06-0208

Efficient tri-metallic anodic electrocatalyst for urea electro-oxidation

Padmini Basumatary, Dimpul Konwar*, Young Soo Yoon*
Gachon University, Korea

The decreasing of fossil fuels and the rapid increase in human energy demands can be balanced by highly efficient energy generators and renewable energy devices. Further, only dependence on the traditional carbon fuel economy could lead to severe outputs such as global warming, respiratory diseases, and smog. Highly efficient engines and alternative renewable energy sources can overcome these adverse issues [1]. Among all the renewable energy generators, fuel cells can play a vital role in achieving clean energy. Recently direct urea fuel cells have been considered as the most suitable indirect hydrogen carrier energy because, it is biodegradable, stable, non-toxic, non-flammable. Besides, it can also be easily stored and transported compared to liquid hydrogen carrier or other volatile liquids [2,3]. However, poor stabilities, low current densities and slow reaction kinetics of anodes in urea fuel cell are the major obstacles for wide-spread applications.

In this study, low cost and efficient anode based on tri-metallic MnNiFe alloy nanoparticles on reduced graphene oxide support were synthesized using a one-pot hydrothermal method. The as-prepared catalysts were characterized using X-ray diffraction, inductively coupled plasma- mass spectroscopy, Brunauer-Emmett-Teller, scanning electron microscopy, and transmission electron microscopy and their catalytic activities were measured using cyclic voltammetry, chronoamperometry. Further, the membrane electrode assembly (unit cell) test was performed supplying 1 M KOH and 0.33 M urea solution at the anode and oxygen (200 sccm) at the cathode in a fuel cell station. In urea electro-oxidation, the Mn0.5Ni2.0Fe0.5/rGO catalyst exhibited superior electrocatalytic activities compared with Ni/rGO and commercial Ni/C catalyst. Furthermore, the Mn0.5Ni2.0Fe0.5/rGO catalyst achieved a mass activity of 1753.97 mA mg-1Ni with an onset potential of 0.34 V (vs. Ag/AgCl) in 1 M KOH and 0.33 M urea solution, which is ~4.2 and 9.8 times higher than that of Ni/rGO and commercial Ni/C. A unit cell with Mn0.5Ni2.0Fe0.5/rGO anode catalyst exhibited a peak power density of 30.06 mW cm-2 in 1 M KOH and 0.33 M urea at 50 C, which is much higher compared to previous reports [2,4].

The Mn0.5Ni2.0Fe0.5/rGO catalyst structural and electronic effects played a crucial role in achieving higher electrocatalytic activity and stability in urea electro-oxidation. Therefore, we propose that Mn0.5Ni2.0Fe0.5/rGO can be a promising electrocatalyst for the urea fuel cell.

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*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

06-0228

Metal-organic framework–derived NiCo@C catalysts for urea oxidation in urea-hydrogen peroxide fuel cells

Nhac Duong Tien, Bo Hyeon Kim, Woo Hyun Yun, Hyon Hee Yoon*

Gachon University, Korea

Urea, a low-cost and benign compound, has been used to generate electricity in urea fuel cells. The low power density is, however, a key issue for the practical implementation of urea fuel cells because of the sluggish anode reaction for the electro-oxidation of urea. Currently, Ni-Co bimetal is widely studied as it is a relatively low-cost material and has high activity toward urea electro-oxidation.

In order to enhance the catalytic activity of the NiCo-based catalysts, various nanostructures having high surface area have been used. Recently, metal-organic frameworks (MOFs), which have high porosity and large surface area with flexible synthesizing methods by changing metal sites and organic ligands, have been drawn wide interest for their application, especially as the electrochemical catalyst. However, stability and electron conductivity of MOFs are major challenges that need to overcome.

In this study, we synthesized a self-assembled hierarchical core-shell structured NiCo and carbon composite using a metal-organic framework (MOF) as a template. A unique NiCo bimetal and carbon composite (NiCo@C) with a core/shell structure were obtained by the calcination of NiCo-MOFs. The structure of NiCo@C particle was characterized by FTIR, XRD, and SEM. The electro-catalytic activity for urea oxidation was evaluated by cyclic voltammetry. The prepared NiCo@C exhibited a promising potential as urea electro-oxidation catalyst due to the porous structure and high electrical conductivity.

*Corresponding author Hyon Hee Yoon
Affiliation Gachon University
E-mail address hhyoon@gachon.ac.kr

06-0244

Carbon Nanotube-supported Ni/Co Sponge for Urea/Hydrogen Peroxide Fuel Cells

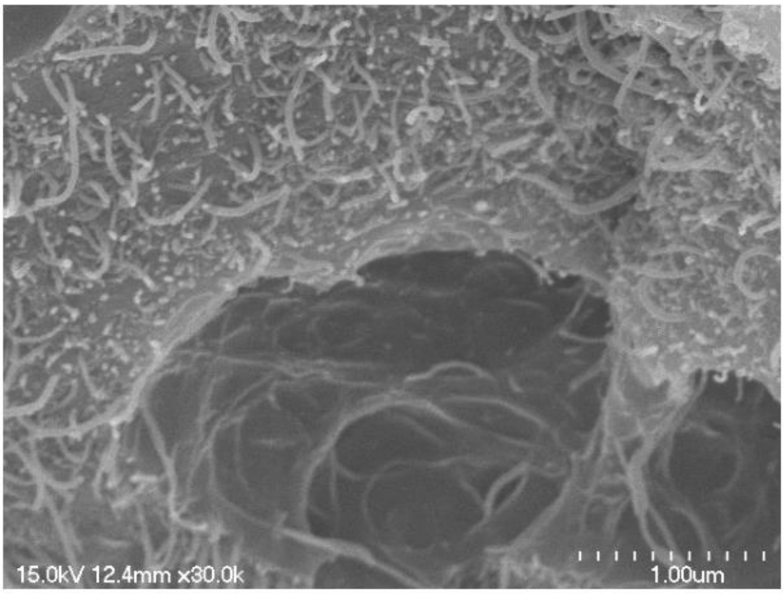
Manh Hoang Tran, Bo Hyeon Kim, Woo Hyun Yun, Hyon Hee Yoon*

Gachon University, Korea

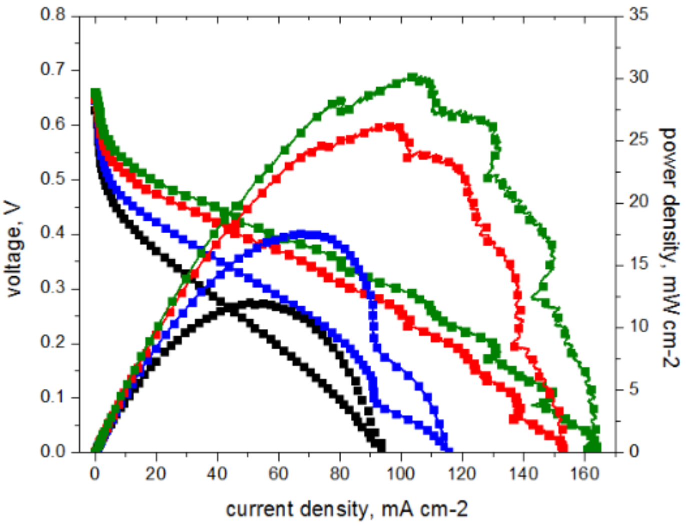
Urea-fueled fuel cells have been gathering much attention because urea is an inexpensive industrial product, non-toxic solid, and easy to store and transport. However, they are not yet competitive with other fuel cells because of their relatively low maximum power density mainly due to to the sluggish urea oxidation rate. Currently, Ni, NiO, $Ni(OH)_2$ and Ni-based bimetallic alloys (e.g. Ni-Co, Ni-Cr, Ni-Mo, Ni-Mn, and Ni-Fe) have been considered as efficient and low-cost catalysts for the urea oxidation in alkaline medium.

Herein, highly porous sea sponge-like nano-structured Ni/Co bimetals and carbon nanotubes (CNT) composites were synthesized via by a combination of sol-gel method and freeze-drying technology.

The morphological and structural properties of Ni-Co/CNT sponges were characterized by X-ray diffraction, scanning electron microscopy, and energy-disperse X-ray spectroscopy. The electrocatalytic activity for urea oxidation was evaluated by cyclic voltammetry and electrochemical impedance spectroscopy. A unique metallic alloy and carbon composite with a porous structure was observed. A urea/H_2O_2 fuel cell with the Ni-Co/CNT sponges as anode exhibited promising maximum power density of 11.7 and 30.2 mW cm^{-2} at 30 ^{o}C and 80 ^{o}C, respectively. The results indicated that the highly porous three-dimensional Ni-Co/CNT sponges can be used for urea oxidation and as an efficient anode material for urea fuel cells.



SEM of Ni-Co/CNT sponge



I-V curves of DUHFC with operating temperature at 30, 60, 70, 80 ℃

*Corresponding author Hyon Hee Yoon
Affiliation Gachon University
E-mail address hhyoon@gachon.ac.kr

06-0301

IMMOBILIZED IONIC LIQUIDS IN HT-PEM FUEL CELLS

Rolf Hempelmann*, Galina Skorikova
Saarland University and KIST Europe, Germany

High-temperature Polymer Electrolyte Membrane Fuel Cells exhibit enhanced tolerance towards traces of CO coming along with hydrogen. State-of-the-art phosphoric acid (PA) doped polybenzimidazole (PBI) membranes, however, degrade rapidly at 180-200°C and poison the catalyst. We have replaced PA partially by a suitable hydrophobic Ionic Liquid (IL): trimethylguanidinium as cation (carrying two protons) and bis(trifluoromethylsulfonyl)imide as anion [1]. This IL was impregnated into a PBI matrix via direct blending into the polymer solution to obtain quasi-solidified ionic liquid membranes with different contents of IL. During the casting process phase separation occurs and the IL forms segregated globules within a percolating PBI network. In order to provide a continuous pathway for a proton transport, this composite membrane was doped with PA to protonate the PBI backbone.

Membrane-electrodes-assemblies were obtained by hot pressing the membranes between two gas diffusion electrodes with a catalyst loading of 1.3 mgPt cm^{-2}. Single cell tests were carried out at constant hydrogen and air flow rates. In order to eliminate the poisoning effect of PA on the Pt/C catalyst, we used our IL as electrolyte also in the catalyst layer. A maximum power density of 110mW cm^{-2} was achieved at 200 ^{o}C and 330 mA cm^{-2}. Besides, durability tests were performed for 135h.

These composite membranes contain up to 3-5 times less free PA in the membrane in comparison with state-of-the-art PA-doped PBI and enable operating temperature above 200 ^{o}C. Therefore these systems are promising for combined heat and power applications.

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*Corresponding author	Rolf Hempelmann
Affiliation	Saarland University and KIST Europe
E-mail address	r.hempelmann@mx.uni-saarland.de

06-0344

Development of rGO-supported OER Electrocatalysts with Low Noble Metal Content for Proton Exchange Membrane Water Electrolysis

Hyokyung Han, Sehkyu Park*
Kwangwoon University, Korea

Noble metals like Ir and Ru as conventional oxygen evolution reaction (OER) catalysts have been used to resist in acid electrolyte and at high operating potentials. However, these noble metals are highly expensive, thus limiting deployment of PEM water electrolyzers for large-scale energy storage systems. In this study, to develop highly active and stable OER electrocatalyst with low noble metal content, various bimetallic Ru-Co catalysts supported on reduced graphene oxide (denoted as RuCo/rGO) are prepared by spray pyrolysis, followed by heat treatment. During the spray pyrolysis, Ru is incorporated into the Co lattice to form RuCo alloy and the optimized concentration of Ru doping is found to be 16wt%. From X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), additional heat treatment stabilizes the catalyst by strengthening the bond between Ru and Co and increases the number of Co^{3+} ion, known as the initiator of oxygen evolution process. Hence, the electrochemical activity is improved after heat treatment, and the catalyst with the annealing temperature of 300°C shows higher electrochemical performance. The overpotential of the optimized RuCo/rGO at 10 mA cm^{-2} is 305 mV in acid electrolyte, which is comparable to that of Ir black. In addition, accelerated durability test (ADT) is conducted to evaluate the stability of the catalyst and the optimized catalyst maintains 70% of its initial performance even after 3,000 potential cycles. Therefore, the RuCo/rGO catalyst exhibits high activity for OER in acidic electrolyte and the preparation method suggested in this study ensures the OER stability and cost-effectiveness.

Keywords: PEMWE, OER catalyst, low loading of noble metal, Ru-Co alloy, Ultrasonic Spray Pyrolysis (USP)

*Corresponding author Sehkyu Park
Affiliation Kwangwoon University
E-mail address vitalspark@kw.ac.kr

06-0356

Infiltration of nanocatalysts for solid oxide fuel cells

Kyung Joong Yoon*
Korea Insititute of Science and Technology, Korea

Solid oxide fuel cells (SOFCs) represent one of the most efficient and environmentally friendly technologies for the generation of electrical power and heat. Although the functionality of SOFC electrodes could be significantly improved by reducing the feature size to the nanoscale, the practical use of nanomaterials has been limited in this area due to the lack of stability and controllability at high temperatures. Herein, we demonstrate an advanced infiltration technique that allows nanoscale control of highly active and stable catalysts at elevated temperatures. Homogeneous precipitation in chemical solution, which is induced by urea decomposition, allows the precise tailoring of the phase purity and geometric properties. Controlling the key characteristics of nanocatalysts allows the construction of rational electrode structure and yields a significant improvement of performance and durability.

*Corresponding author	Kyung Joong Yoon
Affiliation	Korea Insititute of Science and Technology
E-mail address	kjyoon@kist.re.kr

06-0393

Effect of gas Humidity on Carbon Corrosion in PEMFC Cathode

Jaewoo Cho, Sehkyu Park*

Kwangwoon University, Korea

There have been many developments in proton exchange membrane fuel cell for several decades. Especially, the development of perfluorinated sulfuric acid membrane and carbon-supported Pt catalyst has dramatically improved the fuel cell performance. Particularly, the carbon black with a high surface area and an electrical conductivity as a catalyst support improves fuel cell performance because it provides many triple phase boundaries made up of Pt nanoparticle, Nafion ionomer, and reactant gas. However, a potential jump during start-up and shut-down (SUSD) events causes carbon to be readily oxidized, resulting in drastic fuel cell performance decay. The cathode potential jump triggers following reactions in a PEMFC.

$2H_2O \rightarrow O_2+4H^++4e^-$
$C+2H_2O \rightarrow CO_2+4H^++4e^-$ (0.207 V vs.Reversible Hydrogen Electrode)
$C+O_2 \rightarrow CO_2$

In the carbon corrosion reaction, the water is used as a reactant. That is, the amount of water in the reaction site can be a decisive factor on the degree of carbon corrosion reaction. To mimic carbon corrosion during SUSD events, repeated potential step changes (PSCs) between 1.0 V and 1.45 V are performed with different cathode RHs (20, 100, and 200 %) Polarization curves with increasing number of potential step changes are obtained and individual polarization losses of activation, ohmic, and concentration during PSCs are analyzed using electrochemical impedance spectroscopy (EIS) and EIS data fitting. Change in electrochemical surface area (ECSA) was estimated using CV measurements. Pt coalescence associated with carbon support corrosion is observed using transmission electron microscopy (TEM). The experimental polarization and TEM analyses show carbon corrosion rate is coupled with cathode RH (i.e., water concentration). The EIS results presents carbon corrosion increases both charge transfer and concentration resistance at the cathode. The results indicate that carbon corrosion increases hydrophilic surface at the cathode, thus suppressing both molecular oxygen diffusion to catalytically active sites and charge transfer at the interface between the Pt and the ionomer.

*Corresponding author	Sehkyu Park
Affiliation	Kwangwoon University
E-mail address	vitalspark@kw.ac.kr

06-0410

Structural breakthrough of steam air electrode for reversible protonic ceramic electrochemical cells

Jun-Young Park*, John-In Lee
Sejong University, Korea

High-temperature ceramic-based reversible electrochemical cells, such as reversible solid oxide (RSOCs) and reversible protonic ceramic cells (RPCCs), have several advantages to produce electricity and pure hydrogen gas including high energy conversion efficiency (60-80%), diversity of fuel (hydrogen, methane, LNG, etc), non-use of noble metal catalysts, and negligible gas pollutants, compared to the low-temperature polymer electrolyte membrane cells [1]. Recently, RPCCs have received more attentions due to their unique properties, such as intermediate temperature operation (< 700 °C), direct generation of high purity H2, prevention of Ni oxidation at high steam concentrations, and high carbon coking resistance under-hydrocarbon fuels. In particular, low operation temperature alleviates unfavorable characteristics of high-temperature ceramic cells in reliability and long-time durability, such as material compatibility and thermal stress [2-4].

Until now, perovskite-structure-based mixed ionic and electronic conductors (MIECs), such as Ba0.5Sr0.5Co0.8Fe0.2O3-δ and PrBa0.5Sr0.5Co1.5Fe0.5O5+δ, have been most frequently used as steam (air) electrodes due to their high performances in RPCCs. Although RPCCs have many advantages as mentioned, highly electrocatalytic active steam (air) electrodes for oxygen evolution (OER) and oxygen reduction reactions (ORR) are necessary to develop in terms of electrical performance and reliability for making it commercially viable [5, 6].

Herein, we introduce a novel triple conducting (H+/O2-/e-) electrode material for RPCCs at intermediate temperatures. The electrochemical performances of this material investigate in both protonic ceramic fuel cell (PCFC) and protonic ceramic electrolysis cell (PCEC) modes in a single electrochemical device.

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Keywords: Reversible Protonic ceramic cell; Steam (air) electrode; Perovskite; Performance; Durability.

