

SYMP. 06.

Advanced Materials and Devices for Fuel Cell and Electrolysis Technologies

Oral Presentation



6-0130

The Puzzle of Magnetic Field Enhanced Water Oxidation

Zhichuan J. Xu*

Nanyang Technological University, Singapore

Applying an external magnetic field to electrochemical reactions is recently an interesting topic among the electrocatalysis community. Earlier studies have shown that the water oxidation reaction (also called oxygen evolution reaction, OER) can be promoted by an external magnetic field through the promoted bubble removal on the electrode surface. However, that is for the case under the high overpotential and high current applied. In 2019, it has been reported that the promotion of OER in alkaline by applying the field is related to the magnetism of the electrode materials. On the other hand, theoretically, the OER needs to consider the triplet O₂ formation, which involves the spin-polarized electron transfer. The spin-polarized electron transfer can be achieved by ferro(i) magnetic catalysts, however, which may not be easily proved experimentally. That is because in principle, an external magnetic field is not necessary for spin-polarized electron transfer on ferro(i)magnetic materials. It is also unclear about the reaction pathways with a consideration of spin-polarized electron transfer. The pH dependent enhancement has further generated confusion about the relation between magnetic field enhanced OER and the theoretical expectation. In addition, some magnetic catalysts do not exhibit any improvement under the magnetic field. All these phenomena have created a scientific puzzle, appealing to the community. In this talk, I will briefly discuss the progress of this field and several important experimental findings for solving the puzzle. The critical roles of magnetization, pinning effect, and pH dependent increment will be discussed in detail.

Short Bio: Zhichuan is a professor at the School of Materials Science and Engineering, Nanyang Technological University. He received his Ph.D. degree in Electroanalytical Chemistry and his B.S. degree in Chemistry from Lanzhou University, China. His Ph.D. training was received at Lanzhou University, Institute of Physics, CAS, and Brown University. He worked at the State University of New York at Binghamton as a Research Associate and at the Massachusetts Institute of Technology as a Postdoctoral Researcher. Dr. Xu has received several awards such as Chun-Tsung Endowment Outstanding Contribution Award - Excellent Scholar in 2018 and the Zhaowu Tian Prize for Energy Electrochemistry by the International Society of Electrochemistry (ISE) in 2019. He is a Fellow of the Royal Society of Chemistry (FRSC) and a Fellow of the Academy of Engineering Singapore (SAEng). He served as the president of the ECS Singapore Section. Dr. Xu is a Highly Cited Researcher by Clarivate Analytics, Web of Science since 2018.

*Corresponding author	Zhichuan J. Xu
Affiliation	Nanyang Technological University
E-mail address	xuzc@ntu.edu.sg

6-0217

Efficient Water Splitting with PbCrO₄ Thin Film Photoanode Fabricated via Various Synthesis Methods

Sung Ki Cho*

Korea Institute of Science and Technology, Korea

Recently, PbCrO₄ has been considered as a promising material for the efficient photoelectrochemical water splitting. In this study, we introduce various synthesis methods for the fabrication of PbCrO₄ thin film, and report their physical and chemical properties as a photoanode. First, we could electrochemically grow single-crystalline PbCrO₄ microrods on fluorine-doped tin oxide substrate, which exhibited a noticeable activity for the photoelectrochemical water oxidation. The electrochemical growth was based on the electrochemical oxidation of Cr³⁺ to Cr⁶⁺ in the presence of Pb²⁺ in the electrolyte. As-deposited PbCrO₄ microrod had single-crystallinity and semiconducting properties without post-heat treatment, which was achieved with well-organized growth based on a low nucleation rate. The photoactivity of PbCrO₄ microrods was greater than that of PbCrO₄ nanorods, owing to an enhanced minority carrier diffusion length increased by approximately 100 nm. PbCrO₄ microrods decorated with Co-Pi cocatalyst exhibited a noticeable photocurrent (0.5 mA/cm² at 1.23 V vs RHE under 1.5 AMG illumination) and high incident photon-to-current conversion efficiency (30% at $\lambda = 400$ nm) for photoelectrochemical water oxidation. We have also developed various solution-processes (precipitation, solution-combustion, sol-gel, and the Pechini methods) for the fabrication of PbCrO₄ photoanode. For the fabrication of PbCrO₄ film, the formation of the secondary phases such as Pb₂CrO₅ and Cr₂O₃ is thermodynamically feasible, which should be controlled precisely. The Pechini method inherently suppressed the formation of the secondary phase, whereas for the other methods required the additional steps for the precursor optimization or the removal of the secondary phases. PbCrO₄ thin film fabricated using the Pechini method exhibited a reasonable photoresponse superior to other methods, owing to its high surface coverage leading to the highest light absorbance, and owing to better surface state. Our recent results indicate that the crystal structure of electrochemically grown PbCrO₄ can be controlled by using the growth-directing agents, which results in the change on its photoresponse, and that the photodecomposition of PbCrO₄ can be alleviated by using its self-activation.

*Corresponding author	Sung Ki Cho
Affiliation	Korea Institute of Science and Technology
E-mail address	skcho@kist.re.kr

6-0259

Multiscale Modeling and Simulation Approach in Polymer Electrolyte Fuel Cell

Seung Soon Jang*

Georgia Institute of Technology, USA

In an effort to develop innovative polymeric materials for fuel cell applications, we have developed a multiscale modeling approach. In this talk, I will summarize prior studies in the approach, which explored the impact of various molecular variables on nanophase segregation and ion transport. These investigations utilized full-atomistic simulation techniques to predict the most probable nanophase-segregated structures in the presence of water. To assess these structures, researchers analyzed structure factor profiles, local pair correlations, and solvation of hydronium, water, and sulfonate moieties. Findings from these studies suggest that nanophase segregation can be harnessed based on molecular variables, and well-developed nanophase segregation promotes ion transport. Additionally, I will discuss the coarse-grained modeling approach for polymeric material structures, enabling mesoscale simulations, and the outcomes of these mesoscale simulations. The results of these studies demonstrate the assertion that the multiscale modeling protocol can be universally applied to any polymeric material design/development for fuel cell membrane applications.

*Corresponding author	Seung Soon Jang
Affiliation	Georgia Institute of Technology
E-mail address	seungsoon.jang@mse.gatech.edu

6-0261

Highly Durable Pt-based Alloy Catalyst for the Cathode in Polymer Electrolyte Membrane Fuel Cells

Won Suk Jung*

Hankyong National University, Korea

Polymer electrolyte membrane fuel cells (PEMFCs) have high energy density and efficiency, making them a promising zero-emission power source for various applications. However, the sluggish kinetic and poor durability of the cathode catalysts remain significant obstacles to commercialization. Pt-based alloy catalysts are used to improve durability, but their effectiveness is limited due to Pt dissolution, particle agglomeration, and migration. To address this issue, the pre-treatment of fct-structured Pt-based alloy catalysts was studied to enhance durability. The pre-leaching process in a strong acid solution led to faster degradation of the L-PtCo catalyst due to poor particle distribution and detachment, while the annealing of the L-PtCo/NC catalyst under a reducing atmosphere at a mild temperature led to remarkably stable performance and ECSA. Another study prepared a PtCo alloy catalyst using thermal diffusion, resulting in an intermetallic PtCo structure (PtCo/NGC) that was thermally treated under optimized conditions. The PtCo/NGC catalyst showed 3-fold higher mass activity than commercial Pt/C and demonstrated remarkable stability, with a potential loss of only 34 mV and maximum power density loss of 11% after 30,000 potential cycles. The intermetallic structure of the PtCo/NGC catalyst was found to alleviate Pt oxidation and Co dissolution, contributing to its enhanced catalytic performance and stability. These studies highlight the importance of pre-treatment and intermetallic structure in enhancing the durability and performance of Pt-based alloy catalysts for ORR and offer promising solutions for the commercialization of fuel cells.

*Corresponding author	Won Suk Jung
Affiliation	Hankyong National University
E-mail address	jungw@hknu.ac.kr

6-0281

Challenges and Opportunities in Alkaline Water Electrolyzer to Overcome Reduce Ohmic Resistance

Wonchul Cho*

Seoul National University of Science and Technology, Korea

Alkaline water electrolysis has emerged as a promising technology for large-scale hydrogen production due to its low-cost materials and established operation. However, the conventional zero-gap membrane electrode assembly (MEA) approach suffers from the limited catalytic activity of the porous substrates and poor interfacial contact between the catalyst layer and the porous separator. Here, we propose a novel approach to overcome these challenges by introducing a cell design with intrinsic catalytic activity and a separator with higher ionic conductivity. This innovative approach leverages the intrinsic catalytic activity of the electrode material, ensuring high stability while minimizing mass transport resistance through pore engineering. Our findings underscore the importance of optimizing the interfacial contact and mass transport resistance in MEAs to achieve scalable alkaline electrolyzers capable of achieving high current densities.

*Corresponding author	Wonchul Cho
Affiliation	Seoul National University of Science and Technology
E-mail address	wonchul.cho@seoultech.ac.kr

6-0368

Exploring the Interplay of PEMFC Ink Components

Seong Hyeon Woo, Seon-Ho Lee, Sungmin Kim, Beomjun Park, Soo Hwan Lee, Jae Il Lee, Seunghee Woo,
Yun Sik Kang, Seok-Hee Park, Sung-Dae Yim*

Korea Institute of Energy Research, Korea

Colloidal dispersions have been widely utilized in diverse industrial applications, leading to extensive investigations of the underlying physical phenomena that dictate their behavior. Nevertheless, research on the ink used in polymer electrolyte membrane fuel cells (PEMFCs) has only recently commenced. The distinctive properties of the catalysts and ionomer binders that constitute PEMFC ink pose a challenge for characterizing their optimal formulation and predicting their rheological behavior using existing theories. Thus, additional research efforts are necessary to comprehensively elucidate the interplay between the constituents of PEMFC ink and their impact on its behavior.

The properties of PEMFC ink are considered from two major perspectives. The first perspective involves controlling ink properties to achieve coating uniformity, coating shape, and crack characteristics after drying during coating processes such as blade coating, slot die, and spray coating. The second perspective involves structural control of the ink to manipulate the nano interfacial structure of catalysts and ionomers, as well as the pore characteristics of the catalyst layers, which are essential for fuel cell performance and durability. Numerous studies have been conducted from these perspectives recently. However, the variety of variables that originate from ink preparation, including the type and duration of mixing and grinding processes, and ink components such as catalyst (crystallinity and surface area of carbon supports, platinum content), ionomer binder (side chain length and IEC), and solvent (polar aprotic solvents, alcohols, water/monohydric alcohol mixtures), have produced inconsistent research results, making it challenging to draw a comprehensive understanding of the interplay between ink components that determine ink structure.

In this study, we aimed to minimize the ambiguity arising from various variables in PEMFC ink while exploring the correlation between ink structure and ink properties. By fixing the catalyst, ionomer, and solvent components of the ink and maintaining the same ink preparation process, we examined the changes in ink properties such as rheology and sedimentation stability by varying the composition of water and alcohol in a binary solvent. Additionally, we investigated the influence of organic additives on ink properties using the same methodology. To better understand the process of transferring from the ink layer to the catalyst layer, we measured the rheological properties of the ink that changed during the solvent evaporation process, and observed the microstructure and crack characteristics of the catalyst layer formed after the ink was completely dried. Finally, we measured the performance and electrochemical properties of the fuel cell, and discussed our interpretation of the correlation between ink-catalyst layer-fuel cell based on these results.

*Corresponding author	Sung-Dae Yim
Affiliation	Korea Institute of Energy Research
E-mail address	jimmyim@kier.re.kr

Electrodeposition-fabricated Ni-based Porous Transport Electrodes for Proton Exchange Membrane Water Electrolyzer

Kyeong-Rim Yeo¹, Hoyoung Kim², Kug-Seung Lee³, Haesun Park¹, Jinwoo Lee², Soo-Kil Kim^{1*}

¹Chung-Ang University, Korea

²Korea Advanced Institute of Science and Technology, Korea

³Pohang Accelerator Laboratory, Korea

In the face of the worldwide challenge of climate change, hydrogen is central to the transition to a carbon-neutral civilization. Up to now, the majority of hydrogen is produced by reforming of fossil fuels [1], which releases carbon dioxide in addition to hydrogen. In this regard, water electrolysis (WE) in combination with renewable energy sources is eagerly anticipated to produce green hydrogen without the emission of greenhouse gas contaminants. Overcoming the disadvantages of conventional alkaline WE, membrane-electrode-assembly based zero-gap electrolyzers such as proton exchange membrane WE (PEMWE) and anion exchange membrane WE (AEMWE) have been investigated [2,3] due to their merits of enabling compactness, high gas purity, and high current density (efficiency). Particularly, PEMWE is considered as a promising technology as a large-scale energy storage system due to its rapid response to intermittent renewable energy source [4]. However, PEMWE still has a drawback originated from its corrosive environment, which forces the use of expensive platinum group metal (PGM) catalysts for both hydrogen/oxygen evolution reactions (HER/OER) leading to the increase in the system cost. In addition, the durability issues of WE are critical because the high operation voltage affects the electrochemical stability of both electrode and porous transport layer (PTL) [5]. In this viewpoint, it is high important to develop low cost, high activity, and high stability electrocatalysts for both electrodes as well as their fabrication methods to ensure optimized electrode structure with minimized vulnerability to long-term operation.

For those, atomic scale doping, control of the electronic structures, and reconstructing of microstructure of catalysts have been suggested in this work. Unlike conventional electrode fabrication methods such as spray coating or decal coating consisting of synthesis of powder-type catalysts and their coating either on the membrane or PTL, we propose a time-saving technique to fabricate catalyst-integrated electrodes through electrodeposition. All catalysts have been initially constructed in forms of Ni alloys with PGM in appropriate ways using electrochemical deposition and treatment methods. In this method, Ni played a crucial role not only in the facilitation of the electrodeposition process but also in enhancing the catalytic activities to HER/OER. The activity and durability of the developed catalysts were evaluated both in the half-cell and the single-cell level. Within our best knowledge, the performances of the developed catalysts overwhelmed the previously reported results opening the possibility of next-generation electrodes for commercialization.

References

- [1] J.A. Turner, *Science*, 305 (2004) 972-974.
- [2] M. Chatenet, B. G. Pollet, D. R. Dekel, F. Dionigi, J. Deseure, P. Millet, R. D. Braatz, M. Z. Bazant, M. Eikerling, I. Staffell, P. Balcombe, Y. Shao-Horn, H. Schäfer, *Chem. Soc. Rev.*, 51 (2022) 4583–4762.
- [3] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, *Int. J. Hydrogen Energy*, 38 (2013) 4901-4934.
- [4] Y. Yang, S. Bremner, C. Menictas and M. Kay, *Renewable Sustainable Energy Rev.*, 91 (2018) 109–125.
- [5] H. Sun, Z. Yan, F. Liu, W. Xu, F. Cheng and J. Chen, *Adv. Mater.*, 32 (2020) 1806326.

*Corresponding author

Affiliation

E-mail address

Soo-Kil Kim

Chung-Ang University

sookilkim@cau.ac.kr

Modelling of Cold Start-Up Process of Proton Exchange Membrane Fuel Cells Using a Novel Current Density Controlling Strategy

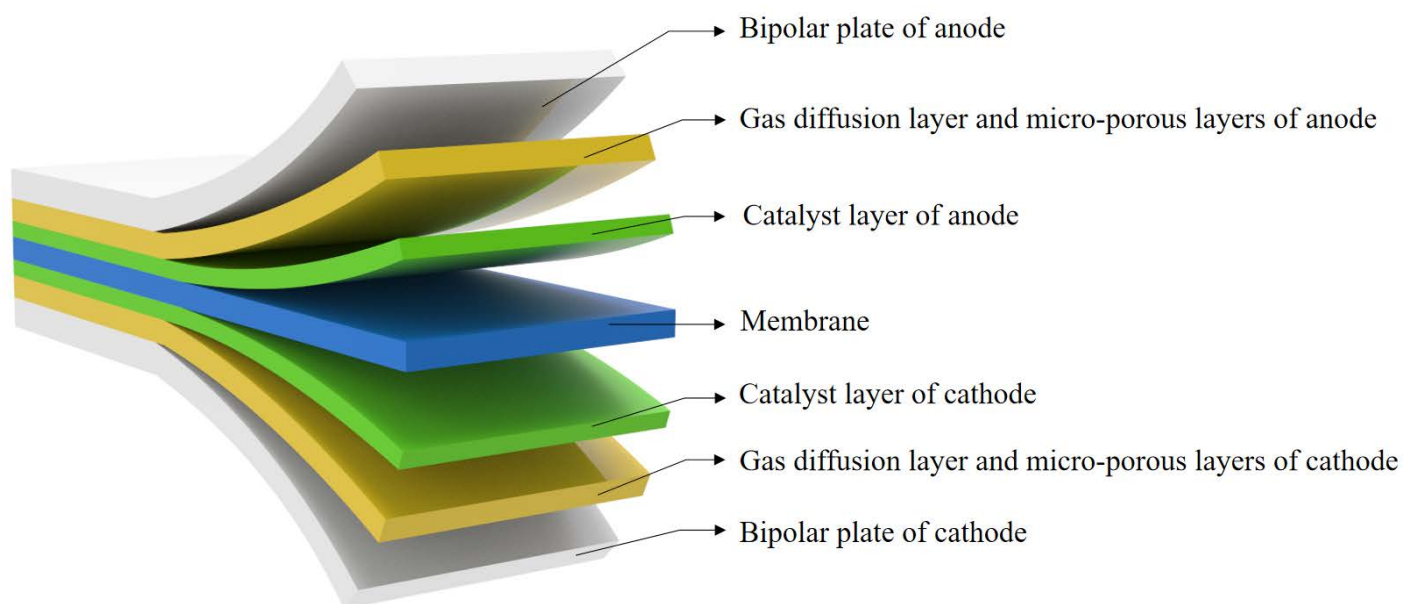
Qianxi Zhang, Hong Cao, Yutong Mu*

Xi'an Jiaotong University, China

Proton exchange membrane fuel cells (PEMFCs) have received much attention due to their environment friendly with the only product of water. Water, on the other hand, can freeze into ice in cold climates, blocking the flow path, resulting in cold start failure, and even shortening cell life. Therefore, adopting a reasonable start-up strategy is the key to successful fuel cell start-up from sub-zero temperatures. The three main start-up strategies used today are constant voltage, constant current, and constant power modes. However, for fuel cell vehicles, it is challenging to adopt a single starting mode due to the complexity of the external environment. This study adopts a variable slope current ramp mode and establishes a three-dimensional fuel cell transient model with the detailed physical model depicted in Fig. 1. This loading mode can regulate the current magnitude using threshold values, and various thresholds can be defined to regulate the starting process more precisely, thus achieving a faster and more efficient cold start process.

References

Lei L, He P, He P, et al. A comparative study: The effect of current loading modes on the cold start-up process of PEMFC stack[J]. *Energy Conversion and Management*, 2022, 251: 114991.



Schematic illustration of the PEMFCs components

*Corresponding author

Affiliation

E-mail address

Yutong Mu

Xi'an Jiaotong University

yutongmu@mail.xjtu.edu.cn

6-0782

Ion-solvating Polybenzimidazole Membranes for Alkaline Water Electrolysis

Hyoung-Juhn Kim*

Korea Institute of Energy Technology, Korea

Currently, proton exchange membrane (PEM) electrolyzers and alkaline electrolyzers are used to produce hydrogen using renewable energy. However, these two electrolysis methods have their own disadvantages, so a new type of water electrolysis technology is required. To overcome the shortcomings of the existing electrolyzers, a new alkaline electrolysis using polybenzimidazole (PBI) was developed. Especially, we synthesized poly(2,2-p-phenylene-5,5-benzimidazole) (p-PBI) which has high crystallinity. Moreover, the crystallinity of p-PBI was increased during membrane fabrication by adding an innovative but very simple biaxial stretching step. The biaxially stretched fe-p-PBI shows high crystallinity and high KOH solution uptake which directly affects electrolysis cell performance. fe-p-PBI was evaluated using platinum group metal (PGM) catalysts and Ni-based catalysts for alkaline electrolysis under 20 wt.% KOH solution feed condition. The electrolysis was performed without severe damage for 1,000 h at 80 °C. The high crystallinity of fe-p-PBI had a great impact on the high performance and long-term stability of the alkaline electrolyzer.

*Corresponding author	Hyoung-Juhn Kim
Affiliation	Korea Institute of Energy Technology
E-mail address	hjk@kentech.ac.kr

Polyelectrolytes Based on Poly (Pentafluorostyrene)

Vladimir Atanasov^{*}, Hyeongrae Cho
University of Stuttgart, Germany

This talk will give an overview on preparation, properties and applications of polyelectrolytes based on functionalized poly(pentafluorostyrene) (PPFS).

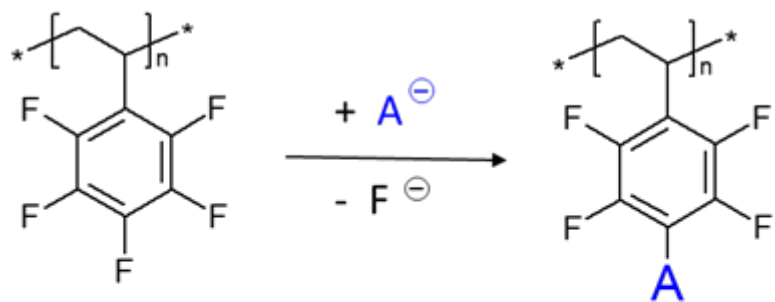
Methods for polymerization of pentafluorostyrene as homo-, block- and graft-copolymers will be introduced and discussed. Among them emulsion free radical polymerization as most scalable and versatile technique will be described and compared to irradiation grafting methods on FTFE as well as preparation of block copolymers obtained by nitroso-mediated control radical polymerization.

To convert PPFS to polyelectrolyte, functionalization with both cation- (phosphonated and sulfonated) and anion-exchange (mercapto- and amino-functionalized) functional groups is going to be presented. Properties related to applications and cell performances in low and high temperature fuel cell (LT- & HT-PEMFC) and vanadium redox flow batteries (VRFB) will be shown. Among them, the resistance to heat is a decisive factor for temperature operation range and stability. Polymers and membranes characterized by thermogravimetric analysis equipped with FTIR analyzer of the outgoing gasses will be compared and discussed. Ion-conductivity is certainly the most important feature of the polyelectrolytes. Conductivity of all polyelectrolytes at conditions relevant to applications will be shown and compared to commercial referents.

The accent of the talk will be on the phosphonated poly(pentafluorostyrene) (PWN).[1-5] This polymer showed high resistance to anhydride formation at temperatures up to 240°C. Because of the low phosphonation degree and the relatively low conductivity of the phosphonic acid in comparison with sulfonic acid, PWN is not suitable as an electrode separator for the fuel cell application. However, due to its stability at elevated temperature, PWN is applicable as a catalyst binder in HT-PEMFC.[6] The best peak power density of 1.74 W.cm⁻² was obtained at 240°C for MEA having ion-pair PEM and PWN as a catalyst binder.

REFERENCES

- [1] V. Atanasov, J. Kerres, *Macromolecules* 2011, 44, 6416.
- [2] V. Atanasov, D. Gudat, B. Ruffmann, J. Kerres, *European Polymer Journal* 2013, 49, 3977.
- [3] V. Atanasov, J. Kerres, *European Polymer Journal* 2015, 63, 168.
- [4] J. Kerres, V. Atanasov, *International Journal of Hydrogen Energy* 2015, 40, 14723.
- [5] V. Atanasov, A. Oleynikov, J. Xia, S. Lyonnard, J. Kerres, *Journal of Power Sources* 2017, 343, 364.
- [6] V. Atanasov, A. S. Lee, E. J. Park, S. Maurya, E. D. Baca, C. Fujimoto, M. Hibbs, I. Matanovic, J. Kerres, Y. S. Kim, *Nature Materials* 2021, 20, 370.



A: S – nucleophile (sulfide & sulfone)
N – nucleophile (amide & ammonium)
P – nucleophile (phosphine & phosphone)

Functionalization of poly(pentafluorostyrene)

*Corresponding author
 Affiliation
 E-mail address

Vladimir Atanasov
 University of Stuttgart
 vladimir.atanasov@icvt.uni-stuttgart.de

Ion-Pair Membrane Based on Imidazolium Functionalized Poly(pentafluorostyrene) for High Temperature Proton Exchange Membrane Fuel Cell Application

Hyeongrae Cho^{*}, Vladimir Atanasov

University of Stuttgart, Germany

Anion exchange membranes based on poly(pentafluorostyrene) (PPFSt) functionalized with tetramethylguanidinium are described in this study. By incorporating flexible thiohexyl groups onto PPFSt followed by functionalization with tetramethylguanidine and its quaternization with dimethylsulfate, free standing anion exchange membranes were fabricated. The resulting membranes were applied in phosphoric acid (PA) doped high temperature proton exchange membrane fuel cells (HT-PEMFCs). The 60 % thiohexylated and 40 % tetramethylguanidinium-functionalized PPFSt membrane (M-PPFSt-TH-TMG) showed higher phosphoric acid doping level than a meta-PBI (m-PBI) membrane. Acid doping level (ADL) of 13.5 PA/guanidinium was achieved for M-PPFSt-TH-TMG in comparison to 4.9 PA/imidazole for the m-PBI. Conductivity of the M-PPFSt-TH-TMG membrane displayed 322 mS·cm⁻¹ (ADL 13.5) and is therefore higher than the m-PBI membrane showing 203 mS·cm⁻¹ (ADL 4.5) at 160 °C. The fuel cell performance measured at 160 °C with non-humidified gases exhibited 150 mA·cm⁻² at 0.6 V and a maximum power peak density of 263 mW·cm⁻². A stability test measured by recording a polarization curve as a function of time indicated no performance decay over 144 hours at 160 °C. A consecutive stability test by monitoring voltages at a constant current density of 217 mA·cm⁻² indicated no significant voltage decay at 160°C assuming that a small decay at the beginning of operation in 20 hours attributed to water evaporation.

