk, we will present the application of atomic layer deposition (ALD) to form nanoscale oxide interfaces with platinum or lanthanum nickel ferrite (LNF or $LaNi_{0.6}$ $Fe_{0.4}O_{3-\Delta}$)-based cathodic backbones to tackle the concomitant issue of thermal instability. The impact of ALD treatments on the ORR kinetics, thermal degradation rate and changes in bottleneck process will be also discussed.

2:00pm **AA2-WeA-3 Bottom-Up ALD Engineering of FexCo1-xSy for Electrocatalytic Hydrogen Evolution***, **Wei Xiong**,* Peking University, China

The development of low-cost, efficient electrocatalyst for hydrogen generation from water (HER) is currently a core task for the hydrogen clean-energy technology. Generally speaking, an efficient electrocatalyst requires its bonding strengths with the reaction intermediates to be neither too high nor too low. Accordingly, the specific activity of a catalyst can be optimized by tuning the elemental composition of the catalyst. Experimentally, the tuning of the catalyst composition can be achieved by atomic layer deposition (ALD). Also, ALD allows for highly conformal loading of the catalyst as a thin coating layer onto a mesoscopically rough electrode support, which has a high surface area and therefore can further boost the overall electrocatalytic activity.

In this presentation, we will show a bottom-up strategy for designing an efficient ternary electrocatalyst by ALD.[1] The strategy involves two separate optimization steps: one is to optimize the specific activity of the catalyst material by ALD, and the other is to optimize the geometric structure of the catalyst support by fabricating a carbon nanotube (CNT) network on mesoscopically rough carbon cloth (CC). As an example, we optimize the composition of a promising ternary electrocatalyst of $Fe_xCo_{1-x}S_y$ via ALD, and the optimized $Fe_{0.54}Co_{0.46}S_{0.92}$/CNTs/CC electrode exhibits a fairly low HER overpotential of −70 mV for achieving −10 mA/cm$^2$ in current density in alkaline solution, which demonstrates the effectiveness of this ALD-based engineering strategy.

Reference

[1] Wei Xiong, Zheng Guo, Hao Li, Ran Zhao, Xinwei Wang,* “Rational Bottom-Up Engineering of Electrocatalysts by Atomic Layer Deposition: A Case Study of $Fe_xCo_{1-x}S_y$-Based Catalysts for Electrochemical Hydrogen Evolution”, ACS Energy Lett., **2017**, *2* (12), pp 2778–2785 .

2:15pm **AA2-WeA-4 Plasma Enhanced Atomic Layer Deposition of Iron Carbide for Electrocatalytic Hydrogen Evolution***, Z Liu, **Yulian Hu**, Q Chen,* Beijing Institute of Graphic Communication, China

A plasma enhanced atomic layer deposition process for depositing iron carbide ($Fe_3C$) thin films is reported, using bis(N,N'-di-tert-butylacetamidinato)iron(II) and $H_2$ plasma. The process shows an ideal self-limiting ALD growth fashion with a saturated film growth rate of 0.041 nm/cycle for a fairly wide process temperature window from 80 to 200°C. The surface morphology of iron carbide film is investigated by atomic force microscopy and scanning electron microscopy. X - ray diffraction, X - ray photoelectron spectroscopy and transmission electron microscopy are used to analyze the crystal phase, film composition and microstructure of iron carbide films. Using this ALD process, Carbon cloth could be uniformly and conformally coated by a thin layer of $Fe_3C$ to afford a nanostructured $Fe_3C$/CC composite. The ALD-prepared $Fe_3C$/CC composite is demonstrated to show excellent performance for electrocatalytic hydrogen evolution.

2:30pm **AA2-WeA-5 Gadolinia-doped Ceria Thin Film Fabricated by Atomic Layer Deposition for Enhancing ORR Kinetics of LT-SOFC***, **Hwichul Yang**, S Kim, Y Lim, Y Kim,* Hanyang University, Republic of Korea

Ceria($CeO_2$)-based material, including gadolinia-doped ceria(GDC), samaria-doped ceria(SDC) and yttria-doped ceria(YDC), has emerged as an electrolyte for low temperature solid-oxide fuel cells(LT-SOFCs) due to the high oxygen ion conductivity and oxygen-reduction reaction(ORR) kinetics compared to yttria-doped zirconia(YSZ) which is a standard electrolyte material for SOFC. Mainly, it has been used as a functional layer on YSZ for enhanced ORR kinetics because it is hard to use ceria-based material as a single electrolyte due to the reduction characteristic in hydrogen environment. Typically, small grain and nanocrystalline structure of this functional layer shows higher ORR kinetics, and thin film fabricated by atomic layer deposition(ALD) is well known for showing that characteristics. In this study, characteristics and effects of GDC functional layer fabricated by atomic layer deposition(ALD) was studied. Surface morphology and crystal structure of ALD/GDC was investigated by physical analysis methods. ALD/GDC functional layer has a small surface grain and nanocrystalline structure, which has lots of oxygen incorporation site and reduces polarization loss. By electrochemical impedance spectroscopy(EIS) method, reduced polarization loss was observed for ALD/GDC-applied cell. Current-voltage characteristic shows enhanced performance of ALD/GDC-applied cell. These results about ALD/GDC indicates that ALD-fabricated functional layer has superior characteristics for SOFC performance.