*Corresponding author	Jun-Young Park
Affiliation	Sejong University
E-mail address	jyoung@sejong.ac.kr

06-0466

The impacts of different carbon support on the platinum catalyst layer for PEM fuel cells

Aniket Kumar, Jae-Woon Hong, Ye Jin Yun, Sun-Ju Song*

Chonnam National University, Korea

In this modern world, polymer-electrolyte fuel cells (PEFCs) have been emerged as a most prominent zero-emission technology for energy conversion due to their thermodynamic efficiency and high energy density. Most commonly platinum (Pt) metals have received a great amount of attention and Pt/C is the most widely used catalyst for PEMFC applications. However, there is a great need to reduce the cost and amount of precious metal catalyst. Additionally, the use of carbon support suffers from a major issue of low durability. So, to overcome this challenge the search of new support material is needed which can act as superior support than tradition Pt/C catalyst. Here, we present a comparative study, showing the relative effects of different carbon support such as multi-walled carbon nanotubes (MWCNT), graphite, graphene Oxide (GO) and reduced graphene oxide (rGO) on the performance and durability as compare to tradition Pt/C catalyst. Such systematic study will provide a new direction towards the goal of achieving a novel catalyst support and will finally open the door for the next-generation PEMFC for “real world” application.

*Corresponding author	Sun-Ju Song
Affiliation	Chonnam National University
E-mail address	song@chonnam.ac.kr

06-0659

Synthesis and Assembly of Metal Phosphide Nanoparticles for Hydrogen Evolution Reaction Catalysis

Don-Hyung Ha*

Chung-Ang University, Korea

For the advanced synthesis of nanoparticles (NPs), chemical transformations of as-synthesized NPs are an emerging and powerful method to tailor the composition and morphology of NPs. Nanosynthetic chemistry has centered on creating new NPs using these transformations. However, beyond works employing empirical qualitative analysis, few works have addressed the underlying atomic mechanisms for these transformations. Works using chemical transformations of NPs for applications are also an under-studied field. This presentation spans from fundamental understandings of the atomic structural evolutions and mechanisms in chemical transformations and synthesis of metal phosphide NPs, to use of these methods to create and characterize new structures, to the assembly of those NPs through electrophoretic deposition, to the final applied stage of electrocatalysts for hydrogen evolution with these metal phosphide NPs. We demonstrated that hydrogen evolution reaction catalytic activity of NPs can be improved by synthetic control such as composition, doping, and crystallinity, as well as film deposition control through utilization of electrophoretic deposition technique.

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

06-0738

Synthesis and property of Poly(fluorosulfonyl maleimide-styrene)s by free radical reaction for Polymer Electrolyte membrane fuel cell(PEMFC)

Sujin Yoon[1], Taewook Ryu[1], Faiz Ahmed[2], Lei Jin[3], Jaewoong Kim[1], Md Mahabubur Rahman[2], Daeho Kim[1], Younghoon Lee[1], Whangi Kim[1*]

[1]*Konkuk University, Korea*

[2]*Konkuk University, Bangladesh*

[3]*Konkuk University, China*

Polymer electrolyte membrane fuel cell (PEMFC) can efficiently generate high power densities, and thereby making it an attractive technology for automobile and portable applications. At present, perfluorinated polymer membranes, such as Nafion® and Flemion® are widely used for PEM materials because of their excellent physical & chemical stability, and high proton conductivity at high relative humidity and low temperature. However, they suffer from such disadvantages as limited operation temperature (0-80 ^{o}C), high cost, and high fuel permeability. This has stimulated the development of research focused on hydrocarbon membranes with low cost and high performance. The recent advances in the development of PEM materials reveal that the performances (like-proton conductivity, power density etc.) of hydrocarbon membranes are close to those of perfluororinated sulfuric acid membranes, and also their production and processing cost is lower. Their characteristics are derived from fluoro atoms and carbonecarbon bonded chemical structures which attribute relatively long lifetime compare to hydrocarbon membranes.Another problem with the comparison of Nafion with hydrocarbon membranes is the acidity. In the case of perfluorinated Nafion, due to the strong electronegativity of Fluoro, the pKa value is lowered and hydrogen migration is easier than the hydrocarbon membrane. Hydrocarbon membranes show low hydrogen ion conductivity due to low acidity. Therefore, the purpose of this experiment is to increase ionic conductivity by attaching a fluorosulf onyl group to the side chain on the hydrocarbon membrane. Fluorosulfonyl maleimde(FMI) was synthesized by nucleophilic addition of fluorosulfonyl isocyanate and maleimde with catalyst trimethylamine(TEA) in Methylene chloride and Benzene as the co-solvent. A series of poly(Fluoro maleimide-styrene)s were prepared by free radical reaction of Fluorosulfonyl maleimide(FMI) and styrene in Poly(Fluoro maleimide-styrene)s containinig the side-chain fluorosulfonyl groups. In order to increase the proton conductivity and mechanical strength of the membrane, PVdF-HFP, a polymer having C-F group with strong electron attracting, was mixed together to prepare a membrane. The membranes were studied by FT-IR, ^{1}H NMR spectroscopy, and TGA. The ion exchange capacity (IEC) water uptake, and proton conductivity were evaluated with increase of degree of fluorosulfonyl groups.

*Corresponding author	Whangi Kim
Affiliation	Konkuk University
E-mail address	wgkim@kku.ac.kr

06-0780

Cerium pyrophosphate (CeP_2O_7): Proton conducting material for intermediate temperature fuel cell

Lakshya Mathur[1], In-Ho Kim[1], Jae-Woon Hong[1], Bhupendra Singh[2], Sun-Ju Song[1*]
[1] *School of Materials Science and Engineering, Chonnam National University, Gwang-Ju61186, Korea*
[2] *CSIR-Advanced Materials & Process Research Institute (AMPRI), Bhopal, India*

In view of sustainable growth and clean energy source, fuel cell is one of the finest technique along with solar cells and battery. Most of the fuel cells are related to stationary application at high temperature. However intermediate temperature operating fuel cell has a wide range of mobile applications. To fulfill this requirement CeP_2O_7 was found suitable, so we have vastly investigated the key features of the same. CeP_2O_7 has been investigated in terms of thermal stability, physical behavior and electrochemical properties. With high durability towards the temperature up to 400℃ CeP_2O_7 shows excellent proton conductivity in humidified conditions at elevated temperature i.e. 2.1×10^{-4}S.cm-1 at 175℃ and pH_2O=0.06 atm[1]. Whereas, the addition of dopant and P/Ce molar ratio in the system, plays an important role in the morphological as well as electrochemical behavior of CeP_2O_7. Effect of both parameters was precisely investigated and it was found that Gd^{+3} –doped cerium pyrophosphate has one order higher protonic conductivity compare to the pure one. Moreover, the effect of variation of P/Ce molar ratio from 2.2-2.8, on CeP_2O_7 was also investigated in terms of morphological and electrochemical behavior. Higher P/Ce molar ratio leads to formation of a core-shell structure, which provides a huge proton conduction path and enhance the protonic conductivity to 2.91×10^{-2} $S.cm^{-1}$at 190℃ and pH_2O = 0.16 atm for P/Ce molar ratio= 2.8[2]. Humidification atmosphere is also a parameter which affects the proton conduction behavior of the system. The mechanism behind the enhancement of proton conductivity with pH_2O was illustrated. This much investigation suggests that cerium pyrophosphate is a suitable candidate to be used as an electrolyte in intermediate temperature fuel cell.

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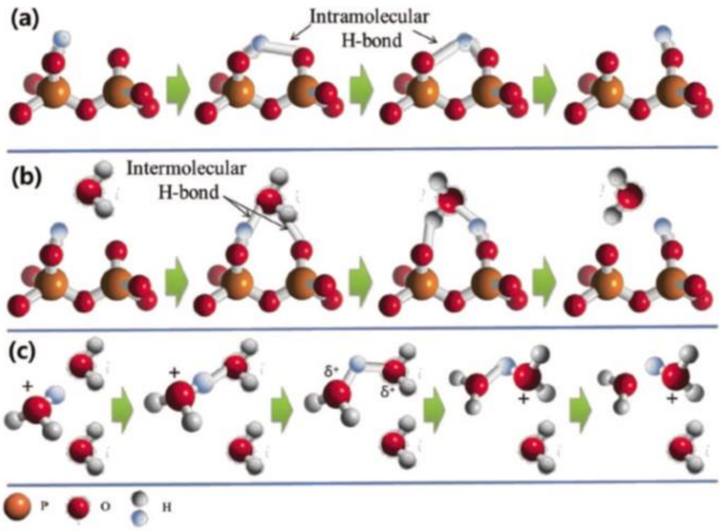

*Corresponding author Sun-Ju Song
Affiliation School of Materials Science and Engineering, Chonnam National University, Gwang-Ju61186
E-mail address song@chonnam.ac.kr

06-0795

Direct Observation of Hydrogen/Deuterium Inserted in CeO_{2-x}

Jeong Seog Kim[1*], Ki-Woong Chae[1], Ta Ryoung Park[1], Yong Nam Choi[2], Seongsu Lee[2]

[1]*Hoseo University, Korea*

[2]*Korea Atomic Energy Research Institute, Korea*

Ceria (CeO2) has been studied as a matrix phase or dopant element for SOFC electrodes, catalyst for water-shift reaction, hydrogen storage, CO/CO2 conversion catalyst, luminescence, and nontoxic biomaterials. The reduction of CeO2 under hydrogen gas has been studied by several research groups in order to resolve the disputed question, “Is there hydrogen uptake by ceria upon reduction with hydrogen?”

Hydrogen atoms have been generally considered as merely chemisorbed on the powder surfaces. Spectroscopic method can hardly depict the presence of hydrogen especially when its concentration is low either chemisorbed or inserted in the matrix structure. In this study we reduced CeO2 powder under both hydrogen and deuterium at high temperature (900 ~1500 K) and at a low gas pressure condition. By using neutron scattering, we investigated the detailed structure of hydrogen/deuterium contained CeO2-x samples (trigonal structure SG P -3 m 1) to find direct evidence of hydrogen/deuterium uptake in the CeO2-x structure. From neutron power diffraction using the maximum entropy (Dysnomia software) and Rietveld (Rietan-fp) methods, we were able to determine the position of hydrogen/deuterium in the CeO2-x powder.

In addition, we characterized the hydrogen inserted CeO2 samples by using Rama and SIMS. These results show that hydrogen/deuterium is up-taken into the bulk C2O3 lattice but the inserted concentration in the lattice structure is 0.5 ~ 1% level. SIMS depth profiling indicated that H (D) ions were uptaken into the reduced Ce-oxide powder.

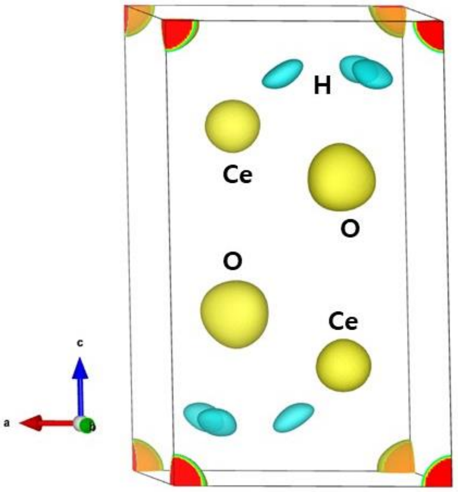

Fig.1. Nuclear density distribution in hydrogen serted Ceria analyzed by Rietan-fp and maximum entropy method (Dysnomia)

*Corresponding author Jeong Seog Kim
Affiliation Hoseo University
E-mail address kimjungs@hoseo.edu

06-0874

Synthesis and Characterization of Sulfonated Poly (Methylisatin Biphenylene) with SiO_2 Nanocomposite Membrane for PEMFC

Sujin Yoon[1], Taewook Ryu[1], Faiz Ahmed[2], Lei Jin[3], Wei Zhang[3], Seungchan Lee[1], Inhwan Choi[1], Whangi Kim[1*]

[1] *Konkuk University, Korea*
[2] *Konkuk University, Bangladesh*
[3] *Konkuk University, China*

High molecular weight polymer containing N-methylisatin was synthesized by superacid-catalyzed polyhydroxyalkylation reactions. Their functionality with sulfonic acid groups and the measurement of apposite parameters for proton exchange membranes (PEMs) were describe. Sulfonic acid groups were introduced into the polymer through sulfonation reaction with chlorosulfonic acid. Composite membranes were prepared by polymer and SiO_2 nanoparticles (20nm, 4~10% wt). The composite membranes were casted from the solution of sulfonated polymer in dimethylsulfoxide (DMSO) to afford 25µm. The structural properties of the synthesized polymers were investigated by ^{1}H NMR spectroscopy. The membranes were studied by thermogravimetric analysis (TGA), ion exchange capacity (IEC), water uptake, dimensional stability and proton conductivity assessment.

*Corresponding author	Whangi Kim
Affiliation	Konkuk University
E-mail address	wgkim@kku.ac.kr

06-1140

On the way towards durable high performance membrane electrode assemblies for proton exchange membrane fuel cells and water electrolysers

Simon Thiele*

Forschungszentrum Jülich, Germany

Membranes and electrodes form the membrane electrode assembly (MEA) in polymer electrolyte membrane (PEM) fuel cells and electrolysis systems which are central for durability, cost and conversion efficiency. The structure of membranes and electrodes including their interfaces are crucial for the creation of high performance MEAs and the potential of improving structural properties has not been fully exploited so far.

In this talk we show how advanced manufacturing methodologies using spray coating and electrospinning can result in strongly improved MEAs. Basis for the presented results is the direct membrane deposition technique which deposits membrane layers directly onto porous catalyst layers. We discuss how to create composite membranes with high conversion efficiencies and durabilties for PEM fuel cells and water electrolysers. Finally, we present results from our advanced catalyst layer manufacturing methodology.

Complementary to manufacturing and analysis of degradation, we show results from tomographic imaging of membranes via Raman imaging and tomographic imaging of catalyst layers by focused ion beam / scanning electron microscopy tomography. These highly advanced techniques allow for 3D reconstruction and analysis at the nanometer scale. Combined with algorithmic methods for the determination of transport parameters and geometric parameters these tomographies allow for an assessment of the structure-property relationship in MEAs.

*Corresponding author	Simon Thiele
Affiliation	Forschungszentrum Jülich
E-mail address	si.thiele@fz-juelich.de

06-1218

Electrodeposition-Fabricated Hydrogen Evolution Catalysts for Proton Exchange Water Electrolysis

Hoyoung Kim[1], Hyanjoo Park[1], SeonHwa Oh[1], Hyeonjeong Park[1], Insoo Choi[2], Soo-Kil Kim[1*]
[1]*Chung-Ang University, Korea*
[2]*Kangwon National University, Korea*

Hydrogen is a clean and efficient energy source that can replace exhaustible fossil fuels, and hydrogen production through water electrolysis is a very attractive way to create an environmental-friendly society [1,2]. In order to minimize the energy required to electrolyze water, catalysts that are highly active for the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) must be developed. The most active catalysts known to date are Pt group metals (PGMs) such as Pt (cathode) and Ir, Ru and their oxides (anode), but the high price of these materials has been a hindrance to commercial development [3]. Therefore, there are two major efforts to achieve economic feasibility.

The first strategy is the use of a low content of PGM catalysts, and the second is the development of PGM-free alloy catalysts. The catalytic activity of PGM-free alloy catalysts can be improved by adjusting the shape, structure and composition [4]. Therefore, studies on metal alloy catalysts consisted of Ni, Co, Fe, Mo, W and Cu, which are known to exhibit relatively good activity among non-PGMs, have been carried out [5,6]. In addition, many studies have been made on compound catalysts of metal carbides, nitrides, phosphides, sulfides, and selenides. Such compounds can facilitate the bond strength-related kinetics of HER through the modification of electronic structures [6].

Electrodeposition is a practical method for fabricating catalysts directly on a porous diffusion layer in a few minutes at room temperature and atmospheric pressure, overwhelming other catalyst manufacturing methods. It also facilitates control of the loading amount, particle shape, structure and composition of catalyst [7]. In this presentation, our recent results of electrodeposition-fabricated HER catalysts for proton exchange membrane water electrolyzer (PEMWE), such as CuMo (η = 165 mV at -10 mA/cm^2), NiW-Cu nanowire (η = 56 mV at -10 mA/cm^2), NiP (η = 105 mV at -10 mA/cm^2), etc. will be introduced along with the considerable advances in the performance of various catalysts recently reported in the literatures.

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*Corresponding author	Soo-Kil Kim
Affiliation	Chung-Ang University
E-mail address	sookilkim@cau.ac.kr

06-1227

Strategies to Improve the Performance of High Temperature PEMFC: Effects of Electrode Structures, Binders, and Humidity

Hyanjoo Park[1], Hoyoung Kim[1], SeonHwa Oh[1], Hyeonjeong Park[1], Won Suk Jung[2], Insoo Choi[3], Hyoung-Juhn Kim[4], Soo-Kil Kim[1*]

[1]*Chung-Ang University, Korea*
[2]*Hankyong National University, Korea*
[3]*Kangwon National University, Korea*
[4]*Korea Institute of Science and Technology, Korea*

In contrast to the low temperature proton exchange membrane fuel cells (LT-PEMFCs) operated at under 100°C using perfluorsulfonic acid (PFSA) membranes as a polymer electrolytes, high temperature PEMFCs (HT-PEMFCs) are operated at an elevated temperature of 120°C or higher. Different types of membrane electrolytes, such as a phosphoric acid (PA)-doped PBI membrane, are mainly used in HT-PEMFC [1,2]. In spite of the advantages of HT-PEMFCs including fast reaction kinetics and unnecessariness of humidifier, several critical issues concerning PA behaviors arise during the operation of HT-PEMFC; uneven PA distribution in the electrodes [3,4], catalyst poisoning by PA [5], and deliquescence of PA.