*Corresponding author	Hyeongrae Cho
Affiliation	University of Stuttgart
E-mail address	hyongrae.cho@icvt.uni-stuttgart.de

Interaction Mediator Assisted Synthesis of Mesoporous Molybdenum Carbide: Mo-Valence State Adjustment for Optimizing Hydrogen Evolution

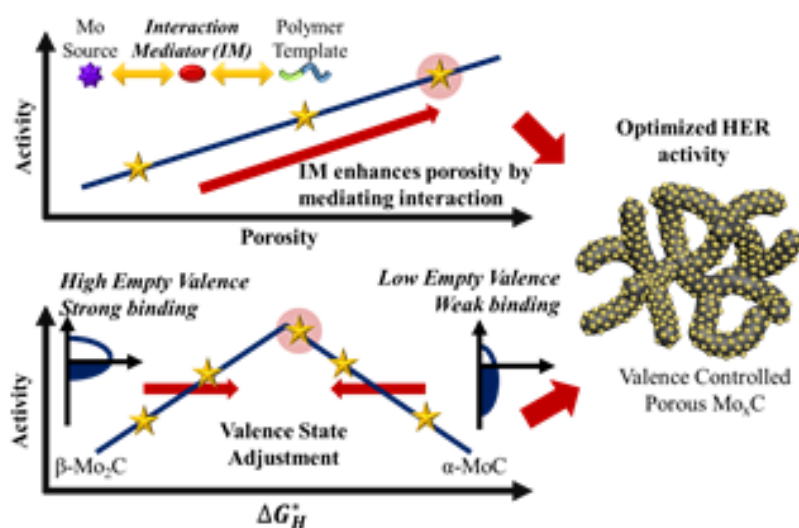
Seongbeen Kim, Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

Molybdenum carbide (Mo_xC) have functioned as promising alternatives for noble metal catalysts due to its low prices and noble metal like catalytic behaviors. In particular, commercial Mo_2C exhibits promising activity for hydrogen evolution reaction (HER) as efficient electrocatalysts. In spite of several research, Mo_xC has suffered from inherent limitations as efficient electrocatalysts for hydrogen evolution reaction (HER), i.e., low density of active site and nonideal hydrogen binding strength. To overcome these limitations, we report synthesis of valence-controlled mesoporous Mo_xC as a highly efficient HER electrocatalyst for both alkaline and acidic conditions.

The synthesis procedure uses an interaction mediator (IM), which significantly increases the density of active site by mediating interaction between PEO-b-PS block copolymer as template and phosphomolybdic acid as Mo source. During the evaporation-induced self-assembly (EISA) process, IM strengthens the interaction between template and Mo source, which causes selective incorporation of precursor into certain block of template. As a results, IM considerably increased the active site density of Mo_xC by increasing porosity, decreasing size of Mo_xC nanoparticles, and increasing dispersity of Mo_xC nanoparticles.

The valence state of Mo is tuned by systematic control of the environment around Mo, by with and without controlled heat treatment (130, 150, 170 °C) under air before thermal treatment at 1100 °C. Theoretical calculations reveal that the hydrogen binding is strongly influenced by Mo valence, and Mo_xC with moderate Mo valence shows optimal intrinsic activity. Consequently, Mo_xC with highest porosity and moderate Mo valence achieves a significant increase in HER activity (exceeding that of Pt/C at high current density $\sim 35 \text{ mA/cm}^2$ in alkaline solution). In addition, a volcano-type correlation between HER activity and Mo valence is identified for the first time. The present strategies can be applied to various carbide and Mo-based catalysts, and the established Mo valence and HER relations can guide development of highly active HER electrocatalysts.



Schemes for abstract

*Corresponding author

Affiliation

E-mail address

Jinwoo Lee

Korea Advanced Institute of Science and Technology

jwlee1@kaist.ac.kr

Modulating Intrinsic Activity of Atomically Dispersed Iron Electrocatalysts through Defect Engineering for Superior PEM Fuel Cell Performance

Seung Yeop Yi, Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

Metal-nitrogen-doped carbon (M-NC) catalysts with atomically dispersed transition metal active sites coordinated to nitrogen on a carbon support have demonstrated significant potential in various electrocatalytic reactions. These catalysts offer high catalytic performance, selectivity, efficient atom utilization, and cost-effectiveness. [1] Specifically, Fe-NC catalysts have emerged as promising alternatives to platinum group metal (PGM)-based catalysts for oxygen reduction reactions (ORR) in acidic environments. However, their performance in membrane electrode assemblies (MEA) within proton exchange membrane fuel cells (PEMFC) falls short of practical application requirements. [2]

To enhance the MEA performance of Fe-NC catalysts, it is crucial to control the intrinsic activity of the Fe-N₄ active sites. One approach to achieving this control involves manipulating the defect sites on the carbon support. [3] By influencing the interaction between Fe-N₄ active sites and the carbon plane, the electronic structure and intermediate adsorption of the Fe center can be altered. Despite the complexity of factors involved, this study proposes a defect engineering strategy based on CO₂ activation, aiming to improve PEMFC MEAs using atomically dispersed Fe-NC catalysts.

The strategy revolves around precisely adjusting the degree of defect formation through CO₂ activation, which is expected to modify the electronic structure of the Fe-N₄ site. This modification, in turn, influences the oxidation state and spin state of the Fe center. The defect-engineered Fe-NC catalysts are then employed in ORR, and their superior half-wave potentials are determined, showcasing their enhanced performance.

To gain further insights into the relationship between the intrinsic ORR activity of Fe-NC catalysts and the degree of defect formation, density functional theory (DFT) calculations are employed. The calculations consider the integrated Crystal Orbital Hamiltonian Population (ICOHP) as a measure of oxygen intermediate adsorption energies. This analysis helps elucidate the impact of defect-induced activity changes, contributing to a deeper understanding of the system.

Finally, the optimized Fe-NC catalyst is evaluated as a cathode in a PEMFC, specifically assessing its peak power density in H₂/O₂ and H₂/air systems. This evaluation determines the catalyst's potential applicability as a material within PEMFC MEAs. The results obtained from this study provide valuable insights into the CO₂ activation-derived defect engineering strategy for enhancing the performance of PEMFC MEAs based on atomically dispersed Fe-NC catalysts. These findings contribute to the development of efficient and sustainable catalyst materials for PEMFCs, facilitating advancements in clean energy technologies.

[1] M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science* 2009, 324, 71-74.

[2] J. Li, M.-T. Sougrati, A. Zitolo, J.M. Ablett, I.C. Oğuz, T. Mineva, I. Matanovic, P. Atanassov, Y. Huang, I. Zenyuk, A.D. Cicco, K. Kumar, L. Dubau, F. Maillard, G. Dražić, F. Jaouen, *Nat. Catal.* 2021, 4, 10-19.

[3] N. Ramaswamy, U. Tylus, Q. Jia, S. Mukerjee, *J. Am. Chem. Soc.* 2013, 135, 15443-15449.

*Corresponding author

Affiliation

E-mail address

Jinwoo Lee

Korea Advanced Institute of Science and Technology

jwlee1@kaist.ac.kr

Ion-pair High-temperature Proton Exchange Membrane Fuel Cells

Yu Seung Kim^{1*}, Ivana Matanovic¹, Emory DeCastro², Katie(H) Lim³, Albert Sung Soo Lee³, Sandip Maurya¹

¹Los Alamos National Laboratory, USA

²Advent Technology, Inc, USA

³Korea Institute of Science and Technology, Korea

High-temperature proton exchange membrane fuel cells (HT-PEMFCs) have the potential to use for heavy-duty automotive applications. However, current polybenzimidazole (PBI)-based HT-PEMFCs are not stable under dynamic operating conditions, and thus, their use in automotive applications has been limited. In 2016, Los Alamos National Laboratory developed ion-pair HT-PEMFCs to resolve the issues associated with PBI-based HT-PEMFCs. After eight years of research, our team found that the working principles of ion-pair HT-PEMFCs are substantially different from the PBI-based HT-PEMFCs. In this presentation, the principles of ion-pair HT-PEMFCs will be discussed. Besides, the remaining challenges and the recent progress of the commercialization of ion-pair HT-PEMFCs will be presented.

References

- 1 Lee, K. S., Spendelow, J. S., Choe, Y. K., Fujimoto, C. & Kim, Y. S. An operationally flexible fuel cell based on quaternary ammonium-biphosphate ion pairs. *Nature Energy* 1 (2016). <https://doi.org:10.1038/nenergy.2016.120>
- 2 Lee, A. S., Choe, Y.-K., Matanovic, I. & Kim, Y. S. The energetics of phosphoric acid interactions reveals a new acid loss mechanism. *J Mater Chem A* 7, 9867-9876 (2019). <https://doi.org:10.1039/c9ta01756a>
- 3 Atanasov, V. et al. Synergistically integrated phosphonated poly(pentafluorostyrene) for fuel cells. *Nat Mater* 20, 370-+ (2021). <https://doi.org:10.1038/s41563-020-00841-z>
- 4 Lim, K. H. et al. Protonated phosphonic acid electrodes for high power heavy-duty vehicle fuel cells. *Nature Energy* 7, 248-+ (2022). <https://doi.org:10.1038/s41560-021-00971-x>
- 5 Jung, J. et al. Dispersing Agents Impact Performance of Protonated Phosphonic Acid High-Temperature Polymer Electrolyte Membrane Fuel Cells. *Acs Energy Letters* 7, 1642-1647 (2022). <https://doi.org:10.1021/acscenergylett.2c00359>

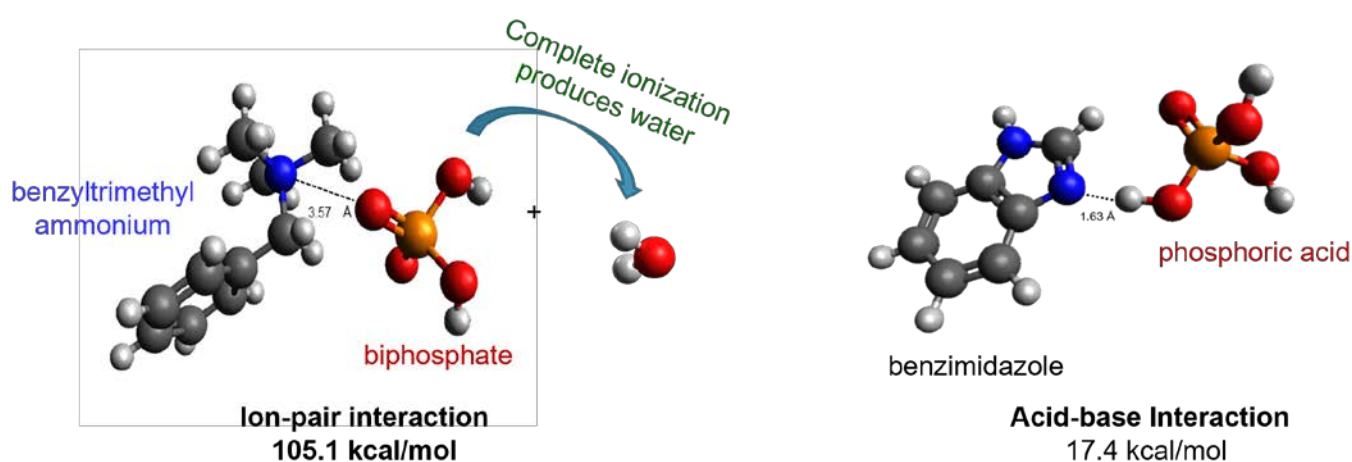


Figure 1. Comparison of interaction energy between acid-base and ion-pair systems

*Corresponding author

Affiliation

E-mail address

Yu Seung Kim

Los Alamos National Laboratory

yskim@lanl.gov

Composition Controlled Colloidal Ni-Fe Oxide Nanoparticles and Investigation of Its Electrochemical Activity for Highly Efficient Water Oxidation Catalyst

Wooseok Jeong, Yun-Kun Hong, Yoonsu Park, Hyungbin Son, Don-Hyung Ha *

Chung-Ang University, Korea

Over the decades, using fossil fuel for a productive life of humanity induces global warming over the world, necessitating the study and utilization of renewable energies. Hydrogen (H₂) is the desirable energy carrier with high energy content and without harmless burning products,¹ leading to consideration of H₂ production methods. Water electrolysis is a candidate for green H₂ production method as it does not allow the generation of toxic by-products. Performing the efficient water electrolysis requires a well-structured catalysts for oxygen evolution reaction (OER) because OER shows slower reaction kinetics than hydrogen evolution reaction (HER) due to the four-electron transfer system, which means that complex OER mechanism can limit the overall reaction of water electrolysis.²

For OER, transition metal based catalysts without platinum group metals are extensively studied due to their stability in alkaline media as well as their low cost. Among the transition metals, Ni and Fe have employed to the OER catalyst through the diverse synthesis strategies. We colloiddally synthesized the Ni-Fe oxide nanoparticles (NFO NPs) by differing the molar ratio of metal precursors. The NFO NPs were analyzed by the X-ray diffraction (XRD) and transmission electron microscopy (TEM), displaying that their morphological characteristics as well as crystalline phases depend on the composition of Ni and Fe. XRD graphs displayed the mixed crystalline phases of Ni metals and Fe oxides in the case of binary metal oxide NPs. TEM images confirmed that the incorporation of Fe causes the decrease in overall NP size and makes the products monodisperse. Additionally, electrochemical performances of the as-synthesized NFO NPs during OER in alkaline media were examined, achieving lower overpotential at 10 mA/cm² than that of the previous reports using Ni and Fe transition metals. Among the various NPs depending on the Ni and Fe composition (from 100:0 to the 0:100, molar ratio of introduced metal precursors), the Ni₃Fe₁ sample using 3 mmol Ni and 1 mmol Fe precursors reached the most efficient OER activity than the other samples. The Ni₃Fe₁ sample was investigated through X-ray photoelectron spectroscopy (XPS) and in-situ Raman spectroscopy analyses to confirm the electronic structures and oxygen intermediates on the catalyst surface during OER. The results provide the insights to design the OER catalyst without precious metals.

References

1. Chatenet, M.; Pollet, B. G.; Dekel, D. R.; Dionigi, F.; Deseure, J.; Millet, P.; Braatz, R. D.; Bazant, M. Z.; Eikerling, M.; Staffell, I.; Balcombe, P.; Shao-Horn, Y.; Schäfer, H. Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments. *Chem. Soc. Rev.* 2022, 51, 4583-4762.
2. Roy, C.; Sebok, B.; Scott, S. B.; Fiordaliso, E. M.; Sørensen, J. E.; Bodin, A.; Trimarco, D. B.; Damsgaard, C. D.; Vesborg, P. C. K.; Hansen, O.; Stephens, I. E. L.; Kibsgaard, J.; Chorkendorff, I. Impact of nanoparticle size and lattice oxygen on water oxidation on NiFeO_xH_y. *Nat. Catal.* 2018, 1, 820-829.

*Corresponding author Don-Hyung Ha
Affiliation Chung-Ang University
E-mail address dhha@cau.ac.kr

CuPd Alloy Catalysts for Gaseous CO₂ MEA-Type Electrolyzer

Gyeong Ho Han, Sang Hyun Ahn*

Chung-Ang University, Korea

Since industrialization, anthropogenic emission of CO₂ into the atmosphere have increased, accelerating global warming, and disrupting the ecological balance. Various investigations are being conducted to reduce atmospheric CO₂. The electrochemical CO₂ reduction with renewable energy sources is attracting attention as a method to convert CO₂ into chemical fuels with high energy density such as CO, CH₄, HCOOH, C₂H₄ and C₂H₅OH. It is essential to fabricate efficient catalysts capable of converting CO₂ into target products with high stability and selectivity. Up to now, numerous studies on Cu-based catalysts as cathode for converting multi carbon products from electrochemical CO₂ reduction are in progress. Since Cu-based catalysts are the only metals capable of C–C coupling, the CO₂ can be converted into valuable C₂₊ products in an electrochemical reaction. However, the Cu-based catalysts have an obstacle in that they are converted into various products rather than selectivity to one product due to its intrinsic properties. To obtain high selectivity to one product and high stability, the studies are being conducted to control properties, which their morphology, composition, facets, and oxidation states.

The conventional H-type cell, which reacts by dissolving CO₂ in an aqueous electrolyte, has a mass transfer problem, so the maximum current density is as low as ~35 mA cm⁻². To solve this problem, the humidified gaseous CO₂ electrolyzer, by applying the zero-gap membrane electrode assembly (MEA) structure, the ohmic resistance has been minimized owing to elimination of electrolyte layer.

Herein, CuPd alloy catalyst was fabricated on microporous layer-coated carbon paper (MPL/CP) using electrodeposition method. The atomic ratio of the fabricated catalyst was change by controlling the concentrations of Cu and Pd precursors. In the XRD analysis, it was confirmed that the Cu and Pd of CuPd/MPL/CP was alloyed, and the shift of the (111) plane was confirmed depending on the composition.

The CuPd/MPL/CP catalysts were used as cathode for electrochemical gaseous CO₂ reduction in electrolyzer. At a certain condition, CO FE of 92.8% and CO partial current density of 67.8 mA cm⁻² were achieved at operating cell voltage (2.4 V_{cell}). Cu/MPL/CP alloy catalyst leads to high performance due to the stabilization of the reaction intermediate due to the fast charge transfer on the surface.

In addition, the CuPd/MPL/CP catalyst was subjected to annealing treatment in a furnace to adjust the phase separation of Cu and Pd. When confirmed through XRD analysis, it was confirmed that the (111) crystal plane formed by the alloy of Cu and Pd was separated according to the annealing temperature. The annealing temperature range from 150 to 300 °C at 50 °C intervals. At a relatively low temperature of 150 to 200 °C, it was confirmed that CH₄ was mainly produce. On the other hand, it was confirmed that C₂H₄ was mainly produced in the catalyst subjected to annealing at high temperature.

*Corresponding author	Sang Hyun Ahn
Affiliation	Chung-Ang University
E-mail address	shahn@cau.ac.kr

In-Situ Growth of a Ni-Fe Layered Double Hydroxide for Exceptional Operational Stability in a Water Electrolysis System

Muhammad Mehdi^{1,2}, Byeong-Seon An¹, Byung-Hyun Kim¹, Chang Hyuck Choi³, Sechan Lee¹, Changsoo Lee¹, MinJoong Kim^{1,2*}, Hyun-Seok Cho^{1,2*}

¹*Korea Institute of Energy Research, Korea*

²*University of Science and Technology, Korea*

³*Pohang University of Science and Technology, Korea*

Nickel-iron layered double hydroxides (Ni-Fe LDHs) consist of stacked Fe³⁺-doped positively charged Ni-hydroxide layers containing charge-balancing anions and water molecules between them. Although Ni-Fe LDHs are highly active catalysts for the oxygen evolution reaction (OER) under alkaline conditions, their poor operational stability remains an issue. Herein, based on density functional theory calculations, it is proposed that the inclusion of a higher Fe content (>40%) than the theoretical Fe³⁺ limit (~25%) allowed by Ni-Fe LDHs can lead to improved structural stability. Therefore, an Fe-rich Ni-Fe LDH electrode is prepared via a growth strategy based on the controlled oxygen corrosion of an Fe substrate by allowing the incorporation of additional Fe²⁺ into the Ni²⁺-Fe³⁺ LDH structure. Indeed, microstructural and elemental analysis confirmed the presence of additional Fe²⁺. This Fe-rich Ni-Fe LDH electrode offers a low OER overpotential (~270 mV at 200 mA cm⁻²) and exhibits excellent operational stability under dynamic operating environments without significant performance degradation or metal ion dissolution. In addition, the role of Co doping on stability was investigated by growing a Co-doped Ni-Fe LDH structure in a customized galvanic cell. The cell also facilitates the advantage of LDH growth on various metal substrates such as Cu, Ni, and stainless steels. Finally, the practical feasibility of the LDH electrodes is demonstrated in a single-cell and 20-cell short stack operation. These findings will aid in the development of reliable OER electrodes for commercial water electrolyzers.

*Corresponding author 1 MinJoong Kim
Affiliation Korea Institute of Energy Research
E-mail address mj.kim@kier.re.kr

*Corresponding author 2 Hyun-Seok Cho
Affiliation Korea Institute of Energy Research
E-mail address hscho@kier.re.kr

Gas Diffusion Electrode Half-Cell System for Characterization of Catalyst Layer in Polymer Electrolyte Membrane Fuel Cells

Hyeon-Seung Jung, Dong Hee Kim, Jong Gyeong Kim, Chanho Pak*

Gwangju Institute of Science and Technology, Korea

The gas diffusion electrode (GDE) half-cell systems were recently introduced as a rapid and efficient tool for the characterization of oxygen reduction reaction (ORR) in the catalyst layer. Typically, the activity of ORR electrocatalysts in proton exchange membrane fuel cells (PEMFCs) is evaluated using the rotating disk electrode (RDE) method. This is a straightforward and rapid analysis technique that requires a minimal amount of catalyst. However, due to the liquid environment of the RDE, O₂ mass transport is restricted, making it accessible only within a narrow potential range of 0.95 to 0.85V.

This system serves as an intermediate step between RDE and membrane electrode assembly (MEA), providing a powerful tool for quickly screening and evaluating electrodes using small amounts of catalyst. Utilizing the GDE allows for the simulation of a unit cell environment, wherein both charge transfer and mass transfer phenomena occurring within the catalyst layer can be concurrently observed. This feature enables its use as a swift and efficient tool for the analysis of catalyst layers and the development of electrodes across a variety of systems. Recent publications from Wilkinson[1] and Gasteiger[2] groups reviewed this new system, proposed new measurement protocols, and suggested improvements.

In this research, we fabricated a half-cell electrode enhanced for gas diffusion and electrical conduction, inclusive of a flow path. The novel system was applied to both the characterization and development of the catalyst layer within the environments of low-temperature and high-temperature PEMFCs. The system was operated at the equivalent temperatures to the MEA, specifically 80°C and 150°C, in acid electrolyte. Analysis was conducted on the characteristics of the ORR and O₂ mass transport in the range of low current density (less than 0.2A/cm²) and high current density (greater than 1A/cm²).

To compare electrochemical properties, which are based on physical attributes such as catalyst layer thickness, active material loading, and binder content, electrochemical impedance spectroscopy (EIS) and distributed relaxation time (DRT) techniques are employed. The DRT method, specifically, separates resistance peaks to compare the disparities between the MEA and the GDE. By deliberately excluding the effects of the electrolyte membrane, anode electrode, and ion transport, the system enables the investigation of the catalyst layer's pure oxygen mass transport properties. Consequently, the GDE half-cell system has been proven to be an effective approach for rapid analysis of electrodes and simulation of high current densities across various PEMFC systems, while requiring minimal amounts of catalyst.

References

- [1] B.A. Pinaud, A. Bonakdarpour, L. Daniel, J. Sharman, D.P. Wilkinson, Key considerations for high current fuel cell catalyst testing in an electrochemical half-cell, *J. Electrochem. Soc.* 164 (2017).
- [2] T. Lazaridis, B.M. Stühmeier, H.A. Gasteiger, H.A. El-Sayed, Capabilities and limitations of rotating disk electrodes versus membrane electrode assemblies in the investigation of electrocatalysts, *Nat Catal* 5 (2022) 363–373.

*Corresponding author

Affiliation

E-mail address

Chanho Pak

Gwangju Institute of Science and Technology

chanho.pak@gist.ac.kr

Cost-Effective and Flexible Monocrystalline Semiconductor via Crack-Assisted Layer Transfer Method for Energy Device Applications

Yonghwan Lee^{*}, Suckin Yun, Nochang Park

Korea Electronics Technology Institute, Korea

Monocrystalline semiconductor-based solar energy conversion devices have attracted huge interest due to its high efficiency compared with other materials. However, the monocrystalline semiconductor-based devices have limited to only high-end applications due to the high cost of the monocrystalline semiconductor substrates such as silicon (Si), gallium arsenide (GaAs) and indium phosphide (InP).

In this work, we show a cost-effective method for producing monocrystalline III-V compound semiconductor thin films via a facile cracking method. The sub 20 μm -thick large-area monocrystalline InP thin films was exfoliated from 350 μm -thick InP substrate via crack-assisted layer transfer method. We confirmed that the material quality (e.g., minority carrier lifetime) of the exfoliated InP thin films remains identical to that of the unprocessed commercial InP substrates. In addition, the approaches enable to produce InP thin films with micro-scale periodic grating structure on the fracture surface by controlling crack propagation direction in InP donor substrate. The dimensions of the periodic grating structure can be controlled by modification of the process parameters of the controlled cracking method. Finally, we propose a new approach for energy bandgap engineering in InP thin films which is further analyzed using computer-aided simulations. By adopting the grating structure of InP thin film, we show that periodically localized stress can be formed on InP thin film with a stress-inducing thin layer. This enables the control of strain as well as energy bandgap in InP thin films. Due to the stress concentration effect, the energy bandgap in InP thin film can be shifted up to 25 meV. In addition, we also present cost-effective photoelectrochemical (PEC) cells using the exfoliated monocrystalline semiconductor thin films for cost-effectively hydrogen fuel generation.

We believe that our proposed facile crack-assisted layer transfer method, which does not require any sophisticated equipment and complex fabrication process, shows a promising way to reduce the cost of monocrystalline silicon and III-V compound semiconductor. In addition, it can be used to realize cost-effective high-performance solar energy conversion devices as well as various (opto)electronic applications.

*Corresponding author	Yonghwan Lee
Affiliation	Korea Electronics Technology Institute
E-mail address	ylee@keti.re.kr

Efficient Alkaline Hydrogen Evolution Reaction Using Superaerophobic Ni Nanoarrays with Accelerated H₂ Bubble Release

Jaerim Kim, Sang-Mun Jung, Yong-Tae Kim, Jong Kyu Kim*

Pohang University of Science and Technology, Korea

Despite the adverse effects of H₂ bubbles adhering to catalyst's surface on the performance of water electrolysis, the mechanisms by which H₂ bubbles are effectively released during the alkaline hydrogen evolution reaction (HER) remain elusive. In this study, we perform a systematic investigation on the effect of nanoscale surface morphologies on H₂ bubble release behaviors and HER performance by employing earth-abundant Ni catalysts consisting of an array of Ni nanorods (NRs) with controlled surface porosities. Both aerophobicity and hydrophilicity of the catalyst's surface vary according to the surface porosity of catalysts. The Ni catalyst with the highest porosity exhibits superaerophobic nature as well as the best HER performance among the Ni catalysts. It is found that the Ni catalyst's superaerophobicity combined with the effective open pore channels enables the accelerated release of H₂ bubbles from the surface, leading to a significant improvement in geometric activities, particularly at high current densities, as well as intrinsic activities including both specific and mass activities. It is also demonstrated that the superaerophobicity enabled by highly porous Ni NRs can be combined with Pt and Cr having optimal binding abilities to further optimize electrocatalytic performance. Our work can provide valuable insights into the design of efficient and robust electrocatalysts consisting of earth-abundant elements toward practical electrochemical HER.

