PCSI
Room Keahou I - Session PCSI-WeA2
Materials for Catalysis, Energy Storage, and Energy Harvesting

Moderator: Mitsuru Takenaka, The University of Tokyo

2:35pm **PCSI-WeA2-14 Scalable Si-Based Metal-Insulator-Semiconductor Photoanodes for Water Oxidation Fabricated Using Nanosphere Lithography and Thin Film Reaction***, E. Yu,* ***Yunho Choi****, S. Wu, J. Risberg, S. Kim,* University of Texas at Austin

Photoelectrochemical (PEC) water splitting is a promising approach for converting solar energy into storable hydrogen, offering a sustainable alternative to fossil-based hydrogen production. PEC cells rely on semiconductor materials to absorb sunlight and generate mobile charge carriers that drive the hydrogen and oxygen evolution reactions. Si-based photoelectrodes are especially attractive due to their optimal bandgap, high charge mobility, long diffusion lengths, and cost-effective, scalable manufacturing process. To improve the stability of Si-based PEC cells, metal-insulator-semiconductor (MIS) structures have emerged as a promising approach [1]. MIS photoanodes integrate ultrathin insulating layers that protect the Si surface while maintaining charge transfer efficiency. The thickness of the insulator is critical:ultrathin layers facilitate effective charge tunneling, whereas thicker layers enhance long-term stability in corrosive environments.

In our previous work, we demonstrated that localized conduction paths formed via an Al/SiO_2 thin-film reaction enable low-resistance charge extraction through thick insulating layers, while also providing excellent stability and scalability to full-wafer photoanodes [2]. However, the performance of such photoelectrodes can be limited by nonuniformity in thin-film reaction behavior. We have now demonstrated a method for creating more controllable and uniform localized conduction paths on the photoanode by employing nanosphere lithography (NSL), a low-cost and highly scalable patterning technique. NSL is used to create a patterned mask for Al deposition that enables the density and locations of Al/SiO_2 thin-film reactions and consequently metal catalysts to be precisely controlled, leading to improvements in both photocurrent density and onset voltage. Moreover, a technique we have recently developed for extremely rapid large-area nanosphere monolayer formation [3] makes this patterning approach easily scalable to fabrication of full-wafer photoanodes and therefore, highly promising for large-scale PEC applications.

2:40pm **PCSI-WeA2-15 Development of Bi_2Te_3-based Thermoelectric Thin Films Using Advanced Pulsed Laser Deposition System***, Yakubu Sani Wudil,* King Fahd University, Saudi Arabia

This study presents the pulsed laser deposition of n-type selenium (Se)-doped bismuth telluride ($Bi_2Te_{2.7}Se_{0.3}$) and n-type bismuth telluride (Bi_2Te_3) nanostructures at varying substrate temperatures. The effects of substrate temperature on the structural, morphological, and thermoelectric properties of these nanostructures were systematically explored. Density functional theory (DFT) simulations were conducted to examine the electronic structures, partial, and total densities of states of the unit cells of the compounds. Surface and structural characterization revealed highly crystalline nanostructures with pronounced grain boundaries. A comparative analysis underscores the impact of Se inclusion on the thermoelectric performance of the Bi_2Te_3 matrix. The study also highlights the substrate temperature-dependent variations in the thermoelectric figure of merit (ZT). Notably, the room temperature thermoelectric power factors (PF) of 2765 μW/mK^2 for pure Bi_2Te_3 and 3179 μW/mK^2 for Se-doped Bi_2Te_3 demonstrate their promise for cooling and power generation applications. The Se-doped Bi_2Te_3 exhibited a room temperature ZT value of 0.92, representing a 30% improvement over the pure phase. This enhancement is attributed to the reduction in thermal conductivity due to increased phonon scattering at the interfaces in the doped material.

2:45pm **PCSI-WeA2-16 Molecularly Engineered Siloxane Binders: Elevating Lfp Cathode Efficiency Under High Active Mass Loading***, Asuman Celik-Kucuk, T. Abe,* Kyoto University, Japan

Previously, we demonstrated that siloxane structures (Sx@04 and Sx#O@06) mitigate the corrosive effects of LiTFSI by forming a protective layer on aluminum current collectors, enhancing lithium stability and battery performance *(Journal of Power Sources 556 (2023) 232520).* Our recent research revealed that siloxane-based polymers (Sx@04) used as binders in LiFePO4 (LFP) cathodes significantly improve rate capability and cycling stability compared to traditional binders like PVDF and PEO *(Journal of Power Sources 581 (2023) 233478).* Building on these findings, we focused on modifying siloxane-based binders (Sx#O@32) to further improve their performance in LFP cathode applications. Testing at 60°C showed that LFP cathodes with Sx#O@32 had superior cyclic stability at 0.5 C, outperforming both Sx@04 and PVDF. Even at high mass loadings, Sx#O@32 maintained better cycling stability than PVDF. Additionally, the Sx#O@32 binder reduced ionic diffusion resistance (Rp) and charge transfer resistance (Rct), facilitating smoother lithiation and delithiation during battery operation. This enhanced performance is attributed to the low internal resistance of the composite electrodes using Sx#O@32. The stronger adhesion observed in these electrodes is likely due to increased cohesion from network formation via anion solvation of low molecular weight siloxane oligomers, enhancing performance over Sx@04 and PVDF binders.