To mitigate these issues, various strategies were applied both to the electrodes and membranes and the performance changes according to them were investigated. First, pulse electrodeposition of pure Pt and Pt-transition metal alloys on the commercial electrodes (BASF Celtec® electrodes, Pt/C for anode and Pt alloy/C for cathode) were tried to control the hydrophilicity (anode) and to improve the oxygen reduction reaction (ORR) activity (cathode). Secondly, different types of binders (Nafion, polytetrafluoroethylene and polyvinylidene difluoride) were applied on the cathode catalysts to check the performance and durability behavior. Lastly, membrane electrode assemblies (MEAs) were prepared with PA-doped PBI membranes (BASF Celtec® membrane) preliminarily exposed to various humidity conditions to find the effects of PA's deliquescence on the performance.

As a result, the electrode modification by pulse electrodeposition exhibited 1.4 times (anode modification for PA distribution) and 1.3 times (cathode modification for ORR enhancement) higher cell performances than pristine MEA under the H_2/O_2 condition. For the effects of binders, polytetrafluoroethylene and polyvinylidene difluoride applied on Pt-transition metal alloys enabled the maintenance of the catalysts performance up to 4000 cycles in the presence of PA. Humidity control was also found to be a critical issue in preserving the MEA performance since high humidity (80%) condition gave 73.4% performance deterioration compared to that of low humidity (~10%) condition. Details will be presented at the conference.

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*Corresponding author	Soo-Kil Kim
Affiliation	Chung-Ang University
E-mail address	sookilkim@cau.ac.kr

06-1245

Fabrication of Large Area Gas Diffusion Ag Electrode for Electrochemical CO_2 Reduction to CO

SeonHwa Oh, Hoyoung Kim, Hyanjoo Park, Hyeonjeong Park, Soo-Kil Kim*
Chung-Ang University, Korea

Electrochemical CO_2 reduction can produce various carbon compounds such as CO, HCOOH, CH_4, etc. Among them, CO in combination with H_2 (syn-gas) can be used in production of longer chain hydrocarbon, through the Fischer-Tropsch process [1]. Electrochemical CO_2 reduction requires catalysts having high selectivity to the target products. For examples, Au and Ag are commonly used in production of CO. Although Au has lower overpotential than Ag in CO production, the lower price and moderate activity of Ag enable the use of Ag as a substitute to Au in practical perspectives. Accordingly, there have been extensive researches on the fabrication and evaluation of various Ag structures as catalysts to produce CO from CO_2 [2, 3]. In addition, scale-up of CO_2 reduction requires membrane-electrode assembly (MEA) type electrolyzer, where gas diffusion electrode (GDE) composed of Ag catalysts formed on gas diffusion layer is necessary. For this purpose, electrodeposition of Ag on carbon paper has been suggested as an efficient method to fabricate GDE [4]. The next step might be the enlargement of the GDE to increase the production rates.

In this study, direct Ag electrodeposition on carbon paper is tried to fabricate large area ($25cm^2$) Ag GDE for proton exchange membrane (PEM)-based MEA type electrolyzer. Electrodeposition methods have the advantage that the morphology, thickness and composition of the catalysts can be easily controlled, and the fabrication process is quick and simple compared with the conventional synthesis method. For the enlargement of the electrodes with electrodeposition, however, uniformity in the characteristics of the deposits such as morphologies and thickness is critical, that are affected by deposition current distribution. The effects of configuration and position of electrodes, mass transport of Ag ions, etc on the deposition uniformity and its subsequent influence to the CO production current and faradaic efficiency were systematically investigated. The results may contribute to the electrodeposition-fabrication of large area electrodes for energy conversion devices.

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Keywords: Electrodeposition, CO_2 reduction, gas diffusion electrode, Ag catalysts, scale-up

*Corresponding author	Soo-Kil Kim
Affiliation	Chung-Ang University
E-mail address	sookilkim@cau.ac.kr

06-1318

Porous flow channel with patterned wettability for fuel cell application

Segeun Jang[1*], Hyean-Yeol Park[2], Sang Moon Kim[3], Sung Jong Yoo[2]
[1]*Hanbat National University, Korea*
[2]*Korea Institute of Science and Technology (KIST), Korea*
[3]*Incheon National University, Korea*

Improving the flow field on water management of polymer electrolyte membrane fuel cell (PEMFC) is critical to realize a practical high-performance energy conversion system. Modifying the channel in conventional flow field have been developed to enhance the mass transport of reactant and water removal. However, the channels of the flow field induce accumulation of water, blocking the transport of the reactants and interfering with the removal of water, which in turn results in reduced fuel cell performance at high current densities. In this work, we proposed to introduce a hydrophilic polymer grafting into the patterned region of a three-dimensional (3D) multi-layered graphene (MLG) coated Ni foams to improve water management in fuel cell. As a result, the MLG-coated Ni foam with patterned wettability provide not only a gas transport pathway via hydrophobic surface of graphene, but also a direct drainage pathway through patterned hydrophilic region, leading to improved mass transport and PEMFC performance at high current densities.

*Corresponding author	Segeun Jang
Affiliation	Hanbat National University
E-mail address	sjang@hanbat.ac.kr

06-1402

Samarium (Sm)-doped ZnO Coupled with g-C3N4 for Photocatalytic Hydrogen Generation

MD RAKIBUDDIN, Mahesh A. Shinde, V. S. V. Prabhakar, Haekyoung Kim*

Yeungnam University, Korea

Hydrogen generation through visible light photocatalysis is harmless, cheap, and highly demandable for the development of sustainable future.[1] Semiconductor nano metal oxides such as ZnO and TiO_2 have received significant attention as photocatalysts due to their high photoactivity, good stability, less-toxicity and cost effectiveness.[2] However, the major drawback is that they are active under UV light due to their wide band gap. Hence, efforts have been developed for making visible light active by doping with metal ions and creating a heterojunction with suitable low band gap semiconductor to suppress electron-hole pair recombination. Graphitic carbon nitride (g-C_3N_4) has been widely utilized as a metal free visible light photocatalyst for its lower band gap.[3] Hence, it is expected that g-C_3N_4 will improve the photocatalytic performance of Sm-doped ZnO by enhancing the charge separation. In the present work, a precursor of Samarium-doped Zn−based organic−inorganic hybrid is prepared by a wet chemical method, and the hybrid precursor is calcined with Urea mixture to get samarium-doped ZnO/g-C_3N_4 hybrid. Different weight percentage of Sm-doped ZnO (1:3, 1:1, and 3:1) is introduced with g-C_3N_4 in the hybrid. The synthesized hybrids are characterized by PXRD, SEM, TEM, XPS, UV-Vis DRS, and photoluminescence techniques to evaluate their structural, morphological and optical properties. The UV-vis studies show that Sm doping increased the visible light absorption of the ZnO nanoparticles. The TEM study confirms the presence of g-C_3N_4 sheet with ZnO particles, and a clear heterojunction is observed between the interfaces. The prepared hybrids are then evaluated for the application in hydrogen generation from water under visible light. The results show that Sm-doped ZnO (1:1) coupled with g-C_3N_4 (SAZOC11) exhibits best photoactivity toward the generation of hydrogen compared to other hybrids and also from the pure Sm-doped ZnO and g-C_3N_4. The SAZOC11 catalyst is found to be stable up to several cycles under visible light. Finally, a photocatalytic mechanism of the hybrid under visible light is proposed. Therefore, the SAZOC hybrid could be a potential candidate for hydrogen generation because of their excellent activity, stability and environmental sustainability.

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*Corresponding author	Haekyoung Kim
Affiliation	Yeungnam University
E-mail address	hkkim@ynu.ac.kr

06-1556

Combination of Thin Film Deposition Methods for Fabrication and Enhancement of Low Temperature Thin Film Solid Oxide Fuel Cells

Suk Won Cha*, Sangbong Ryu

Seoul National University, Korea

Thin film solid oxide fuel cells are attracting greater attention and are being actively studied. While these thin film solid oxide fuel cells (TF SOFCs) retain potential merits of conventional solid oxide fuel cells operating at 650~850 ℃, the lower operating temperature of TF SOFCs allows them to reduce costs and temperature thresholds for balance-of-plant and surrounding components for SOFC stacks. Despite these strengths, the lower operating temperature reduces charge transfer kinetics, catalytic activity and ion conductivity of electrolytes of TF SOFCs. Improving these factors is, therefore, the primary research aim for TF SOFCs. Platinum is mainly used as a catalyst electrode of TF SOFCs due to its superior catalytic activity in the lower operating temperature regime. Its vulnerability in thermal stability has driven much research to focus on improving microstructural stability in the operating environment of SOFC. Our research group succeeded to enhance the thermal stability of the Pt electrode by covering Pt with ceramic thin films. Sputter or atomic layer deposition process was used for the ceramic covering process and GDC or YSZ were mainly used ceramic materials for coating. TF SOFCs with the ceramic-treated electrode were able to operate stable more than 9 hours at 500 ℃, a remarkable result given that a cell with pure Pt electrode failed to continue even for an hour. Apart from the electrode, the solid electrolyte is another hurdle for high performance of TF SOFCs since highly thin electrolyte has weakness in its reliability and also ionic conductivity depends on the temperature in Arrhenius form. Various recipes have been investigated, such as introducing multi-layered electrolyte or hybrid methods combining a couple of deposition processes. Combination of multiple deposition processes could enhance not only performance but also productivity of the fabrication process by substituting time-consuming atomic layer deposition with physical vapor deposition. Furthermore, the method expanded the applicability of TF SOFCs to diverse substrates ranging from anodic aluminum oxide (AAO) supports to anode supports. For AAO support, a couple of hundreds of nanometer electrolyte thickness was realized by using the hybrid method. In case of anode support, TF SOFC with a micrometer thick electrolyte were nicely settled on micro-porous anode support via the method.

*Corresponding author	Suk Won Cha
Affiliation	Seoul National University
E-mail address	swcha@snu.ac.kr

06-1632

Catalytic Property of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ / $Ce_{0.9}Gd_{0.1}O_{2-x}$ (LSCF/GDC) Prepared by Ultrasonic Infiltration of Multi-doped Ceria Nanoparticles

Hafiz Ahmad Ishfaq[1, 2], Rak-Hyun Song[1, 2*], Jong-Eun Hong[2], Amjad Hussain[1, 2], Seung-Bok Lee[1, 2], Tak-Hyoung Lim[1, 2]

[1]Korea University of Science and Technology, Korea

[2]Korea Institute of Energy Research, Korea

The reduction of polarization resistance to oxygen reduction reaction (ORR) at the cathodes is one of the greatest challenges in solid oxide fuel cells. Nano scale based solution infiltration is one of the most promising approaches to overcome this technical barrier in SOFCs. In this study we systematically designed the nano-structured cathode, which was prepared by ultrasonic infiltration of ionically conducting phase of Sm and Nd-doped ceria (SNDC) into the commercial composite cathode of Sr- and Fe-doped $LaCoO_3$ (LSCF) and Gd-doped ceria (GDC) in order to enhance the electrochemical performance. The performance of tailored cathode was evaluated in fuel cell mode under practical operating conditions and the results indicated that there was ~40% improvement in peak power density at 700℃ with 5.4mg/cm^2 loading of SNDC. The microstructural analysis showed that the enhanced performance of the nano-structured cathode was attributed to formation of additional three phase boundary by ionically conductive nano-particles, which extend the cathode reactive sites and facilitate the oxygen reduction reaction.

*Corresponding author	Rak-Hyun Song
Affiliation	Korea University of Science and Technology
E-mail address	rhsong@kier.re.kr

06-1818

Synthesis and Characterization of Chemically Durable Anion Exchange Membranes for Fuel Cell Application

Adam F. Nugraha[1, 2], Da-Hee Kwak[2], Dongwon Shin[2], Byungchan Bae[1, 2*]
[1]*University of Science and Technology, Korea*
[2]*Korea Institute of Energy Research, Korea*

Anion exchange membranes (AEMs) have garnered a great deal of research interest in the past decade due to their potential for applications in redox flow batteries, water electrolysis, water purification, and anion exchange membrane fuel cells (AMFCs). In particular, AMFCs have received much attention due to their cost-effectiveness compared to proton exchange membrane fuel cells (PEMFCs) by virtue of the alkaline environments that enable the use of non-noble metals as an electrocatalyst. However, the existing AEMs underperform compared to proton exchange membranes (PEMs) in term of ion conductivity and chemical stability.

In the past decade, there have been a variety of polymers with aromatic main backbone chains such as poly(sulfone)s, poly(phenylene oxide), poly(arylene ethers), and others, being used as AEM material. However, the degradation of the polymer backbone in aromatic AEMs has been one of the main issues under alkaline conditions. The recent finding showed that the aryl-ether cleavage with the electron-withdrawing functional group was easily triggered at high pH condition. Thus, aromatic AEMs free from any aryl-ether bonds are desired for chemically durable membranes. In this report, AEM based on phenylene-structure were synthesized via a nickel coupling reaction. Polymerization followed by quaternization and ion exchange reaction to obtain tough and bendable membranes by a solution casting method. The membranes were characterized by ^{1}H NMR, water uptake, ion conductivity, and chemical stability test.

*Corresponding author Byungchan Bae
Affiliation University of Science and Technology
E-mail address bcbae@kier.re.kr

06-1904

Macromolecular Antioxidants for Chemically Durable Electrolyte Membranes for PEMFC Applications

Abdul Kodir[1, 2], Sung-Hee Shin[1], Mutya Rahmah Arbi[1, 2], Dongwon Shin[1], Byungchan Bae[1, 2*]
[1]*Korea Institute of Energy Research, Korea*
[2]*University of Science and Technology, Korea*

Chemical durability of electrolyte membranes has been a challenge for the last decade because the longevity of the PEMFC is profoundly affected by the lifetime of the membranes. Some of the additives have been reported to be successful to increase the durability of electrolyte membranes by scavenging free radical species. For examples, cerium ions are well-known antioxidants that could increase the durability of the membranes, but leaching-out and lower conductivity had been addressed as the issues [1]. Thus, it is crucial to find alternative antioxidants without sacrificing conductivity. Organic antioxidants can be one of the candidates to fulfill the aims [2].

We have tried to investigate macromolecular antioxidant which can avoid leaching-out issue during the fuel cell operation. Scavenging activity of five different kinds of antioxidants was checked not only by hydrogen-peroxide exposure experiment but also by Fenton's oxidative test. FT-IR, GPC, fluoride emission, conductivity, as well as tensile strength, were employed to monitor the antioxidant effect on membrane degradation. Proton conductivity and water absorption of the composite membranes were also comparable to that of the pristine one, which could solve the issue of metal antioxidant.

Moreover, the open circuit voltage (OCV) holding test was conducted to confirm their effect during the fuel operation. OCV holding test result showed that the membrane with macromolecular antioxidants could maintain higher OCV than the pristine membrane as verified by in situ analysis. These results showed that macromolecular antioxidants are useful to increase the chemical durability of the membranes.

*Corresponding author	Byungchan Bae
Affiliation	Korea Institute of Energy Research
E-mail address	bcbae@kier.re.kr

06-1914

Synthesis and characterization of advanced sulfonated polyphenylene semi-block copolymer for proton exchange membranes fuel cell application

Farid Wijaya[1, 2], Dongwon Shin[2], Byungchan Bae[1, 2*]
[1] *University of Science and Technology, Korea*
[2] *Korea Institute of Energy Research, Korea*

Proton exchange membranes fuel cells (PEMFCs) have considered as clean energy devices which can convert chemical energy to electrical and thermal energy by an electrochemical reaction between hydrogen and air. [1] However, commercial perfluorinated polymer membranes such as Nafion are expensive, and alternative hydrocarbon-based polymer membranes have poor electrochemical performance and chemical stability. [2] Therefore, one of the important challenges is to make hydrocarbon-based polymer electrolyte membranes with an intentionally designed chemical structure for obtaining high fuel cell performance as well as long-term durability. [3] In this research, sulfonated polyphenylene semi-block copolymers were synthesized for high proton conductive and chemically stable polymer electrolyte membrane. The polymerization was carried out with Colon's Nickel catalyzed cross-coupling reaction. The chemical structure and molecular weight were confirmed by nuclear magnetic resonance and gel permeation chromatography, respectively. The ion exchange capacity was controlled in 2.0 meq g^{-1}. The resulting membrane was transparent and bendable. In addition, the membrane showed higher proton conductivity than Nafion membrane. Consequently, fuel cell performance of polyphenylene semi-block copolymer outperformed that of Nafion even at a low relative humidity condition.

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*Corresponding author	Byungchan Bae
Affiliation	University of Science and Technology
E-mail address	bcbae@kier.re.kr

06-1953

Fabrication and Electrochemical Characteristics of High Performing planar type IT-SOFC half Cell with a Thin and Dense GDC Buffer layer

Amjad Hussain Hussain[1, 2], Rak-Hyun Song[1, 2*], Jong-Eun Hong[1], Seung-Bok Lee[1, 2], Tak-Hyeong Lim[1, 2]
[1]*Korea Institute of Energy Research, Korea*
[2]*University of Science and Technology, Korea*

To ensure the development of next-generation solid oxide fuel cell (SOFCs) the fabrication of a thin, dense and defect-free GDC buffer layer is essential. However, the sintering constraints have been posing significant challenges to achieve this goal. Planar-type (SOFCs) fabrication methods have been customized to achieve higher power at intermediate temperature, high degree of flatness, and reduced fabrication cost. In this study, anode supported planar half-cell is fabricated in single step via co-sintering of NiO-YSZ/NiO-ScSZ/ScSZ/GDC with dimension 120×120×0.7mm through the optimization of tape casting and lamination process. The warping occurs due to the different sintering behavior of each layer during co-sintering process. The process allows for minimization of mismatch thermal expansion coefficient (TEC) to avoid the unnecessary cracks and warping. Monitor the shrinkage of each material and warping evolution of multi-structure SOFC in real time. The electrolyte and buffer fabricated by tape casting and co-sintering process had the excellent microstructural characteristic like gas permeability, thin and dense microstructure at 1320°C and there were no structural defects observed. The flatness of cell is obtained by applying a dead load fast-heating step. Finally obtained four-layer structured SOFC shows the maximum power density 791mW/cm2 at 750°C. This method is time efficient, reproducible, cost effective and highly manageable to enhance the performance and durability.