*Corresponding author	Jong Kyu Kim
Affiliation	Pohang University of Science and Technology
E-mail address	kimjk@postech.ac.kr

Poster Presentation



6-0387

Alloy Electrocatalysts for Alkaline Hydrogen Evolution with Enlarged Surface Area Using Nanowire Template

Hong Seong Park, Kyeong-Rim Yeo, Soo-Kil Kim*

Chung-Ang University, Korea

Water electrolysis (WE) is an environmentally friendly technology that uses electrical energy to split water to produce high-purity hydrogen. In contrast to proton exchange membrane WE (PEMWE), which depends on the use of expensive platinum group metals as catalysts, anion exchange membrane WE (AEMWE) operates in an alkaline environment enabling the use of low-cost transition metal (TM) catalysts. However, the mechanism of hydrogen evolution reaction (HER) in AEMWE is more complicated than that in PEMWE due to the inclusion of a water dissociation step, diminishing the advantages of AEMWE. Therefore, the development of low-cost HER catalysts with high activity is essential to improve the efficiency of AEMWE. Various studies have been conducted to improve the activity of TM catalysts. As one of the strategies, templates to increase the active surface area of catalysts have been conducted, where the templates were in the form of nanowires (rods) of SnO₂, WO₃, and Cu(OH)₂ fabricated through various methods such as heat treatment, thermal evaporation, anodization, and reduction [1-3].

In this study, TM nanowires were fabricated by electrodeposition as templated substrates for the subsequent electrodeposition of Ni-based alloy catalysts to enhance the active surface area of the catalysts. The alkaline HER activity as well as various electrochemical characteristics of the prepared catalysts were evaluated to present the effectiveness of the area-enlargement. A series of spectroscopic analysis to observe the surface morphologies, compositions, crystallographic and electronic structures of the catalysts were conducted to identify the origin of the enhanced activity in comparison with non-templated alloy catalysts and templated single metal catalysts.

References

- [1] M.S. Saha, R. Li, X. Sun, Composite of Pt–Ru supported SnO₂ nanowires grown on carbon paper for electrocatalytic oxidation of methanol, *Electrochemistry Communications*, 9 (2007) 2229-2234.
- [2] L. Li, Y. Zhang, X. Fang, T. Zhai, M. Liao, X. Sun, Y. Koide, Y. Bando, D. Golberg, WO₃ nanowires on carbon papers: electronic transport, improved ultraviolet-light photodetectors and excellent field emitters, *Journal of Materials Chemistry*, 21 (2011) 6525-6530.
- [3] S. Zhao, J. Huang, Y. Liu, J. Shen, H. Wang, X. Yang, Y. Zhu, C. Li, Multimetallic Ni–Mo/Cu nanowires as nonprecious and efficient full water splitting catalyst, *Journal of Materials Chemistry A*, 5 (2017) 4207-4214.

*Corresponding author

Soo-Kil Kim

Affiliation

Chung-Ang University

E-mail address

sookilkim@cau.ac.kr

Effect of Membrane-Electrode Assembly Parameters for Superior Anion-Exchange Membrane-Based Unitized Regenerative Fuel Cells

Kyung Ah Lee^{1, 2}, Ji Eun Park^{3*}, Yung-Eun Sung^{1, 2*}

¹*Seoul National University, Korea*

²*Institute for Basic Science, Korea*

³*Tech University of Korea, Korea*

The optimization of integrated renewable fuel cell, a next-generation fuel cell technology, was investigated. In an Alkaline Membrane Regenerative Unitized Fuel Cell (AEM-URFC), it is important to optimize the oxygen electrode to enable both green hydrogen production and fuel cell operation. In this study, the effects of ionomer contents, catalysts mass amounts, porous transport layer (PTL) and different catalysts of hydrogen, oxygen electrode on high-efficiency AEM-URFC were investigated. The hydrogen electrode PtRu/C was 0.4mgpt/cm², the oxygen electrode was Pt 1mg/cm² (Ionomer 10wt%), and the IrO₂ was 0.2mg/cm². Measured 1200mA/cm² at 0.6V in fuel cell mode (FC mode) and 130mA/cm² at 1.6V in water electrolysis mode (WE mode). Also, the performance of AEM-URFC (1200 mA cm⁻² at 0.6 V) is superior to AEM-URFC reported in the literature due to Carbon GDL.

*Corresponding author 1	Ji Eun Park
Affiliation	Tech University of Korea
E-mail address	cathypark7@naver.com
*Corresponding author 2	Yung-Eun Sung
Affiliation	Seoul National University
E-mail address	ysung@snu.ac.kr

6-1003

Investigating the Experimental Parameters Influencing Sulfur Poisoning on YSZ SOFCs

Rameez Zafar, Hyung-Tae Lim*
Changwon National University, Korea

Sulfur poisoning is a condition that leads to performance degradation of a solid oxide cell due to the presence of sulfur in the supplied fuel gas. It is of significant concern when using hydrocarbon gases with solid oxide electrochemical cells, as they typically contain small amounts of sulfur. To better understand sulfur poisoning and its parameters, solid oxide fuel cells (SOFCs) were tested before, during, and after sulfur poisoning. Anode-supported (AS) cells were prepared for sulfur poisoning. These cells were tested under various atmospheric and physical conditions during the poisoning and recovery phases, which include constant current densities of 250 mA/cm², 500 mA/cm², and 750 mA/cm², as well as at constant voltages of 0.5 V, 0.7 V, and 0.9 V for poisoning and recovery. The gases used for poisoning were 50 ppm and 5 ppm H₂S, while pure H₂ was used for recovery in all cases. The changes in performance, severity, and reversibility of sulfur poisoning were observed with varying current density, cell voltage, and sulfur concentration of the supplied gas. It was found that for AS cells, the initial performance degradation (which occurs when the supplied gas is switched to H₂S) increased linearly with increasing current density. However, the second performance degradation (which occurs gradually over time) and recovery (which occurs when the supplied gas is switched back to H₂) remained within a range of 2%–3% for current densities of 250 mA/cm² and 500 mA/cm² but were more than twice as high for a current density of 750 mA/cm². These results indicate that AS cells are particularly susceptible to initial performance degradation as well as higher recovery with increasing current density, but the second degradation and recovery phases remain relatively stable at lower current densities.

*Corresponding author	Hyung-Tae Lim
Affiliation	Changwon National University
E-mail address	htaelim@changwon.ac.kr

Entangled Iridium Oxide Nanotube Catalyst for Stable Water Electrolysis with Low Loaded Amount

Gyu Seong Yi^{1,2}, Hui-Yun Jeong³, Jinho Oh^{1,4}, Daehyeon Ko¹, Yung-Eun Sung^{2,5}, Hyun S. Park^{1,4*}

¹*Korea Institute of Science and Technology, Korea*

²*Seoul National University, Korea*

³*Lawrence Livermore National Laboratory, USA*

⁴*University of Science and Technology, Korea*

⁵*Institute for Basic Science, Korea*

A polymer electrolyte membrane (PEM) water electrolysis has been attracted big interest from the hydrogen industry to achieve the goal to produce green hydrogen. For producing green hydrogen, renewable energy has to be used as energy source. Due to the energy power fluctuations of renewable energy, rapid response and dynamic operating range of PEM water electrolysis (PEMWE) are required. In spite of these advantages, PEMWE has a fatal drawback of high stack cost result from the usage of iridium-based catalyst and titanium-based cell component to endure acidic environment and high anode potential. High cost of iridium is due to the extreme rarity of iridium in earth crust and it is only produced as a byproduct during the production of platinum group metals. In this study, iridium nanotube (IrNT) was synthesized to reduce the loaded amount of iridium. To synthesize the iridium nanotube, firstly Ag@Ir core-shell structure was synthesized through hydrothermal reaction on the silver nanowire and the silver core was eliminated during the annealing and etching process. When this IrNT was sprayed on the titanium porous transport layer, IrNTs are entangled due to their one-dimensional structure. Entangled iridium nanotubes ensure the interconnection with adjacent catalyst in ultralow loaded amount as low as 0.05 mg/cm²⁺. This entangled structure also enables to lessen the loaded amount of catalysts without diminishing the stability compare to the nanoparticles.

*Corresponding author	Hyun S. Park
Affiliation	Korea Institute of Science and Technology
E-mail address	hspark@kist.re.kr

6-1596

Fabrication of Stainless Steel-Supported Solid-Oxide Fuel Cells by Co-Sintering Process and Their Electrochemical Properties

Sang Eun Lee, Hee Jung Park^{*}

Dankook University, Korea

The metal-supported solid-oxide fuel cell with excellent thermal and mechanical properties can be applied to various fields from portable devices and transportation to fuel cells for power generation. In particular, the use of stainless-steel support is very advantageous in terms of cost. However, due to the irreversible redox characteristics of stainless steel, it requires to be manufactured in a reducing atmosphere. In this study, all components (solid electrolyte/anode/contacting layer/metal support) except for a cathode have been stacked and then co-sintered in a reducing condition. Then, the Ba-Sr-Co-Fe-O perovskite cathode with high performance has been coated on the sintered solid electrolyte. A very thin blocking layer (dense ceria) has been inserted between the zirconia solid electrolyte and the cathode to prevent the chemical reaction not desired. The electrochemical properties of the metal-supported solid-oxide fuel cell have been investigated by 2-probe ac impedance and dc measurements as a function of temperature. High performance has been obtained due to both the optimal microstructure of each layer and the thin ceria-blocking layer.

*Corresponding author	Hee Jung Park
Affiliation	Dankook University
E-mail address	parkjang@dankook.ac.kr

6-1815

Tailoring Pr-Doped PtFeP Nano Alloy on N-rGO Support for an Efficient Ethanol Oxidation Reaction

Padmini Basumatary, Ji Hyeok Choi, Dimpul Konwar^{*}, Young Soo Yoon^{*}
Gachon University, Korea

Tailoring Pr-doped PtFeP Nano Alloy on N-rGO Support for an Efficient Ethanol Oxidation Reaction

Padmini Basumatary¹, Ji Hyeok Choi¹, Dimpul Konwar^{*}, Young Soo Yoon^{*}

Department of Materials Science and Engineering, Gachon University, Bokjung-dong, Seongnam-si, Gyeonggi-Do, 1342, Republic of Korea.

¹These authors contributed equally.

Corresponding Author:

Prof. Y. S. Yoon (E-mail: benedicto@gachon.ac.kr)

Prof. D. Konwar (E-mail: dkonwar@gachon.ac.kr)

Abstract

Hydrogen is considered as a valuable renewable energy fuel with promising capabilities. At standard temperature and pressure the generation of hydrogen from water electrolysis requires theoretical cell voltage of 1.23 V whereas only 0.084 V from ethanol [1]. Again, ethanol fuel cells can offer higher efficiency and are also environmentally benign. However, ethanol dissociation is a multi-electron oxidation reaction with slow reaction kinetics because scission of C–C is difficult [2]. Herein, a novel Pr-doped PtFeP electrocatalyst with three different dopants (1, 5, and 10 wt%) configurations on N-rGO support was synthesized using a modified solvothermal method and are characterized using various analytical techniques. For comparison, PtFeP/N-rGO was further prepared and investigated for hydrogen evolution and ethanol oxidation. Pr5PtZnP/N-rGO exhibited a lower overpotential of 45 mV for hydrogen production in presence of 0.5 M of H₂SO₄ electrolyte solution, which was ~32 times lower than theoretical value for water electrolysis for hydrogen production. The optimized Pr5PtZnP/N-rGO (~20% Pt) achieved better EOR mass and specific activity, which was ~8 times higher compared with commercial Pt/C (40% Pt). Furthermore, Pr5PtFeP/N-rGO exhibited outstanding stability and tolerance towards CO_{ad} and their intermediated species during the ethanol oxidation reaction in acidic media, which was mainly associated to its bifunctional and intrinsic effect [3]. In addition, Pr5PtZnP/N-rGO was highly stable even after 5000 cycles.

Keywords: Electrocatalyst, Hydrogen evolution, Ethanol oxidation, Ethanol fuel cell, Current density, Power density.

References

[1] M. Chatenet, B. G. Pollet, D. R. Dekel, F. Dionigi, J. Deseure, P. Millet, R. D. Braatz, M. Z. Bazant, I. Staffell, P. Balcombe,

Y. S. Horn, H. Schäfer, Chem. Soc. Rev. 2022, 51, 4583–4762.

[2] M. D. R. Lutz, B. Morandi, Chem. Rev. 2021, 121, 300–326.

[3] P. Basumatary, D. Konwar, Y. S. Yoon, Appl. Catal. B: Environ. 2020, 267, 118724.

*Corresponding author 1	Dimpul Konwar
Affiliation	Gachon University
E-mail address	dimpulkonwar@gmail.com

*Corresponding author 2	Young Soo Yoon
Affiliation	Gachon University
E-mail address	benedicto@gachon.ac.kr

Relationship between Operating Condition and Degradation of Ni-YSZ Steam Electrode Material for Solid Oxide Electrolysis Cells

Jaewoo Park, Ki-Tae Lee *

Jeonbuk National University, Korea

A solid oxide cell (SOC) is a future energy system with high efficiency because it enables reversible operation modes of a solid oxide fuel cell (SOFC) and a solid oxide electrolysis cell (SOEC). In particular, SOEC can produce electricity and hydrogen by electrolyzing water and has very high energy conversion efficiency. In addition, SOC systems operating in reversible mode can be easily combined with renewable energy systems. Therefore, hydrogen production through SOEC combined with renewable energy sources is an essential energy system for realizing a sustainable hydrogen economy. Meanwhile, in the case of conventional nickel-yttria stabilized zirconia (Ni-YSZ) electrodes used in SOFCs, the correlation between microstructure, performance and degradation has been extensively studied. However, the cause of the performance degradation occurring in the SOEC cell has not yet been clearly identified. Because SOFC and SOEC have different operating conditions, even materials optimized for SOFC may not be suitable for SOEC electrode material applications. Therefore, if the cause of degradation of the SOEC steam electrode is clearly understood, it can be of great help in improving the durability of the entire cell.

In this study, the effect of factors such as operating temperature, steam concentration and current density on the degradation of Ni-YSZ steam electrodes was investigated. The performance and electrochemical properties of SOEC were analyzed using current density-voltage (j -V) measurement and electrochemical impedance spectroscopy (EIS), and the correlation with microstructure-performance-degradation was identified through microstructure observation of the single cells before and after electrochemical measurement.

*Corresponding author Ki-Tae Lee
Affiliation Jeonbuk National University
E-mail address ktleee71@jbnu.ac.kr

6-2043

Support Role for Non-Noble NiMo Electrocatalyst in Alkaline Hydrogen Oxidation

Hakyung Min, Jinkyu Park, Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

The Pt-based catalyst for the hydrogen oxidation reaction (HOR) must be replaced for commercialization of anion exchange membrane fuel cells (AEMFCs). Contrary to comprehensive investigations of platinum group metals (PGMs)-free catalysts, systematic analysis of supporting materials are rarely discussed. Here, we demonstrate a design approach that enhances the catalytic activity of PGM-free catalysts by using a support made of N-doped mesoporous carbon. To illustrate the support effect, we looked at the electrochemical properties of NiMo alloys over N-doped mesocellular carbon foam (NiMo/N-MSUF-C), NiMo/N-CMK-3, and NiMo/MSUF-C. By incorporating large pores, the diffusion of OH⁻ into the catalyst layer is facilitated, resulting in an increased limiting current density. Additionally, the strong interactions between NiMo and N species cause modifications to electronic structure of NiMo, leading to improved H and OH⁻ binding energy. The AEMFC with NiMo/N-MSUF-C as the anode showed an outstanding performance at the peak power density of 152 mA cm⁻².

*Corresponding author	Jinwoo Lee
Affiliation	Korea Advanced Institute of Science and Technology
E-mail address	jwlee1@kaist.ac.kr

6-2067

Designing Amorphous CoMoP_x with Abundant Active Sites for Efficient Water Splitting

Hyunwoo Jun, Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

We have devised a novel method for synthesizing highly efficient catalysts, specifically amorphous bimetallic phosphides (a-CoMoP_x/CF), used in water splitting. This approach entails utilizing porous Co-MOF/CF and defective CoMoO₄/CF as templates to induce the formation of abundant defects and large voids, which facilitate the creation of amorphous a-CoMoP_x/CF. The bimetallic components exhibit synergistic behavior, as confirmed by theoretical calculations, resulting in hierarchical amorphous nanosheet arrays with advantageous characteristics such as enhanced mass transfer capacity and a high ratio of exposed atoms. Consequently, the electrochemical active surface area (ECSA) increases. This unique combination of structural advantages and synergistic catalytic effects renders a-CoMoP_x/CF exceptionally active for the hydrogen evolution reaction (HER) under alkaline conditions, displaying a low overpotential of 59 mV at the current density of 10 mA cm⁻². Additionally, we successfully demonstrated that our comprehensive electrolysis apparatus employing a-CoMoP_x/CF as both the cathode and anode exhibits comparable performance to a noble metal-based catalyst configuration (Pt/C-CF || RuO₂-CF), achieving stable operation at 100 mA cm⁻² for over 100 hours and a current density of 10 mA cm⁻² at a potential of 1.581 V. These findings present a groundbreaking approach for designing robust structured catalysts utilizing earth-abundant materials, paving the way for large-scale electrocatalytic applications in energy conversion technologies.

*Corresponding author

Jinwoo Lee

Affiliation

Korea Advanced Institute of Science and Technology

E-mail address

jwlee1@kaist.ac.kr

Stabilizing Yttria-Stabilized Zirconia via Nano-Alumina for Stable and Durable Long-Term SOFC Operation

Muhammad Measam Ali^{1,2}, Amjad Hussain^{1,2}, Rak Hyun Song^{1,2*}, Dong Woo Joh², Jong Eun Hong^{1,2},
Seong Bok Lee^{1,2}, Tak Hyoung Lim^{1,2}

¹*University of Science and Technology, Korea*

²*Korea Institute of Energy Research, Korea*

Over the last decade, the pursuit of new energy sources has been at its peak. In this pursuit, hydrogen became the center of attraction. As a result, fuel cells became popular energy conversion devices that convert chemical energy into electrical energy such as solid oxide fuel cells (SOFC), proton exchange membrane fuel cells (PEMFC), molten carbonate fuel cells (MCFC), direct methanol fuel cell (DMFC), etc. SOFCs are widely accepted due to their various advantages like fuel flexibility, high power density, high efficiency, and zero emissions. SOFCs are classified into three main types depending on their geometry (planar, tubular, and flat tubular) and structural support (anode-supported, electrolyte-supported, metal-supported, etc.). Planar anode-supported SOFCs with NiO-8YSZ anode support have been commercialized because of their low operating temperature (600-750 °C), easy stack design, high power density, and easy fabrication procedures. During the lifetime of SOFC stack operation, the cell must tolerate numerous thermal shocks, mechanical shocks, and redox cycles. And to withstand these challenges, the cell should have appropriate structural integrity, materials compatibility, and good interface adhesion. However, NiO-8YSZ anode-supported SOFC has low structural strength (<100 MPa) for stable and durable long-term operation. The mechanical strength can be enhanced by utilizing low molar yttria-stabilized zirconia (3 mol.% yttria-stabilized zirconia-3YSZ) but it comes with trade-offs. The crystal lattice phase of 3YSZ is not stable under humid reduction environments. The tetragonal phase of 3YSZ is susceptible to transforming into the monoclinic phase which can greatly reduce the performance of SOFC. In this work, the crystal lattice phase conversion was suppressed via the addition of nano-alumina into the anode support. The SOFC was fabricated using the conventional tape-casting technique, co-laminated, and co-fired till electrolyte at the final temperature of 1300-1400 °C. The weight percentages of 0, 1, and 2 were added to the NiO-3YSZ anode support to investigate its effect on the stability and durability of the cell. The electrochemical investigation has shown that the NiO-3YSZ with 1wt.% nano-alumina is quite stable at accelerated conditions (wet H₂@300mAcm⁻²) having superior strength than the NiO-8YSZ anode-supported SOFC.

*Corresponding author

Rak Hyun Song

Affiliation

University of Science and Technology

E-mail address

rhsong@kier.re.kr

Degradation Features Triggered by Renewable Energy-Mimicking Fluctuating Loads in Proton Exchange Membrane Water Electrolysis

Anastasiia Voronova^{1,2}, Sol Kim^{1,2}, Hee-Young Park¹, Jong Hyun Jang^{1,2}, Bora Seo^{1,2*}

¹*Korea Institute of Science and Technology, Korea*

²*University of Science and Technology, Korea*

The growth of the hydrogen economy necessitates cost reduction in the manufacturing and operation of proton exchange membrane water electrolysis (PEMWE), which can be achieved by PEMWE coupling with renewable energy sources. With this regard, precise durability estimation of RES-coupled PEMWE and subsequent durable materials development become a significant challenge. The lack of systematic degradation processes analysis in PEMWE, particularly under fluctuating loads that simulate RES conditions currently is a main challenge for the PEMWE implementation into the hydrogen economy. In this work, a set of stability tests based on steady-state loads and cycling loads with various voltage ranges was applied for systematic comparison with high-resolution simulated solar profile. Resulting degradation features were systematically analyzed with combined analysis of electrochemical and spectroscopic characterizations, giving valuable insights toward performance change, membrane degradation, catalyst dissolution, and migration/diffusion, and Ti porous transport layer passivation. Notably, the simulated solar profile was featured by elevated fluoride release rate, activation overpotential recovery during “night time” periods, and Pt dissolution/diffusion. Among the comparison stability profiles, the steady-state profile at elevated load and dynamic profile with cycling from 5 % of nominal to elevated load could jointly mimic and induce the solar profile-derived degradation features. The results obtained provide important clues in bridging the gap between laboratory-scale research and the on-site operation of RES-coupled PEMWE. Findings also offer a rational guideline for developing an accelerated stress test protocol.

*Corresponding author	Bora Seo
Affiliation	Korea Institute of Science and Technology
E-mail address	brseo@kist.re.kr

Development of a Conversion of CH₄ and a Hydrogen Storage by Reactions with Magnesium Based Alloy

Young Jun Kwak, Ki-Tae Lee, Myoung Youp Song*

Jeonbuk National University, Korea

There is a growing interest in hydrogen product and storage processes based on the use of renewable energy resources. In a renewable energy-based hydrogen economy, the distribution of hydrogen from the producer to the consumer is currently the missing key technology. In this work, a new approach for CH₄ conversion to hydrogen and storage uniting has been developed based on magnesium alloy. With Ni as the catalytic source, CH₄ converts and generates hydrogen that is utilized by hydrogen absorb-release reaction in magnesium. MgH₂-12Ni (composition 88wt% MgH₂ + 12wt% Ni) was prepared in a planetary ball mill by milling in high-purity hydrogen gas at 12 bar at a disc rotation speed of 400 rpm for 6 h. X-ray diffraction (XRD) analysis was performed on the samples after reaction-related milling and after reaction with CH₄. The variation of absorbed or released hydrogen quantity with time was measured by at 773K with a Sievert-type high-pressure device. The microstructures of the powders were observed using scanning transmission microscope (STEM) with energy-dispersive X-ray spectroscopy (EDS). The synthesized samples were also characterized using Fourier transform infrared (FT-IR) spectroscopy. XRD pattern of MgH₂-12Ni after reaction with CH₄ of 12 bar at 773 K and decomposition under 1.0 bar H₂ at 773 K showed MgH₂ and Mg₂NiH₄ phases. This indicates that conversion of CH₄ occurred, and hydrides were formed. MgH₂-12Ni absorbed 0.8 wt% H within 1 min in a reaction with CH₄ of 12 bar at 773 K and then released 0.8 wt% H within 1 min under H₂ of 1 bar at 773 K. Attenuated total reflectance FT-IR spectroscopy (ATR-FTIR) spectra of MgH₂-12Ni after reactions under 12 bar CH₄ at 723 K and 773 K showed peaks of C-H bending, C=C stretching, O-H stretching, O-H bending, and C-O stretching. EDS analysis of MgH₂-12Ni after reaction under 12 bar CH₄ at 773 K exhibited the presence of carbon on the surfaces of particles.

*Corresponding author	Myoung Youp Song
Affiliation	Jeonbuk National University
E-mail address	songmy@jbnu.ac.kr

Graphitic Carbon Nitride-Supported Ir-Based Catalyst for Efficient Acidic Oxygen Evolution Reaction

Yen-Linh Thi Ngo¹, Sol Kim^{1,2}, Anastasiia Voronova^{1,2}, Jong Hyun Jang^{1,2}, Bora Seo^{1,2*}

¹*Korea Institute of Science and Technology, Korea*

²*University of Science and Technology, Korea*

To enable large-scale hydrogen production, it is important to reduce the noble metal content used in the anode of proton exchange membrane water electrolysis (PEMWE). Graphitic carbon nitride (g-C₃N₄) has gained significant attention in recent years due to its exceptional properties and diverse applications including electrocatalysis. However, there is still a lack of research on electrocatalytic oxidation reactions in acidic environment. Since g-C₃N₄ endows a highly hydrophilic surface, it can enhance the exposure of active sites and facilitate mass transfer, making it a suitable substrate for constructing active and robust oxygen evolution reaction (OER) catalysts. In this presentation, iridium metal/metal oxide catalysts dispersed on g-C₃N₄ (IrO₂@g-C₃N₄) will be proposed as an efficient and durable electrocatalyst for acidic OER. The IrO₂@g-C₃N₄ exhibited high intrinsic catalytic activity toward acidic OER, achieving an overpotential as low as 253 mV at a current density of -10 mA cm⁻². The high catalytic activity can be attributed to the synergistic effects between the metal and carbon nitride. Furthermore, the catalyst showed negligible activity decay after 1000 cyclic voltammetry cycles, indicating excellent long-term durability. Notably, the IrO₂@g-C₃N₄ catalyst exhibited comparable performance and durability to commercially available carbon-supported IrO₂ (IrO₂/C).