2:45pm **AA2-WeA-6 Atomic Layer Deposition of Palladium Nanoparticles on Nickel for Direct Methanol Solid Oxide Fuel Cell Catalysts***, **Junmo Koo**, D Jang, H Choi, J Kim,* Korea University, Republic of Korea*; H Jeong,* University of Illinois at Urbana-Champaign*; J Shim,* Korea University, Republic of Korea

Direct usage of methanol as a fuel of solid oxide fuel cells (SOFCs) has several advantages compared to hydrogen gas fuel. Liquide form of methanol enables easy and safe storage, and it can be utilized as fuel without any cumbersome reforming process. These advantages of methanol have drawn much attention in the field of fuel cell society. However, catalyst poisoning originated from residual carbon monoxide and slow reaction of DMSFOC electrode is the most urgent issue of DMSOFC. Among various catalyst for DMSOFC, platinum-ruthenium bimetallic catalyst has shown the best performance for methanol oxidation. High cost of Pt, however, hinders the widespread commercialization of DMSOFC. Recently, nickel is regarded as promising substitute of Pt/Ru catalyst for its reforming performance of alcohol and hydrocarbon and inexpensive price. However, unwanted carbon formation is occurred during electrochemical oxidation of methanol using Ni catalyst. Therefore, nickel-based alloys have been widely studied for the effective oxidation of methanol and avoid unwanted carbon coking of nickel catalyst. Palladium (Pd) is one of the strong candidate material for bimetallic nickel-based catalyst. Previous studies reported the enhanced catalytic activity and unwanted carbon deposition on anode surface originated from the existence of Pd.

Optimum structure of Ni/Pd bimetallic catalyst would be composed of well-dispersed Pd nanoparticles on Ni substrate due to relatively high price of Pd compared to that of Ni. Atomic layer deposition (ALD) was used in order to fabricate Pd nanoparticles because of its unique availability to deposit uniform film even on complex structures. In this study, Ni/Pd bimetallic catalyst for DMSOFC were evaluated by fuel cell performance, electrochemical impedance spectroscopy, and long term-stability. ALD-made Ni/Pd catalyst revealed enhanced performance and stability compared to sputter-made Ni/Pd catalyst, which represents the effectiveness of ALD technique for fabricating surface-modified catalyst with increase surface area for desired reactions.

3:00pm **AA2-WeA-7 Diffusion-Limited Atomic Layer Deposition: Realizing the Encapsulation of Homogeneous Catalysts**, ***Bin Zhang***, *S Zhang, H Liang, Y Qin,* Institute of Coal Chemistry, Chinese Academy of Sciences, China

The homogeneous metal complex catalysts play an important role in chemical engineering, biology and medicine industry. The heterogenization of homogeneous metal complex catalystshas performed both advantages of homogeneous (high activity and selectivity) and heterogeneous catalysts (reusability).Generally, the encapsulation of metal complexes via physical adsorption in the pore channels of porous materials is preferred, because it can maintain the properties and freedom of metal complexes. The big challenge is to precisely tailor the pore entrance size of the porous materials. Recently, we have realized the encapsulation of metal complexes into nanochannels of mesoporous materials by building a "hollow plug" at the pore entrance via diffusion-limited ALD[1]. The pore size of the hollow plug is precisely controlled on the sub-nanometer scale by changing the number of ALD cycles to encapsulate various metal complexes with different molecular sizes. Moreover, we have also investigated the effect of ALD parameters and cycles on the activity and reusability of heterogeneous catalysts by the encapsulation. This ALD-assisted encapsulation method has a wide application and can be applied to the encapsulation of most homogeneous catalysts into different mesoporous materials for various heterogeneous reactions.

1. Zhang, S.; Zhang, B.*; Liang, H.; Liu, Y.; Qiao, Y.; Qin Y.* *Angew. Chem. Int. Ed.* 2018, 57, 1091.

3:15pm **AA2-WeA-8 Ultrathin ALD Yttria-Stabilized Zirconia Overcoating on Metal Electrodes for Low Temperature Solid Oxide Fuel Cell**, ***Byung Chan Yang***, *D Go, S Oh, J Shin, J An,* Seoul National University of Science and Technology, Republic of Korea

Solid oxide fuel cells (SOFC) have attracted much attention as highly efficient, fuel-flexible, and eco-friendly energy conversion device. However, conventional SOFC have practical issues in applications to various fields due to high operating temperature (up to 1000℃). Recently, studies on low temperature SOFC (LT-SOFC) (≤ 500℃) which can be operated at a relatively low temperature have been actively conducted. However, since it is operated at a low temperature, electrochemical reaction at the electrode is lowered; therefore, the use of noble metal electrode is essential. However, thermal stability, in this case, is also reduced by using noble metal electrode at elevated temperature.

In this study, we show how to improve the thermal stability of metal electrode by depositing yttria-stabilized zirconia (YSZ) overlayer. We have improved the SOFC performance and thermal stability by applying the ultrathin (2-3nm) YSZ overlayer with varying composition. YSZ overlayers were deposited by atomic layer deposition (ALD) on Pt electrodes with 0, 8, 15, 30, and 100 mol% of $Y_2O_3$-doping in $ZrO_2$, respectively. Doping level was controlled by the relative cycle ratio between $Y_2O_3$ and $ZrO_2$ in of ALD process. Fuel cell performance were analyzed through I-V-P and EIS measurements, and the thermal stability was measured using chronoamperometry. The performance of the reference cell decreased by more than 50% after 10 hours of operation, while that of the cell with YSZ overlayer was maintained at > 90% even after 10 hours of operation. Also, the performance of 8mol%-doped YSZ overlayer was 450℃ to 1.46mW / $cm^2$, which was not different from 1.4mW / $cm^2$ of the reference cell. However, the performance of the cell with 15mol%-doped YSZ overlayer was ~10% higher than that of reference cell. These results show that ALD can effectively tune the composition of the 2-3nm-thick YSZ overlayer, which can hugely affect the SOFC performance as well as the thermal stability.

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