Keywords: Solid oxide fuel cell, Co-sintering, Warping, Buffer layer, Flatness.

*Corresponding author	Rak-Hyun Song
Affiliation	Korea Institute of Energy Research
E-mail address	rhsong@kier.re.kr

06-1954

Manufacturing of poly(phenylene sulfide)–graphite composites for fuel cell bipolar plates

Moon Hee Lee[1], Byung Choon Kim[1], Kwang Sang Park[1], Jong Seok Woo[1], Soo-Young Park[2*]
[1]*Morgan Advanced Materials, Korea*
[2]*Kyungpook National University, Korea*

Polymer–graphite composites have been the focus of a number of studies as the materials for bipolar plates, which are one of the most important components in fuel-cell stacks, because of their low cost, low weight, and chemical inertness. In particular, inertness to phosphoric acid, and high electrical, thermal, and mechanical properties are required for polymer–graphite composites used in the bipolar plates of phosphoric acid fuel cells. Composites of poly(phenylene sulfide) (PPS) and graphite with high concentrations of graphite (up to 40 wt%) were prepared by both compression and extrusion–compression methods. The PPS–graphite composite prepared by compression (PPS–graphite$_{\text{com}}$) exhibited high anisotropic electrical and thermal conductivities, with the in-plane components much higher than the through-plane components because of the planar orientation of the graphite sheets. The PPS–graphite composite prepared by the extrusion–compression method (PPS–graphite$_{\text{ext}}$) exhibited more isotropic properties than the PPS–graphite$_{\text{com}}$ composite because the shearing force during extrusion made the graphite randomly oriented in the composite. Thus, the through-plane electrical and thermal conductivities of the PPS–graphite$_{\text{ext}}$ composite were higher than those of the PPS–graphite$_{\text{com}}$ composite, even though their in-plane properties were much lower. The in-plane electrical conductivity of the PPS–graphite$_{\text{ext}}$ composite was more reduced than its thermal conductivity, indicating that the electrical conductivity was more sensitive to the internal graphitic structure of graphite than the thermal conductivity. The flexural strength of the PPS–graphite$_{\text{ext}}$ composite was higher than that of the PPS–graphite$_{\text{com}}$ composite even though the thermal stabilities of the two composites were not much different from each other. Thus, this study offers insights into the effect of the orientation of conductive two-dimensional fillers on the anisotropic properties; it also provides basic information on the structure and relationships between various properties of the PPS–graphite composites.

*Corresponding author	Soo-Young Park
Affiliation	Kyungpook National University
E-mail address	psy@knu.ac.kr

06-1955

Effect of Thermal Annealing for Perfluorosulfonic Acid Membranes

Juniko Nur Pratama[1, 2], Sung-Hee Shin[2], Dongwon Shin[2], Byungchan Bae[1, 2*]
[1]*University of Science and Technology, Korea*
[2]*Korea Institute of Energy Research, Korea*

Perfluorosulfonic acid (PFSA) polymer membrane such as Nafion have been known as the benchmark in PEMFC application because of its high proton conductivity. However, it showed a limitation on its operating temperature due to the lower glass transition temperature.[1] Recently, the PFSA membrane bearing short-side chain (SSC) has been widely adopted for their high crystallinity and better thermal durability in spite of lower equivalent weight to sulfonic acid. The better thermal properties of SSC PFSA is known that shorter branch would help for the main chain to crystallize more than those with the long side chain.[2] It also has been reported that heat treatment could increase its thermal stability.[3]

However, their systemic study has not been conducted yet, thus, we tried to find a more precise relationship between thermal annealing and physicochemical properties of the membranes. Two types of SSC PFSA membranes having different equivalent weight was annealed and its response to the different temperatures was investigated. The membranes were characterized by dynamic mechanical analysis to measure its Tg and followed with water uptake, dimensional stability in water, and ion conductivity. Also, a similar procedure was applied to the reinforced PFSA with PTFE substrate. Not only pristine also reinforced membranes showed a high response to thermal annealing, which might act an important role in determining terminal electrochemical properties of the membranes.

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*Corresponding author	Byungchan Bae
Affiliation	University of Science and Technology
E-mail address	bcbae@kier.re.kr

06-1957

Synthesis of aliphatic polymer ionomer for alkaline membrane fuel cell applications

Seunghyun Lee[1, 2], Byungchan Bae[1, 3], Dongwon Shin[1*], Da-Hee Kwak[1]
[1]*Korea Institute of Energy Research, Korea*
[2]*Chungnam National University, Korea*
[3]*University of Science and Technology, Korea*

Alkaline membrane fuel cells (AMFCs) have an advantage of low cost comparing to proton exchange membrane fuel cells (PEMFCs), since precious metal catalysts can be replaced by non-precious metal catalyst because of fast oxygen reduction reaction (ORR) under alkaline condition. [1] Although new high records in AMFC performance were achieved recently, AMFC performance still needs to be improved further for real application. [2] There are several factors affecting the AMFC performance. In the view of ionomer, low anion conductivity diminishes the AMFC performance. In addition, it is known that benzene adsorption is also one of the main inhibitors for the hydrogen oxidation reaction (HOR). [3] For, these reasons, we developed new polymer ionomer to enhance the AMFC performance.

The effect of benzene adsorption on the AMFC performance was investigated using aliphatic-based ionomer. Fumatech FAA-3 ionomer solution was used for the comparison. The AMFC performance was obtained using Fumatech FAA-3-30 membrane and platinum catalyst. The single cell test was conducted at 70°C. Both aliphatic-based ionomer and aromatic-based ionomer showed similar ion conductivity, while single cell performance was significantly different. When the aliphatic-based ionomer used as a binder, the AMFC performance was improved. This may be due to elimination of benzene adsorption, which reduces catalyst activity.

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*Corresponding author	Dongwon Shin
Affiliation	Korea Institute of Energy Research
E-mail address	dwshin@kier.re.kr

06-1967

A study on optimization of nickel-mediated polymerization for the synthesis of polymer electrolyte membrane

Songmi Kim[1, 2], Adam F. Nugraha[1, 3], Dongwon Shin[1], Byungchan Bae[1, 3*]
[1]*Korea Institute of Energy Research, Korea*
[2]*Yonsei University, Korea*
[3]*University of Science and Technology, Korea*

Polymer electrolyte membrane fuel cells (PEMFCs) are clean energy devices which generate electricity and heat at the same time. [1]Polymer electrolyte membrane (PEM) is one of the key components in the fuel cell system. Most commercial PEMs are perfluorinated polymers. Although perfluorinated polymer membranes have excellent electrochemical performance and chemical stability, they are too expensive. [2]For this reason, hydrocarbon-based polymer membranes have been developed to alternated perfluorinated polymer membranes. However, there are still some drawbacks such as low electrochemical performance and long-term stability. [3]

Here, we synthesized polyphenylene semi-block copolymers. Semi-block architecture can lead to high ion conductivity and polyphenylene structure have outstanding chemical stability. However, expensive metal catalyst is needed for C-C coupling polymerization. Therefore, we tried to optimize nickel-mediated polymerization conditions with less usage of nickel catalyst. The molecular weight of polymers were monitored using gel permeation chromatography. Reduced amount of nickel catalyst resulted in low molecular weight. In addition, the amount of bipyridine ligand, which activated and regenerated nickel catalyst, also affect the degree of polymerization.

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*Corresponding author	Byungchan Bae
Affiliation	Korea Institute of Energy Research
E-mail address	bcbae@kier.re.kr

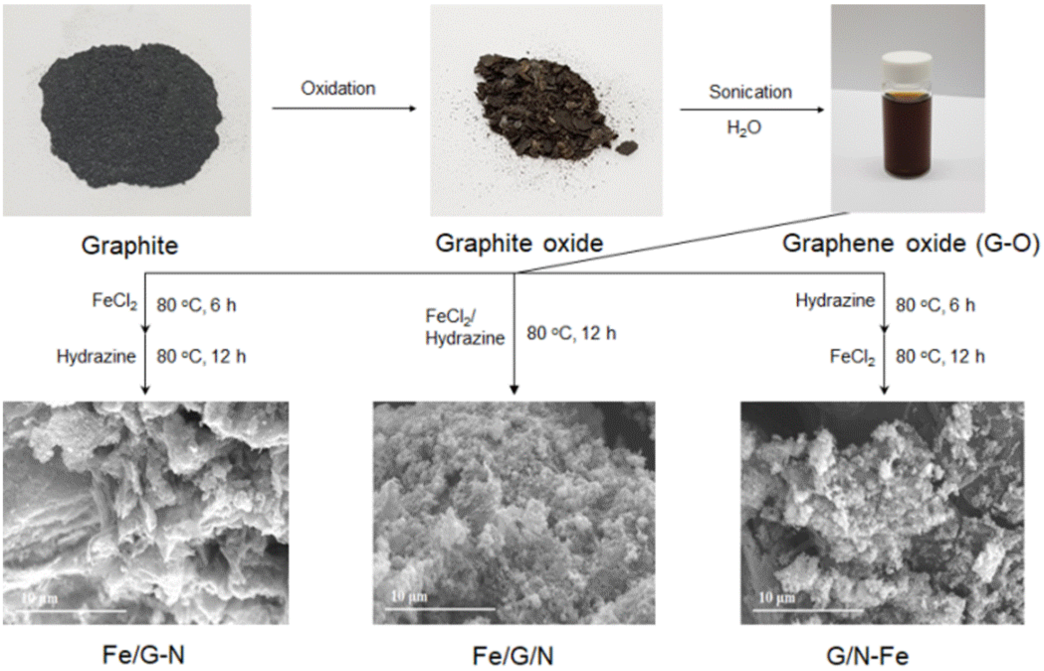
06-2018

Synthesis of N-doped Reduced Graphene Oxide/Fe_3O_4hybrids and Effect of Order of synthesis Steps on Electrocatalytic Performances for Oxygen Reduction Reaction.

Sungjin Park*, Yunseok Shin

Inha University, Korea

Oxygen reduction reactions (ORRs) occur at cathodes in fuel cells and require efficient electrocatalysts. Because of the cost and limited durability and stability of commercial Pt/C catalysts, the development of efficient Pt-free electrocatalysts is an active research topic. Here, we explain the solution-based production of iron oxide nanoparticles/N-doped graphene-based materials from $FeCl_2$, graphene oxide (G−O), and hydrazine. Orders of synthesis steps were varied by; i) reacting $FeCl_2$ and G−O first and then adding hydrazine (Fe/G−N), ii) reacting G−O, $FeCl_2$, and hydrazine at the same time (Fe/G/N), or iii) reacting G−O and hydrazine first and then adding $FeCl_2$ (G/N−Fe). The hybrids produced showed better ORR electrocatalytic activity in alkaline media than single components such as N-doped graphene-based materials or Fe_3O_4. Furthermore, the electrocatalytic properties of the resulting hybrids were found to depend on orders of addition. Fe/G/N was found to be the best electrocatalyst and had better onset and half-wave potentials, thermodynamic current density, and 4-electron selectivity. All three hybrids show good cyclic durability and methanol tolerance.



*Corresponding author Sungjin Park
Affiliation Inha University
E-mail address sungjinpark@inha.ac.kr

06-2041

Facile preparation of three-dimensional nitrogen-doped inverse opal carbon by utilizing heterogeneous polymer as a carbon and nitrogen precursor

Katie Lim[1], Heejun Kweon[2], Hansol Choi[2], Hansung Kim[2*], Hee-Young Park[1], Hyun S. Park[1], Jong Hyun Jang[1*]
[1]Korea Institute of Science and Technology, Korea
[2]Yonsei University, Korea

Nitrogen-doped carbon materials have been extensively studied for decades with an application to electrode in electrochemical energy device, due to its high conductivity and electrocatalytic activity toward oxygen reduction reaction. Many synthetic strategies for nitrogen doping were studied such as thermal ammonia treatment, heat treatment with nitrogen-containing chemicals like melamine, and chemical vapor deposition with a heteroatom polymer in the presence of metal catalyst. On the other hand, those methods have been known to be not favorable to the industry due to high toxicity and high cost of the procedure.

Recently, mussel-inspired polydopamine(PDA) has been demonstrated to be an effective source for the preparation of nitrogen-doped carbon by virtue of its versatile coating ability associated with the high nitrogen content. Through coating a PDA layer on main carbon source and following heat treatment, nitrogen-doped carbon with favorable nitrogen-doping structure was successfully synthesized and evaluated to be electrochemically active toward oxygen reduction reaction. Based on this possibility of PDA as a nitrogen precursor, more improved nitrogen-doped carbon material with higher nitrogen content and favorable structure was developed in this study. In order to achieve higher nitrogen content, PDA was utilized as both the nitrogen and carbon precursor simultaneously, without applying any other carbon source. Moreover, favorable porous structure which is highly ordered and interconnected was introduced by using thermally decomposable polystyrene(PS) as a sacrificial template.

As a result, self-standing three-dimensional nitrogen-doped inverse opal carbon with ordered macropores was prepared from PS vertical deposition, ultra-fast PDA polymerization, and following pyrolysis. Inverse opal structure with completely interconnected macropores was optimized with the PDA coating amount. Several analyses, such as FE-SEM, XPS and mercury porosimeter, were conducted in order to examine the physical characteristics of the synthesized inverse opal carbon material. This three-dimensional nitrogen-doped inverse opal carbon can be widely applied in electrochemical energy device with high possibility.

*Corresponding author 1	Hansung Kim
Affiliation	Yonsei University
E-mail address	elchem@yonsei.ac.kr

*Corresponding author 2	Jong Hyun Jang
Affiliation	Korea Institute of Science and Technology
E-mail address	jhjang@kist.re.kr

06-2047

Nickel-containing Species Molecularly Dispersed on the Carbon Nitride as Hybrid Electrocatalysts for the Oxygen Evolution Reaction.

Sujin Seok, Sungjin Park*

Inha University, Korea

Water electrolysis is a type of oxygen electrochemistry that has been studied as a sustainable and effective energy conversion and storage device. The reaction occurring at the anode electrode is referred to as OER (oxygen evolution reaction). The OER reaction is slow because of the four-electron reaction, which is a major cause of the efficiency degradation. There is a need to develop new catalysts that allow the OER reaction to occur rapidly.

Hybrid catalytic materials containing single atoms or molecule-based active species immobilized on nano-materials have been suggested as advanced catalyst for various reactions. In this study, novel hybrid system consisting of molecularly dispersed Ni-based species on a graphitic carbon nitride (g-C_3N_4) framework show excellent electrocatalytic performance for the OER. Various chemical and structural analyses show that the Ni-based species are well-dispersed on the C_3N_4 network without agglomeration and does not affect the network structure of C_3N_4. In addition, electrochemical characterization results suggest dispersed Ni-containing molecular entities are active species for the OER. Our approach using hybridized molecular nanomaterials would be highly valuable for developing new electrocatalytic systems.

*Corresponding author	Sungjin Park
Affiliation	Inha University
E-mail address	sungjinpark@inha.ac.kr

06-2053

Cobalt organometallic active species immobilized on carbon-based materials at the molecular level for the oxygen reduction reaction

Dawoon Jang, Sungjin Park*
Inha University, Korea

Electrocatalysts for the oxygen reduction reaction (ORR) are essential elements for the redox reactions in fuel cells and metal–air batteries. Pt-based ORR catalytic systems show excellent catalytic activities but their high costs and low durability are inherent critical drawbacks. Pt-free systems, other metal systems, carbon-based metal-free materials, and nonprecious-metal–carbon hybrids have been suggested as alternative candidates for this purpose. Organometallic complexes with transition metal coordination are an important class of molecular catalysts in various applications owing to their highly tunable properties, such as coordination numbers, oxidation states of metal centers, and binding structures between metals and ligands. Consequently, the coordination of such organometallic active centers to nanomaterials, which have huge steric bulk and variable electrical properties, can influence their catalytic performances in a dramatic way. In particular, electrocatalysts composed of low-cost transition metals (Co or Fe), nitrogen, and carbon materials (M-N-C) have shown promising catalytic performances for the ORR. However, most of the M-N-C catalysts require high-temperature treatment for a high ORR activity. This energy- and time-consuming processing step makes it hard to prepare such catalysts in rational, predictive, and cost-effective ways. Owing to the high abundance and good catalytic activity of cobalt, cobalt-based composite materials have been investigated widely as electrocatalysts for the ORR. Chemically modified graphenes, carbon nanotubes (CNTs), and other carbonaceous materials were often used as supports in the composites. Cobalt or cobalt oxide nanoparticles dispersed on the surfaces of carbon-based materials and Co-N-C species embedded into carbon-based networks are efficient active species for the ORR. In this work, we developed a hybrid ORR catalyst through the coordination of Co-based organometallic molecules to N-doped carbon-based materials. Notably, our method offers a room-temperature reaction pathway for the formation of a stable catalytic complex through the exploitation of N-doped structures. The hybrid ORR catalyst shows excellent catalytic performance with an onset potential of 0.95 V (RHE), superior durability, and good methanol tolerance. Chemical and structural characterization after many reaction cycles reveals that the Co-based organometallic species maintained the original structure of cobalt(II) acetylacetonate with coordination to the carbon-based materials. Also chemical and morphological characterization demonstrate after many reaction cycles reveals that a molecular well-dispersed active species at the surfaces of the carbon-based materials.