Biography: I hold dual PhDs in applied chemistry from Tohoku University (MEXT scholarship) and polymer chemistry from Gebze Technical University. With a strong background in organic and inorganic polymeric materials, I specialize in the design and application of advanced hybrid materials for electrochemical devices, including rechargeable batteries and fuel cells. My career includes work as an assistant professor at Marmara University and a visiting researcher at Kyoto University, contributing to significant projects like NEDO's RISING-2. I have authored 37 journal articles, hold two patents, and received prestigious awards such as the L'Oréal–UNESCO National Fellowship and a Hirose Foundation fellowship.

2:50pm **PCSI-WeA2-17 Minimizing Ion/Electron Pathways Through Ultrathin Conformal Holey Graphene Encapsulation in Li- and Mn-Rich Layered Oxide Cathodes for High-Performance Lithium-Ion Batteries***, Heejoon Ahn,* 222 Wangsimni-ro, Seongdong-gu, Republic of Korea*; S. Kim,* Hanyang University, Korea

Lithium-ion batteries (LIBs) are increasingly favored due to their attractive features. The design of the cathode in LIBs plays a critical role in determining cell capacity, operating voltage, and overall cost. Lithium- and manganese-rich (LMR) cathode materials stand out as promising candidates for the next generation of cathode materials due to their ability to operate at high voltages and provide capacity exceeding 250 mAh g^{-1}. However, despite these appealing characteristics, LMR faces challenges in commercialization due to factors such as poor rate capability and rapid capacity and voltage decay during cycling. These are closely associated with the fundamental structural issues arising from the two distinct phases of LMR materials, slow reaction kinetics and structural degradation occurring through side reactions between the electrode and electrolyte. In this study, we introduce a carbon encapsulation technique that integrates polyethylenimine (PEI) and holey graphene onto the LMR surface, aiming not only to augment electrical conductivity but also to facilitate ionic conductivity. Despite its low carbon content of 0.1 wt%, the suggested PEI/holey graphene-encapsulated LMR demonstrates enhanced cycle stability and rate performance for the LMR electrode. Moreover, the thin and uniform PEI/holey graphene encapsulation layer serves a dual purpose by easing the movement of Li^+/e^- on the LMR surface and providing a protective barrier against physical and chemical aggressions. Throughout cycling assessments, the PEI/holey graphene-encapsulated LMR mitigates the leaching of transition metals, mitigating microcrack formation and irreversible structural alterations compared to bare LMR. Consequently, the proposed PEI/holey graphene encapsulation emerges as an attractive technology for high-performance LIB design, concurrently elevating the cycle stability and rate performance of LMR electrodes.

2:55pm **PCSI-WeA2-18 The Interplay between Gaseous Water and Surface Hydroxyl on Diamond(001) via Hydrogen Bonding***, Huiqun Xiao, K. Huang,* Guangdong Technion Israel Institute of Technology, China

Hydrogen bonding plays a pivotal role in water sciences, governing dynamics such as proton transfer,[1-3] phase transition,[4]solvation,[5] and dissociation.[6]For example, Kumagai et al.[1] have demonstrated a relay reaction of proton-transfer of a chain of $H_2O(OH)n$ (n≤4) on Cu(110) via hydrogen bonding by inelastic electrons. For thermal reaction, Huang et al.[6] reported on the enhanced dissociation of $(H_2O)_2$ on Si(001) by intermolecular hydrogen bonding; the dissociation barrier of $(H_2O)_2$ was computed as 73-87 meV as against that of a single H_2O of 273-307 meV. Here, we describe the interplay between a surface hydroxyl on diamond(001) and a gaseous water via hydrogen bonding, as revealed by density functional theory simulations given in parts.

