

Tuesday Afternoon Poster Sessions, July 23, 2019

ALD Applications

Room Evergreen Ballroom & Foyer - Session AA3-TuP

Catalysis and Sensor Applications Poster Session

AA3-TuP-1 Highly Dispersed Uniform Pt Catalysts on Carbon Support by Atomic Layer Deposition with Fluidized Bed Reactor(FBR), Jung-Yeon Park, W Hong, S Oh, Hyundai Motor Group, Republic of Korea; *W Lee, S Kwon,* Pusan National University, Republic of Korea

One of the key issues for fuel cell study is to increase the active surface area by controlling the size of Pt catalyst and reduce Pt loading to achieve high performance and cost savings. Atomic layer deposition (ALD) has recently received attention as an effective method for synthesis of nano catalyst since it allows precise control at the atomic level. In this study, Pt catalyst is synthesized using ALD directly on the surface of porous carbon support floated by fluidizing bed reactor (FBR). The oxygen functional group introduced on carbon surface through acid solution treatment provides reaction site of Pt precursor. In initial cycle, nucleation occurs on carbon surface, and high density 1-2 nm size uniform nanoparticle is formed. The Pt precursor adheres to the surface of already generated Pt and grows the Pt nanoparticle. Because of this growth mechanism, the size distribution of the particle is slightly wider at high cycles, but the size of the particle is controlled by the cycle and grows up to about 4 nm in 30 cycles. About 1 nm size particles have the highest active surface area, but in terms of catalyst performance, about 3 nm size particles show the best results under the Pt loading fixed condition. When the size of particle is not less than 3 nm, Pt exhibit physical properties as a catalyst and agglomeration of particles can be suppressed. To evaluate the catalyst performance of new processes, MEA optimization is important and this remains as a future plan.

AA3-TuP-3 Stabilizing Ultrasmall Colloidal Platinum Diphosphide (PtP₂) Nanocrystals with Atomic Layer Deposition Oxide for Neutral H₂O₂ Electrosynthesis, Hui Li, S Geyer, Wake Forest University

Despite recent demonstrations of various electrocatalysts for small amount hydrogen peroxide (H₂O₂) production with rotating ring-disk electrode technique, it is still a great challenge to develop an efficient, selective, and stable O₂-to-H₂O₂ electrocatalyst for realizing continuous on-site production of neutral hydrogen peroxide. Here we synthesize ultrasmall and monodisperse colloidal PtP₂ NCs which achieves nearly zero-overpotential and unit H₂O₂ selectivity at 0.27 V vs. RHE for ORR. DFT calculation suggests that the P play a key role in promoting associative hydrogenation of OOH* to H₂O₂ and suppressing the dissociative OOH* to O*. With precise ALD Al₂O₃ overcoat and activation, the proton-exchange membrane fuel cell (PEMFC) with 42Al₂O₃/PtP₂-600 catalyst achieves a maximum r(H₂O₂) of 2.26 mmol h⁻¹ cm⁻² and a highest current efficiency of 78.8% for 120 h. Under recycle mode, the accumulated neutral H₂O₂ concentration reaches up to 3wt% for 65 h and 1.21 mol L⁻¹ for 120 h, and which can be readily used for medical, food, and environmental applications.

AA3-TuP-5 Synthesis of Core Shell Nanocatalysts using Atomic Layer Deposition with Fluidized Bed Reactor for PEMFC, Seung-Jeong Oh, W Hong, J Park, Hyundai Motor Group, Republic of Korea; *W Lee, S Kwon,* Pusan National University, Republic of Korea

Proton Exchange Membrane Fuel Cells(PEMFC) have attracted significant interest as sources of renewable energy due to higher energy conversion efficiency than conventional internal combustion engines and zero-emission characteristics. Despite its great advantages, it is difficult to commercialize due to high stack cost. Among the parts, Platinum(Pt) catalyst is expensive and scarce, so it is important to maximize the catalyst activity with minimal usage. Many researchers have significantly focused on core shell nanocatalysts due to their great activity, selectivity and stability with reducing the Pt loading. To optimize the characteristics of core shell nanocatalysts, it is necessary to precisely control shell composition and thickness. With the Atomic Layer Deposition(ALD) process, the size of nanocatalysts and shell thickness could be finely tuned at atomic scale. In order to uniformly deposit the nanocatalysts on the porous carbon support with large surface area, ALD with Fluidized Bed Reactor(ALD-FBR) offers the solution. By dispersing the carbon powder in the chamber, particle agglomeration is prevented and nanocatalysts can be uniformly deposited.