*Corresponding author	Sungjin Park
Affiliation	Inha University
E-mail address	sungjinpark@inha.ac.kr

06-2054

Enhanced electrocatalytic activity of oxygen reduction reaction of borane-modified graphene oxide with well-dispersed Pt

Haeju Kim, Sungjin Park*

Inha University, Korea

In fuel cells and meta-air batteries, the oxygen reduction reaction (ORR) progresses at the cathode during redox reactions and has challenge to overcome the high activation energy using effective electrocatalysts. In order to supplement the disadvantage, various studies using Pt particle with good catalytic activity such as Pt/C have been carried out. However, it is still difficult to develop Pt containing catalysts with excellent ORR catalytic performance at a low-temperature solution processes. In this work, we suggest a new method to produce composites containing borane-modified graphene oxide (BG) with well-dispersed Pt nanoparticles with uniform size distribution using a low-temperature solution process and their outstanding electrocatalytic performances for ORR in basic media. The composites are synthesized by reaction between $H_2PtCl_6{\cdot}6H_2O$ and BG at a solution process. The Pt particles are distributed uniformly on the surface of BG without agglomeration with lateral dimensions of 10-15 nm. The composites have excellent ORR activity, which is equal to that of Pt/C and previously reported Pt-containing catalysts, with onset and half-wave potentials of 0.99 and 0.84 V, respectively, and show excellent four-electron selectivity and superior kinetics.

*Corresponding author	Sungjin Park
Affiliation	Inha University
E-mail address	sungjinpark@inha.ac.kr

06-2103

Two step synthesis of metal free N-doped carbon blacks and their excellent electrocatalytic performance of ORR.

Sunghee Park, Sungjin Park*

Inha University, Korea

N-doped carbon black is two step synthesized from melamine as a N source (one step) and 1000oC in N2 (two step). This metal free carbon material is a excellent electrochemical oxygen reduction reactions (ORRs) catalysts, in terms of efficient, durable, and cost-effective catalysts. In this regard, the development of metal-free catalysts with excellent activity is essential. Herein we report the development of a novel two-step heating route to produce metal-free N-doped carbon blacks. The prepared materials exhibit superior electrocatalytic performance for ORRs in a basic media, which is comparable to commercial Pt/C catalysts. Among the various heating temperatures tested, sequential two-step heating at 750 and 1000 °C produced the most efficient catalysts with onset and half-wave potentials of 0.97 and 0.82 V, respectively. The prepared materials show excellent selectivity for 4-electron transfer, durability, and stability in response to methanol poisoning. Control experiments with one-step heating and no N-doping confirm the superiority of the two-step heating process for producing efficient electrocatalysts.

*Corresponding author	Sungjin Park
Affiliation	Inha University
E-mail address	Sungjinpark@inha.ac.kr

06-2291

Nickel-based Chalcogenide Electrocatalysts For Efficient Water Splitting

Sungwon Kim[1], Masaki Saruyama[1], Masanori Sakamoto[1], Taro Yamada[2], Hee-Young Park[3], Jong Hyun Jang[3], Kazunari Domen[2], Toshiharu Teranishi[1*]

[1]*Kyoto University, Japan*

[2]*The University of Tokyo, Japan*

[3]*Korea Institute of Science and Technology, Korea*

Hydrogen is a clean and high-density energy source. An ever-increasing demand for clean energy technologies in this era of global climate change has triggered unprecedented attention toward electrochemical water splitting to generate hydrogen as renewable and sustainable approach. Among the currently available water electrocatalysts, noble metal-based electrocatalysts (Pt, Ir, Ru, and etc.) have arrange of advantages, such as high current density and chemical stability. Although noble metal-based electrocatalysts have shown a promise for water splitting reaction, the scarcity of these noble metals present barriers for their scale-up deployment. Furthermore, the sluggish kinetics is the main obstacles for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which results in a large overpotential for overall water splitting. Thus, abundant and more active electrocatalysts are essential for efficient storage of electrical energy with small overpotentials. A great deal of efforts and progress have been made towards efficient HER and OER electrocatalysts with chalcogenide-based materials, such as Mn, Fe, Co, Ni, Mo, and etc. Among them, Ni-based chalcogenide electrocatalysts have shown a great promise for similar chemical properties with Pt which originate from the same group in periodic table. In this presentation, we will show our recent research studies on the nanostructured Ni-based chalcogenides synthesized by wet chemical method including electrocatalytic activities for water splitting by engineering the exposed facets and architectural nano-composites. Furthermore, experimental methodology and detailed characterization will be showed to reveal the reaction kinetics with electrocatalytically active species of Ni-chalcogenide. This will provide insights toward fundamental understanding on the reaction mechanism and better design concepts for HER/OER electrocatalysts.

*Corresponding author	Toshiharu Teranishi
Affiliation	Kyoto University
E-mail address	teranisi@scl.kyoto-u.ac.jp

06-2321

A Study on the Ion Behavior for Metal Recovery from Organic Acid Coating Waste Fluid through Electrodialysis Process

Sang-Mi Park*, Soong-Keun Hyun*
Inha University, Korea

The plating industry is not only an industry that has a close relationship with the electric materials and electronic parts industry, which is the core competence business area of the country, but also has a great influence on the quality of determining the price by improving the functional characteristics and value-added of core parts and materials. The plating solution used here contains metals and various additives and is discarded due to the deterioration of metal deposition efficiency due to aging of organic materials over time. The effluent wastewater is classified as a main hazardous substance emission management subject and is under intensive management.

In this study, electrodialysis was used as a method for recovering and reusing exhausted metal from the waste wastewater. The experiment was investigated on the ion behavior of waste solutions that is methanesulfonic acid electrolyte containing copper and tin, bismuth. We carried out varying current density and metal content.

*Corresponding author 1	Sang-Mi Park
Affiliation	Inha University
E-mail address	friends0126@naver.com

*Corresponding author 2	Soong-Keun Hyun
Affiliation	Inha University
E-mail address	skhyun@inha.ac.kr

06-2482

Scalable synthesis of nanoparticle electrocatalyst via sputtering on soluble powder substrates

Hee-Young Park, Injoon Jang, Jong Hyun Jang, Sung Jong Yoo*
Korea Institute of Science and Technology, Korea

Carbon supported nanoparticles (NP/C) have been widely utilized as a catalyst for electrochemical energy conversion devices such as, fuel cell, metal-air battery, and electrolyzer. As the efficiency of the devices are mainly governed by the activity of catalysts, much effort have been focused on synthesis of highly active catalyst with high surface area. Wet chemical methods have been used to make NP/C catalysts as the process provided NPs with finite size and fine size distribution. The wet chemical methods often requires hazardous and/or expensive chemical reagents to produce fine NPs.

Here, we report a clean way to prepare NP/Cs based on magnetron sputtering of bulk materials on soluble powder substrate, followed by the deposition of the NPs on carbon supports. Using a powder substrate having OH moieties, we prepared ultrafine NPs without agglomeration of particles. The NP/Cs showed improved activity for various electrochemical reactions, mainly due to their high surface area.

*Corresponding author	Sung Jong Yoo
Affiliation	Korea Institute of Science and Technology
E-mail address	ysj@kist.re.kr

06-2848

Engineered metal oxides for solar fuels

Gang Liu*

Institute of Metal Research, Chinese Academy of Sciences, China

Extending the light absorption range of wide-bandgap photocatalysts into the visible light region is significant in terms of fully harvesting and converting solar light. The desirable band-to-band redshift of the absorption edge of semiconducting binary metal oxides such as prototypical photocatalyst $TiO2$ by doping has long been targeted but remains a challenge, up to date. Here, by taking the advantage of abundant one-dimensional diffusion channels with rhombus-like cross-sections along the c-axis in the crystal structure of titanium oxalate hydrate to promote the entrance of nitrogen dopant species into the bulk and subsequent thermal topotactic transition in an atmosphere of gaseous ammonia, the homogeneous doping of substitutional carbon/nitrogen for oxygen in the $TiO2$ decahedral plates with a dominant anatase phase was obtained for the first time. The resultant $TiO2-x(CN)y$ with an unusual band-to-band visible light absorption spectrum can induce photocatalytic water oxidation to release oxygen under visible light irradiation. On the other hand, integrating a semiconducting light absorber with an appropriate co-catalyst appears almost indispensable for photocatalytic solar fuel generation. Although ferroelectric materials with the spontaneous electrical polarization are considered promising light absorbers with the ability to induce the oppositely directed transports of photogenerated electrons and holes in the bulk, their applications are intrinsically restricted by the large Schottky barrier at the interface of the ferroelectric and the cocatalyst which has a larger work function. Here, we demonstrate that, by the selective chemical epitaxial growth of anatase $TiO2$ islands on the positively poled (00-1) facet of $PbTiO3$ single-crystal particles to form an atomically smooth interface with a small potential difference, the material shows significantly improved photocatalytic hydrogen and oxygen generation under both UV-visible and visible light, while the islands-free $PbTiO3$ is inactive in visible light.

*Corresponding author	Gang Liu
Affiliation	Institute of Metal Research, Chinese Academy of Sciences
E-mail address	gangliu@imr.ac.cn

06-2853

Mussel-Inspired Polydopamine Treated Reinforced Composite Membranes with Self-Supported CeO_x Radical Scavengers for Highly Stable PEM Fuel Cells

Ki Ro Yoon*

Korea Institute of Industrial Technology, Korea

The physical and chemical degradations of a state-of-the-art proton exchange membrane (PEM) composed of a perfluorinated sulfonic acid (PFSA) ionomer and polytetrafluoroethylene (PTFE) reinforcement are induced through the repeated expansion/shrinkage of the ionomer and free radical attacks. Such degradations essentially originate from the loose structure of the materials and the low interactive binding force among the PEM constituents. In this study, the need for simplified design principles of adhesives led to the use of mussel-inspired polydopamine (PD) as an interfacial modifier for the fabrication of highly durable PEM. Indeed, a self-polymerized dopamine layer acts as an interfacial glue, and enables efficient impregnation of a hydrophilic PFSA ionomer into porous hydrophobic PTFE with high packing density, resulting in strong adhesion between the PTFE and the PFSA polymers in the membrane. In addition, the redox property of the PD end groups spontaneously reduces the partial Ce salts in the ionomer solution and anchors them to the PD@PTFE substrate as defective cerium oxide (CeO_x) nanoparticles, reducing the dissolution and subsequent migration under cell operations. Finally, a CePD@PTFE membrane shows outstanding durability in fuel cells under an accelerated humidity cycling test with a reduction in the degree of physical and chemical failures.

*Corresponding author	Ki Ro Yoon
Affiliation	Korea Institute of Industrial Technology
E-mail address	kryoon@kitech.re.kr

06-2905

Pt-Co Alloy Nanoparticles with Organic Reducing Agent Induced Pt Shell for Highly Stable Proton Exchange Membrane Fuel Cells

Sehyun Lee, Injoon Jang, Jue-Hyuk Jang, Hee-Young Park, Sung Jong Yoo*
Korea Institute of Science and Technology, Korea

To improve the oxygen reduction reaction (ORR) activity, which is the decisive factor for proton exchange membrane fuel cells (PEMFCs), alloy Pt with transition metals is widely used as a promising strategy. However, the transition metals are vulnerable to liquid electrolyte and fuel gases under cell operation that lead to degrade the catalytic activity. To overcome this problem, Pt protection layers are introduced in PtCo alloy core through chemical method. A robust Pt shell on the carbon-supported PtCo intermetallic core nanoparticles are achieved via the organic hydride donor, a Hantzsch ester. The hydride from Hantzsch ester reduces residual Cl on Pt skeleton surfaces and slowly affects the negatively charged defect sites without damaging the core structure. The secondary Pt reduction reaction via hydride is conducive to cover the negatively charged Pt skeleton surfaces and acquire the optimum thickness without the formation of isolated Pt nanoparticles. PtCo@Pt with a unique Pt shell shows higher catalytic activity and durability than commercial Pt/C for ORR electrocatalysts in PEMFCs.

*Corresponding author	Sung Jong Yoo
Affiliation	Korea Institute of Science and Technology
E-mail address	ysj@kist.re.kr

06-2920

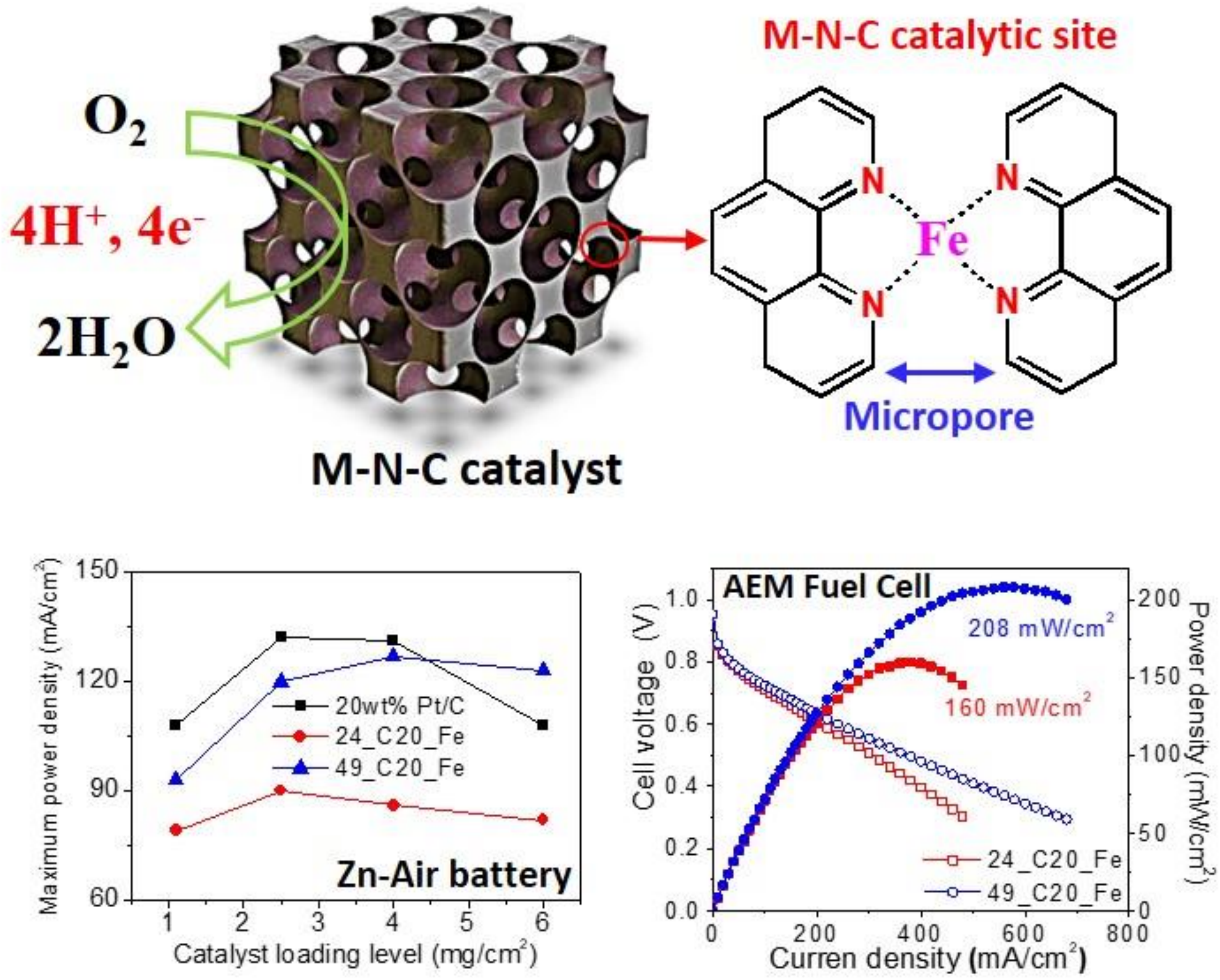
Effect of M-N-C (Metal-Nitrogen-Carbon) Catalyst Support Pore Size on the Performance for Fuel Cells and Zn-Air Battery.

Hee Soo Kim[1], Jue-Hyuk Jang[1], Hyun S. Park[1], Sung Jong Yoo[1*], Won Cheol Yoo[2*]

[1]*Korea Institute of Science and Technology, Korea*

[2]*Hanyang University, Korea*

The development of highly active, cost-effective and lusty non-Pt based electrocatalyst for Oxygen Reduction Reaction (ORR) is the important point to enhance the application of fuel cell and metal-air battery application. Thus, appropriate morphology and structure for improving active catalyst site density and enhancing mass transport of reactant are necessary. Therefore, development of non-Pt based catalyst such as M-N-C (Metal-Nitrogen-Carbon) are required in recently. In this study, various size (36nm and 60nm) of silica template was utilized to synthesize different metal (Fe, Co and Ni) and nitrogen co-doped three dimensional ordered mesoporous carbon (3DOmC) for ORR application. Especially, CO2 activation was used to develop the micropore to form and increase the M-N-C catalytic activity density. As a result, micro and mesoporosity controlled 3DOmC-M-N-C electrocatalysts were successfully synthesized. Due to its highly catalytic activity density and excellent mass transfer property by wide pore structure, these 3DOmC-M-N-C showed an excellent ORR performance compared with various ORR catalyst (onset potential : - 0.056 V and Half-wave potential : -0.106 V vs Ag/AgCl (V) of 49_C20_Fe) Furthermore, 3DOmC-M-N-C were used as a catalyst for AEMFC (Anion Exchange Membrane Fuel Cell) and Zn-air battery to observe the effect of the pore structure on the full cell configuration. Hence, because of the excellent diffusion capacity and due to its wide mesopore structure and highly catalytic activity density, 49_C20_Fe showed the best performance in those samples. In addition, the performance of the AEMFC and Zn-air battery of 49_C20_Fe (127 mW/cm2 for Zn-Air battery and 208 mW/cm2 for AEMFC, respectively) was better than 24_C20_Fe (90 mW/cm2 for Zn-Air battery and 160 mW/cm2 for AEMFC, respectively) catalyst. This result is highly suggesting that fabrication of the Fe-N4 active sites and formation of mesoporous structure were obtained simultaneously in the simple hard-template-assisted and activation process, and in that the advantages of ordered mesoporous structure with wide pore size (24 and 49nm) in metal-containing 3DomC-M-N-C were elucidated for outstanding single cell performance.