*Corresponding author	Bora Seo
Affiliation	Korea Institute of Science and Technology
E-mail address	brseo@kist.re.kr

Low-Content Ir-Based Catalyst with Modulated Electronic Structure for Efficient Proton Exchange Membrane Water Electrolysis

Sol Kim^{1,2}, Jinwoo Woo¹, Yen-Linh Thi Ngo¹, Jong Hyun Jang^{1,2}, Bora Seo^{1,2*}

¹*Korea Institute of Science and Technology, Korea*

²*University of Science and Technology, Korea*

Decades of fossil fuel use have led to severe environmental pollution, driving the need for alternative energy sources. Hydrogen, in particular, has emerged as an attractive energy carrier due to its high gravimetric energy density. However, the majority of hydrogen is still produced using the steam-to-methane reforming method, which emits significant amounts of CO₂. In contrast, water electrolysis (WE) techniques offer a carbon-free approach enabling sustainable hydrogen production. In particular, proton exchange membrane water electrolysis (PEMWE) is well-suited for integration with renewable energy sources due to its high efficiency, compact design, and rapid response to load fluctuations. Nevertheless, the sluggish kinetics of the oxygen evolution reaction (OER) at the anode of PEMWE necessitates the use of noble metal catalysts like Ir and Ru, impeding its practical application. To overcome this challenge, IrO₂ has conventionally served as an OER catalyst in acidic environments, thanks to its superior activity and stability. Hence, developing low-content Ir-based catalysts becomes crucial to improve the cost-effectiveness of PEMWE. In this presentation, tin oxide-supported iridium oxide (IrO_x/SnO_y-NaCl) catalysts was proposed as an efficient acidic OER catalyst. Tin oxide was employed to enhance Ir dispersion and reduce its usage, while NaCl was introduced to improve OER activity by modulating the valence state of Ir. The prepared IrO_x/SnO_y-NaCl catalysts exhibited high OER activity and mass activity, comparable to the state-of-the-art Ir-based acidic OER catalysts. In addition, electrochemical and X-ray spectroscopic analyses validate that the presence of NaCl enhanced the catalytic activity of IrO_x by optimizing the mixed valence state of Ir³⁺/Ir⁴⁺ on the catalyst surface, a favorable configuration for OER. Notably, the IrO_x/SnO_y-NaCl catalysts demonstrate excellent single-cell performance in PEMWE, achieving a mass activity 2.6 times higher than that of commercial IrO₂.

*Corresponding author	Bora Seo
Affiliation	Korea Institute of Science and Technology
E-mail address	brseo@kist.re.kr

6-2212

Promoting Oxygen Evolution Activity via Electronic Structure Modification of MnO₂ with F and Ru Incorporation for Proton Exchange Membrane Water Electrolysis

Jegon Lee¹, Sol Kim¹, Jong Hyun Jang^{1, 2}, Bora Seo^{1, 2*}

¹*Korea Institute of Science and Technology, Korea*

²*University of Science and Technology, Korea*

Hydrogen production through proton exchange membrane water electrolysis (PEMWE) offers a promising solution for achieving a sustainable and environmentally friendly energy society, addressing the existing energy crisis and environmental concerns. However, the practical implementation of PEMWE faces obstacles due to the high cost of cell stacks, primarily attributed to the use of precious metals as anode catalyst. To overcome this challenge, non-precious metal-based transition metal oxide catalysts have been proposed as alternatives for the anode catalyst. Unfortunately, these alternatives often exhibit limited activity for the oxygen evolution reaction (OER), which is the sluggish anode reaction in PEMWE. Therefore, there is a need to develop non-precious metal catalysts with reasonable OER activity. In this presentation, an approach for enhancing the OER activity of MnO₂ catalysts by modulating their electronic structure through F incorporation, while reducing the reliance on precious metal. The resulting F-incorporated Mn_{1-x}Ru_xO₂ catalyst demonstrated improved OER activity compared to pristine MnO₂ catalyst. Especially, the (Mn_{0.94}Ru_{0.06})O₂:2.5F catalyst, synthesized under optimal conditions, exhibited superior mass activity. In addition, X-ray spectroscopic and electrochemical characterizations revealed that the increase in the Mn³⁺/Mn⁴⁺ ratio and oxygen vacancies contribute to the enhancement of the OER activity. Moreover, practical application of the (Mn_{0.94}Ru_{0.06})O₂:2.5F as the anode catalyst for a PEMWE was demonstrated with a single-cell test. Our findings provide an activation strategy for inactive transition metal oxide catalysts.

*Corresponding author	Bora Seo
Affiliation	Korea Institute of Science and Technology
E-mail address	brseo@kist.re.kr

Enhanced Electrochemical Properties for the Oxygen Evolution Reaction of NiAl-LDH Nanoplates on NiFe Foam: A Density Functional Theory Study

Yoojin Lee, Jeong Woo Han*

Pohang University of Science and Technology, Korea

Fossil fuels have played a crucial role in global development, but their carbon emissions contribute to global warming. To ensure sustainable development, it is essential to develop clean energy alternatives. Hydrogen is a promising eco-friendly energy source due to its abundance, wide availability, and high energy density. However, the efficiency of water electrolysis, the primary method for carbon-neutral hydrogen production, remains a challenge. The slow kinetics of the oxygen evolution reaction (OER) in water electrolysis hinder its efficiency. Previous studies explored noble metal-based electrocatalysts (Ru, Ir, Pt, etc.) to enhance OER efficiency, but their limited reserves and high cost pose obstacles. To address these issues, active research focuses on layered materials, particularly 4th-period transition metals.

Nickel aluminum-layered double hydroxide (NiAl-LDH) is a highly promising electrocatalyst material due to its improved structural stability and increased ratio of low-coordinated nickel achieved through the introduction of aluminum. Employing foam as a growth environment for electrocatalysts offers numerous advantages, including high specific surface area, efficient material utilization, low mass density, versatile porous channels, and good conductivity. By utilizing a foam composed of nickel and iron, which are well-established elements, we can maximize the potential of NiAl-LDH while addressing the limitations of existing rotating disk electrodes.

Previous studies in electrocatalysis have primarily focused on the interaction between catalyst materials and their interfaces using density functional theory (DFT) calculations of the OER. However, recent research on catalysts directly grown on substrates, such as single-atom catalysts, has revealed that changes in catalytic activity can arise not only from the interaction between reactants and the catalyst surface but also from the interaction between the catalyst and the substrate. This study aims to investigate the impact of foam on the electrocatalytic reactions and thoroughly examine the interface between NiAl-LDH and foam through heterostructure modeling. When comparing the OER overpotential of NiAl-LDH@NiFe foam (NFF) and NiAl-LDH@Ni foam (NF) heterostructures, it was found that LDH@NFF showed a lower overpotential. Through Bader charge analysis of the heterostructure where LDH was formed on foam, it was confirmed that charge transfer occurred at the interface. When comparing NFF and NF, it was found that more electron transfer occurred at the interface of LDH@NFF than that of LDH@NF due to the electron supply from Fe in NFF. In conclusion, it was found that LDH was better formed on NFF with stronger interfacial binding energy, leading to better OER performance.

Our findings reveal that the interactions between catalysts and substrates can control the electronic structures of the catalyst through charge transport from the metal substrate, similar to the charge transport-induced enhancement observed in single-atom catalysts. These results offer a promising approach for the rational design of oxygen evolution catalysts, enabling electronic structure control through interactions with metal substrates, not only at the atomic scale but also at larger scales for practical applications.

*Corresponding author Jeong Woo Han

Affiliation Pohang University of Science and Technology

E-mail address jwhan@postech.ac.kr

6-2217

A DFT Study of Ni and Co-Based Nitride and Its Reconstructed Heterostructure Catalysts for Electrochemical Water Splitting

Miyeon Kim, Jeong Woo Han *

Pohang University of Science and Technology, Korea

Renewable energy has become increasingly important in mitigating climate change and achieving carbon neutrality. Electrochemical water splitting is a crucial reaction for utilizing renewable hydrogen energy. This reaction consists of two half-reactions: oxygen evolution reaction (OER) at the anode and hydrogen evolution reaction (HER) at the cathode. Oxyhydroxides and nitrides of 3d transition metals, such as nickel and cobalt, are regarded as promising catalysts due to their cost-effectiveness and stability in alkaline electrolyte.

However, there is limited research on the reconstructed structures that occur during electrochemical reactions. We focused on the reconstruction of nitrides into oxyhydroxides through the dissolution of metal and nitrogen under oxidizing conditions. In this study, we investigated Ni- and Co-based nitrides (NiMN and NiCoMN) and its reconstructed heterostructure (NiCoOOH/NiCoMN).

Density functional theory (DFT) calculations were performed to figure out the effect of cobalt incorporation in NiMN. Firstly, cobalt incorporation in NiMN was found to improve structural stability by strengthening metal-nitrogen covalency. The differences in the d-band center of metals and the p-band center of nitrogen decreased, and the formation energy became more stable as the cobalt ratio in NiCoMN increased. This demonstrated the potential to alleviate the undesired dissolution by controlling cobalt ratios. Secondly, the core-shell heterostructure of NiCoOOH/NiCoMN formed under oxidizing conditions exhibited superior OER activity compared to bare NiCoOOH. We investigated that the optimal electronic structure of heterostructure is a key factor in enhancing the OER activity. On the other hand, NiCoMN displayed comparatively poorer HER activity than NiMN, resulting in a higher theoretical overpotential for HER.

This study reveals that cobalt incorporation can effectively control the dissolution rate of NiMN by strengthening the metal-nitrogen covalency. Furthermore, we suggest a more stable and energy-efficient heterostructure catalyst for the development of electrochemical water splitting. Moreover, we propose that it is essential to analyze not only pristine catalysts but also reconstructed heterostructures to fully understand their catalytic behavior.

*Corresponding author

Jeong Woo Han

Affiliation

Pohang University of Science and Technology

E-mail address

jwhan@postech.ac.kr

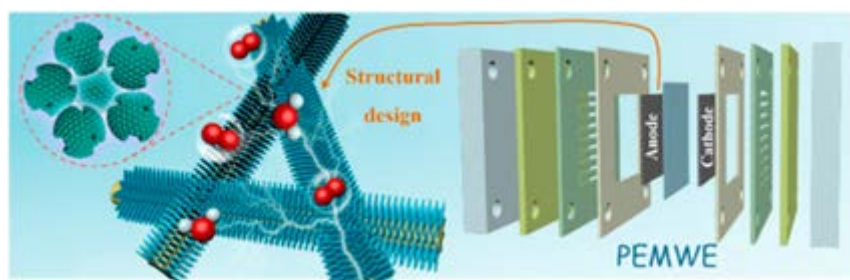
Porous and Defect-Rich Self-Supporting RuO₂ Nanosheets Oxygen Evolution Electrocatalysts for Proton Exchange Membrane Water Electrolyzer

Jaeho Byeon¹, Huawei Huang², Hoyoung Kim¹, Jinwoo Lee^{1*}

¹Korea Advanced Institute of Science and Technology, Korea

²King Abdullah University of Science and Technology, Saudi Arabia

Proton exchange membrane water splitting is acknowledged as a green and sustainable technology for producing high purity hydrogen due to its advantages of a compact electrolyzer, higher energy efficiency. In this study, we employed in-situ transformation and heat treatment to produce self-standing porous RuO₂ nanosheets on carbon fiber paper for oxygen evolution reaction. The resulting hierarchical open structure helped to increase the mass transfer and gas release capabilities, increasing the exposure of active sites with great catalytic activity. The RuO₂-NS/CF subsequently displayed outstanding long-term durability at a high current density (100 mA cm⁻² for 50 h), excellent catalytic activity for OER under acidic conditions (212 mV @ 10 mA cm⁻²). With current densities of 7.905 A cm⁻² at 2.0 V_{cell}, RuO₂-NS/CF also displayed strong performance as an anode in the PEMWE single cell, suggesting a significant potential for use in commercial PEMWE. The results of this study offered fresh perspectives on the structural layout of reliable and durable catalysts and showed how significantly the PEMWE anode structure affects catalytic performance.



Rational Structure Designing of Anode Catalyst for Proton Exchange Membrane Water Electrolysis

*Corresponding author

Jinwoo Lee

Affiliation

Korea Advanced Institute of Science and Technology

E-mail address

jwlee1@kaist.ac.kr

Proton-Conductive Fused Aromatic Networks (FANs) with High Stability and Crystallinity

Soo-Young Yu¹, Yoon-Kwang Im², Hyuk-Jun Noh³, Javeed Mahmood⁴, Sang-Young Lee⁵, Hee-Young Park¹, Jonghyun Jang^{1*}, Jong-Beom Baek^{2*}

¹*Korea Institute of Science and Technology, Korea*

²*Ulsan National Institute of Science and Technology, Korea*

³*Dartmouth College, USA*

⁴*King Abdullah University of Science and Technology, Saudi Arabia*

⁵*Yonsei University, Korea*

The advent of graphene in 2004 prompted the development of two-dimensional (2D) materials, such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs) and a fused aromatic networks (FANs). FANs have been developed as a new approach to make stable 2D materials for practical applications. Their fully conjugated aromatic linkages and non-rotatable bonds provide excellent chemical stability, but developing well-defined structure is still challenge. Here we synthesized highly stable and crystalline FANs via self-cyclotetramerization. The porphyrazine(Pz)-linked FANs is constructed from a single type of building block, which is designed to increase Pz-FAN crystallinity. The newly prepared Pz-FAN showed high crystallinity, stability and nitrogen content, providing a high proton conductivity ($1.16 \times 10^{-2} \text{ S cm}^{-1}$). Furthermore, Pz-FAN-based membrane evaluated as promising potential material for application in proton exchange membrane fuel cell (PEMFC).

*Corresponding author 1	Jonghyun Jang
Affiliation	Korea Institute of Science and Technology
E-mail address	jhjang@kist.re.kr
*Corresponding author 2	Jong-Beom Baek
Affiliation	Ulsan National Institute of Science and Technology
E-mail address	jbbaek@unist.ac.kr

A Method for Estimating PEM Fuel Cell States Using Probability Distribution-Based Loss Component Analysis

Dong Hoon Shin^{1*}, Hee-Young Park¹, Jong Hyun Jang¹, Seungryeol Yoo²

¹*Korea Institute of Science and Technology, Korea*

²*Korea University of Technology and Education, Korea*

This study proposed a novel method referred to as the loss component analysis (LCA) to represent the current state of fuel cells. This method determined three weights related to each loss component reflecting the fuel cell states, and the fuel cell conditions were diagnosed using deviations in weight from the reference weight at the normal state. The maximum increase in weight allocated to each loss component was found to have the most significant impact on changes in the state of the fuel cell from its normal state.

In this study, LCA was applied to both the data obtained from empirical models and acquired through experiments that mimic the three faults that could occur during fuel cell operation. The results were compared to demonstrate the validity of the proposed method.

*Corresponding author	Dong Hoon Shin
Affiliation	Korea Institute of Science and Technology
E-mail address	sdh13ok@kist.re.kr

Zn-Based Nanowire Electrocatalyst for Electrochemical CO₂ Conversion to CO

Junhyeong Kim¹, Hee-Young Park¹, Sang Hyun Ahn^{2*}

¹*Korea Institute of Science and Technology, Korea*

²*Chung-Ang University, Korea*

Electrochemical CO₂ conversion system has been recognized as one of the eco-friendly technologies that overcomes the climate problems caused by global warming and produces the useful fuels. In particular, CO production via electrochemical CO₂ conversion requires only two electrons and proceeds in a simple mechanism. In general, Au and Ag-based catalyst exhibits the high CO production selectivity through the electrochemical CO₂ conversion. However, their high cost and scarcity hinder commercial application. Zn, also shows the high selectivity for CO production, has been recognized as one of the candidates for alternative of these noble metals.

In this study, we fabricate the Zn-based nanowire electrocatalyst for application as the electrochemical CO₂ conversion cathode. First, the hexagonal Zn catalyst with a predominant (101) facet is fabricated by electrodeposition. Subsequently, solution-phase reconstruction of the hexagonal Zn catalyst is conducted by immersed into the KHCO₃ solution in which the hexagonal morphology is transformed to nanowire form. After, the thermal treatment for Zn-based nanowire catalyst is conducted to modify the surface electron structure. The electrochemical CO₂ conversion performance of fabricated Zn-based electrocatalysts is investigated in CO₂-purged 0.5 M KHCO₃.

*Corresponding author	Sang Hyun Ahn
Affiliation	Chung-Ang University
E-mail address	shahn@cau.ac.kr

Support Effect in Atomically Dispersed Pt on WO₃-x for Hydrogen Evolution Reaction

Jiwon Kim, Jinkyu Park, Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

Currently, hydrogen production is primarily based on the steam reforming of fossil fuels, which is accompanied by environmental issues such as substantial increase in atmospheric CO₂, and thus it is necessary to find sustainable and clean alternatives. The electrochemical water splitting, consisting of hydrogen and oxygen evolution reaction, is considered as potentially cost-effective and promising approach for clean hydrogen production.[1] For the cathodic hydrogen evolution reaction (HER), platinum (Pt)-based materials are the most effective electrocatalysts but the high cost and scarcity of Pt are key obstacles for the commercial applications of water electrolyzers. So, it is necessary to reduce the amount of platinum used and increase the intrinsic activity.

Numerous efforts on the design strategy for nanostructured electrocatalysts have been made to improve the utilization of Pt and thereby to reduce the use of Pt in HER. For examples, core-shell and hollow structures can significantly improve the utilization by diminishing the buried non-active Pt atoms inside the particles. From this point of view, single-atom catalysts (SACs), in which all metal species are individually dispersed on a desired support, could be the best candidates for meeting this goal because they offer the maximized number of surface exposed Pt atoms. Several studies have also demonstrated that Pt SACs show greatly boosted Pt mass activity compared to commercial Pt/C. [2] However, surprisingly, research into understanding the role of support in the field of Pt SACs for HER is rarely found.

By using tungsten oxide material as a support, we unveiled the effect of the support on a single-atom. The change in the electronic structure of single-atom and support was characterized by X-ray photoelectron spectroscopy. In particular, the kinetics of hydrogen insertion/extraction behavior of tungsten oxide compared with nanoparticle/support was characterized by electrochemical analysis such as cyclic voltammetry. The strategy proposed in this study can provide new insight to the single-atom catalyst research fields on enhancement of the utilization of the noble metal.

*Corresponding author	Jinwoo Lee
Affiliation	Korea Advanced Institute of Science and Technology
E-mail address	jwlee1@kaist.ac.kr

Modulating Electron-Withdrawing/Donating Properties of Atomically Dispersed Fe-N-C for Oxygen Reduction Reaction

Yeju Jang¹, Seonggyu Lee², Jinwoo Lee^{1*}

¹*Korea Advanced Institute of Science and Technology, Korea*

²*Kumoh National Institute of Technology, Korea*

Platinum-based catalysts, which are frequently employed in oxygen reduction reactions (ORR), account for 25% of fuel cell costs, making them a significant barrier to commercialization. As a result, recently, research has focused on M-N-C catalysts, which are low-cost transition metals (Fe, Co, Mn) coordinated to nitrogen functions in carbon plane. However, the studies on regulating the kinetic activity of the M-N_x active site are scarce. By modulating the electronic structure of the catalytic site, The ORR activity can be enhanced by controlling the adsorption energy of *O, *OH, and *OOH (ORR intermediates). The heteroatom doping on Fe-N-C site can tune the electronic structure of active site. In this study, the ORR activity of a single Fe-N₄ catalytic site was controlled by introducing electron-withdrawing and donating groups to the carbon basal plane by simple S doping. The volcano correlation of ORR activity is shown with the atomic composition of oxidized sulfur and thiophene-like sulfur. The d-orbital energy of the Fe ion is effectively reduced by electron-withdrawing oxidized S functionalities, which also reduce the adsorption of ORR intermediates. Therefore, oxidized S induced an increase of ORR activity of Fe-N₄ sites, whereas electron-donating thiophene-like S functionalities induced a decrease of ORR activity. According to several experimental characterizations, the change in ORR activity was discovered to result from the electronic influence of the sulfur functionality rather than the change in carbon crystallinity, the quantity of active sites, or the structural alteration of the catalytic site.

*Corresponding author	Jinwoo Lee
Affiliation	Korea Advanced Institute of Science and Technology
E-mail address	jwlee1@kaist.ac.kr

6-2912

Mosaic CrO/Co₉S₈ Heterostructure with a Maximized Synergy Effect for Hydrogen Evolution Reaction in Neutral Media

Yeji Park, Kwangyeol Lee*

Korea University, Korea

Generating hydrogen, an eco-friendly energy carrier, through electrochemical water splitting from the neutral media has attracted considerable attention due to the much less corrosion of the water electrolyzer and the feasibility of the direct usage of seawater sources without pH adjustment. To enhance the catalytic performance in neutral media by modulating the HER mechanism, electrocatalysts with dual-site were required for facilitating fast water adsorption/dissociation and sequential hydrogen desorption, respectively. Therefore, designing the well-defined heterostructures by integrating the H₂O adsorption-active materials with HER-active materials is a promising strategy to heighten the HER performance. Herein, we embedded the numerous oxophilic cluster into the metal sulfide matrix to synthesize the mosaic hetero-nanostructure with the maximized interface, increasing the active sites for hydrogen evolution reaction. The efficient charge redistribution at the interface is significantly enhanced the catalytic performance. This study provides a promising design strategy to synthesize the electrocatalysts with hetero-interface and a realization to understand the fundamental HER mechanism in neutral media.

*Corresponding author	Kwangyeol Lee
Affiliation	Korea University
E-mail address	kylee1@korea.ac.kr

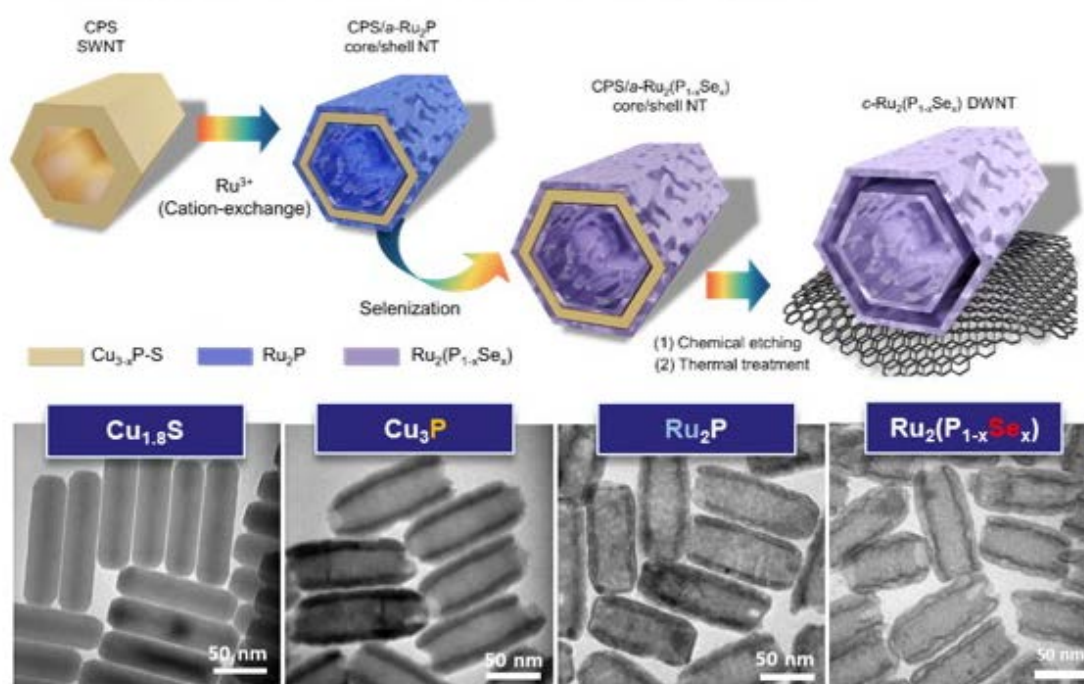
Selenium-Incorporated Ruthenium Phosphide Nanotubes for Accelerated Hydrogen Evolution Reaction in Alkaline Media

Eunsoo Lee, Kwangyeol Lee*

Korea University, Korea

Hydrogen(H_2) generation via electrocatalytic reduction of water is a promising technology that can provide sustainable and eco-friendly energy. However, the hydrogen evolution reaction (HER) in alkaline conditions remains challenging because of its sluggish reaction kinetics due to the additional water dissociation step. Herein, we synthesize the Selenium-incorporated ruthenium phosphides (Se-Ru₂P) nanotubes via alternating anion and cation exchange reactions of Cu_{2-x}S hexagonal nanorod templates. The selenization of Ru₂P nanotubes improved the robustness of structure, which accounts for increased catalytic activity and stability toward alkaline HER. Moreover, an in-depth X-ray photoelectron spectroscopic study found the less formation of hydroxylated Ru species in Se-Ru₂P during hydrogen production. The advantages of these features, the Se-Ru₂P nanotubes achieved superior hydrogen evolution catalytic properties with low overpotentials of 39 mV at a current density of 10 mA/cm² after 15,000 CV cycles in 1.0M KOH. Beyond that, the Tafel slope of Se-Ru₂P nanotubes was only 32.8 mV dec⁻¹, the result indicates that the introduction of Se can positively alter the reaction kinetics of the HER.