In this work, we synthesized core shell nanocatalysts using ALD-FBR. We utilize Nickel(Ni), Ruthenium(Ru) for the core materials, and Pt for the shell

material. Ni(1-dimethylamino-2-methyl-2-butanolate)₂, η⁴-1,3-cyclohexadiene ruthenium tricarbonyl, and Trimethyl(methylcyclopentadienyl)platinum(IV) are used as Ni, Ru and Pt precursor, respectively. The size of nanocatalysts and shell thickness is controlled by changing each ALD cycles. TGA, XRD and HRTEM are used to examine the structural and chemical properties of core shell nanocatalysts. From EDX line profile analysis, shell material(Pt) is preferentially deposited on core nanoparticles(Ni, Ru). Electrochemical Surface Area(ECSA) and cell performance were measured by Cyclic Voltammetry(CV) and MEA test. Core shell nanocatalysts by ALD-FBR show higher ECSA and cell performance than commercial catalyst.

AA3-TuP-6 Porous Nanomembranes Grown by Atomic Layer Deposition: Self-Rolling in Solvent and their Sensing Applications, F Ma, Y Zhao, G Huang, Yong Feng Mei, Fudan University, China

Tubular microstructures of various materials have emerged as active agents for large-scale detoxification, sensing, and many other promising applications [1]. Generally, for sensing application, binding of specific recognition sites on tubular structures for targets molecule is engaged to achieve capture and detection of certain molecular [2]. The rolled-up technology [3,4] provide the possibility of producing microtubular structures with desired geometries and surface decoration on surface, which should be of great importance for real-time bio-sensing. In this study, porous nanomembranes were fabricated with high productivity by depositing active material on the surface of 3D polymer porous template with rough surface via atomic layer deposition technique [5]. The free-standing porous ZnO nanomembranes were obtained after the sacrificial template was removed at high temperature in oxygen. The rough surface of the template and the high temperature treatment make the surface of the nanomembrane with porous microstructure. Self-rolled porous ZnO nanomembranes were then prepared by sonication in chemical solvent. The porous surface was used as cysteine recognition sites for effective and selective binding of neurotransmitter compounds like dopamine (DA). Such selective binding is significantly enhanced by the high surface-to-volume-ratio of the porous structure. For sensing applications, dispersion solution containing rolled-up structures was dropped on the surface of glassy carbon electrode, and then cysteine recognition sites was self-assembled on porous ZnO nanomembrane to capture target DA molecules which induces concentration-dependent electrical signals. Detailed analyses demonstrate that increased mass transfer leads to the enhanced sensitivity for DA. The current strategy provides an opportunity to develop 3D biosensor for high-affinity capture-based detection of nerve agents and can be extended to environmental contamination field.

References:

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AA3-TuP-7 Fabrication and Characterization of Atomic Layer Deposited ZnO-based Ultra-thin Films for Hydrogen Sensing, Yan-Qiang Cao, A Li, Nanjing University, China

As a high-energy density, non-polluting renewable energy source, hydrogen is widely used in many fields such as industrial synthesis, fuel cells, and rocket propulsion. It is of great importance to develop reliable, fast, and precise hydrogen sensors so as to avoid possible explosion risks and harm. Due to the low cost, chemically and thermally stability, extremely abundant nanostructures and simple fabrication technique, ZnO as n-type semiconductor is widely used to detect reductive gases, such as hydrogen. Usually thin film-based sensor is more effective for improved gas sensing performance due to its small size, larger surface to volume ratio, and feasibility in integrated circuits. To date, research on ZnO ultra-thin film-based H₂ sensor is still lacking.

In this work, the ZnO ultra-thin films with varied thicknesses from 5 nm to 30 nm were grown on SiO₂ substrate at 200 °C using diethyl zinc (DEZ) and H₂O by atomic layer deposition (ALD), which could precisely control the thickness of the films down to values comparable to the Debye length. The effect of ZnO thickness and post-anneal on H₂ sensing, such as detection concentration, work temperature, and sensitivity has been carefully investigated. It is found that H₂ sensor based on 10 nm-thick ZnO ultrathin film exhibits better room temperature sensing performance with R_{air}/R_{gas} of 29 in 4000 ppm H₂. We also attempted to prepare Pt nanoparticles-decorated ZnO ultra-thin films by ALD. The impact of Pt NCs size and areal

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density on enhanced H₂ sensing of ZnO film sensor has been evaluated. The improved mechanism has been proposed.

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