*Corresponding author 1	Sung Jong Yoo
Affiliation	Korea Institute of Science and Technology
E-mail address	ysj@kist.re.kr
*Corresponding author 2	Won Cheol Yoo
Affiliation	Hanyang University
E-mail address	wcyoo@hanyang.ac.kr

06-2937

Investigation of ordered and disordered PtRhSn/C electrocatalysts for electrochemical ethanol oxidation reaction

Myeong Jae Lee, Eung-Jun Lee, Kyungmin Yim, Dong Wook Lee, Daeil Choi, Sehyun Lee, Hee Soo Kim, Sung Jong Yoo*

Korea Institute of Science and Technology (KIST), Korea

Polymer Electrolyte Membrane Fuel Cell (PEMFC) is an electrochemical energy conversion device which converts chemical energy into electrical energy. One kind of PEMFC, Direct Ethanol Fuel Cell (DEFC) has several advantages, such as easy fuel storage, high energy density, low operating temperature and environmental benefit. However, there is problem that a large amount of precious metal catalyst with scarcity and high prices is required to overcome substantially slow kinetics of electrochemical ethanol oxidation and obstacles of C-C bond breaking. In order to resolve this issue, several researches on structural design of active PtRhSn electrocatalyst which has high ethanol oxidation reaction (EOR) activity and great C-C bond breaking ability were carried out. However, it is still lack of understanding whether structural ordering of the catalyst has positive effect on EOR or not. In addition, in-depth investigation on correlation between degree of ordering and dissolution of the catalyst during electrochemical measurement was still not achieved.

In this work, degrees of ordering of the catalysts were controlled by heat treatment and they were characterized by electrochemical and physicochemical measurements. By this approach, higher EOR activity of disordered catalyst and higher stability of ordered catalyst in EOR condition were figured out. In addition, carbon barrier was introduced to the surface of the catalyst and further characterization of enhanced activity and stability of the catalyst with carbon barrier was conducted.

*Corresponding author	Sung Jong Yoo
Affiliation	Korea Institute of Science and Technology (KIST)
E-mail address	ysj@kist.re.kr

06-2956

Bio-derived Multifunctional Electrocatalyst: Co2P Nanoparticles Supported on Nitrogen-Doped Carbon for Highly Efficient Electrochemical Reaction.

Dong Wook Lee[1, 2], Daeil Choi[1], Myeong Jae Lee[1], Sehyun Lee[1], Kwan Young Lee[2], Sung Jong Yoo[1*]
[1]*Korea Institute of Science and Technology, Korea*
[2]*Korea University, Korea*

The viability of energy conversion devices such as fuel cell and metal-air batteries are closely related to the price of the oxygen reduction reaction (ORR) catalyst which is applied to the electrode, especially the cathode. Until now, platinum has been mainly used as a catalyst, and this has been a hindrance to commercialization in terms of economy. To overcome this problem, nanostructured catalysts synthesized without non-precious metal for ORR have been actively studied. Among them, cheap and abundant biomass as a starting material has stood out an attractive method to obtain electrocatalysts when converted to activated carbon.

In this study, we developed the Co2P nanoparticles supported on abundant nitrogen-doped carbon catalyst through the eco-friendly and simple method by using bean sprouts (NBSCP). The catalyst can exhibit activity in various electrochemical reactions. In particular, superior performance is noted for the oxygen reduction reaction (ORR). Compared to the commercial Pt/C, NBSCP exhibits a lower onset potential, higher current density, and superior stability. This excellent ORR activity and durability is attributable to the synergistic effect between Co2P nanoparticles with carbon shell and nitrogen-doped carbon. In addition, NBSCP has been applied to anion exchange membrane fuel cells and it exhibited excellent performance. At the optimized cathode, the NBSCP exhibited the max power density of 172 mW cm-2. It is considered to be a competitive performance and it has demonstrated the possibility for application to energy conversion systems.

*Corresponding author	Sung Jong Yoo
Affiliation	Korea Institute of Science and Technology
E-mail address	ysj@kist.re.kr

06-3003

Low loading of Noble-catalysts in Highly Efficient Polymer Electrolyte Membrane-Unitized Regenerative Fuel Cells (PEM-URFC)

Ahyoun Lim[1], Junyoung Kim[1], Hye Jin Lee[1], Jong Hyun Jang[1], Yung-Eun Sung[2*], Hyun S. Park[1*]
[1]*Korea Institute of Science and Technology, Korea*
[2]*Seoul National University, Korea*

Unitized regenerative fuel cell (URFC) is promising energy device, which is combined form of water electrolyzer (WE) and fuel cell (FC) to generate hydrogen fuel from renewable energy and provide electricity from produced fuel. It has high specific energy (3660 Wh/kg) which is five times higher than that of Li-ion battery (700 Wh/kg) [1]. However, round efficiency of URFC is poor, around 40-50 % unlike battery (more than 90 %). In URFC, high loading of noble catalysts, i.e. 1-5 mg cm-2, has been inevitable to obtain high performance although the state of technology itself is mature to be commercialized [2]. Here, 49 % round trip efficiency at 0.4 Acm-2 is achieved with low loading of total noble catalysts, 0.8 mg(Pt+IrO2) cm-2, by electrodeposition of platinum and iridium oxide. In single cell tests, mass transfer resistance is reduced compared to that of general spray electrode due to catalysts structure produced by electrodeposition. In addition, dual electrodeposition leads synergy effect from platinum, e.g. reduction of contact resistance and enhancement of electrochemical surface area of iridium oxide. In the aspect of water electrolysis in URFC, the electrode shows highly active and stable performance during 300 h operation, e.g. 7.1 A cm-2 at 2.0 Vcell with only 0.16 mgIr cm-2 and 115 µV h-1 at 0.4 A cm-2.

*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

06-3008

Effect of operating conditions on performance and durability of anion exchange membrane water electrolyzer

Katie Lim[1], Sungwon Kim[1], Ohsub Kim[1, 2], Min Kyung Cho[1], Hee-Young Park[1], Hyun S. Park[1, 2], Jong Hyun Jang[1, 3*]

[1]Korea Institute of Science and Technology, Korea

[2]University of Science and Technology, Korea

[3]Green school, Korea University, Korea

Accompanying to the soaring interest in fuel cells, hydrogen production becomes another center of great attention recently. These days, hydrogen is mainly produced from the steam reforming of natural gas these days, which results in the emission of greenhouse gases such as carbon dioxide or hydrocarbons. Thus, it is necessary to search for alternative methods for hydrogen production, such as water electrolysis powered by renewable energy sources, in order to realize a clean energy cycle from hydrogen production to power generation by fuel cell systems. Alkaline anion exchange membrane water electrolysis (AEMWE) is one of the promising methods for producing hydrogen with high purity, efficiency and safety. Many studies have been conducted on AEMWE for improving the ionic conductivity and catalytic activity of the system, and it is revealed that the operating conditions affect the performance and durability as well. In this regard, fabrication of the electrode and operating condition of AEMWE system are studied and optimized in this study, to achieve a AEMWE with a high-performance and durability consequently.

*Corresponding author	Jong Hyun Jang
Affiliation	Korea Institute of Science and Technology
E-mail address	jonghyun.jang@gmail.com

06-3019

Effect of transition metal alloying on the phosphoric acid adsorption of carbon supported Pt nanoparticle electrocatalyst

In Gyeom Kim[1], Chang Seob Kim[1], Dong-Hee Lim[2], Hyung Chul Ham[1*], Jong Hyun Jang[1, 3*], Hee-Young Park[1*]
[1]Korea Institute of Science & Technology (KIST), Korea
[2]Chungbuk National University, Korea
[3]Green School, Korea University, Korea

With the increasing potential of safe, green, and sustainable energy resources, polymer electrolyte membrane fuel cell (PEMFC) has recently attracted considerable attention due to their intrinsic advantages: no (or low) emissions, high efficiency, and high energy density. Specially, high temperature-PEMFC (HT-PEMF) utilizing phosphoric acid-doped polybenzimidazole (PBI) as a proton exchange membrane has several advantages, compared to low-temperature PEMFC (< 80°C), such as higher tolerance towards carbon monoxide poisoning, easier water management, efficient heat utilization, and faster reaction rate due to its high operating temperatures (above 120 °C up to 200 °C).

However, the phosphoric acid and its anions typically tends to adsorb onto the surface of the platinum catalyst and significantly decreases the ORR activity (Pt poisoning). Thus, high phosphoric acid tolerance is very important as well as higher intrinsic activity of electrocatalysts for improved the ORR activity in HT-PEMFCs. To decreasing the phosphoric acid coverage on the surface of Pt catalysts, it is considered necessary to decrease the adsorption strength of phosphoric acid on the Pt.

Herein, in this study, we investigated the adsorption strength of phosphoric acid on carbon supported Pt skin Pt_3M alloy (M = Ni, Co, and Fe) nanoparticles ($Pt@Pt_3M/C$), using electrochemical analysis and density functional theory (DFT) calculations. The electrochemical results showed that the adsorption charge density near the onset potential region decreased when Pt_3M alloy (M = Ni, Co, and Fe) was formed. Furthermore, the DFT calculations predicted weaker adsorption of phosphoric acid with alloying by Co, Fe, or Ni in the subsurface layers. Both the experimental and theoretical results demonstrated that $Pt@Pt_3Ni/C$ has the higher phosphoric acid tolerance, with the weakest adsorption of phosphoric acid due to the lower density of states at the Fermi level (DOS_{Ef}).

*Corresponding author 1	Hyung Chul Ham
Affiliation	Korea Institute of Science & Technology (KIST)
E-mail address	hchahm@kist.re.kr

*Corresponding author 2	Jong Hyun Jang
Affiliation	Korea Institute of Science & Technology (KIST)
E-mail address	jhjang@kist.re.kr

*Corresponding author 3	Hee-Young Park
Affiliation	Korea Institute of Science & Technology (KIST)
E-mail address	parkhy@kist.re.kr

06-3020

Development of Iridium oxide coated Ti mesh electrode for durable oxygen electrode of polymer electrolyte membrane water electrolyzer

Hye Jin Lee[1, 2], Hye Young Jung[1, 2], Ahyoun Lim[1], Sungwon Kim[1, 2], Hyun-Seo Park[1, 3], Hee-Young Park[1, 2*], Jong Hyun Jang[1, 2*]

[1] *Korea Institute of Science and Technology (KIST), Korea*
[2] *KU-KIST GreenSchool, Korea University, Korea*
[3] *University of Science and Technology (UST), Korea*

Research on hydrogen energy has attracted much attention as a capable medium for storing large capacity and surplus power. Especially, polymer electrolyte membrane water electrolyzer (PEMWE) is the fastest growing system due to its advantages such as high rate of hydrogen production, high purity in produced hydrogen, compact system and clean byproducts (O_2), etc. In this regard, PEMWE research has been focused on reducing the high cost of the system by developing inexpensive catalysts, which can substitute the noble metal catalysts (platinum, iridium metal, etc.). Moreover, improving cell durability and energy efficiency have been ciritical objectives of the recent studies. In this respect, it is necessary to study on preventing the passivation and corrosion of the diffusion layer and bipolar plate under various operating conditions and anode potentials, for achieveing more durable PEMWE system consequently. Ti, which is known to be stable under acidic environment, is one of the promising candidates for application to diffusion layer and bipolar plate in PEMWE.

Herein, by utilizing the highly stable Ti, the electrodeposited IrO_2 catalyst layer on the Ti mesh electrode was suggested as a durable oxygen electrode. In particular, the result of the IrO_2 coated on Ti mesh electrode showed that the performance was stable at the low amount of catalyst. Furthermore, through the corrosion polarization test, the coated IrO_2 physically confirmed the exposure of the Ti mesh diffusion layer and low dissociation rate of electrode in the aging experiment at 1.72 V. These results indicate that the plated IrO_2 serves as a catalyst layer for oxygen evolution reaction (OER) and a corrosion inhibitor of Ti mesh. Moreover, it has excellent stability obtained with a small amount of catalyst.

*Corresponding author 1	Hee-Young Park
Affiliation	Korea Institute of Science and Technology (KIST)
E-mail address	Parkhy@kist.re.kr

*Corresponding author 2	Jong Hyun Jang
Affiliation	Korea Institute of Science and Technology (KIST)
E-mail address	jhjang@kist.re.kr

06-3029

Synthesis of polyethylene glycol-modified Au nanoparticles for electrochemical reduction of carbon dioxide via liquid medium sputtering

Min Gwan Ha[1, 2], Ara Jo[1], Young Sang Park[1], In Young Cha[1], Hee-Young Park[1], Hyun S. Park[1*], Jong Hyun Jang[1, 3*]

[1]Korea Institute of Science and Technology, Korea
[2]Pusan National University, Korea
[3]Green school, Korea University, Korea

As a consequence of industrialization, CO_2 emissions form fossil fuel consumption have been increasing, leading to global warming. The electrochemical CO_2 conversion is considered to be an attractive strategy to mitigate the impacts of global warming by recycling emitted CO_2 reduction to CO. In order to develop the practical use of CO_2 conversion techniques, selective and efficient electrocatalysts are crucial. Despite the remarkable efforts, these techniques still suffer from low catalytic activity as well as a complex catalyst synthesis procedure.

In this study, an effective and stable Au nanoparticles on carbon support coated polyethylene glycol (PEG) was developed by a one-step liquid medium sputtering deposition method. PEG layers on the Au surface provide high catalytic activity and stability and lead to enhance the performance of CO production. The prepared PEG modified Au/C catalyst exhibited a Faradaic efficiency for CO production of 100 % at -0.57 V_{RHE} and outstanding stability during 10 h because of prevention of sulfur poisoning and high solubility of PEG for CO_2 .

*Corresponding author 1	Hyun S. Park
Affiliation	Korea Institute of Science and Technology
E-mail address	hspark@kist.re.kr
*Corresponding author 2	Jong Hyun Jang
Affiliation	Korea Institute of Science and Technology
E-mail address	jhjang@kist.re.kr

06-3049

Development of Strategy for Tuning ORR Activity by Controlling Electron Properties of a Fe-N_4 sites embedded Carbon Plane

Seunghyun Lee[1], Jinwoo Lee[2*]
[1]*Pohang University of Science and Technology, Korea*
[2]*Korea Advanced Institute of Science and Technology, Korea*

Replacement of Pt-based oxygen reduction reaction (ORR) catalysts with non-precious metal catalysts (NPMCs) such as Fe/N/C is one of the most important issues in the commercialization of proton exchange membrane fuel cells (PEMFCs). Despite numerous studies on Fe/N/C catalysts, a fundamental study on the development of a versatile strategy is still required for tuning the kinetic activity of a single Fe-N_4 site. Herein, we report a new and intuitive design strategy for tuning and enhancing the kinetic activity of a single Fe-N_4 site by controlling electron-withdrawing/donating properties of a carbon plane with the incorporation of sulfur functionalities. The effect of electron-withdrawing/donating functionalities was elucidated by experimentation and theoretical calculations. Finally, the introduction of an oxidized sulfur functionality decreases the d-band center of iron by withdrawing electrons, thereby facilitating ORR at the Fe-N_4 site by lowering the intermediate adsorption energy. Furthermore, this strategy can enhance ORR activity without a decrease in the stability of the catalyst. This simple and straightforward approach can be a cornerstone to develop optimum NPMCs for application in the cathodes of PEMFCs.

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

06-3065

Hydrogen-selective Behavior of Carbon-encapsulated Metal Nanoparticles to Tolerate Frequent Shutdown/startup Cycling

Daeil Choi, Dong Wook Lee, Eungjun Lee, Myeong Jae Lee, Sehyun Lee, Sung Jong Yoo*
Korea Institute of Science and Technology, Korea

When environmental issues are coming to the fore, fuel cells have been paid worldwide attention as an eco-friendly energy devices for upcoming generation thanks to no emission of pollutants. Among others, proton exchange membrane fuel cells (PEMFCs) have received spotlighted owing to their merits of high energy density and conversion efficiency for automobile applications even though there are several types of fuel cells. However, commercialization of the PEMFCs is still challenging since there are pragmatic issues to overcome such as economic efficiency derived by the usage of precious metal, catalytic activity, and durability. For automobile applications, it is crucial that the PEMFCs have a tolerance against endure electrochemically harsh conditions such as long-term operation, localized fuel starvation, and frequent startup/shutdown cycles. In particular, in case of the reverse current flow induced by localized hydrogen starvation in the anode, it accelerates the degradation of catalyst layers and consequently brings down the PEMFCs system. Fuel starvation occurs when oxygen is in the anode which only hydrogen exists on account of O¬2 crossover from the cathode to the anode or air from outside. For example, when the PEMFCs shutdown and startup, air from outside is introduced into the anode and oxygen/hydrogen boundary is formed in an instant. Although it is temporary phenomenon, undesired oxygen reduction reaction (ORR) occurs because of oxygen. Once the ORR takes place in the anode, it leads to an increase of cathode potential up to ~1.5 V. Then, as a result, the catalysts are agglomerated and degraded. Herein, so as to overcome this practical issues, we report carbon-encapsulated Pt core-shell nanoparticles which can fundamentally interrupt the formation of the localized fuel starvation region. The carbon-shell of core-shell nanoparticles with nanopores accept hydrogen selectively by blocking access of oxygen to Pt surface via size-dependent reaction. Furthermore, even after accelerated degradation test, it is demonstrated that the catalysts exhibit not only high hydrogen oxidation reaction (HOR) selectivity but also still restrains the ORR activity owing to excellent stability of carbon shell under electrochemically stressful condition. After the repetitive cycles of shutdown/startup in single-cell, in addition, the MEA with the HOR-selective catalysts shows the constant performance compared to that with commercial catalysts. The hydrogen-selective behavior of the core-shell catalysts is also observed in single-cell measurement compared to commercial Pt/C. Therefore, this research will suggest innovative strategy to design the catalyst for anode to boost the durability of the PEMFCs system for automobile applications.