1. *Migration of hydroxyl on C(001) catalyzed by water.* It is found that surface hydroxyl on diamond(001) is capable of interacting with a gaseous water via hydrogen-bonding, forming a complex, OH(surf)...H_2O(ad), which exhibits enhanced adsorption energies of 0.47 eV. By a series of cooperative motions of this complex and the underlying substrate atoms, the adsorbed water molecule is dissociated; the resulting fragment of hydrogen recombines with the prior OH(surf) to form water, whereas the other fragment of hydroxyl is deposited to the adjacent carbon-dimer site. Effectively, this process represents the water-catalyzed migration of surface hydroxyl on C(001), exhibiting an isotropic barrier of 0.33 eV. These findings are in contrast to anisotropic migration of hydroxyl on diamond(001) in the absence of water; the barriers vary from 1.96 eV along [10] to 2.24 eV along [110].
2. *Self-catalyzed dissociation of water on C(001).*It has been established that the water physisorbs on C(001), from which there is a competition that strongly favors desorption (adsorption energy computed as 0.24 eV) over dissociation (barrier computed as 0.39 eV). The dissociation products are fragments of hydrogen (H) and hydroxyl (OH) at a surface dimer of C(001), at which the dynamics of a new incoming water molecule is altered. We find that this new incoming water is molecularly adsorbed over the surface hydroxyl via hydrogen bonding, leading to an enhanced adsorption energy of 0.52 eV. Subsequent dissociation proceeds in two steps, in which the adsorbed water first overcomes a barrier of 0.25 eV to a metastable state, and thereafter dissociates to form surface hydroxyl and hydrogen atoms at the neighboring dimer site (dissociation barrier computed as 0.39 eV). It follows that the dissociation of water proceeds in a self-catalyzed fashion, in which one product fragment (surface hydroxyl) enhances the dissociation significantly.

3:00pm **PCSI-WeA2-19 Development of High-Performance Hydrogen Generation Catalyst Based on Fluorine-Doped Tin Oxide Aerogel***, **Hyung-Ho Park,*** Yonsei University, Korea

The electrochemical hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are efficient methods for generating clean, sustainable, and dense energy sources. Nørskov's theoretical study states that Pt is the most effective catalyst for HER due to its low Gibbs free energy (ΔG ~0) or moderate M-H bonding toward H* adsorption. Unfortunately, its scarcity and high cost limit its practical use. To overcome these drawbacks, high surface area carbon in the form of core-shell, wrapped, or dispersed structures has been used as a metal catalyst support, forming complexes with the metal and providing impressive resistance against corrosion.

In this presentation, an "aerogel" system is introduced to fabricate an ultra-low-density and highly porous metal support of SnO_2.[1] The aim is to meet the fundamental criteria for an ideal metal support structure, including resistance to corrosion, high conductivity, high porosity, large specific surface area, and strong metal-support interaction. SnO_2 aerogel was synthesized using a sol-gel method, leveraging the benefits of an aerogel system to impart three significant advantages to SnO_2: ultra-low density, which reduces the electrode's weight; a large surface area to achieve optimal metal catalyst dispersion; and high porosity, facilitating ion insertion and mass transfer. Additionally, anion doping of SnO_2 with fluorine at the atomic level during synthesis was conducted to improve conductivity. This doping resulted in an observable bandgap expansion, and the one-step synthesized F-doped SnO_2 (F-SnO_2) exhibited higher conductivity, significantly reducing the electrochemical charge transfer resistance compared to undoped SnO_2. Subsequently, a sputtering technique was used to deposit nanometer-scale Pt on the colloidal F-SnO_2 surface. The resulting hybrid structure (F-SnO_2@Pt) demonstrated enhanced HER activity and impressive catalytic stability even after prolonged oxidation activity.[2]

[1] V. G. Parale, T. Kim, H. Choi, V. D. Phadtare, R. P. Dhavale, K. Kanamori, H.-H. Park, Adv. Mater. **2307772** (2024).

[2] T. Kim, S. B. Roy, S. Moon, S. Yoo, H. Choi, V. G. Parale, Y. Kim, J. Lee, S. C. Jun, K. Kang, S. Chun, K. Kanamori, H.-H. Park, ACS Nano. **16**, 1625 (2022)

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3:05pm **PCSI-WeA2-20 In Situ X-Ray Absorption Spectroscopy (XAS) Study of CeO_2-Based Catalysts for CO_2 to Methane Conversion***, **Irene Barba-Nieto,** Y. Wang, J. Moncada, J. Jimenez,* Brookhaven National Laboratory*; M. Fernández-García,* Instituto de Catálisis y Petroleoquímica (CSIC), Spain*; J. Rodriguez,* Brookhaven National Laboratory

Carbon dioxide (CO_2) is the primary gas responsible for the greenhouse effect in Earth's atmosphere, leading to higher global temperatures and climate change. In order to limit global warming to 1.5 ºC and achieve net zero carbon dioxide emissions by 2050, it is essential to advance industrial processes that facilitate the generation of clean fuels from CO_2; one of the most promising strategies in this regard is the utilization of CO_2 and its transformation into valuable chemicals.