Summary of Synthesize $c\text{-Ru}_2(\text{P}_{1-x}\text{Se}_x)$ Nano-catalyst for HER



*Corresponding author

Kwangyeol Lee

Affiliation

Korea University

E-mail address

kylee1@korea.ac.kr

6-3032

Hydrocarbon; Patterning; GO; PEMWE; Durability; Gas Crossover; MEA;

YeonJae Lee, Yeonghwan Jang, Segeun Jang^{*}

Kookmin University, Korea

Polymer electrolyte membrane water electrolysis (PEMWE) with Nafion membrane has higher current density and energy efficiency compared to existing alkaline water electrolysis. However, there is a rising interest in hydrocarbon membranes as an alternative to Nafion membranes which has high cost, high gas permeability, and mechanical instability at high temperature. Hydrocarbon-membrane-based PEMWE has the advantages of low gas permeability, excellent thermal stability, low cost, and non-fluorine. However, membrane/electrode interfacial adhesion problems between hydrocarbon-based membrane and electrode of fluorinated ionomer exist, and this is closely related to low performance and durability degradation during operation. In this study, we derived optimal pattern shapes on the surface of the membrane and additional graphene oxide (GO) loadings by comparing hydrogen crossover and the PEMWE performance. Also, through performing diverse electrochemical measurements and mechanical characterizations, we developed a highly durable hydrocarbon-based membrane-electrode assembly.

*Corresponding author	Segeun Jang
Affiliation	Kookmin University
E-mail address	sjang@kookmin.ac.kr

Development of Symmetric Injection System for Fabricating Reinforced Composite Membrane-Electrode Assembly and Applying It to Fuel Cells

Yeonghwan Jang, YeonJae Lee, Segeun Jang^{*}

Kookmin University, Korea

Traditionally, MEA fabrication procedures have been carried out with membrane and electrode fabrication separate from each other. Therefore, it requires a lot of time and process. Here, we devised a symmetric deposition system that accelerated the MEA fabrication process and minimize the number of steps required to make reinforced composite membranes. The system included infrared lights and spray nozzles arranged in pairs. With this setup, we were able to achieve better impregnation deep into the PTFE sheet by overlapping each spraying location on both sides, which was made possible by the symmetrical injection of ionomer to the PTFE sheet. In addition, a functional Nafion/CeO₂ thin film can be created on the anode side of the membrane by adding a ceria solution near the end of the membrane fabrication. Heat treatment was performed using an infrared lamp for a short time to evaporate any remaining solvent and enhance crystallization. Both anode/cathode electrodes are performed continuously after membrane fabrication using a symmetrical injection nozzle for electrodes located next to the ionomer nozzle. Fabrication of the MEA took less than 30 minutes thanks to its symmetric injection characteristics, and it outperformed commercial Nafion membrane-based MEAs in terms of chemical/mechanical durability and performance.

*Corresponding author	Segeun Jang
Affiliation	Kookmin University
E-mail address	sjang@kookmin.ac.kr

6-3043

3D Structured Highly Active Oxygen Evolution Electrocatalysts for Water Electrolyzer

Minhui Kim, Seonggyu Lee *

Kumoh National Institute of Technology, Korea

In essence, the primary challenge in substituting fossil fuels with sustainable and environmentally friendly energy carriers such as hydrogen lies in the creation of an efficient energy storage system on a large scale. Within the realm of water electrolyzers, surplus electrical energy is converted into chemical energy through the electrochemical splitting of water into hydrogen fuel and oxygen. Nonetheless, the efficacy of the electrolyzer is constrained by the sluggish kinetics and substantial overpotential resulting from the intricate four-electron process known as the oxygen evolution reaction (OER). This impediment significantly obstructs the broad adoption and commercial viability of water electrolyzers. To mitigate this challenge, the development of a comprehensive approach to augment the kinetic activity of electrocatalysts engaged in the oxygen evolution reaction (OER) is imperative. Accordingly, we have devised a novel design featuring three-dimensional (3D) structured OER electrocatalysts with meticulous control over the incorporation of heteroatoms at the atomic scale. This design has been formulated with the primary objective of enhancing the kinetic activity specifically in relation to the process of oxygen evolution.

*Corresponding author	Seonggyu Lee
Affiliation	Kumoh National Institute of Technology
E-mail address	seonggyulee@kumoh.ac.kr

6-3053

Optimization of Membrane-Electrode Assembly Fabrication Conditions for High-Performing Low Temperature Direct Ammonia Fuel Cells

Dohoon Kim, Segeun Jang*

Kookmin University, Korea

Hydrogen-based polymer electrolyte membrane fuel cells (PEMFCs) attained early commercialization due to their high efficiency and performance. Nonetheless, they are yet suffering from low volumetric energy density, pricey noble catalysts, start-up/shutdown durability, etc. However, ammonia—a hydrogen atom carrier— could easily convert to liquid, which has a higher density than gas, under mild conditions compared to hydrogen molecules. Originating from this characteristic, liquid ammonia-feeding type fuel cells have come out: the concept of direct ammonia fuel cells (DAFCs).

In DAFCs, sluggish ammonia oxidation reaction (AOR) takes place instead of hydrogen oxidation reaction (HOR) at the anode: a major factor for low performance.

State-of-the-art DAFCs require aqua form ammonia anolyte. Feeding liquid-based ammonia fuel on DAFCs results in the severe liquid crossover from an anode to an oxygen-gas-based cathode, leading to mixed potential and catalyst poisoning.

The aforementioned two points are the main hurdles for commercializing DAFCs. To overcome inferior performance and propose optimizing direction, in this study, authors investigated the effect of MEA components: mainly catalyst, ionomer and their content. The optimization was confirmed by comparing the performance, ammonia crossover and durability.

*Corresponding author	Segeun Jang
Affiliation	Kookmin University
E-mail address	sjang@kookmin.ac.kr

6-3057

Deteriorated Balance between Activity and Stability via Ru Incorporation into Ir-Based Oxygen Evolution Nanostructures

Kyu-Su Kim¹, Shin-Ae Park², Sang-Mun Jung¹, Jaeik Kwak¹, Jae-Sub Kwon¹, Yoona Kim¹, Hyun-Woo Jung²,
Yong-Tae Kim^{1*}

¹*Pohang University of Science and Technology, Korea*

²*Pusan National University, Korea*

Proton exchange membrane water electrolysis is actively researched to improve the oxygen evolution reaction for the effective hydrogen production. However, commercialization an application for the electrodes still requires nanostructure integration and further improvements. We studied the effects of representative materials: iridium (has high stability and maintains high surface area with nanosized pores), ruthenium (has high intrinsic activity but causes structural agglomeration), and osmium (facilitates the formation of nanostructures) in various combinations. As reported other results, it was confirmed that the catalytic activity and stability could be remarkably improved through the alloying with iridium and ruthenium, but the balance between activity and stability was notably deteriorated when nanostructure was applied. Even in the subsequent annealing steps to preserve its stability, it could not restore the balance due to the aggregation of nanostructures in thermal treatment. Based on these results, we propose OER catalyst design directions that achieve to both enhancing activity and preserving stability simultaneously.

*Corresponding author	Yong-Tae Kim
Affiliation	Pohang University of Science and Technology
E-mail address	yongtae@postech.ac.kr

Cathodic Protection System against a Reverse-Current after Shut-Down in Zero-Gap Alkaline Water Electrolysis

Sang-Mun Jung¹, Yoona Kim¹, Kyu-Su Kim¹, Hyun-Yup Kim¹, Jaesub Kwon¹, Jinhyeon Lee¹, Hyun-Seok Cho², Yong-Tae Kim^{1*}

¹*Pohang University of Science and Technology, Korea*

²*Korea Institute of Energy Research, Korea*

Growing the hydrogen economy requires improving the stability, efficiency, and economic value of water-splitting technology, which uses an intermittent power supply from renewable energy sources. Alkaline water electrolysis systems face a daunting challenge in terms of stabilizing hydrogen production under the condition of transient start-up/shut-down operation. Herein, we present a simple but effective solution for the electrode degradation problem induced by the reverse-current under transient power condition based on a fundamental understanding of the degradation mechanism of nickel (Ni). It was clearly demonstrated that the Ni cathode was irreversibly oxidized to either the β -Ni(OH)₂ or NiO phases by the reverse-current flow after shut-down, resulting in severe electrode degradation. It was also determined that the potential of the Ni electrode should be maintained below 0.6 V_{RHE} under the transient condition to keep a reversible nickel phase and an activity for the hydrogen evolution reaction. We suggest a cathodic protection approach in which the potential of the Ni electrode is maintained below 0.6 V_{RHE} by the dissolution of a sacrificial metal to satisfy the above requirement; irreversible oxidization of the cathode is prevented by connecting a sacrificial anode to the Ni cathode. In the accelerated durability test under a simulated reverse-current condition, lead was found to be the most promising candidate for the sacrificial metal, as it is cost effective and demonstrates chemical stability in the alkaline media. A newly defined metric, a reverse-current stability factor, highlights that our system for protecting the cathode against the reverse-current is an efficient strategy for stable and cost effective alkaline hydrogen production.

*Corresponding author	Yong-Tae Kim
Affiliation	Pohang University of Science and Technology
E-mail address	yongtae@postech.ac.kr

Controlled Colloidal Synthesis of Gold-Based Nanoparticles with Transition Metal and Their Electrocatalytic Properties

Yun Jae Hwang, Don-Hyung Ha^{*}

Chung-Ang University, Korea

Colloidal synthesis is a facile and versatile strategy that can suggest a new direction for conventional gold-based nanoparticles. In this study, we redevelop the crystalline phase regulation of several gold-based nanostructures including Au-Ni hetero-nanoparticles and Au-Cd intermetallic nanoparticles. The gold-metal nanoparticles were synthesized through the heat-up nucleation method with co-reduction of the metal precursor. The crystalline phase and structure were controlled by varying the synthetic conditions such as reaction precursor ratio, reaction temperature, and reaction time. The crystalline phase of Au-Cd NPs could be tuned by varying the compositional stoichiometries of the alloy. The Au and Cd atoms were intermixed to form the atomically ordered intermetallic phase with crystalline phase transition. Several factors such as reaction temperature and composition determine the formation of Au-Ni heterostructures. The Au particles appeared darker than the Ni in the High-resolution TEM images, exhibiting clearly defined Au-Ni heterostructure. STEM-EDS characterizations reveal that Au and Ni separate into two domains. Au-metal nanostructure has been analyzed as an electrocatalyst for hydrogen evolution reactions in a three-electrode system, using linear sweep voltammetry. We also examined the plasmonic properties of gold-based plasmonic nanoparticles with various structures and diverse metal stoichiometries which resulted in controlled plasmonic characteristics. As such, a broad plasmon resonance band emerged as the Au-Cd nanoparticles converted into an intermetallic compound and a slight peak shift is detected in Au-Ni optical characterization.

*Corresponding author	Don-Hyung Ha
Affiliation	Chung-Ang University
E-mail address	dhha@cau.ac.kr

6-3100

Selective Electrocatalysis Imparted by Metal–Insulator Transition for Durability Enhancement of Automotive Fuel Cells

Sang-Mun Jung, Yong-Tae Kim*

Pohang University of Science and Technology, Korea

Repetitive start-up and shut-down events in polymer electrolyte membrane fuel cells for automotive applications lead to serious corrosion of the cathode due to an instantaneous potential jump that results from unintended air leakage into the anodic flow field followed by a parasitic oxygen reduction reaction (ORR) on the anode. Here we report a solution to the cathode corrosion issue during the start-up/shut-down events whereby intelligent catalyst design is used to selectively promote the hydrogen oxidation reaction (HOR) while concomitantly suppressing the ORR on the anode. Platinum thin layers supported on hydrogen tungsten bronze (Pt/HxWO₃) suppressed the ORR by converting themselves into an insulator following exposure to oxygen, while selectively promoting the HOR by regaining metallic conductivity following subsequent exposure to hydrogen. The HOR-selective electrocatalysis imparted by a metal–insulator transition in Pt/HxWO₃ demonstrated a remarkably enhanced durability of membrane electrode assemblies compared to those with commercial Pt/C catalysts.

*Corresponding author	Yong-Tae Kim
Affiliation	Pohang University of Science and Technology
E-mail address	yongtae@postech.ac.kr

Iridium-Ruthenium Oxygen Evolution Catalysts with Enhanced Mass Activity for Proton Exchange Membrane Water Electrolysis (PEMWE)

Suji Lee^{1,2}, Chaeyeon Yang^{1,2}, Yung-Eun Sung^{2*}, Hyun S. Park^{1*}

¹*Korea Institute of Science and Technology, Korea*

²*Seoul National University, Korea*

Hydrogen has received much attention in recent years due to its ability to replace the fossil fuels as a clean energy carrier. Currently, the water electrolysis for hydrogen production is more getting popular due to its zero emission of greenhouse gases. Among various ways to produce hydrogen, alkaline water electrolysis (AWE), which utilizes a diaphragm separator in a strong KOH aqueous solution, has been researched for a long time. However, it suffers from a significant drawback of limited partial load operation to being operated by intermittent renewable energy sources.

On the other hand, proton exchange membrane water electrolysis (PEMWE), which uses a proton conducting polymer membrane, offers numerous advantages, including high operating current density, a wide partial load operating range, high hydrogen purity, and enhanced operational safety. Nevertheless, one of its shortcomings is the high loading of noble metals required for hydrogen and oxygen evolution reactions. Since most metals cannot withstand harsh acidic conditions, iridium, an exceptionally rare and expensive precious metal, is necessary to synthesize electrocatalyst to ensure stability under acidic conditions.

In this presentation, to reduce the amount of iridium while maintaining high activity and stability for OER, ruthenium-iridium catalyst were scrutinized for PEMWE. By using appropriate catalyst structures, OER electrode with ruthenium-iridium catalyst was fabricated with a reduced amounts of iridium, showing higher OER performance than commercial IrO_x based electrode. The improved mass activity of iridium incorporated with the ruthenium was studied in the practical devices.

*Corresponding author 1 Yung-Eun Sung
Affiliation Seoul National University
E-mail address ysung@snu.ac.kr

*Corresponding author 2 Hyun S. Park
Affiliation Korea Institute of Science and Technology
E-mail address hspark@kist.re.kr

Exploring the Effectiveness of Alkaline Ion-Solvating Water Electrolysis Copolymer Membranes in the Polybenzimidazole Family Groups: Delving into Enhanced Performance and Emerging Applications

Hyungkyu Cho, Byeol-Nim Lee, Md Abu Zafar Al Munsur, Hyoung-Juhn Kim*

Korea Institute of Energy Technology, Korea

The long-term stability of anion exchange membrane water electrolysis (AEMWE) remains a significant obstacle in its commercialization efforts. This is primarily attributed to the degradation caused by the strong alkali hydroxide ions towards the functional groups of AEMWE membrane's cation exchange sites. Although the degradation of functional groups does not significantly affect the mechanical strength of the membrane, it results in decreased hydroxide ion conductivity, thereby reducing the efficiency of water electrolysis. This degradation occurs through SN2 and Hofmann elimination E2. Therefore, the development of a promising electrolyte membrane that simultaneously satisfies mechanical strength and chemical durability while ensuring high hydroxide ion conductivity in KOH solutions with low concentrations or deionized water, enabling the utilization of non-precious metal catalysts, is a top priority in large-scale green hydrogen water electrolysis technology integrated with renewable energy sources. The ion-solvating membrane water electrolysis (ISMWE) is gaining attention as the ultimate electrolysis technology for green hydrogen production, allowing for the reduction of KOH solution concentration. The key component of this electrolysis is the ion-solvating membrane, which consists of a polymer-based separator doped with KOH, forming a single electrolyte system comprising polymer, water, and KOH. Polybenzimidazole (PBI) family groups including Poly(2,5-benzimidazole) (AB-PBI), poly[2,2'-(p-phenylene)-5,5'-bisbenzimidazole] (p-PBI), and poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (m-PBI) have been studied regarding its performance in KOH doping, dimensional stability, hydroxide ions conductivity, and mechanical strength for ISMWE. In this research, copolymers of AB-PBI and p-PBI were synthesized specifically for their application in Ion-solvating water electrolysis. As the polycondensation reaction progressed, 3,4-diaminobenzoic acid and 3,3-diaminobenzidine were added at varying ratios to terephthalic acid to regulate copolymer composition. The polymer solutions were cast onto a glass plate using an adjustable digital doctor blade. Once cooled to room temperature, the obtained brown PBI film was immersed in deionized water for several days to remove phosphoric acid. Subsequently, the PBI film was rinsed with isopropyl alcohol (IPA) to eliminate any remaining solvent and water. The membrane electrode assembly (MEA) was fabricated by applying the catalyst coating onto PBI film. The slurry catalyst was uniformly distributed using an auto-spray machine with ultrasonic dispersion. The membranes were evaluated under various conditions using the alkaline water electrolysis cell station. This involved testing two different temperatures for cell operation, 60 °C and 80 °C, and three different concentrations of KOH: 10wt%, 15wt%, and 20wt%. The aim was to determine the optimal conditions that would be suitable for the adapted ion solvating membrane (ISM). As a result, the selected ISM in this study exhibited significantly superior performance and durability compared to the commercial anion exchange membrane, Sustain®. These findings were attributed to the use of PBI copolymer as Ion-solvating membrane, which allowed for the utilization of high-efficiency and durable alkaline water electrolysis. This study highlights the potential of PBI structures as the backbone and cation exchange sites for ISMWE operating with low KOH concentration solutions and/or pure water.

*Corresponding author

Affiliation

E-mail address

Hyoung-Juhn Kim

Korea Institute of Energy Technology

hjk@kentech.ac.kr

6-3161

Polybenzimidazole-Based Polymer Electrolyte Membranes Form an In-Situ Thermally Induced Semi-Interpenetrating Polymer Network between PVA and PAA

Munsur Md Abu Zafar Al, Hyungkyu Cho, Byeol-Nim Lee, Hyoung-Juhn Kim*

Korea Institute of Energy Technology, Korea

The polymer electrolyte membrane has gained enormous interest in the last three decades in energy conversion technology for renewable electricity generation. There are a great variety of polymer electrolyte membranes that have developed, such as perfluorosulfonic acid, polystyrene, polyether sulfone, polyether ketone, polyphenylene, polyolefine, polybenzimidazole, etc., which are used for modern electrochemical devices such as fuel cells and water electrolyzers. Polybenzimidazole is widely used as a polymer electrolyte that conducts ions between the cathode and anode and separates reactants due to its unique features, such as excellent electrochemical properties, chemical stability, and well-ordered chain-packed crystallinity. Unfortunately, despite those advantages, polybenzimidazole shows considerably high hydrogen crossover, phosphoric acid dissolution, and low mechanical flexibility¹. Therefore, the hydrogen crossover and phosphoric acid dissolution have a big impact on the durability of the electrochemical device for long-term operation.

Herein, we adopt an efficient polymer electrolyte membrane with enhanced electrochemical properties, high phosphoric acid retention capacity, and reduced hydrogen crossover. An in-situ semi-interpenetrated polymer network² composite membrane was formed by an esterified PVA/PAA cross-linked network with interpenetrated polybenzimidazole. The thermally induced esterification reaction between PVA and PAA forms a three-dimensional crosslinked network, which is expected to improve mechanical robustness and reduce hydrogen crossover. Therefore, the physicochemical properties of the prepared composite membranes, together with their applications as new polymer electrolyte membrane (PEM) materials for both fuel cell and water electrolyzer applications, will be systematically investigated and discussed in detail.

*Corresponding author	Hyoung-Juhn Kim
Affiliation	Korea Institute of Energy Technology
E-mail address	hjk@kentech.ac.kr

The Effect of Temperature and Electrolyte Concentration on the AEMWE Performance with P-Polybenzimidazole Membrane

Byeol-Nim Lee, Hyungkyu Cho, Md Abu Zafar Al Munsur, Hyoung-Juhn Kim*

Korea Institute of Energy Technology, Korea

The anion exchange membrane water electrolysis (AEMWE) is a promising technology for water electrolysis due to its cost-effectiveness and potential for large-scale hydrogen production at a low cost. However, further development is needed to enhance the performance of AEMWE cells, focusing on improving efficiency, durability, and optimizing operating conditions.

In this study, we aimed to investigate the factors influencing the performance of AEMWE using the p-polybenzimidazole(p-PBI) membrane. We conducted an analysis of the polarization curve and impedance to evaluate the electrolysis performance based on the concentration of the KOH solution and the operating temperature. The concentration of KOH solution was varied at 10, 15, and 20 wt.%, while the temperature was maintained at either 60 or 80 °C. The analysis of the polarization curve revealed that increasing the concentration of KOH solution at the same temperature resulted in a decrease in the ohmic resistance.

In addition, a remarkable reduction in the cell voltage was observed, indicating the enhanced performance of the electrolysis. This can be attributed to the improved ion conductivity of the p-PBI membrane in higher concentrations of KOH solution. Moreover, we observed that increasing the temperature from 60 °C to 80 °C at a 10 wt.% KOH concentration significantly improved performance in the high voltage region. However, at a concentration of 20 wt.%, the performance improvement was less pronounced compared to that observed at 60 °C. This result confirms that the change in concentration of the KOH solution has a more substantial impact on the cell polarization behavior compared to temperature. In conclusion, concentrated KOH solutions and higher temperatures have been proven beneficial for achieving highly efficient performance by reducing the energy needed for electrolysis.

*Corresponding author	Hyoung-Juhn Kim
Affiliation	Korea Institute of Energy Technology
E-mail address	hjk@kentech.ac.kr

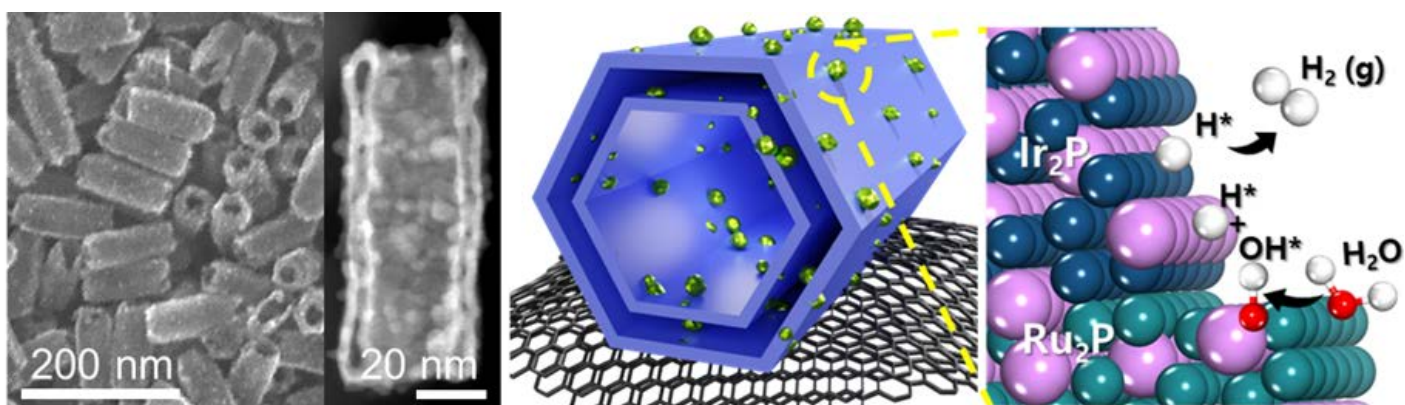
Interfacial Engineering of Ru₂P/Ir₂P Heterostructure for Alkaline Hydrogen Evolution Catalysis with Efficient Hydrogen Spillover

Kwangyeol Lee^{*}, [Sangyeon Jeong](#)

Korea University, Korea

For hydrogen evolution reaction (HER) in alkaline media, it is vital to trade-off hydrogen adsorption, hydroxyl adsorption, and water dissociation. Therefore, the rational design of electrocatalysts with excellent ability to dissociate water and bind hydrogen species at the same time can offer a pathway towards highly efficient alkaline HER catalysts. While various single-phase catalysts such as Ru₂P have been developed as HER catalysts, many failed to overcome the inherent sluggish reaction kinetics of HER in alkaline media.

Herein, we report the in-situ growth of Ir₂P clusters on Ru₂P hollow nanotubes, which are highly efficient electrocatalysts for alkaline HER. Density functional theory calculations reveal that the geometrical features of protruded Ir₂P clusters on the surface of Ru₂P promote fast cascade water dissociation and H₂ production by favoring hydrogen spillover from the Ru₂P surface to the adjacent Ir₂P cluster. This work highlights that rational synthesis of hybrid catalysts is a viable strategy for developing active and durable alkaline HER catalysts.



*Corresponding author

Affiliation

E-mail address

Kwangyeol Lee

Korea University

kylee1@korea.ac.kr

High-Performance Internal Reforming Methanol Fuel Cell with Novel HT-PEM Fuel Cells Technology

Joonbyum Kim, Gyeongseok Gwak, Seongwoo Kim, Junghwan Kim, Yeong Cheon Kim, Suk-Woo Nam^{*},
So Young Lee^{*}

Korea Institute of Science and Technology, Korea

The demand for hydrogen as a renewable energy source has increased due to global warming. Energy storage and conversion devices require the use of polymer electrolyte membrane fuel cells (PEMFCs) in integrated power and heat systems, because they offer higher energy density than current battery systems. Methanol, in particular, serves as promising hydrogen carrier with higher energy densities than pressurized hydrogen, overcoming technical obstacles associated with the use, storage, and transportation of pure hydrogen. However, a key challenge in utilizing methanol as a fuel for PEMFCs lies in the development of high-temperature polymer electrolyte membrane fuel cells (HT-PEM) that can operate above 210°C. Typically, HT-PEMFCs operate within the temperature range of 140-180°C and exhibit several advantages, including enhanced reaction kinetics, high power output, CO tolerance, and relatively simple water management [1]. However, current HT-PEMFCs based on phosphoric acid (PA) doped polybenzimidazole (PBI) membranes show limited long-term stability at higher operating temperatures and exhibit a significant drop in performance due to the PA leaching. Thus, one of the major challenges is the development of a membrane with excellent physicochemical stability and high performance at the temperature of 210°C and above. The aforementioned challenges have been successfully addressed and satisfied via the development of a cerium hydrogen phosphate (CeHP) membrane that allows for proton conduction above 200°C through a self-assembled network (SAN) nanofibrous structure by SY Lee et al. [1]. Consequently, it is feasible to design an internal reforming methanol fuel cell (IRMFC) by utilizing the novel HT-PEMFC and methanol as a liquid hydrogen carrier (LHC).