*Corresponding author	Sung Jong Yoo
Affiliation	Korea Institute of Science and Technology
E-mail address	ysj@kist.re.kr

06-3083

Electrochemical impedance spectroscopy analysis for carbon support degradation in polymer electrolyte membrane fuel cell.

Jeawoo Jung[1, 2], Chang Seob Kim[1], Myungsu Lim[1], Seung-hyeon Oh[1], Hee-Young Park[1], Hyun S. Park[1, 3], Jong Hyun Jang[1, 2*]

[1]*Korea Institute of Science and Technology, Korea*
[2]*Green School, Korea University, Korea*
[3]*University of Science and Technology (UST), Korea*

Proton exchange membrane fuel cells (PEMFCs), which are environmentally friendly and efficient, have been intensively researched and developed for automobile and stationary applications. Several companies are introducing fuel cell electric vehicles into the market, but the problem of improving durability remains, of which performance degradation due to carbon corrosion within electrodes is the biggest issue. To produce more reliable and economical systems, further development of PEMFCs to achieve higher durability and low cost is required. In particular, carbon corrosion within electrode needs to be analyzed accurately to improve durability.

The effect of voltage and relative humidity in accelerated degradation of fuel cells was analyzed by electrochemical impedance spectroscopy. For this, a transmission-line model based equivalent circuit was used, where the resistance to proton transport in the cathode was considered. As the degradation voltage increased from 1.3 V to 1.5 V, the performance decay, and the charge transfer resistance, gradually increased. This change was larger when the relative humidity (RH) was increased from 50% to 100%. However, the ionic resistance was higher at RH 50% condition than RH 100% condition. This result occurred due to increased water evaporation from the ionomer in cathode catalyst layer. There was a similar trend of changing ohmic resistance. However, when degraded at 1.5 V, ionic resistance and charge transfer resistance increased due to carbon corrosion. It appears that the change in charge transfer resistance lead to the change in ionic resistance.

*Corresponding author	Jong Hyun Jang
Affiliation	Korea Institute of Science and Technology
E-mail address	jhjang@kist.re.kr

06-3095

Synthesis and fuel cell application of new solid acid composite-Polybenzimidazoles (PBIs) for Intermediate temperature

Seung Ju Lee, Min Jae Lee, Yeong Cheon Kim, Young Suk Jo, Suk Woo Nam, Hyoung Juhn Kim, So Young Lee*

Korea Institute of Science and Technology, Korea

Recently, fuel cells are considered as an alternative to solve energy problems and pollution problems in the future. High temperature proton exchange membrane fuel cells (HT-PEMFC) using phosphoric acid-doped polybenzimidazole (PBI) electrolytes, which can be operated at high operating temperatures of 150-160℃, have high energy density, and It is an efficient energy conversion device. The performance shows 500 to 800 mW/cm^2 peak power density without external humidification under H_2 / air.

However, HT-PEMFCs are limited in operating temperature due to the leaching of PA when the fuel cells are exposed to water below 140℃, also the loss of weakly bound phosphoric acid when operated above 200℃. In addition, high temperature fuel cells such as solid oxide fuel cells (SOFCs) operating at temperatures of 800℃, achieve a power density of 1400 mW/cm^2 at 700℃, but the fuel cell performance of high temperature fuel cells at low temperatures are as weak as 100 mW/cm^2 at 350℃. Therefore, it is most important to improve the performance of intermediate temperature fuel cells. Current intermediate temperature fuel cells show relatively poor performance and require commercial application study.

In this study, we have developed a one-step process by adding solid acid composite to polymer electrolyte membrane which can operate at 150 ~ 250℃ and able to intermediate temperature polymer electrolyte fuel cell application. The result is peak power density of 1200 mW / cm^2 at 250℃ under H_2 / O_2. It can be seen that the performance has increased almost three times compared to conventional CsH_2PO_4 ITFC (a peak power density of 415mW/cm^2). Also compared with conventional p-polybenzimidazole (p-PBI) membranes, toxicity due to reactant impurities such as carbon monoxide or sulfur dioxide is low, which can be applied to indirect methanol reforming reactors.

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

06-3109

Novel Hydrocarbon Polymer-Based Electrode Ionomer for Alkaline Anion Exchange Membrane Fuel Cells

Ji Eon Chae[1, 2], So Young Lee[1], Kwang Ho Song[2], Hyoung-Juhn Kim[1*]
[1] *Korea Institute of Science and Technology, Korea*
[2] *Korea University, Korea*

Alkaline anion exchange membrane fuel cells (AEMFCs) are an attractive alternative to proton exchange membrane fuel cells because it has an advantage for cost reduction due to the use of non-precious metal catalysts. Since AEMFCs have charge carriers of hydroxide ions, anion exchange membranes having various cationic groups substituted on the hydrocarbon polymer backbone have been actively studied for high hydroxide conductivity, mechanical properties and durability. As well as, among the core materials of membrane electrode assembly, an electrode ionomer serves as a binder for uniformly dispersing the catalyst and fixing the catalyst layer and the anion exchange membrane. And it also acts as a transfer pathway for hydroxide ions generated from cathode to anode. Especially, the electrode ionomer is important that greatly affects the catalyst layer morphology and fuel cell performance. In this research, polymers with various molecular weights were synthesized for the electrode ionomer for AEMFCs, and the polymer molecular weight was controlled by chain transfer reaction of sulfonyl chloride containing monomer with styrene in radical polymerization. To introduce functional groups, long bromo-alkyl chains were attached to styrene, and the quaternary ammonium groups could be substituted to conduct hydroxide ions. The synthesized anion conducting polymers were investigated with various characterizations. Finally, the fuel cell performance was evaluated by applying it as the electrode ionomer. The details will be discussed in presentation.

*Corresponding author	Hyoung-Juhn Kim
Affiliation	Korea Institute of Science and Technology
E-mail address	hjkim25@kist.re.kr

06-3116

A Study on the Demonstration Evaluation of PEM Fuel Cell according to Fuel Gas Composition

MinWoo Kim*, SooJin Han, JungWoon Lee, HyoJung Bang

Institute of Gas Safety R&D, Korea Gas Safety Corporation, Korea

Recently, there has been a growing interest in renewable energy worldwide due to problems such as depletion of fossil fuels and environmental pollution. hydrogen society gradually emerging in korea, and the development and dissemination of fuel cells are gradually expanding, and overseas exports of fuel cell products are also actively promoted. However, in order to export products, the status of overseas fuel gas composition, power system, and quality of supply water should be grasp first, and fuel cell demonstration evaluation using this should be accompanied.

Especially, the composition of the city gas supplied to the fuel cell varies from country to country, and impurities that can cause poisoning effect in the fuel cell, such as an odorize, hydrogen sulfide, ammonia and carbon monoxide are exists. Therefore, it is deemed necessary to verify that the safety performance of the fuel cell can be fully implemented under the conditions of impurities by simulating the composition of fuel gas in the country to be exported.

In this study, product certification and test gas standards of overseas countries were analyzed, and analyzed the city gas components that are actually supplied to overseas countries. In addition, we tried to secure technical bridgeheads for exporting products by producing demonstration gas simulating overseas city gas components and supplying and demonstrating them to low temperature type PEM fuel cells to secure safety performance data.

*Corresponding author	MinWoo Kim
Affiliation	Institute of Gas Safety R&D, Korea Gas Safety Corporation
E-mail address	mwkim@kgs.or.kr

06-3117

Review on evaluation of safety performance methods and evaluation of safety performance for Stationary SOFC stack.

TaeSeong Park, EunKyung LEE[*], HyoJung Bang

Institue of Gas Safety R&D, Korea Gas Safety Corporation., Korea

As the interest on the New and Renewable energy is rising around the globe over recent years, Korean government has encouraged the diffusion and the adoption, as well as its development through the deregulation and the expansion of the investment policy for the new industry. This would enhance the rapid increase and the growth of related domestic market such as green sources, including wind power, solar photovoltaic energy, and fuel cell system. Through its continuous development of relevant technology, it is expected to make progress in the skills and technology development for the New and Renewable Energy.

The fuel cell system is highly advanced among other new regeneration energy, like solar photovoltaic energy, or wind power, in which it is capable to supply active energy easily with a less amount of space for installation from anytime and anywhere by using various methods, such as reforming the hydrogen fuel to hydrocarbon, and water electrolysis etc. In advance, the fuel cell energy can provide much higher generating efficiency through the use of solid oxide fuel cell that operates at a higher temperature compares to other types of fuel cells, including PEM fuel cell. The solid oxide fuel cell can raise the thermal efficiency in connection with other related equipment and these benefits effect on the continuous technological development process on the various categories from KW class to MW. However, the nature of the solid oxide fuel cell that it performs at a fairly high temperature, above 700 ℃, makes it hard on the structural design and the selection of materials and it requires advanced technological capabilities in designing the SOFC. Furthermore, it is essential for enhancing more public interests to secure the technology on the evaluation of safety performance for SOFC stack, which operates at the highest temperature among other types of solid oxide fuel cells as well as developing the system of safety performance assessment.

After a careful selection of the evaluation criteria, this study has successfully operated the safety performance of the SOFC stack assessment through the analysis of both internal and external evaluation standards for fuel cells. It also provides a comprehensive review of the risk factors within the Hot-box with respect to the process risk resolution method of HAZOP(Hazard and operability study). This study will contribute to the universalization and to provide much safe environment of operating the solid oxide fuel cell system.

*Corresponding author	EunKyung LEE
Affiliation	Institue of Gas Safety R&D, Korea Gas Safety Corporation.
E-mail address	eklee0123@kgs.or.kr

06-3121

Anion Exchange Membrane Water electrolysis Operating at High Temperature using KOH doped Polybenzimidazole

Min Jae Lee[1, 2], Ahyoun Lim[1], Hyun S. Park[1], Kwang Ho Song[2], Hyoung-Juhn Kim[1*]
[1]*Korea Institute of Science and Technology, Korea*
[2]*Korea University, Korea*

Hydrogen is one of the most promising sustainable and renewable energy. The advantages of hydrogen are high energy density, high reversible conversion efficiency and low environmental pollution. However, since most of the current methods of producing hydrogen like steam reforming generate greenhouse gases, a lot of research is under way on water electrolysis, environmentally friendly hydrogen production methods. There are two main methods of water electrolysis: alkaline water electrolysis and proton exchange membrane water electrolysis (PEMWE). Alkaline water electrolysis is the oldest method and because it can use non-precious metal catalyst, it is excellent in price competitiveness. However, due to the corrosion and precipitation caused by liquid electrolyte, performance and stability can be reduced. And it requires a large volume of device because of its low current density and has a slow start/stop response because the pressure of the anode and cathode must be adjusted to prevent gas crossover. PEMWE has the advantages of higher energy efficiency, hydrogen production rate and purity than alkaline water electrolysis. However, proton exchange membranes such as Nafion, which are mainly used in PEMWE, are expensive and since the electrolyte is acidic environment, low-cost transition metals are not stable and there is a limit to use noble metal catalysts.

Anion exchange membrane water electrolysis (AEMWE) has been developed to combine the advantages of the two techniques. Since AEMWE operates under alkaline conditions, it is possible to use cheaper non-precious metal catalysts, and by using a membrane, high hydrogen production efficiency and purity can be obtained. However, the performance is still lower than other water electrolysis methods. So many research has been conducted to improve performance.

Higher operating temperatures can increase catalysts activity ion conductivity, which can increase the performance of water electrolysis. However, anion exchange membranes now in use have a limitation of low stability and degradation at high temperatures above 100 ℃. Polybenzimidazole (PBI) has excellent heat and chemical stability. Also, the imidazole group in PBI is an amphoteric compound, so ion conduction in the -NH- group is possible under alkaline conditions.

So in this study, KOH-doped PBI membrane, which is stable at high temperature and alkaline conditions, was employed to operate AEMWE cell at high temperature above 100 ℃ and compared the conventional anion exchange membrane.

*Corresponding author	Hyoung-Juhn Kim
Affiliation	Korea Institute of Science and Technology
E-mail address	hjkim25@kist.re.kr

06-3128

A Study on the Safety Performance Evaluation according to the Operational Conditions of the Water Electrolysis System

MinWoo Kim*, JiHye Kim, EunKyung Lee, JungWoon Lee

Institute of Gas Safety R&D, Korea Gas Safety Corporation, Korea

Currently, various problems are being researched all over the world as new and renewable energy is emerging because of problems such as depletion of fossil fuels and environmental pollution. Renewable energy refers to energy sources such as wind energy, solar energy, geothermal energy, and hydropower. And technology to produce hydrogen using surplus power generated from renewable energy is attracting attention. Techniques for producing hydrogen include steam reforming and carbon dioxide reforming using fossil fuels. There are technologies such as water electrolysis using non-fossil fuels, thermochemical decomposition, and biological decomposition. Among them, the water electrolysis technology has the advantage of producing high purity hydrogen compared to other technologies, and is a system for producing hydrogen and oxygen using electric power and water.

In this study, the hydrogen production system using water electrolysis is also being studied. The water electrolysis system has different efficiency and performance under various operating conditions such as operating temperature and operating pressure, and safety performance is evaluated according to operating conditions in order to identify the risk. Based on the results of this study, it is thought that it will be a great contribution to constructing a water electrolysis system by deriving the appropriate operating condition for each water electrolysis technology.

*Corresponding author	MinWoo Kim
Affiliation	Institute of Gas Safety R&D, Korea Gas Safety Corporation
E-mail address	mwkim@kgs.or.kr

06-3133

Analysis and Evaluation of Risk Assessment for Solid Oxide Fuel Cells

EunKyung Lee*, TaeSung Park, HyoJung Bang
Institute of Gas Safety R&D, Korea Gas Safety Corporation, Korea

Demand and supply for hydrogen energy are increasing. Fuel cells that use hydrogen as fuel are in the spotlight. Fuel cells have advantages such as high power generation efficiency and space efficiency. Also, can be installed in various applications because they are easy to adjust the size of power generation. Fuel cells can be divided into low temperature fuel cells and high temperature fuel cells. In particular, the development of Solid Oxide Fuel Cells among high-temperature fuel cells is carried out in various fields, ranging from several KW classes to several MWs, as they have high power generation efficiency and can be enhanced in conjunction with other equipment. However, because it operates at high temperatures, it requires high technical skills in system design, such as structural design or material selection. In particular, securing technology for operation characteristics and performance evaluation of stacks, which are key technologies of fuel cells, is essential. An analysis of the SOFC stack is essential such as safety management and evaluation of risk assessment.

In this study, we analyzed the safety management of SOFC stack. The items for safety management of the SOFC stack were derived through analysis of international regulations, codes, and standards on hydrogen. Possible rick factors were analyzed through Hazard and Operability (HAZOP). Finally, this study results can contribute escalate in demand for Fuel cell safety technology and activation of supply.

*Corresponding author	EunKyung Lee
Affiliation	Institute of Gas Safety R&D, Korea Gas Safety Corporation
E-mail address	eklee0123@kgs.or.kr

06-3149

Development of Prototype for Standardization of Stationary Fuel Cell Efficiency Evaluation Method

EunKyung Lee, GunWoo Oh*, MinWoo Kim, JungWoon Lee

Institute of Gas Safety R&D, Korea Gas Safety Corporation, Korea

Fuel cells are widely seen as renewable energy to replace greenhouse gas emissions. Fuel cells have advantages such as utilization rates and regular power generation as well as environmental aspects. In addition, demand for fuel cells is expected to increase further as they can be installed by application such as stationary, residential, portable, depending on the size of power generation. These fuel cells need to be evaluated for performance. Currently, the performance evaluation of fuel cells is in accordance with KGS AB 934. The efficiency values are derived by evaluating thermal and electrical efficiency. Domestic fuel cell assessment standards differ in part from international standards. Domestic standards suggest that the efficiency performance is more than the value indicated by the manufacturer. Detailed evaluation methods for measuring efficiency are not given in EN 50465, IEN 62282 etc. overseas. Therefore, it is intended to standardize the thermal and electric evaluation methods for inspection of fuel cells in the country.

This study aims to standardize the evaluation method of the electrical and thermal efficiency of fuel cells. To this end, the prototype for fuel cell evaluation is manufactured. We evaluate the reliability of the fuel cell by evaluating the result as a prototype product. Finally, this study results can contribute escalate in demand for fuel cell technology and activation of supply.

*Corresponding author GunWoo Oh
Affiliation Institute of Gas Safety R&D, Korea Gas Safety Corporation
E-mail address ohkw@kgs.or.kr

06-3208

Investigation of Support Effect in Atomically Dispersed Pt on WO_{3-x} for High Utilization of Pt in Hydrogen Evolution Reaction

Jinkyu Park, Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

Single-atom catalysts (SACs) have attracted growing attention because they maximize the number of active sites, with unpredictable catalytic activity. Despite numerous studies on SACs, there is little research on the support, which is essential to understanding SAC. Herein, we systematically investigated the influence of the support on the performance of the SAC by comparing with single-atom Pt supported on carbon (Pt SA/C) and Pt nanoparticles supported on WO_{3-x} (Pt NP/WO_{3-x}). The results revealed that the support effect was maximized for atomically dispersed Pt supported on WO_{3-x} (Pt SA/WO_{3-x}). The Pt SA/WO_{3-x} exhibited a higher degree of hydrogen spillover from Pt atoms to WO_{3-x} at the interface, compared with Pt NP/WO_{3-x}, which drastically enhanced Pt mass activity for hydrogen evolution (up to 10 times). This strategy provides a new framework for enhancing catalytic activity for HER, by reducing noble metal usage in the field of SACs.

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

06-3360

The Effect of Metal Foam as Flow Field on Performance in the Non-Humidified Dead-End System

Myo-eun Kim[1, 2], Young-Jun Sohn[1, 2*]
[1]*Korea Institute of Energy Research, Korea*
[2]*University of Science and Technology, Korea*

In recent years the interest in drones, mobile power sources, etc. has been increasing at rapid pace and the attention has been focused on simplification of system volume. Thus, the fuel cell system on dead-end operation system, which is more fuel-efficient and compact compared to conventional fuel cell system, is often applied. In the fuel cell system on dead-end operation, the fuel may be supplied in a non-humidified condition to minimize the balance of plant (BOP). The management of relative humidity is a very important to maintain fuel cell power on non-humidified operation mode and it is closely related to the water management of the system.