This study examines the effectiveness of two catalyst types, Ru-CeO_2 and Ru-CeO_2-TiO_2 systems, for the conversion of CO_2 into methane. The results demonstrate that, despite a lower Ru content, TiO_2-containing systems exhibit significantly enhanced catalytic activity for CO_2 conversion to methane. To understand this fact, in situ X-ray absorption measurements have been carried out on the Ru K-edge and Ce L_3-edge analyzing their behavior under H_2, CO_2 and H_2+CO_2.

The XAS findings indicate that the presence of TiO_2 in the catalysts stabilizes the metallic state of Ru, which remains in this state during the methanation reaction. Moreover, TiO_2 promotes the formation of Ce^{3+}, enhancing the catalysts' reactivity. This effect is attributed to TiO_2 facilitating an electronic transfer at the interface and perturbing the regular fluorite geometry of ceria, thus promoting the presence of Ce^{3+}. The presence of Ce^{3+} significantly impacts the catalytic properties of the sample, aiding in the oxidation-reduction of Ce and stabilizing Ru. Consequently, the presence of reduced cerium plays a crucial role in determining the surface chemistry of the catalyst, crucial for efficiently converting CO_2 into methane.

3:10pm **PCSI-WeA2-21 Properties of Spongy Structured $BaTiO_3$ Prepared by R.F. Magnetron Sputtering for Energy Harvester***, S. Kim,* Department of Energy Materials & Chemical Engineering, Kyungpook National University, Republic of Korea*; **Sang-Shik Park,*** 1Department of Energy Materials & Chemical Engineering, Kyungpook National University, Republic of Korea

A sustainable energy-harvesting technique, which can transfer various forms of energy from the surrounding environment into electricity, could be an alternative to remedy the shortcomings of traditional battery technology [1-3]. New piezoelectric and triboelectric materials for energy harvesting are being widely researched to reduce their processing cost and complexity and to improve their energy conversion efficiency. In this study, $BaTiO_3$films of various thickness were deposited on Ni foams by R.F. magnetron sputtering to study the piezoelectric and triboelectric properties of the porous spongy structure materials. Then piezoelectric nanogenerators (PENGs) were prepared with spongy structured $BaTiO_3$and PDMS composite. The output performance exhibited a positive dependence on the thickness of the $BaTiO_3$film, pushing load, and poling. The PENG output voltage and current were 4.4 V and 0.453 μA at an applied stress of 120 N when poled with a 300 kV/cm electric field. The electrical properties of the fabricated PENG were stable even after 5,000 cycles of durability testing. The triboelectric nanogenerators (TENGs) were fabricated using spongy structured $BaTiO_3$and various polymer films as dielectrics and operated in a vertical contact separation mode. The maximum peak to peak voltage and current of the composite film-based triboelectric nanogenerator were 63.2 V and 6 μA, respectively. This study offers new insights into the design and fabrication of high output nanogenerators using spongy structured materials.

Author Index

Bold page numbers indicate presenter

— A —
Abe, Takeshi: PCSI-WeA2-16, 1
Ahn, Heejoon: PCSI-WeA2-17, **1**
— B —
Barba-Nieto, Irene: PCSI-WeA2-20, **2**
— C —
Celik-Kucuk, Asuman: PCSI-WeA2-16, **1**
Choi, Yunho: PCSI-WeA2-14, **1**
— F —
Fernández-García, Marcos: PCSI-WeA2-20, 2
— H —
Huang, Kai: PCSI-WeA2-18, 1
— J —
Jimenez, Juan D.: PCSI-WeA2-20, 2
— K —
Kim, Seon-A: PCSI-WeA2-21, 2
Kim, Suhun: PCSI-WeA2-14, 1
Kim, Sungwook: PCSI-WeA2-17, 1
— M —
Moncada, Jorge: PCSI-WeA2-20, 2
— P —
Park, Hyung-Ho: PCSI-WeA2-19, **2**
Park, Sang-Shik: PCSI-WeA2-21, **2**
— R —
Risberg, Joseph: PCSI-WeA2-14, 1
Rodriguez, José: PCSI-WeA2-20, 2
— W —
Wang, Yuxi: PCSI-WeA2-20, 2
Wu, Shang-Hsuan: PCSI-WeA2-14, 1
Wudil, Yakubu Sani: PCSI-WeA2-15, **1**
— X —
Xiao, Huiqun: PCSI-WeA2-18, **1**
— Y —
Yu, Edward: PCSI-WeA2-14, 1