In this study, we developed a high-performance IRMFC in combination with the novel HT-PEMFC. The objective of our research is to enhance the operating temperature range, overall performance, and long-term stability of the fuel cell systems. Based on an innovative ultra-thin reformer design using double reformer and metallic bipolar plates proposed by Avgouropoulos et al. [2], we have designed an internal methanol reformer configuration that effectively utilizes methanol and achieves high current density. Through comprehensive experimental investigations, we have examined various operating parameters, overcome technical challenges, and introduced advancements in the performance, weight, and volume of the whole system. Our system has demonstrated remarkable results with maximum power densities of 1.15 W/cm² at 250°C and long-term stability over 180 hours with a voltage decay rate of 370μV/h at 220°C. The single cell of the HT-PEMFC with an external reformer exhibited efficient performance with long-term stability over 1000 minutes at 250°C, achieving a cell voltage of 600mV at 0.2A/cm².

By utilizing methanol as a LHC and integrating reformer within the high-performance HT-PEMFC, the IRMFC offers a sustainable and environmentally friendly alternative for energy conversion. This technology not only contributes to mitigating the challenges of climate change but also opens up new possibilities for sustainable future.

[1] Lee S et al. Self-assembled network polymer electrolyte membranes for application in fuel cells at 250°C. 2021.

[2] Papavasiliou J et al. Technological aspects of an auxiliary power unit with internal reforming methanol fuel cell. International Journal of Hydrogen Energy. 2019

*Corresponding author 1 Suk-Woo Nam
Affiliation Korea Institute of Science and Technology
E-mail address swn@kist.re.kr

*Corresponding author 2 So Young Lee
Affiliation Korea Institute of Science and Technology
E-mail address sylee5406@kist.re.kr

Development of Thin Film Assembled Membrane with High Gas Barrier for Anion Exchange Membranes Water Electrolysis Applications

Yung Bin Choi, Ju Yeon Lee, So Young Lee*

Korea Institute of Science and Technology, Korea

Alkaline water electrolysis (AWE) is a well-known technology for hydrogen production, as it uses inexpensive non-precious metal catalysts and is highly durable. However, AWE has a problem with hydrogen and oxygen crossover between the electrodes, which can lead to decreased hydrogen production and safety hazards. Attempts to mitigate this problem by using thicker porous diaphragms have increased overall resistance, leading to performance degradation.

To address the disadvantages of AWE, research on anion exchange membrane water electrolysis (AEMWE) using anion exchange membranes (AEMs) or ion-solvating membranes is actively being conducted. This approach has the advantage of reduced gas crossover and membrane resistance due to the non-porous dense polymeric membrane. However, AEMWE often exhibits low durability due to mechanical and thermochemical instability. Additionally, the non-porous structure may impede hydroxide ion transport in highly alkaline conditions.

Recently, a high-performance, durable asymmetric electrolyte membrane with a porous and dense structure has been developed to address the disadvantages of AWE and AEMWE [1]. Additionally, an advanced porous separator with a thin selective skin layer has been developed for AWE application with the goal of increasing cell performance and reducing hydrogen permeation [2,3].

In this study, we propose a thin film assembled (TFA) membrane as a high gas barrier for AEMWE systems. The TFA membrane consists of an AEM as thin film and a porous diaphragm as thick porous support. We used a commercial Zirfon diaphragm as porous structure. Also, Polybenzimidazole (PBI) and Poly(diphenyl-terphenyl piperidinium) (PDTP) were used as an AEM. The PBI and PDTP prevent gas crossover, resulting in superior current density and improved performance. Zirfon improves mechanical and thermochemical stability by facilitating electrolyte transport through the membrane.

Herein, we fabricated each TFA membranes and performed water electrolysis tests. Experiments were conducted at various KOH concentrations and temperatures to evaluate the water electrolysis performance of the fabricated Zirfon-PBI and Zirfon-PDTP TFA membranes. In addition, a long-term test was conducted at a high current density of 2 A cm^{-2} at $80 \text{ }^\circ\text{C}$ to confirm the durability of the TFA membrane.

As a result, the TFA membrane, a hybrid membrane combining a porous diaphragm and a non-porous AEM, was able to improve water electrolysis performance by preventing gas crossover and improving ionic conductivity in the AEMWE system. Additionally, it was also confirmed that they exhibit high durability even at high current densities. We are confident that the TFA membrane we proposed will contribute to future hydrogen production technology by showing higher performance and durability than previously studied membranes.

- [1] J. Y. Lee, S. Y. Lee, High Performance Asymmetric Polybenzimidazole Membranes for Anion-Exchange Membrane Water Electrolysis. EuroMembrane 2022 Abstract
- [2] Choi J et al. Thin Film Composite Membranes as a New Category of Alkaline Water Electrolysis Membranes. Small. 2023
- [3] Kim S et al. Highly selective porous separator with thin skin layer for alkaline water electrolysis. Journal of Power Sources. 2022

*Corresponding author	So Young Lee
Affiliation	Korea Institute of Science and Technology
E-mail address	sylee5406@kist.re.kr

Tailored Cu-Sb Catalysts via Electrodeposition for Selective CH₄ Production from CO₂ Electrolysis

Jungmin Yoo, Gyeong Ho Han, Sang Hyun Ahn*

Chung-Ang University, Korea

In recent decades, the rapid increase in anthropogenic carbon dioxide emissions released into the atmosphere has been a major contributor to the exacerbation of climate change. Electrochemical CO₂ reduction reaction (CO₂RR) using renewable energy sources is one of the good ways to respond to these problems and are a way to convert carbon dioxide into other high-value fuels or chemicals. Methane (CH₄) particularly benefits from the advantage of an already well-established infrastructure for its storage, distribution, and utilization. Converting CO₂ to CH₄ at high rates and energy efficiency, the development of efficient electro-catalysts plays a crucial and indispensable role, as it is essential for achieving high activity and selectivity. Copper (Cu) continues to be recognized as highly promising catalysts for the conversion of CO₂ into various C₁ and C₂₊ products. However, Cu-based catalysts are limited in application in the industry because of their poor stability and low selectivity in the target product. The poor properties of Cu-based catalysts can be attributed to the morphological changes resulting from degradation or the uncontrolled oxidation state of Cu, which occur during CO₂RR process. Alloying copper with other elements offers potential alternatives for controlling and adjusting the properties of catalysts.

By alloying a second metal antimony (Sb) into Cu, herein, we synthesized bimetallic copper-antimony catalysts, denoted as CuSb/MPL/CP, by co-electrodeposition on microporous layer-coated carbon paper (MPL/CP) under room temperature. FESEM and EDS CO₂RR tests were performed in a gas flow membrane electrode assembly (MEA) single cell using humidified gaseous CO₂. FE-SEM, EDS measurements revealed that Cu and Sb were well dispersed onto substrate. CO₂RR tests were performed in a gas flow MEA single cell using humidified gaseous CO₂. With the synergistic effect between Cu and Sb, the CuSb/MPL/CP catalysts achieve the highest CH₄ Faradaic efficiency (FE) of 55.4% with a CH₄ partial current density of 125.8 mA cm⁻². In addition, The Sb/Cu ratio of the catalyst can be adjusted by changing the deposition solution concentration, which, like other literature reports on Cu-Sb alloy catalysts, enhances the selectivity for CO and inhibits the selectivity for CH₄ and C₂₊ products. Now we are looking to improve performance with additional post-processing methods in the future, which has the potential to significantly improve overall performance levels.

*Corresponding author	Sang Hyun Ahn
Affiliation	Chung-Ang University
E-mail address	shahn@cau.ac.kr

6-3254

CuS Electrodes for Electrochemical CO₂ Reduction

Juho Ha, Hyunki Kim, Sang Hyun Ahn^{*}

Chung-Ang University, Korea

Electrochemical CO₂ reduction reaction (CO₂RR) is one of the promising solutions for carbon neutrality as it can recycle emitted CO₂ for clean production of industrial chemicals. Focusing on the catalyst, only Cu based materials show the unique feature about C₂₊ production. For decades, various studies have been conducted on the development of Cu catalyst through alloying, oxidation state control and about grain boundaries, crystal facet, dopants. However, it still has low partial current density and insufficient stability for commercialization.

Herein, copper sulfide was fabricated on carbon gas diffusion layer with microporous surface. First, Cu was electrochemically deposited on the carbon paper. Subsequent immersing in Na₂S solution enables simple exchange of surface oxygens with S ions. By adjusting the exchange condition, catalyst morphology and surface composition can be easily controlled. The fabricated electrodes were employed as cathodes for CO₂RR electrolyzer and its faradaic efficiency(FE) were computed. It was revealed that the CO₂RR performance was highly affected by S coverage on Cu surface.

*Corresponding author	Sang Hyun Ahn
Affiliation	Chung-Ang University
E-mail address	shahn@cau.ac.kr

In-Situ Metal Oxide Modification of PA/PBI Composite Membranes for High-Temperature PEMFC Applications

Seong Woo Kim, Joonbyum Kim, Gyeongseok Gwak, Junghwan Kim, Yeongcheon Kim, Sukwoo Nam*, So Young Lee*

Korea Institute of Science and Technology, Korea

High-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) exhibit adequate CO tolerance and high reaction kinetics [1]. Among them, phosphoric acid doped polybenzimidazole (PA/PBI) membranes are known to be the most promising membranes used in HT-PEMFCs. In PA/PBI membranes, PA acts as a proton conductor, with protons being transferred via hydrogen bond rearrangement between the PA molecules and PBI backbone. [2]. However, there is a temperature limit (<180 °C) exists due to the condensation of PA, which makes it challenging to achieve operation in PEMFC above 200 °C. Recently, research on using metal oxides into the PA/PBI membrane has been pursued to develop a polymer electrolyte membrane that can be operated at temperature above 180 °C. The metal oxides in PA solution change into a metal hydrogen phosphate form that can prevent the evaporation of PA at high temperatures above 180 °C, showing no performance degradation. In addition, The transfer of protons to the metal hydrogen phosphate surface is facilitated, which improves the ionic conductivity at temperatures above 200°C. Herein, we prepared poly(2,2'-(1,4-phenylene)-5,5'-bibenzimidazole) (pPBI) composite membranes through an in-situ method in which metal oxides (SnO₂, TiO₂, ZrO₂) were added to the synthesis solution during pPBI synthesis. In this work, the effects of metal compounds on fuel cell performance and durability at high temperature above 200 °C will be discussed.

*Corresponding author 1 Sukwoo Nam
Affiliation Korea Institute of Science and Technology
E-mail address swn@kist.re.kr

*Corresponding author 2 So Young Lee
Affiliation Korea Institute of Science and Technology
E-mail address sylee5406@kist.re.kr

A Simulation Model for Ruthenium-Catalyzed Dry Reforming at Different Temperatures and Gas Compositions

Young Bae Jun*

Korea Institute of Science and Technology, Korea

Dry-reforming of methane (DRM) is a promising environmental-friendly technology for the production of syngas (a combination of H₂ and CO) and the concurrent consumption of CO₂. However, the widespread adoption of such technology is impeded by several challenges, particularly the short lifespan of the employed catalysts due to metal sintering, coke deposition, and sulfur poisoning.

To address such issue, researchers have explored catalysts with varying catalyst configurations, morphologies, and topologies. One promising type of catalyst is perovskites, in which active metals embedded in the B-sites are reduced and exsolved to the surface of the structure as nanoparticles. Such perovskite-structured catalysts exhibited superior performance and resistance to coke formation and poisoning compared to catalysts prepared by conventional impregnation methods.

In this study, using COMSOL Multiphysics software, the authors constructed a comprehensive simulation model of a DRM reactor that employs Sr_{0.92}Y_{0.08}Ti_{0.95}Ru_{0.05}O_{3-d}, a metal-exsolved-perovskite catalyst that was previously investigated by the author's research group [1].

To effectively simulate the reactor, five main reactions were considered: DRM reaction, reverse water-gas-shift, CH₄ decomposition, CO disproportionation (Boudouard reaction), and carbon-steam gasification [2]. The viscosity, thermal properties, and diffusivity of the gas mixture were calculated across a range of temperatures and gas compositions. The reaction efficiency (η) of the simulation model was derived by comparing empirical and simulated data. The evaluation of the parameter is of significant importance to accurately calculate fundamental information, such as reactor consumption and heat transfer.

Following validation against the experimental data, the effects of temperature, gas composition, and gas flow rate on the dry reforming reaction were investigated.

The analysis focused particularly on CH₄ and CO₂ conversion and H₂ yield. The findings demonstrated that increasing the temperature leads to higher conversions and yield. It was also observed that such increase led to a higher temperature differential between the operating and catalysts bed temperatures, in which the latter drops due to the endothermic nature of the reforming reaction. The same effect was observed when increasing the amount of CO₂ in the feed, yielding higher methane conversion rates. On the other hand, decreasing the gas flow rate reduced the temperature differential between the operating and catalysts bed temperatures, shifting the reaction towards equilibrium.

This study aims to contribute to the understanding of the intricate dynamics of DRM processes via utilizing simulation models.

[1] Kim, G. S., Lee, B. Y., Ham, H. C., Han, J., Nam, S. W., Moon, J., Yoon, S. P., (2019), Highly active and stable sr_{0.92}y_{0.08}ti_{1-x}ru_xo_{3-d} in dry reforming for hydrogen production, International Journal of Hydrogen Energy, 44(1), 202-212.

[2] Benguerba, Y., Dehimi, L., Virginie, M., Dumas, C., Ernst, B., (2015), Modelling of methane dry reforming over ni/al₂o₃ catalyst in a fixed-bed catalytic reactor, Reaction Kinetics, Mechanisms and Catalysis, 114(1), 109-119.

*Corresponding author

Affiliation

E-mail address

Young Bae Jun

Korea Institute of Science and Technology

jun971216@kist.re.kr

Electrodeposited Transition Metal Phosphide Electrocatalysts for Selective CO₂ Reduction to Multi-Carbon Products

Dong Young Hwang, Gyeong Ho Han, Sang Hyun Ahn*

Chung-Ang University, Korea

The global energy demand is continuously rising, leading to an annual increase in carbon dioxide (CO₂) emissions resulting from the combustion of fossil fuels such as coal, oil, and natural gas. Accordingly, many technologies have been utilized for minimizing amount of CO₂, which accounts for the largest share of greenhouse gases. Electrochemical CO₂ reduction have many benefits, including operation at room temperature and ambient pressure, easy to modularization and scale-up, and less restricted space.

In the CO₂ reduction reaction (CO₂RR), CO₂ is reduced at the cathode, and the products can vary depending on the number of reacting protons, electrons, and the applied potential. Also, the choice of catalyst plays a crucial role in determining the types of products formed. These products can be categorized as either liquid or gas and can also be classified based on the number of carbon atoms, such as C₁, C₂, C₃, and C₄ products. For example, Cu-based catalysts show good performance for C₂₊ products. However, they have lower selectivity for C₃₊ products because of higher energy barrier in multi-carbon formation. In the case of Cu, the binding energy of CO intermediates (*CO) is controlled to regulate the formation of C₂₊ products. This is because the process of *CO dimerization occurs during C-C coupling, leading to the formation of C₂₊ products. The other way to produce C₂₊ products is formate (*HCOO⁻) pathway with self-condensation of formaldehyde (H₂CO) from formate. Considering that, transition metal phosphide (TMP) are promising CO₂ electrocatalysts due to the formation of surface hydrides (*H⁻) on their surface. It is known that the formation of hydrides on the surface allows for their reaction with CO₂ to produce formate (*HCOO⁻). Also, TMP catalysts are known as good hydrogen evolution reaction (HER) catalysts. However, by applying a potential lower than the theoretical potential for the HER, such as 0 V_{RHE} (standard hydrogen electrode potential), it is possible to avoid HER, providing an advantage in the CO₂ reduction process.

In this study, TMP was synthesized on carbon paper (TMP/CP) using electrodeposition, including FeP/CP, NiP/CP, and CoP/CP. For morphological and crystalline changes, electrochemical etching or Ar annealing were employed. The CO₂RR performances of these catalysts were then evaluated in H-type cell operating at low potential regions where the HER doesn't occur. The expected products included C₃ (methylglyoxal) and C₄ (2,3-furandiol), which have standard electrochemical potentials (E⁰) lower than that of the HER. Gas products were analyzed using gas chromatography (GC), while liquid products were analyzed using ¹H nuclear magnetic resonance (¹H NMR) to determine the generated products and their quantities.

*Corresponding author	Sang Hyun Ahn
Affiliation	Chung-Ang University
E-mail address	shahn@cau.ac.kr

6-3320

Development of Highly Active and Durable Fe-N-C Catalyst for Anion Exchange Membrane Fuel Cells

Sourabh Sunil Chougule, Namgee Jung*

Chungnam National University, Korea

Abstract: Anion exchange membrane fuel cells (AEMFCs) have emerged as a promising technology for clean energy conversion, offering advantages such as the utilization of non-platinum group metal (NPGM) catalysts and alkaline electrolytes [1-2]. However, further development of this technology is hindered since its required high Pt loading catalyst at anode and cathode to achieve high performance in the fuel cell [2-4]. Among all identified NPGM candidates, iron-nitrogen-doped carbon (FeNC) single atom catalyst is most promising to catalyze the sluggish oxygen reduction reaction (ORR). FeNC single atom catalyst (SACs) were successfully synthesized by impregnating Fe precursor into carbon matrix followed high temperature pyrolysis. FeNC single atom catalyst was confirmed by XRD, XPS and HAADF-STEM images and optimized catalyst examined for electrochemical activity. Due to the uniformly dispersed single atom Fe with high density and Strong interaction between Fe-N₄ with carbon support, FeNC catalyst showed best catalytic activity as well as durability among many other state-of-the-art catalysts and the commercial Pt/C.

Objective: This research aims to investigate the feasibility and performance of FeNC SACs as catalysts for the ORR in AEMFCs. By achieving atomic dispersion of Fe on carbon supports, we are expecting enhanced catalytic activity and stability. Moreover, understanding the structure-property relationship of FeNC SACs in alkaline media will provide valuable insights into their application potential in AEMFCs.

Methods: FeNC SACs Synthesized by grinding Iron phthalocyanine and carbon support precursor with ethanol solvent. As prepared catalysts annealed at different temperature 600-900° C in Ar atmosphere to form chemically absorbed Fe-N₄ structure on carbon support. Furthermore, Annealed samples washed with 0.5 M H₂SO₄ to remove excess nanoparticle and kept in vacuum oven for overnight to dry.

Results:

The ORR performance of the all catalysts were evaluated using O₂-saturated 0.1M KOH solutions, in which half-wave potentials ($E_{1/2}$) of the catalysts decreased in the following order FeNC600 > FeNC 700> FeNC 800> FeNC 900. Among all samples FeNC 600 sample Shows high ORR activity ($E_{1/2}$ = 0.875 V RHE) than that of commercial Pt/C catalyst ($E_{1/2}$ = 0.86 V RHE). FeNC 600 catalyst selected for durability test and The ADTs were performed by 10,000 (10 k) potential cycling in O₂-saturated 0.1 M KOH solution, at a scan rate of 100 mV s⁻¹ between 0.6 and 1.0 V. After 10 k potential cycles, FeNC 600 sample shows high durability that Pt/C catalyst.

Conclusion: The activity and stability behaviors of Pt/C and FeNC catalysts were investigated with different temperature Annealed samples. The optimized catalyst, FeNC 600-Ar, achieves high activity ($E_{1/2}$ = 0.875 VRHE in 0.1 M KOH). This work has not only provided a promising precious-metal-free ORR catalyst candidate but also invented a versatile synthetic method for highly tunable heterogeneous electrocatalysts.

Referances:

1] J. Huo, J. Mater. Chem. A, 2020, 8(32), 16271-16282

2] L. Wang, J. Mater. Chem. A. 2020, 8, 13166-13172

3] M.Assad, Journal of Colloid and Interface Science 2021, 596, 148–157

4] J. Lilloja, Journal of Power Sources Advances, 2021, 8, 100052

*Corresponding author

Namgee Jung

Affiliation

Chungnam National University

E-mail address

njung@cnu.ac.kr

Enhanced Oxygen Evolution Reaction Performance in Water Splitting: Synthesis of Ru-Doped NiFe Catalysts

Sun Beom Ahn, Gyeong Ho Han, Sang Hyun Ahn*

Chung-Ang University, Korea

Hydrogen energy is receiving significant attention as a potential replacement for future energy resources. Among various methods of hydrogen production, electrolysis is highly environmentally friendly as it does not emit carbon dioxide as a byproduct. Electrolysis consists of two reactions: oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Due to the involvement of four-electron transfer, OER generally exhibits slower reaction kinetics compared to the two-electron transfer involved in HER. Therefore, improving the performance of OER is crucial for enhancing the efficiency of electrolysis since it is the rate-determining step.

IrOx and RuOx are considered the most effective catalysts for the OER due to their high activity and stability compared to other metals. However, their use is limited in commercial applications due to the high cost and limited availability of these precious metals. As an alternative, research has been conducted on non-precious transition metal compounds such as Ni, Co, and Fe. Among them, Ni-based catalysts, including NiP, NiFe, and NiCo₂O₄, have shown promising OER performance. Nevertheless, these compounds still fall short of the performance exhibited by IrOx and RuOx. To address this, doping small amounts of Ir or Ru into the catalysts can enhance their performance.

Various methods can be employed for catalyst fabrication, including chemical precipitation, chemical vapor deposition, hydrothermal synthesis, sol-gel method, and electrodeposition. Among these, electrodeposition offers several advantages. By controlling the current density, potential, and deposition time, one can precisely manipulate the thickness, morphology, and composition of the catalyst layer. Furthermore, electrochemical deposition enables uniform coating on the electrode surface and reduces contamination from other impurities, thus facilitating the production of high-purity catalysts.

Galvanic displacement is an oxidation-reduction reaction that occurs based on the difference in standard reduction potentials between two metals. The metal with a relatively higher standard reduction potential (more negative value) undergoes oxidation, while the metal with a lower standard reduction potential is spontaneously reduced. This reaction occurs spontaneously, requiring no complex equipment or sophisticated procedures, making it easily accessible. Additionally, it can be easily scaled up for industrial production.

Herein, we aimed to enhance the performance by synthesizing a NiFe compound and preparing a catalyst with a small amount of Ru doping. First, a film was fabricated onto carbon paper using electrodeposition, followed by the Ru doping through a galvanic displacement method. The performance of the prepared catalyst was evaluated under 1.0 M KOH conditions. The results showed that NiFe/CP exhibited decent performance with an overpotential of 257 mV at 10 mA/cm², while Ru-NiFe/CP demonstrated enhanced performance with an overpotential of 227 mV.

Furthermore, we are conducting experiments with the expectation of synergy effects between the catalyst electrodeposited on stainless steel fiber paper composed of Ni, Fe, and Mo, known for their good OER performance.

*Corresponding author

Sang Hyun Ahn

Affiliation

Chung-Ang University

E-mail address

shahn@cau.ac.kr

6-3341

Development of a Normalized Test Protocol for PEM Fuel Cell Characterization

Youngseung Na, Choeun Kim *

University of Seoul, Korea

Fuel cells utilizing hydrogen have gained significant attention as eco-friendly energy sources. To enable their application in diverse fields such as automotive, building, and portable systems, fuel cells need to be optimized and their performance under various geometries, parameters, and operating conditions must be thoroughly examined. A crucial aspect of accurate testing lies in the adoption of a normalized test protocol and experimental setup. This study highlights three critical factors in a test protocol: reproducibility, degradation prevention, and evaluation of influential parameters.

This study focuses on the development of a normalized test protocol that ensures reproducibility, even in the presence of device or experimenter changes. The protocol aims to prevent contamination of results caused by deterioration, regardless of the number of parameter variations and test repetitions. However, existing test protocols often struggle to satisfy these requirements, hindering reproducibility and accurate analysis of parameter influences. This research aims to address these challenges by proposing a robust test protocol that enables consistent results, minimizes contamination, and facilitates the analysis of changed parameters with significant differentiation. The development of such a protocol contributes to enhancing the reliability and reproducibility of fuel cell testing methodologies.

Reproducibility failures often arise due to the hysteresis effect observed in initial humidity experiments or flooding caused by water accumulation in the flow path. The presence of deterioration further complicates accurate analysis, as it can be accelerated depending on the amplitude condition of the impedance. To address these challenges, a comprehensive test protocol is proposed by optimizing the combination of Open Circuit Voltage (OCV), Electrochemical Impedance Spectroscopy (EIS), IV curve measurements, and other relevant techniques.

Furthermore, novel strategies are devised to mitigate the impact of prior experiments on subsequent ones, ensuring that various factors from previous tests do not interfere with later experiments. This approach enables the development of a test protocol that satisfies the aforementioned conditions. Additionally, the protocol accounts for the diverse parameters associated with fuel cells, allowing for a thorough analysis of their influence.

We are committed to supporting your study analysis by providing valuable insights and guidance in the development of an effective test protocol. By incorporating these advancements, the field of fuel cell testing can overcome existing limitations and achieve more accurate and reliable results.

*Corresponding author	Choeun Kim
Affiliation	University of Seoul
E-mail address	cho509@uos.ac.kr

RuO₂ Supported on the PdPb Multi-frame for Strengthened Electrocatalytic Activity and Stability for OER in Acidic Media

Doyeop Kim, Kwangyeol Lee*

Korea University, Korea

Electrochemical water splitting suggests a promising carbon-free method for hydrogen production, which can greatly reduce reliance on fossil fuels. However, one major challenge in enhancing the efficiency of this process depends on the sluggish kinetics of the oxygen evolution reaction (OER). Existing catalysts based on Ru nanoparticles exhibit remarkable activity for acidic OER but are susceptible to dissolution in acidic conditions, limiting their stability. We have developed a novel approach to synthesizing RuO₂ catalysts supported by PdPb multi-frames to address this issue. This involved a seed-mediated growth method followed by thermal oxidation, stabilizing the Ru-based nanocatalyst. Through temperature control of thermal oxidation, it is possible to adjust the degree of doping of Pd into RuO₂, and the presence of Pd doped in RuO₂ prevents overoxidation, leading to exceptional catalytic activity and remarkable stability for the acidic OER. This study suggests an ideal synthesis method for efficiently introducing dopants into RuO₂-based catalysts while providing a new understanding of catalyst development with improved performance in acidic conditions for the OER.

*Corresponding author	Kwangyeol Lee
Affiliation	Korea University
E-mail address	kylee1@korea.ac.kr

Efficient Hydrogen Evolution Reaction over Edge-Exposed 1T Phase WS₂ Grown Directly on the Surface Modified 3D WO₃ Nanohelical Array

Bongwon Kim, Jaerim Kim, Noho Lee, Jong Kyu Kim *

Pohang University of Science and Technology, Korea

The electrochemical hydrogen evolution reaction (HER) in water splitting has been widely considered as a promising technology to produce clean and renewable hydrogen fuel. As promising catalytic materials for the electrochemical HER, layered 2 dimensional (2D) transition metal dichalcogenides (TMDCs) such as MoS₂ and WS₂ have drawn great attention as alternatives to precious metals such as platinum (Pt) and gold (Au).

In this study, a hierarchical catalyst consisting of edge-exposed 1T phase WS₂ grown on an array of surface-modified WO₃ nanohelices (NHs) and its enhanced electrochemical HER performance are presented. The oxygen-deficient WO₃ NHs surface modified by controlled annealing facilitates the formation of the edge-exposed WS₂ during sulfurization. The metallic 1T phase WS₂ is preferentially grown on the WO₃ NHs owing to the strain induced between WS₂ and curved WO₃ NHs. Furthermore, ion irradiation enables the formation of the higher density of oxygen vacancies in the WO₃ NHs, and thus, the growth of a rich edge-exposed 1T phase WS₂ during sulfurization. The resulting catalyst exhibits an exquisite combination of desirable structural properties, including a metallic 1T phase and a wealth of edge-exposed morphologies, leading to a remarkable enhancement in HER performance for efficient water splitting.

*Corresponding author	Jong Kyu Kim
Affiliation	Pohang University of Science and Technology
E-mail address	kimjk@postech.ac.kr

6-3456

Effect of Heat Treatment Process on Pt-C Hybrid Catalysts for Fuel Cells

Khikmatulla Davletbaev, Namgee Jung*

Chungnam National University, Korea

Abstract

Proton exchange membrane fuel cells (PEMFCs), which can directly transform chemical energy into electrical energy, are considered as one of the promising energy technologies due to their high efficiency [1-2]. PEMFC performance significantly relies on electrocatalysis at the cathode due to the sluggish kinetics of oxygen reduction reaction (ORR). In PEMFCs, carbon-supported Pt nanoparticles (Pt/C) are mainly used as catalysts for ORR because of their outstanding electrochemical property [3]. Nevertheless, it is well known that Pt/C suffers from durability issues due to agglomeration and dissolution of Pt nanoparticles under harsh conditions during fuel cell operation [4]. Herein, our research focuses on Pt encapsulation by carbon shells and the protective effect by carbon shells on the durability of Pt nanoparticles. The microstructure of the carbon shell is elaborately controlled by the flow rate of H₂ gas and annealing time. As a result, the robust porous carbon shell effectively prevents dissolution and Ostwald ripening of the Pt nanoparticles while exhibiting high electrochemical performance during long-term operation.

Objectives

The main objective of this study is to develop Pt-C hybrid catalysts with carbon-encapsulated Pt nanoparticles (Pt@C/C) to demonstrate the protective effect by carbon shells on the ORR activity and durability of Pt nanoparticles. To achieve this purpose, the pore size of the carbon shell layer is regulated by changing the heat treatment conditions in H₂ gas atmosphere.

Methods

The Pt@C/C catalysts is synthesized via solvothermal reaction using Pt(acac)₂ and carbon supports. Carbon atoms derived from the organic ligands, acetylacetonates (acac) can be incorporated into the lattice of metal nanoparticles during high-temperature reaction, and subsequent heat treatment forms ultrathin carbon shells on Pt nanoparticles. To regulate the pore size of the carbon shell layer without changing the particle size, the flow rate of H₂ gas and annealing time are rationally optimized in the heat treatment process.

Results

As-prepared samples are heat-treated in H₂/N₂-mixed gas atmosphere by changing the experimental conditions such as gas flow rate and annealing time. The carbon shell formation on Pt nanoparticles is clearly demonstrated by transmission electron microscope (TEM) and electrochemical tests. As a result, the exposed metal surface area of the Pt@C/C catalysts changes with heat treatment conditions due to the regulated porosity of the carbon shell, exhibiting different ORR activity and durability.

Conclusion

Carbon shell-encapsulated Pt catalysts are successfully synthesized by a solvothermal method followed by heat treatment. The pore structure of the carbon shell is modulated at the atomic level by altering the post-annealing conditions. It is demonstrated that the robust porous carbon shell layer contributes to the enhanced durability of the Pt nanoparticles while exhibiting high ORR activity during long-term operation.

References

- 1] N. Jung, Nano Today, 2014, 9,433-456
- 2] S. Ji, ACS Catal, 2022, 12, 7317-7325
- 3] J. Min, Curr Opin Electrochem, 2023, 39:101257
- 4] S.Chougule, Carbon Energy, 2023, 10.1002

*Corresponding author	Namgee Jung
Affiliation	Chungnam National University
E-mail address	njung@cnu.ac.kr

High Performance and Durability Para Polybenzimidazole Composite Membrane for Anion Exchange Membrane Water Electrolysis Applications

Se Hak Kim^{1,2}, Ju Yeon Lee¹, Yun Jeong Hwang^{2*}, So Young Lee^{1*}

¹*Korea Institute of Science and Technology, Korea*

²*Seoul National University, Korea*

As global warming becomes a more pressing issue, hydrogen energy has been touted as a promising new energy source. Water electrolysis is a process that can produce hydrogen efficiently and environmentally friendly, and anion exchange membrane water electrolysis (AEMWE) has recently been developed as an alternative to conventional water electrolysis. Hydrogen produced using an anion exchange membrane water electrolysis (AEMWE) is more efficient and pure rather than liquid typed alkaline water electrolysis (AWE). Additionally, non-precious metal catalysts can be used in AEMWE, which could make it cheaper than proton exchange membrane water electrolysis (PEMWE). However, it has been reported that AEMs for water electrolysis still exhibit low ion conductivity and alkaline stability, which limits their performance and durability compared to PEMWE.

In this study, we developed high-performance and durable para-polybenzimidazole (p-PBI) membranes with cerium nanofillers for AEMWE applications. To understand the role of cerium nanofillers on the composite membrane structure and AEMWE performance, composite membranes were prepared with various amounts of cerium nanofiller loading level from 0 to 50 wt%. The relationship between the structural properties of the composite membranes and cerium nanofiller content was investigated in terms of membrane morphology, ion conductivity, mechanical properties, and water or KOH mass transport. Electrochemical performance was also evaluated for the various types of prepared composite membranes. Finally, long-term stability test at high constant current density and high temperature (> 60 oC) was conducted to confirm membrane durability. These results will be presented in the poster section of the International Conference on Advanced Electromaterials 2023 (ICAE 2023).

*Corresponding author 1 Yun Jeong Hwang
Affiliation Seoul National University
E-mail address yjhwang1@snu.ac.kr

*Corresponding author 2 So Young Lee
Affiliation Korea Institute of Science and Technology
E-mail address sylee5406@kist.re.kr

Effect of Catalyst Post-Heat Treatment on Microstructure of Electrode in Polymer Electrolyte Fuel Cells

Sungmin Kim, Yun Sik Kang, Iksung Lim, Hyunjoon Lee, Eunjik Lee, Seunghee Woo, Seok-Hee Park, Gu-Gon Park, Sung-Dae Yim*

Korea Institute of Energy Research, Korea

Polymer electrolyte membrane fuel cells (PEMFCs) are gaining recognition as a future energy device due to their high conversion efficiency and minimal environmental impact compared to conventional energy sources. However, PEMFCs have not yet achieved a significant advantage in terms of performance or economic aspects to fully replace traditional energy sources. To address this, enhancing the performance of fuel cell components can lead to a higher power density, allowing for a reduction in the number of cells in a stack, resulting in cost savings and improved economic feasibility. In PEMFCs, the membrane electrode assembly (MEA) is a critical component where the electrochemical reactions actually occur, and the structure of the MEA determines the performance of a single cell and, consequently, the PEMFC stack and system. Therefore, understanding and optimizing the structure of the MEA, particularly the electrode, are crucial for the development of PEMFCs. As one way to improve the performance of PEMFCs, many researchers have focused on the development of electrode structures. The structure of the electrode, where catalytic reactions take place, such as the oxygen reduction reaction, significantly affects the performance and durability of PEMFCs. Typically, the electrode is produced by depositing and drying a slurry composed of electrode catalyst, ionomer, solvent, or other materials. The internal microstructure of the slurry is determined by the characteristics of the materials used and their interactions, ultimately influencing the microstructure of the final electrode and, as mentioned earlier, the performance and durability of the PEMFCs.

In this study, we aim to analyze the effect of post-heat treatment in various gas atmospheres on the surface characteristics of carbon-supported Pt catalyst and investigate the changes in the interaction between the catalyst and ionomer resulting from catalyst modification. Ultimately, we seek to find the correlation between the internal microstructure of the electrode and the performance of PEMFCs. To achieve this, a slurry containing the modified catalyst was prepared, and the interactions between the catalyst and ionomer were analyzed using dispersion analyzer and rheometer. Additionally, MEAs with the slurries were fabricated, and various electrochemical evaluations were conducted. Through these analyses, we investigated the correlation between the rheological properties of the slurry, the physical characteristics of the electrode, and the electrochemical characteristics of MEAs.

*Corresponding author	Sung-Dae Yim
Affiliation	Korea Institute of Energy Research
E-mail address	jimmyim@kier.re.kr

6-3475

Boosting Polymer Electrolyte Membrane Fuel Cells Performance under Low Platinum Loading through Direct Current Power Variation in Platinum and Cobalt Co-Sputtering

Hyoummyoung Oh, Taehyun Park*

Soongsil University, Korea

This study seeks to overcome the barriers to commercializing proton exchange membrane fuel cells (PEMFCs), primarily the reliance on platinum (Pt), a rare and expensive metal. Instead of depositing Pt, we utilized Pt₃Co as a catalyst, also aimed to identify the optimal sputtering conditions that would yield higher performance relative to the same Pt usage. Pt₃Co offers improved oxygen reduction reaction (ORR) and a larger surface area, demonstrating superior performance compared to Pt alone. As various sputtering deposition methods exist, our experiment strived to find the optimal conditions. We conducted sputtering processes using On-Off and Stair methods, with a Pt loading of 0.05 mg/cm² for all samples. Among these, the Pt₃Co-Stair exhibited the highest peak power density of 247 W/cm², followed by Pt₃Co-On Off at 228 W/cm², while Pt alone had the lowest value of 211 W/cm². Furthermore, we verified the characteristics of the catalyst through SEM, XRD, and EIS analyses. The following study facilitates the commercialization of PEMFCs by improving performance and reducing reliance on costly materials.

*Corresponding author	Taehyun Park
Affiliation	Soongsil University
E-mail address	taehyunpark@ssu.ac.kr

Bismuth Doped Nickel Oxide Catalyst for Efficient Hydrogen and Oxygen Evolution Reaction in Alkaline Media

Seunghyun Jo, KwangSup Eom*

Gwangju Institute of Science and Technology, Korea

To substitute noble metal-based electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), the development of nickel oxide catalysts has attracted intense research interest due to their cost-effectiveness and high activity. In particular, nickel oxide exhibits remarkable catalytic activity because nickel has a strong affinity for protons in the HER pathway, and the easy electrochemical oxidation on the surface of nickel oxide triggers reconstruction, forming hydroxide structures that are suitable intermediates for the OER. However, nickel oxide has a relatively higher activation energy for the desorption of protons (the second step of HER, $\text{Ni-H}_{\text{ads}} \rightarrow \text{Ni} + \text{H}_2$) and the reaction step from nickel(II) oxide to nickel(III) oxyhydroxide (the third step of OER, $\text{Ni-O} \rightarrow \text{Ni-OOH}$) compared to other steps. Consequently, these steps become the rate-determining steps (RDS) of HER and OER, respectively. The significantly high activation energy of the RDS seriously reduces the reaction rate, necessitating the control of the electric structure of nickel oxide to optimize the adsorption energy of intermediates.

In this context, bismuth additives are incorporated into nickel oxide electrocatalysts to enhance the HER and OER activities. Bismuth, being more electronegative than nickel, reduces the positive charge on nickel during HER steps, resulting in lower attraction to protons. Moreover, the positively charged nickel oxide exhibits a higher attraction to hydroxide ions during OER steps. Consequently, the activation energy of the RDS for HER and OER is reduced compared to pristine nickel oxide. In practical terms, the bismuth-doped nickel oxide demonstrates a 107 mV and 59 mV lower overpotential at 20 mA cm^{-2} in alkaline HER and OER, respectively, compared to nickel oxide. Furthermore, the bismuth-doped nickel oxide also demonstrated extended durability exceeding 67,000 hours for both HER and OER.

*Corresponding author	KwangSup Eom
Affiliation	Gwangju Institute of Science and Technology
E-mail address	keom@gist.ac.kr

Impact of Relative Humidity on Open Circuit Voltage in Proton Exchange Membrane Fuel Cells

Choeun Kim, Youngseung Na*

University of Seoul, Korea

Fuel cells have gained significant attention as a clean and sustainable energy source. Proton Exchange Membrane Fuel Cells (PEMFCs) stand out due to their quick response and low operating temperature. One crucial performance parameter of PEMFCs is the Open Circuit Voltage (OCV), electrochemical potential between the hydrogen fuel and the oxidant, which directly affects their power output and overall efficiency. This study focuses on investigating the relationship between relative humidity and PEMFC OCV to provide valuable insights into optimizing the operation of these fuel cells.

The experimental setup consisted of a single-cell PEMFC, which was operated under different relative humidity conditions. OCV and Electrochemical Impedance Spectroscopy (EIS) was employed to analyze the impact of humidity on electrical resistance. The relative humidity levels were controlled by adjusting the water content in the hydrogen and air streams.

The experimental results indicate a decrease in open-circuit voltage (OCV) with increasing relative humidity. To gain deeper insights into this phenomenon, the theoretical voltage loss is calculated using the Nernst equation. A comparison between the experimental and theoretical results demonstrates that the experimental voltage loss exceeds the value predicted by the theoretical model. Analysis of the electrochemical impedance spectroscopy (EIS) data reveals variations in the electrical resistance of the components, which can be attributed to changes in humidity levels. These fluctuations in electrical resistance directly impact the overall system performance, thus accounting for the observed disparities between the experimental and theoretical voltage losses.

Overall, this study provides valuable insights into the relationship between relative humidity and PEMFC OCV. The findings highlight the importance of humidity control in optimizing the performance and efficiency of PEMFCs, shedding light on potential strategies for enhancing the operation of these fuel cells in practical applications.

*Corresponding author	Youngseung Na
Affiliation	University of Seoul
E-mail address	ysna@uos.ac.kr

High-Performance Water Electrolyzer with Minimum Platinum Group Metal Usage: Iron Nitride-Iridium Oxide Core-Shell Nanostructures for Stable and Efficient Oxygen Evolution Reaction

Jinoh Oh¹, Hui-Yun Jeong², Hyun S. Park^{1*}

¹*Korea Institute of Science and Technology, Korea*

²*Lawrence Livermore National Laboratory, USA*

To reduce the usage of rare-earth metals in a proton-exchange-membrane water electrolyzer (PEMWE), a highly active water-oxidizing anode based on a core-shell catalyst structure was developed. Earth-abundant metal-based iron-nitride nanostructure was adopted to support thin, electrodeposited iridium-oxide films. PEMWEs with core-shell nanostructure has substantially low ohmic and mass-transfer resistances, suggesting that the introduction of Fe₂N nanostructure on Ti PTL enhances the transfer of protons, water, and oxygen on the catalyst layer. Furthermore, a high Ir mass activity of 103 A/mg_{Ir} was achieved with reduced Ir loading of 0.036 mg/cm² on the Ti PTL. The well-known weakness of transition-metal nitrides (TMNs) for use in PEMWEs, that is, their chemical instability in corrosive acidic environments, was overcome by carefully passivating the surfaces of the TMNs with chemically stable Ir catalyst layers. As a result, the prepared core-shell-structured catalysts were stable under the PEMWE operating condition.

*Corresponding author	Hyun S. Park
Affiliation	Korea Institute of Science and Technology
E-mail address	hspark@kist.re.kr

Enhancing Water Electrolysis with NiFe@NiMoP@ZnO Nanorods: A Simple and Efficient Synthesis Approach

Yeosol Yoon, Taeho Lim*

Soongsil University, Korea

Water electrolysis is gaining attention as a sustainable method for hydrogen production, owing to its eco-friendly nature. The process involves two reactions: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), for which Pt and IrO₂ have been considered as the state-of-the-art catalysts, respectively. However, the limited availability and high cost of noble metals present challenges in scaling up production. As a result, there is active research focused on developing inexpensive and high-performance non-noble metal catalysts, including nitrides, oxides, phosphides, and sulfides based on transition metals. Among these alternatives, nickel-based phosphides have emerged as potential candidates, with nickel (Ni) and phosphorus (P) playing crucial roles as hydride-acceptor and proton-acceptor, respectively. Their catalytic activity can be enhanced by reducing the energy barrier to water dissociation. Nevertheless, nickel-based phosphides still fall short of the performance exhibited by noble metal-based catalysts, hindering their practical application. One approach to improving their activity is through the use of templates. Nanostructures such as nanoplates, nanorods, and nanowires can augment mass transfer by increasing the surface area, thereby facilitating better contact with electrolytes. Furthermore, the presence of numerous exposed active sites contributes to the enhancement of activity. Another strategy involves doping with heterogeneous elements. Introducing additional elements promotes charge transfer by modifying the electronic structure through element interactions.

In this study, we were inspired by these concepts and synthesized NiFe@NiMoP using ZnO nanorods as a template. The ZnO nanorods were electrodeposited on a nickel foam (NF) substrate. Subsequently, NiFe@NiMoP was electrodeposited on the ZnO template to evaluate its activity in both the HER and OER. Remarkably, the catalyst exhibited outstanding activity compared to the catalyst electrodeposited directly on bare NF without the nanorods. This improvement in catalytic activity was attributed to the increased surface area resulting from the formation of nanorods. Moreover, the interaction between elements achieved through doping with heterogeneous elements facilitates fast charge transfer. Consequently, the electrodeposited NiFe@NiMoP catalyst demonstrated enhanced activity due to the increased number of exposed active sites and efficient charge transfer.

*Corresponding author	Taeho Lim
Affiliation	Soongsil University
E-mail address	taeholim@ssu.ac.kr

A Study on the Electrochemical Oxidation Behavior of Catechol Derivatives as Fuels for Direct LOHC Fuel Cells

Ha Neul Baek, Tae Ho Lim*

Soongsil University, Korea

Many governments and global companies have made significant efforts to address the depletion of fossil fuels and the escalating issue of global warming. In light of these challenges, hydrogen is being considered as a prospective alternative energy carrier for the future. However, gaseous hydrogen itself presents challenges due to its low volumetric energy density and risk of explosion. As an alternative to gaseous hydrogen, Liquid Organic Hydrogen Carriers (LOHC) have gained attention as a viable option. LOHCs are organic compounds that remain in a liquid state at room temperature and can securely store hydrogen through chemical bonding within the organic compound. Nevertheless, in order to use hydrogen stored within LOHCs, a separate high-temperature/high-pressure hydrogen extraction process is necessary. This process introduces inefficiency in terms of energy and the overall hydrogen utilization process. Consequently, among various LOHCs, recent attention has been focused on an LOHC that can be directly used as a fuel for fuel cells. One prominent material among these LOHCs is methanol. While numerous electrochemical studies have been reported on this substance, methanol has a significant drawback of emitting carbon dioxide during electrochemical oxidation. Therefore, alcohol-based LOHCs that do not generate carbon dioxide, such as isopropanol, have been investigated as a potential fuel for direct LOHC fuel cells.

Within this context, catechol has emerged as a newly proposed liquid-state hydrogen carrier. Catechol, which has an aromatic ring with two adjacent hydroxyl groups, undergoes electrochemical oxidation to form o-benzoquinone. Notably, catechol exhibits high electrochemical reversibility and reactivity, enabling efficient energy production through electrocatalytic oxidation reactions without relying on noble metals such as Pt. As a fundamental study, this study explores the potential as fuels of catechol derivatives (catechol, 4-methyl-catechol, 4-tert-butyl-catechol), which feature different electron-donating groups, using electrochemical measurements. Through this investigation, we have confirmed the positive influence of the electron donating group on the electrochemical oxidation of catechol derivatives.

*Corresponding author	Tae Ho Lim
Affiliation	Soongsil University
E-mail address	taeholim@ssu.ac.kr

Investigating the Influence of Cathode Catalyst Layer Fabrication Conditions on Toluene Electrochemical Hydrogenation in PEM Electrolyzers

Jaeyeon Park, Taeho Lim*

Soongsil University, Korea

Global energy consumption continues to rise, while Earth's reserves are increasingly depleted. As a result, our society is actively exploring numerous solutions, and hydrogen has emerged as a highly promising alternative that is extensively researched across various fields. However, due to hydrogen's low volumetric energy density and risk of explosion, storage and transportation pose significant challenges, prompting the investigation of diverse methods to overcome them. Among these approaches, the Liquid Organic Hydrogen Carrier (LOHC) offers a notable advantage as it possesses a relatively high volumetric energy density and remains in a stable liquid state at room temperature, enabling the utilization of existing petroleum infrastructure. Toluene, in particular, has received significant attention as a favorable LOHC due to its affordability and high selectivity in converting to methylcyclohexane, a hydrogenated form.

The objective of our study was to store hydrogen in toluene through the electrochemical hydrogenation process. For this purpose, we employed a Proton Exchange Membrane (PEM) electrolyzer, which consisted of a PEM, anode, cathode, separators with flow fields, and current collectors. We specifically investigated the influence of various fabrication conditions of the cathode catalyst layer on the electrochemical hydrogenation of toluene. Through electrochemical analysis, we explored different factors such as catalyst types, composition of the catalyst ink used to form the catalyst layer, the method of catalyst layer formation, and the type of Liquid/Gas Diffusion Layer (LGDL). By integrating the experimental and analytical results, we successfully developed an optimized cell for toluene hydrogenation.

*Corresponding author	Taeho Lim
Affiliation	Soongsil University
E-mail address	taeholim@ssu.ac.kr

A Study on the Effect of Toluene/Water Crossover on the Electrochemical Hydrogenation of Toluene in a PEM Electrolyzer

Junbeom Jeon, Taeho Lim^{*}

Soongsil University, Korea

Hydrogen is increasingly being considered as a potential alternative to traditional hydrocarbon energy sources. Extensive research is being conducted to produce hydrogen without harmful emissions. However, the inherent challenges associated with hydrogen, particularly in terms of storage and transportation, present significant obstacles. For instance, when storing hydrogen in liquid form, it necessitates supercooling it to a temperature as low as -253°C. Similarly, when storing hydrogen in its gaseous state, it requires pressurization up to 700 bar. These methods, relying on extreme temperatures and pressures, pose physical limitations.

In response to these challenges, researchers are exploring a chemical approach called Liquid Organic Hydrogen Carrier (LOHC). LOHCs offer the advantage of conveniently storing and transporting hydrogen under ambient temperature and pressure conditions. Recently, there have been attempts to directly store hydrogen in LOHC through water splitting, with toluene being a widely used LOHC material for this purpose. Toluene, which hydrogenates to form methylcyclohexane, is considered a promising LOHC due to its high stability under ambient conditions and compatibility with existing petroleum infrastructure. However, there is a lack of comprehensive studies on the electrochemical hydrogenation of toluene, particularly in terms of the implementation of a Proton Exchange Membrane (PEM) electrolyzer.

This study investigates the impact of toluene/water crossover, a phenomenon that can occur in a PEM electrolyzer, on the electrochemical hydrogenation of toluene. During the hydrogenation process, a small amount of toluene migrates from the cathode to the anode through the PEM, negatively affecting the oxygen evolution reaction of the anode. Conversely, a significant amount of water also passes from the anode to the cathode, influencing the hydrogenation reaction of toluene. We conducted a detailed investigation of these phenomena using various electrochemical measurement methods.

*Corresponding author	Taeho Lim
Affiliation	Soongsil University
E-mail address	taeholim@ssu.ac.kr

Diagnostic Analysis of the Electrode Degradation by Carbon Corrosion Reaction in Polymer Electrolyte Membrane Fuel Cells Using the Electrochemical Impedance Spectroscopy Analysis

JunHwa Kwon, Seunghyun Jo, Ki-Yeop Cho, KwangSup Eom*

Gwangju Institute of Science and Technology, Korea

In compliance with the global energy paradigm shift from fossil to fuel, there has been increasing demand for advanced polymer electrolyte membrane fuel cell (PEMFCs) technologies for automobile and power generator systems as well. Nevertheless, the present PEMFC systems are still insufficient to meet the ultimate target, specifically with regard to the durability, suggested by U.S department of energy (DoE) [1]. Among the various causes limiting the lifespan of PEMFC, the corrosion of the support carbon is the most problematic issue, which has an enormous impact on the performance and durability of PEMFC systems. To elucidate the corrosion mechanism under diverse atmosphere, previous studies have conducted several analysis using in-situ techniques such as gas chromatography and non-dispersive infrared to identify the released corrosion by-products while measuring the electrode potential changes [2, 3], and electrochemical analysis to evaluate the degraded performance of PEMFCs. However, fundamental studies for electrode degradation behaviors during corrosion reactions are not fully understood even though carbon corrosion-induced structural deformation and collapse of supporting carbon are well-known for major factors affecting PEMFC performance decays [2]. Therefore, it is necessary to study the impact of structural properties of porous electrode on the performance and durability of PEMFCs.

In this study, we verified an exquisite methodology using the electrochemical impedance analysis with complex capacitance analysis based on transmission line model (TLM) equivalent circuit and performed two typical accelerated stress tests (ASTs); a load cycling test between 0.4 and 0.95 V vs. RHE and a high potential holding test at 1.4 V vs. RHE, mimicking the dynamic fuel cell operation and startup/shutdown cycles, respectively. In particular, to identify the effects of the deformation behaviors of carbon support on performance decaying of PEMFC during the consecutive degradation processes, the comprehensive results of the capacitive and faradaic impedance analysis are discussed in detail. Overall, the quantitative analysis of capacitive elements of degrading electrode would facilitate the extraction of physicochemical insight for diagnosis in the systemic point of view.

References

- [1] DOE Technical Target for Fuel Cell Systems for Stationary at <https://www.energy.gov/eere/fuelcells/doe-technical-targets-fuelcell-systems-stationary-combined-heat-and-power>
- [2] J. Electrochemical Society, 165,6, F3148-3160, 2018
- [3] J. Electrochemical Society, 164, 14, F1580-F1586, 2017

*Corresponding author

KwangSup Eom

Affiliation

Gwangju Institute of Science and Technology

E-mail address

keom@gist.ac.kr

Investigation of Cerium (IV) Hydrogen Phosphate as a Durability Booster for High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFCs)

Gyeongseok Gwak, Joonbyum Kim, Seongwoo Kim, Junghwan Kim, Yeong Cheon Kim, Suk-Woo Nam^{*},
So Young Lee^{*}

Korea Institute of Science and Technology, Korea

Fuel cell is electrochemical device which convert chemical energy into electrical energy from chemical reaction of hydrogen and oxygen or air. They are a promising research area for addressing modern global climate change. If hydrogen is supplied from electrolysis using green energy sources such as wind, solar, bio, and geothermal, power generating systems utilizing fuel cells emit no carbons to atmosphere, helping to prevent global warming caused by carbon emission.

Among the various types of fuel cell, low temperature proton exchange membrane fuel cells (LT-PEMFCs, below 100 °C), which combined perfluorosulfonic acid (PFSA) membranes and platinum-based electrodes, generate high electrical power at mild operation temperature. In addition, LT-PEMFCs is attractive as power sources for transportation applications, because these devices have advantages such as low noise and long driving distances on a single charge of hydrogen. However, LT-PEMFCs requires high-purity hydrogen (>99.97%) and water management systems for their realistic and stable operation. Slightly elevated temperature operation, enhancing the tolerance to impurities within hydrogen feed stream, is necessary, which also attribute to simplifying water management systems. However, PFSA membranes for LT-PEMFCs, with low glass transition temperature ranges (T_g , ~ 110 °C), is not applicable to higher temperature operation.

Compared to PFSA membranes, para-polybenzimidazole (p-PBI) membranes are more resistant to higher operating temperatures (T_g , ~ 430 °C). Phosphoric acid (PA) doped p-PBI membranes fuel cells show high and stable performance at 160 °C, which results from the proton conduction properties of doped phosphoric acid. However, at operating temperature above 180 °C, proton conduction through PA decreases due to its condensation of phosphoric acid and leakage.

We recently studied p-PBI membranes mixed with cerium hydrogen phosphate (CeHP) using in-situ composite membrane fabrication processes. These composite membranes overcome the reduction of proton conductivity by forming fibrous CeHP proton conduction pathway in p-PBI polymer matrix. The fibrous CeHP is stable above 180 °C, and in addition, the proton conductivity of CeHP increases as the operating temperature increases. We showed unprecedented high performance composite membrane fuel cells, which reach a maximum power density of 2.35 W/cm² (250 °C, H₂/O₂) and good durability of 7000 min at 0.2 A/cm².

However, these in-situ composite membrane fuel cells were analyzed using electrochemical impedance spectroscopy (EIS) to evaluate their long-term stability at 250 °C. The results showed that the electrode experienced significant degradation. To address this issue, in this study, we developed a new high performance and durability electrode using CeHP nanofibers. The CeHP nanofibers were incorporated into the electrode to form a three-phase interface with the binder (polytetrafluoroethylene, PTFE), catalyst (Pt/C, Pt alloy/C), and phosphoric acid (PA). We also investigated the role of CeHP and Ce within the membrane electrode assembly (MEA). Our results suggest that CeHP can improve the long-term durability and performance of high-temperature proton exchange membrane fuel cells (HT-PEMFCs) at harsh operating temperatures. Detailed results will be discussed in the ICAE 2023 poster presentation.

*Corresponding author 1	Suk-Woo Nam
Affiliation	Korea Institute of Science and Technology
E-mail address	swn@kist.re.kr
*Corresponding author 2	So Young Lee
Affiliation	Korea Institute of Science and Technology
E-mail address	sylee5406@kist.re.kr

Effect of pH of Electrolyte on Non-Noble Metal-Based Electrocatalysts in Oxygen Reduction Reaction

Jinyeop Kim, Dong Young Chung*

Korea Advanced Institute of Science and Technology, Korea

Due to its high cost and stability issues, efforts to replace platinum, which has unrivaled activities for the oxygen reduction reaction (ORR) of fuel cells, have recently increased. Platinum-group-metal free candidates such as N-doped carbon (N-C) and Fe-N-C exhibit comparable performance with platinum-based catalysts. Despite this possibility, the catalyst design is constrained by a lack of knowledge regarding active sites and mechanisms. Noting that it is important to understand the inner-sphere behaviors such as proton and electron transfer to identify the precise mechanism, efforts to accurately understand the reaction activity trend according to the pH of the electrolyte are required.

Herein, after identifying the pH dependence of polycrystalline platinum and gold which can provide a criterion of direct adsorption for oxygen species, the mechanism for the ORR on N-C and Fe-N-C catalysts was proposed by confirming the pH dependence of each catalyst and the rate-determining step (RDS) analysis through Tafel slopes. Both the activity trend according to pH and RDS analysis show that N-C and Fe-N-C can provide better ORR active sites which bind with oxygen directly than materials with low oxygen affinities, and that the case of Fe-N-C results in more efficient catalysis. Revealing that the pH effect of electrolyte on ORR activity allows us to know the circumstance of the active sites, the findings in this work can suggest a strategy in designing ORR catalysts.

*Corresponding author

Dong Young Chung

Affiliation

Korea Advanced Institute of Science and Technology

E-mail address

dychung@kaist.ac.kr

Development of Efficiency of Anion Exchange Membrane Water Electrolysis Using Transition Metal Based Catalysts

Chaeyeon Yang^{1,2}, Yung-Eun Sung^{2*}, Hyun S. Park^{1*}

¹*Korea Institute of Science and Technology, Korea*

²*Seoul National University, Korea*

As global fossil-energy consumption continues to rise, green hydrogen becomes a crucial energy vector in achieving carbon net-zero objectives. The conversion of renewable electricity into the chemical energy of hydrogen through water electrolysis provides a suitable and scalable method for achieving environmentally sustainable hydrogen production. Among various water electrolysis, alkaline water electrolysis (AWE) has been researched for a long time. However, AWE faces limitations in generating high purity and pressured gas products. Another challenge is the occurrence of gas crossover between hydrogen and oxygen dissolved in the electrolyte through a diaphragm separator employed in AWE. In contrast, Anion Exchange Membrane Water Electrolysis (AEMWE) employs a polymer membrane, which minimizes gas crossover and enables a compact system design with high-pressure operation. The alkaline conditions of AEMWE allow the use of cost-effective transition metal-based catalysts compared to noble metal-based catalysts. Nevertheless, transition metal-based catalysts have exhibited lower activity and durability compared to precious metal catalysts. In this presentation, we present nickel-based transition metal catalysts for AEMWE with enhanced catalytic activity by incorporating additional transition metals. The performance of the catalyst in water electrolysis was evaluated using a practical device.

*Corresponding author 1 Yung-Eun Sung
Affiliation Seoul National University
E-mail address ysung@snu.ac.kr

*Corresponding author 2 Hyun S. Park
Affiliation Korea Institute of Science and Technology
E-mail address hspark@kist.re.kr

Mitigating Surface Poisoning of Pt-Based Electrode for Stable Isopropanol Electrooxidation by Acetone Removal Process

Hanjoo Kim, Dong Young Chung*

Korea Advanced Institute of Science and Technology, Korea

Direct isopropanol fuel cell (DIFC) has received less attention than other direct alcohol fuel cells (DAFCs) because isopropanol (IPA) is selectively oxidized to acetone and not fully oxidized to CO₂, resulting in lower power output. However, DIFC has shown a new opportunity for generating electricity in closed, fully reversible cycle when combined with liquid organic hydrogen carrier (LOHC) without external input of heat. This system is applicable to on-board electricity generation on mobile platforms [1].

Despite the usefulness of DIFC, it is hard to commercialize due to its performance decay over time [2]. Many studies have conducted mechanistic understanding for IPA oxidation in half cell (3-electrode system) to find out the reason of the performance decay in DIFC. Most of in situ vibrational spectroscopies have shown that performance decay in DIFC is mainly related to increasing acetone coverage with time, leading to electrode surface poisoning and deactivation of catalyst [3][4].

Still, acetone-poisoned surface cleaning process for overcoming instability in DIFC have remained unclear. So, in this study, we study IPA oxidation on polycrystalline Pt and Pt/C electrode in half cell by applying various types of potential ranges. We identify a possibility of poisoned surface cleaning using acetone reduction. This finding will help in enhancing stability of DIFC.

References

1. G. Sievi, D. Geburtig, T. Skeledzic, A. Bosmann, P. Preuster, O. Brummel, F. Waidhas, M. A. Montero, P. Khanipour, I. Katsounaros, J. Libuda, K. J. J. Mayrhofer and P. Wasserscheid, *Energy Environ. Sci.* 12, 2305 (2019).
2. M. Brodt, K. Muller, J. Kerres, I. Katsounaros, K. Mayrhofer, P. Preuster, P. Wassercheid and S. Tiele, *Energy Technol.* 9, 2100164 (2021).
3. D. S. Mekazni, R. M. Aran-Ais, E. Herrero, J. M. Feliu, *J. Power Sources* 556, 232396 (2023).
4. F. Waidhas, S. Haschke, P. Khanipour, L. Fromm, A. Gorling, J. Bachmann, I. Katsounaros, K. J. J. Mayrhofer, O. Brummel, J. Libuda, *ACS Catal.* 10, 6831 (2020).

*Corresponding author

Dong Young Chung

Affiliation

Korea Advanced Institute of Science and Technology

E-mail address

dychung@kaist.ac.kr

6-3745

Evaluation of Electrochemical Performance of Bipolar Plate Free Polymer Electrolyte Membrane Fuel Cells: Operating in Low and High Relative Humidity

Gyutae Park, Taehyun Park*

Soongsil University, Korea

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) have emerged as a promising technology for a wide range of applications. The bipolar plate, a critical component of PEMFCs, plays a pivotal role in providing reactive gas, collecting electricity, and managing water and heat. Due to its significant volume contribution (more than 60% of the PEMFC stack) and significant cost impact (about 30% of the total cost), optimizing the bipolar plate design is critical for large-scale commercial deployment. Balancing mechanical strength, corrosion resistance, and cost reduction requires the exploration of innovative approaches.

In this study, we investigate the effects and trends of removing the bipolar plate on the cathode side of the PEMFC. A series of experiments were conducted by removing the bipolar plates from the anode and cathode sides, respectively. In addition, the experiments included varying the relative humidity of the inlet gas.

The power and impedance of a unit cell assembled with two serpentine bipolar plates were measured while varying the relative humidity at the anode and cathode. Remarkably, performance improvements were observed in all cases where the anode or cathode bipolar plate was removed.

Typically, the conventional unit cell exhibits sensitivity to the relative humidity of the cathode, meaning that performance is primarily affected by the humidification of the cathode inlet gas. However, when the cathode bipolar plate was removed, performance increased by approximately 60% and became more sensitive to the relative humidity of the anode inlet gas. The improved performance can be attributed to improved contact between the current collector and the gas diffusion layer, which facilitates homogeneous gas distribution, and the presence of water generated at the cathode, which provides sufficient humidification.

Electrochemical impedance spectroscopy (EIS) measurements revealed significant differences in resistance. When the cathode bipolar plate was removed, the dry state of the cathode inlet gas exhibited a lower ohmic resistance compared to the gas at 100% relative humidity. In addition, the decrease in charge transfer resistance exceeded the decrease in ohmic resistance.

In addition, we analyzed the performance trend as a function of the relative humidity of the inlet gas when the cathode bipolar plate was removed. In all cases, performance showed significant improvements over the conventional bipolar plate setup, with significant reductions in both ohmic resistance and charge transfer resistance. Interestingly, the dry cathode exhibited superior performance compared to the dry anode, contrary to the behavior of conventional bipolar plates. These results suggest that the effect of humidification is less significant when the bipolar plate is removed.

This research advances the understanding of the electrochemical performance of bipolar plateless PEMFCs and provides valuable insight into design considerations aimed at improving the efficiency and cost effectiveness of these

fuel cells in various applications.

*Corresponding author	Taehyun Park
Affiliation	Soongsil University
E-mail address	taehyunpark@ssu.ac.kr

Fabrication of Porous Tungsten Oxide Catalyst Controlled by Ethanol/DI Water Ratio for Highly Efficient Hydrogen Evolution Reaction

Minju Chae, Su Jeong Suh*
Sungkyunkwan University, Korea

Hydrogen is considered an excellent replacement fuel for the efficient and environmentally friendly production of energy. The hydrogen evolution reaction (HER), which occurs due to electrochemical water splitting, is a highly efficient and sustainable approach for achieving clean energy.

Tungsten oxide (WO_3) had received much attention due to its applications in various fields, such as in lithium-ion batteries, gas sensors, and as electrochromic and photochromic devices. Among all other transition metal oxides, being excellent corrosion resistant, WO_3 stands apart due to its stability in aqueous and acidic electrolytic solutions. In this study, WO_3 can be fabricated through a facile hydrothermal synthesis method in a different Ethanol:DI water ratio.

To examine the HER performance of WO_3 catalyst, electrochemical testing was carried out in a three-electrode system with 0.5M H_2SO_4 standard electrolyte. The morphology and composition of the materials were analyzed by SEM and EDS. XRD was performed to confirm the crystal structures of the prepared materials. Raman spectroscopy and TEM were performed to determine the structures and size of the materials. The chemical composition was confirmed by XPS

*Corresponding author	Su Jeong Suh
Affiliation	Sungkyunkwan University
E-mail address	suhsj@skku.edu

Cellulose Nanocrystals–Blended Zirconia/Polysulfone Composite Separator for Alkaline Electrolyzer at Low Electrolyte Contents

Jung Won Lee, Won Chul Cho*

Seoul National University of Science and Technology, Korea

Power-to-gas technology requires the use of water-electrolyzers with improved coupling properties with fluctuating systems in a large scale for cost-effective hydrogen production. Alkaline electrolyzers have been applied to MW-scale hydrogen production under constant current operation. Recently, alkaline electrolyzers with advanced electrodes and separators showed quick response time to variable power input. Typically, alkaline electrolyzers adopt a porous separator with high electrolyte concentration (25–30 wt%) owing to its ability to provide high ionic conductivity. However, the circulation of the concentrated electrolyte in the electrolyzer block causes loss of Faraday efficiency and corrosion. Herein, we show that a cellulose nanocrystals (CNCs)-blended zirconia/polysulfone composite porous separator exhibits both low area resistance of $0.18 \Omega \text{ cm}^2$ and low hydrogen permeability of $4.7 \times 10^{-12} \text{ mol bar}^{-1} \text{ s}^{-1} \text{ cm}^{-1}$ at low electrolyte contents (10 wt.% KOH solution). Meanwhile, a commercial Zirfon® separator exhibited poor performances of the high area resistance of $0.71 \Omega \text{ cm}^2$ and high hydrogen permeability of $305 \times 10^{-12} \text{ mol bar}^{-1} \text{ s}^{-1} \text{ cm}^{-1}$ under the same condition. The cell comprising the optimized composite separator displayed a remarkable capability of 1.83V at 0.6 A cm^{-2} with 10 wt.% KOH solution for 300 h in a stable mode. Hydrophilic cellulose nanocrystals were successfully incorporated into the hydrophobic polymer network, resulting in lowering the area resistance and gas permeability of the separator. These results demonstrate that AWE equipped with (CNCs)-blended zirconia/polysulfone composite porous separators can achieve high performance using low concentration electrolytes, contributing to lifetime.

*Corresponding author

Won Chul Cho

Affiliation

Seoul National University of Science and Technology

E-mail address

wonchul.cho@seoultech.ac.kr

A Study on the Effect of TiO₂ Nanoparticle Size on the Performance of Composite Separators in Alkaline Water Electrolysis

YooJin Jo, Min Hee Seo, Jung Won Lee, Won Chul Cho^{*}

Seoul National University of Science and Technology, Korea

The intermittent and volatile nature of renewable energy sources threatens the stable operation of power grids, necessitating dynamically operated energy storage. Power-to-gas technology is a promising method for managing electricity variations on a large GW scale. The electrolyzer is a key component that can convert excess electricity into hydrogen with high flexibility. Composite separators comprising ceramic filler and thermoplastic polymer are widely used in alkaline electrolyzers due to their stability in harsh conditions. The ceramic filler should possess high chemical stability and strong interaction with the polymer binder. TiO₂ is a good filler candidate due to its hydrophilicity and potential capabilities. However, the impact of TiO₂ size on composite separator properties has yet to be studied. Herein, we investigated the size effect of various TiO₂ nanoparticles (18, 40, and 100 nm) on the performance of the titania/polysulfone-based separators. Smaller TiO₂ nanoparticles increased bubble point pressure (BPP) and decreased H₂ permeability. Meanwhile, the ohmic resistance decreased with increasing TiO₂ size. The interaction between TiO₂ nanoparticles and polysulfone increased with the smaller sizes of TiO₂ nanoparticles. Robust interactions increased resistance by reducing the pore size distribution. The separator of 100TiO₂/PSU (445 ± 5 μm thickness) exhibited both low ohmic resistance (0.15 Ω cm²) and high BPP (3.0 ± 0.2 bar). The cell operated stably, maintaining a cell voltage of 2.10–2.12 V for 1000 h at 2.0 A cm⁻² at 80 °C with 30 wt.% KOH. These results demonstrate that the use of titanium dioxide nanoparticle-based separators can achieve high performance compared to commercial zirconia-based separators.

*Corresponding author

Won Chul Cho

Affiliation

Seoul National University of Science and Technology

E-mail address

wonchul.cho@seoultech.ac.kr

Cobalt Nanoparticles Integrated Nitrogen-Doped Carbon Nanotube: A Bifunctional Electrocatalyst for Direct Methanol Fuel Cell

Kousik Bhunia, Keyru Serbara Bejigo, Sang-Jae Kim*

Jeju National University, Korea

Direct methanol fuel cells (DAFCs) hold great potential for portable to stationary power sources. However, apart from the Platinum (Pt) catalyst cost, the current state of the DAFC device suffers performance loss due to severe methanol crossover from anode to cathode and poisoning of the anode catalyst from intermediates carbonaceous species accumulated at the catalyst surface. The methanol migration to cathodes tends to deteriorate Pt active sites from oxygen reduction reaction (ORR). The adsorption of the carbonaceous species degrades the alcohol electrooxidation efficiency of the Pt-sites. Therefore, methanol-tolerant cathodes and efficient anodes are highly desired for DAFC application. Cobalt (Co) nanoparticles integrated nitrogen-doped carbon nanotube (Co@NCNT) is synthesized as an excellent methanol tolerance ORR catalyst. The catalyst shows excellent methanol tolerance ability with comparable ORR in alkaline electrolytes. The Co@NCNT improved the methanol electrooxidation reaction (MOR) of the Pt nanoparticles (NPs). DMFC tests were carried out at constant methanol concentrations using Co@NC cathode and Pt NPs decorated Co@NCNT anode catalyst systematically. The Pt NPs-Co@NCNT || Co@NCNT cells exceed that of a Pt/C || Pt/C cathode. This work will demonstrate the nonprecious Co@NC cathode, as well as excellent support for anode catalysts for advanced DMFC technologies with increased performance.

*Corresponding author	Sang-Jae Kim
Affiliation	Jeju National University
E-mail address	kimsangj@jejunu.ac.kr

Non-Nobel Metal Single-Atom Anchored Cation Defective NiFe-LDH for Water Electrolysis

Jae Kwan Lee¹, Jin Ho Seo¹, Young Min Kim¹, Ho Won Jang^{1, 2*}

¹*Seoul National University, Korea*

²*Advanced Institute of Convergence Technology, Korea*

Layered double hydroxide (LDH) is deemed a promising catalyst for electrochemical applications because of its favorable adsorption/desorption energy and cost-effectiveness. NiFe-LDH, one of the LDHs, consists of positively charged host layers (brucite-like Ni(OH)₆ and Fe(OH)₆ octahedra) and interlayer anions such as sulfate, chloride, and nitrate. It has been studied as an excellent candidate for industrial applications of water splitting, particularly as a catalyst for both the anode and cathode reactions due to its bifunctional catalytic activity. However, despite its outstanding catalytic activity, it has shown poor long-term stability in alkaline media, due to the dissolution of iron.

The stability of the catalyst can significantly increase with the formation of cation vacancies by suppressing the dissolution of iron. For example, Peng et al. demonstrated enhanced stability through vacancy-rich NiFe-LDH obtained by alkaline etching of NiFeZnAl-LDH and more recently, Wu et al. proved that cation vacancies in NiFe-LDH are a motif of reconstruction. Although vacancy engineering has enhanced the stability and catalytic activity of NiFe-LDH, the activity is not sufficient for application in industrial fields.

We achieved higher catalytic activity performance by decorating single tungsten atoms onto the pre-formed cation vacancies of NiFe-LDH. The single tungsten atoms were deposited onto the vacancy-rich NiFe-LDH using the simple and mass-producible hydrothermal method. Tungsten ions preferentially deposited onto the cation vacancies due to their higher positive charge density. Through the synergistic effect of the tungsten single atom and lattice distorted NiFe-LDH, a highly active and durable catalyst was successfully synthesized.

*Corresponding author	Ho Won Jang
Affiliation	Seoul National University
E-mail address	hwjang@snu.ac.kr

6-4195

Durability Test for Pt Catalyst Supports in SiC-Graphene System of Polymer Electrolyte Membrane Fuel Cells

KyeongHo Lee, Chaelin Moon, Joon Heo, JiHun Choi, HyukJun Youn, HyeonSeok Jeong, SoonMok Choi*

Korea University of Technology and Education, Korea

Commercial Polymer Electrolyte Membrane Fuel Cells (PEMFCs) use carbon supported Pt catalyst(Pt/C) to achieve cost competitiveness. Well-dispersed nano particles have been researched to reduce the amount of expensive Pt. However, catalysts using conventional carbon supports suffer from durability problems under repeated cycling. In this case, the separation of Pt particles causes an increase in the resistance, which ultimately shortens the lifetime of the PEMFC. This study aimed to improve the durability and conductivity of platinum catalyst supports. Nano sized SiC support was used instead of carbon. Graphene with a large surface area makes it suitable as a carrier. Graphene layers are deposited on the SiC core using CVD process. The crystallinity due to the high-temperature process of over 1400 °C using CVD was analyzed by XRD, and the core-shell structure of the SiC-based support was confirmed by TEM. Nano Pt particle was coated by Polyol process on SiC-graphene support. SiC-graphene support was analyzed by the CV measurement and tried to confirm a longer life time than those the conventional carbon support.

*Corresponding author

SoonMok Choi

Affiliation

Korea University of Technology and Education

E-mail address

smchoi@koreatech.ac.kr

Hierarchically Designed Co₄Fe₃@N-doped Graphitic Carbon Derived from Prussian Blue Analogues (PBAs) as Electrocatalysts for Oxygen Evolution Reaction in Anion Exchange Membrane Water Electrolysis

Seohyun Park¹, Jeong-Hyang Jo^{2, 3}, Ji-Hoon Lee², Wook Jo^{1*}

¹*Ulsan National Institute of Science and Technology, Korea*

²*Korea Institute of Materials Science, Korea*

³*Pusan National University, Korea*

Anion exchange membrane water electrolyzers (AEMWEs) have been strongly emerged beyond the established water electrolysis systems with the unique merits of electrode reaction of Alkaline water electrolysis (AWE) and system configuration and product quality of Proton exchange membrane water electrolyzers (PEMWEs). Despite numerous merits of AEMWEs, relatively low efficiencies and limited long-term durability raised from insufficient electrochemical activity of transition metal-based electrocatalysts remain to be resolved. It is emphasized that above issues are more pronounced in oxygen evolution reaction (OER) electrodes, which are more kinetically sluggish and exposed to corrosive environments compared to hydrogen evolution reaction (HER) electrodes. In order to overcome the aforementioned challenges through the development of highly active and durable OER electrocatalysts, several efforts are proposed. From the activity point of view, the transition metal solid solutions can provide an intrinsic electrochemical behavior accompanied by intermetallic interactions and the generation of microstructural defects. In addition, the application of protective layers on the surface of the electrocatalyst effectively prevents the direct contact between the electrocatalysts and electrolyte solution under oxidative operating conditions, which is an effective strategy to improve the long-term stability. However, these strategies require additional precursors or a complex synthesis process.

Herein, to fabricate the hierarchically designed OER electrocatalysts composed of bimetallic alloys with oxide layer@N-doped graphitic carbon electrocatalyst, the Prussian blue analogues (PBAs) were suggested as an effective template. PBAs can guarantee such advantages of i) systematic adjustment of the species and relative ratios of transition metal ions, ii) highly porous structure and porosity for rich active site and surface functionality and iii) a cyano group ($-C\equiv N-$), which is the structural bridge of the PBAs, can be converted into the highly conductive and durable surface protective structure during the pyrolysis process without additional precursors. Accordingly, PBAs were utilized with a simple one-pot synthesis process with control of the pyrolysis condition, which can successfully produce the final product with conductive alloy cores and durable top surface as versatile electrocatalysts. Under an optimized heat treatment condition, the PBA structure was converted into a hierarchically structured electrocatalyst of Co-Fe bimetallic alloys with N-doped graphitic carbon shell, the OER activity and long-term durability under alkaline media (1.0 M KOH) were significantly improved. In short, Co/Fe PBA-derived electrocatalysts provided 25 % relieved overpotential and 15 times higher electrochemical surface area compared to commercial IrO₂ catalysts. The chemical structure, which achieved high valence states on the surface of the alloy core, and the local arrangement enhanced the electrocatalytic performance. It is strongly believed that the hierarchical structure of PBA-based OER electrocatalysts proposed in this study can contribute to the cost-effectiveness and the early commercialization of AEMWEs.

*Corresponding author	Wook Jo
Affiliation	Ulsan National Institute of Science and Technology
E-mail address	wookjo@unist.ac.kr