In recent studies, it has been found that when the metal foam is applied to flow field as the way to improve the fuel-diffusion and water management of the fuel cell stack, the performance can be better compared to the conventional channel.

In this study, we fabricated a fuel cell using a metal foam as flow field and conducted experimental studies on a dead-end operation mode. And we optimized the operating conditions such as temperature, pressure, and purge conditions and compared the performance with conventional channels.

As a result, it was found that the performance of the fuel cell using the metal foam as flow field was improved compared to the conventional channel on the dead-end operation mode. It is believed that the porous structure of the metal foam is advantageous for holding water, i.e. on the non-humidified operation system metal foam is better to maintain humidity inside of cell, and for preventing the reduction of active area due to condensed water.

*Corresponding author	Young-Jun Sohn
Affiliation	Korea Institute of Energy Research
E-mail address	yjsohn@kier.re.kr

06-3387

Development of radial directional channel in circular shape of proton exchange membrane water electrolysis cells

Yena Choi, Gun Woo Kim, Youngseung Na*
University of Seoul, Korea

Various sustainable energy sources have been tried around the world. Most clean energy technologies, such as solar power generation or wind power generation facilities have difficulty in balancing production and demand. Energy Storage Systems (ESS) using hydrogen have emerged to complement the imbalance of demand and supply. Hydrogen storage systems are cheaper than lithium-ion batteries for large scale capacity. Various electrolysis systems using surplus electricity from solar power generation or wind power generation facilities have been developed and commercialized. These water electrolysis systems are also considered as clean hydrogen production among the other hydrogen production methods, reforming natural gas, pyrolysis using nuclear power, and so on. Proton Exchange Membrane Water Electrolysis(PEMWE) is attracting attention because of high-power and high-pressure operation. Electrolyte membranes, catalysts, electrodes of PEMWE are developed for low cost, long endurance, and high performance. The flow field design is also essential to supply water and educt oxygen from electrodes.

Especially, as the size of the water electrolysis increases, water is likely to deplete at the high current region, which results in performance degradation. This study focuses on the new channel design of the PEMWE for uniform distribution of reactants for electrochemical reaction. So, the optimal pattern in which reactant can be well delivered is designed. The present invention proposes a design to minimize the dead zone by using a circular flow path instead of a conventional square flow path to use a wide active area as possible. Besides, the circular flow path can discharge the oxygen generated through the electrochemical reaction and can water flow uniformly supply. Two-phase flow analysis is analyzed by computational fluid dynamics to elucidate the numerical comparison of the performance much improved than the conventional square flow path shape through simulation. The optimal results of the flow path with the circular flow path are found in terms of pressure drop, generated hydrogen amount, and temperature distribution.

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

06-3392

Ni-based hydrogen oxidation catalysts in alkaline media

Hyeonjeong Park, Hoyoung Kim, Hyanjoo Park, Seonhwa Oh, Soo-Kil Kim*

Chung-Ang University, Korea

Anion exchange membrane fuel cells (AEMFCs) enables use of non-Pt group metal (PGM) catalysts due to its less corrosive environmental, which is an important factor in consideration of production cost of FCs suggesting an alternative to proton exchange membrane fuel cells (PEMFCs). Nevertheless, the relatively sluggish reaction kinetics for both hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) on non-PGM catalysts remain as hurdles to overcome. Particularly, the kinetic of HOR in alkaline environmental is much slower than that in acidic media such as PEMFC [1]. Therefore, development of highly active non-PGM HOR catalysts in alkaline media is one of the critical research issues for AEMFCs [2].

In this study, Ni-based binary alloy (NiM) catalysts for HOR in alkaline media have been prepared and evaluated. The Ni-based alloy catalysts were electrodeposited on the glassy carbon (GC) rotating disk electrode (RDE) and the composition of NiM were controlled by adjusting the concentration of each metal precursor (Ni and M). The HOR performance of Ni-M catalysts in alkaline medium was examined in 0.1 M potassium hydroxide (KOH) with potentiostatic method. The surface morphology, bulk composition and crystal structure of the catalysts were analyzed by field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD), respectively. The performance of alloy catalysts toward HOR including durability will be discussed.

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*Corresponding author	Soo-Kil Kim
Affiliation	Chung-Ang University
E-mail address	sookilkim@cau.ac.kr

06-3418

Surface engineering of one-dimensional coaxial AuPt@RuO$_x$ nanowires for efficient oxygen evolution reaction under acidic media

Taehyun Kwon, Heesu Yang, Kwangyeol Lee*

Korea University, Korea

With increasing demand for renewable energy sources, electrolytic water splitting has become one of the most promising technologies to overcome environmental issues. For the successful penetration of the water electrolysis to the hydrogen society, efficient electrocatalysts with excellent activity and stability need to be developed and, for the development of nanostructured catalysts, the thorough understanding of surface energy and atomistic structures on the catalyst surface is required. Among various nanocatalyst designs, one-dimensional nanostructured catalysts with metallic core are particularly promising because of the facilitated electron conduction along nanocatalyst axis as well as increased number of active sites due to the inherently high surface area per volume. Recently we have demonstrated that the interfacing of Pt-rich phase and catalytic RuO$_x$ phase greatly promotes the catalytic stability of the RuO$_x$ due to the Pt doping. In order to combine the Pt-assisted stabilization of RuO$_x$ phase and the inherent conductivity of 1-D metal core, we have prepared one-dimensional coaxial nanowires with Au@Pt core and RuO$_x$ shell. In this presentation, we report the synthesis and surface engineering of core-shell ternary AuPt@RuO$_x$ nanowires as well as their greatly enhanced activity and stability toward OER under acidic media.

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

06-3421

Transition metal doping in the IrRuO$_x$ enhances the overall water splitting performance in acidic conditions

Ye Ji Park, Jinwhan Joo, Kwangyeol Lee*

Korea University, Korea

We have recently reported that cactus-like Cu$_{2-x}$S@IrRu nanostructures exhibit excellent catalytic activity and stability toward the hydrogen evolution reaction and oxygen evolution reaction serving as bifunctional catalysts. It has been previously demonstrated that the presence of vacant sites in the metal oxide is essential to the stability enhancement of metal oxide toward OER. In order to develop bifunctional catalysts with further enhanced catalytic activity and stability, we have attempted the transition metal doping of IrRu phase on the Cu$_{2-x}$S substrate to create vacant sites in the RuIrO$_x$ phase. We have systematically investigated the effects of Cr, Mn, Fe, Co, and Ni dopants on the IrRu oxide phase toward the OER. Among the transition metal dopants tested, the effect of Mn dopant was most significant in the improvement of the electrocatalytic activity of IrRu catalyst. Herein, we report our efforts to understand the underlying principle behind Mn-assisted performance boosting of IrRu oxide.

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

06-3426

IrNi nanoframes supported on the mixed metal sulfides show enhanced electrocatalytic stability and activity toward OER due to the vacant site control and S-doping effect

Minki Jun, Haneul Jin, Kwangyeol Lee*
Korea University, Korea

Sluggish reaction kinetics of the oxygen evolution reaction (OER) poses as a formidable hurdle to the realization of carbon-zero hydrogen economy. Therefore, great efforts are being made to develop the nanocatalysts with high performance for the OER. Among various nanostructures, nanoframe structure has attracted enormous attention due to its high surface-to-volume ratio. However, nanoframe structures are prone to structural degradation during electrocatalysis. Recently, significant progress has been made in hetero-interface-based nanocatalysts in terms of the electrocatalytic activity and stability. Herein, we report the synthesis of IrNi nanoframes (IrNi NFs) supported on the mixed metal sulfides and its electrocatalytic performance. The prepared IrNi NFs supported on mixed metal sulfides showed enhanced activity and stability for the OER as compared to those of Ir/C due to the vacant site formation as well as S replacement of oxygen atoms.

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

06-3430

Colloidal based synthesis of Ni_xS_y as a stable non-noble electrocatalyst for OER

Jinhyoung Jo, Jun Kim, Kwangyeol Lee*
Korea University, Korea

The ever-escalating consumption of fossil fuels has engendered numerous environmental problems, thus calling for the development of clean energy sources. Water splitting via electrolysis has received a great attention as a hydrogen production method due to its potential carbon-zero nature, and its commercial success is largely dependent on the performance of catalytic oxygen evolution reaction (OER), which is the rate-determining step. Although Ir-based catalysts have been widely used, the high cost and scarcity of Ir overburden the commercial applications. Therefore, it is crucial to develop catalysts of cheaper ingredients that show a great performance comparable to that of commercial Ir-based catalysts. Transition metal sulfides have been extensively investigated as alternative catalyst materials, and among them nickel sulfides have received the most notable attention due to the stability and activity toward OER. Most of nickel sulfide catalysts have been prepared by reacting nickel foam with sulfur sources, and the understanding of intrinsic catalytic performance of nanocrystalline nickel sulfides is rather little known. Herein, we report the solution-based synthesis of well-defined Ni_xS_y octahedral nanocage (ONC), that show a great electrocatalytic activity and stability toward OER.

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

06-3435

Ir-based nanoframes as active and stable electrocatalysts toward the oxygen evolution reaction

Songa Choi, Kwangyeol Lee*

Korea University, Korea

IrO_x and RuO_x have proven to be the most active electrocatalysts for oxygen evolution reaction (OER). However, the IrO_x and RuO_x based nanoparticles can easily agglomerate under higher operating potential due to the fast restructuring of the metal oxide surface, which leads to a severe deterioration of the catalytic activity and stability. We posited that the overall catalytic stability of the iridium oxide phase can be greatly enhanced if the iridium oxide nanostructures are confined to a small size regime but are unable to touch each other due to the physical separation enabled by the inner-residing Pt-based dendritic core. The electroconductivity of Pt phase is also conducive to the catalytic activity due to facile electron transfer. Herein, we present the synthesis of heterophase IrNi nanoframe with PtNi axis by controlling the differences in decomposition kinetics of each metal precursor and gas type between argon and carbon monoxide. The Ir oxide phase, obtained from electrochemical oxidation, on the metallic PtNi phase efficiently catalyzed the OER and showed superb stability in acidic media.

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

06-3455

Soft Templated Synthesis of Mesoporous Non-precious Metal Catalyst with Fe-N_x/C Active Sites for Oxygen Reduction Reaction

Ahryeon Lee[1], Yeongdong Mun[2], Jinwoo Lee[1*]

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

[2] *Pohang University of Science and Technology, Korea*

We synthesized ordered mesoporous non-precious metal catalyst (NPMC) with highly active Fe-N_x/C sites denoted as m-FePhen-C for the oxygen reduction reaction in fuel cells. This was the first study that incorporated a catalyst precursor with Fe-N coordination directly in a block co-polymer-assisted soft-template method for the synthesis of mesoporous Fe/N/C. The synthesized catalyst (m-FePhen-C) showed a high catalytic performance comparable to that of Pt/C in half-cell tests. In single-cell tests, a membrane electrode assembly (MEA) with an m-FePhen-C cathode exhibited 40% higher power density than did an MEA with a commercial Pt/C cathode with comparable electrode thicknesses. This result is highly meaningful in that simultaneous formation of the Fe-N_x/C active sites and ordered mesoporous structure were achieved in the simple soft-template-assisted process, and in that the advantages of mesoporous structure with appropriate pore size in metal containing NPMC were elucidated for high-performance MEAs.

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

06-3631

A eutectic mixture of biphenyl and diphenylmethane as a high-capacity, reversible liquid organic hydrogen carrier (LOHC)

Chang Won Yoon*

Korea Institute of Science and Technology, Korea

Mismatch between renewable energy potentials and energy needs makes hydrogen highly attractive as a sustainable energy carrier because of its high gravimetric energy storage density of ca. 33.3 kWh·kg-1. However, the low volumetric energy density of gaseous hydrogen (2.97 Wh·L-1@273 K & 1 atm) limited its use for numerous energy applications. In the regard, a safe and efficient hydrogen storage system that enables to reversibly store and release large amounts of hydrogen has attracted significant attention. Liquid organic hydrogen carriers (LOHCs) are promising candidate materials for the purpose because they possess high volumetric hydrogen storage densities (>45 g-H2·L-1). In addition, the stored hydrogen at LOHCs can readily be released by catalytic dehydrogenation in the presence of an appropriate catalyst. Moreover, LOHCs have high compatibility with the existing fossil fuel infrastructure. Here, we present a new eutectic mixture of biphenyl and diphenylmethane which has the 6.9 wt % and 60 g-H2 L−1 of gravimetric and volumetric hydrogen storage capacities, respectively, and its H2 storage and release properties. Finally, a dehydrogenation system is designed and operated in conjunction with a polymer electrolyte membrane fuel cell (PEMFC), generating ca. 0.5 kW of electrical power in a continuous manner.

*Corresponding author Chang Won Yoon
Affiliation Korea Institute of Science and Technology
E-mail address cwyoon@kist.re.kr

06-3645

Platinum-Rare-Earth Metal Alloy Fuel Cell Catalysts. Making the Impossible Simple

Jens Oluf Jensen*, Yang Hu, Benedikt Axel Brandes, Lars Nilausen Cleemann, Qingfeng Li
Technical University of Denmark, Denmark

Platinum-rare earth metal (Pt-RE) alloy nano-particles are reported to be among the most active electrocatalysts for the oxygen reduction reaction in PEM fuel cells. Ten years ago, the Pt-RE catalysts were initially predicted theoretically at DTU Physics [1] and the activity was later verified experimentally on the nanogram scale [2] and on polycrystalline films [3]. However, the making of such alloy nano-catalysts has proven extremely challenging and until now, nobody has managed to devise a process that can be scaled up with proper control of particle size, composition and activity.

The strongly electropositive nature of all RE elements and their high affinity to oxygen exclude aqueous processes. The standard reduction potentials of RE metals are extremely negative (like -2.279 V for Gd^{3+}/Gd) compared to late transition metals (e.g., -0.25 V for Ni^{2+}/Ni) that are normally alloyed with platinum. Platinum, on the other hand, has very positive standard reduction potentials (1.188 V for Pt^{2+}/Pt) and this gives a reduction potential difference of more than 3 V. Thus, simultaneous reduction requires extreme conditions.

The paper presents a simple and fully scalable method to synthesize Pt-RE alloy nano-catalysts via a one-step heat-treatment in hydrogen of a mixture of common metal salts, a carbon-nitrogen precursor and a carbon support. [4] The simplicity experienced from the outside contrasts the complexity of the mechanism of the process. It involves the formation of a carbon-nitrogen network accommodating atomically dispersed metal ions of both kinds. Alloying happens through a step-wise thermal collapse of the network and simultaneous reduction by hydrogen in a flow furnace.

Examples of alloys manufactured as nano-particles on carbon are Pt_3Y, Pt_5La, Pt_5Ce, Pt_2Gd and Pt_3Tb. The synthesis mechanism is explained and justified by XRD, TEM and XPS at different stages of the formation process. The catalyst activities were verified on rotating disk electrodes with area-specific activities of up to 6 times that of pure platinum.

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*Corresponding author	Jens Oluf Jensen
Affiliation	Technical University of Denmark
E-mail address	jojen@dtu.dk

06-3660

The Role, Current Status and Prospect of PEM Water Electrolyzer in South Korea's Hydrogen Economy

Sangbong Moon*, Charlie Moon
Elchemtech Co., Ltd, Korea

Energiewende Policies(Germany, 2010), the Hydrogen Roadmap(Japan, 2014), and the Hydrogen Economy Roadmap(South Korea, 2019)were announced.

The fundamental of the roadmap is to reduce CO_2, and in order to attain the target, renewable energy was introduced, alongside production of renewable energy-related hydrogen, storage and transportation of hydrogen, and the utilization.

One of the most important elements in the hydrogen economy is the production of renewable energy-derived hydrogen.Hydrogen derived from renewable energy is produced by electrolyzing water using renewable energy. Unlike grey hydrogen(hydrogen produced by reforming methods), it is called CO_2 free hydrogen or green hydrogen. There are countries that give incentives on green hydrogen. This presentation will talk about types and characteristics of water electrolysis, producing hydrogen using renewable energy, requirements when linking renewable energy with the electrolyzer, introduction of PEM water electrolysis system, the most suitable electrolyzer to link with renewable energy and development of related materials.

*Corresponding author	Sangbong Moon
Affiliation	Elchemtech Co., Ltd
E-mail address	sbmoon@elchemtech.com

06-3781

Nanorods of Platinum-Tellurium Alloy on Metallic Transition Metal Dichalcogenide as Hybrid Electrocatalyst for Hydrogen Evolution

Dongyeon Bae[1], Hagyeong Kwon[1], Dongyeon Won[2], Byungdo Ji[2], Heejun Yang[2], Suyeon Cho[1*]
[1]*Ewha Womans University, Korea*
[2]*Sungkyunkwan University, Korea*

The development of an effective and inexpensive electro-catalyst for hydrogen production has been received enormous attentions because of tremendous needs for clean, renewable and sustainable energy for future life. Even though noble metal platinum (Pt) has been regarded as an irreplaceable effective electrocatalyst for hydrogen evolution reaction (HER), there have been intensive efforts to reduce or replace platinum-based catalysts due to its high price. Here, we demonstrate a new and facile pathway for fast electrochemical synthesis of nanorod-shaped electrocatalyst with the controllable chemical composition of tellurium and platinum. For the synthesis of tellurized platinum electrocatalyst, metallic two-dimensional single crystal, molybdenum ditelluride ($MoTe_2$), has been used as a dynamic support with abundant chemically active sites in its basal plane. X-ray diffraction study combined with transmission electron microscopy measurement reveals that nanorods grown on metallic $MoTe_2$ surface have stoichiometric chemical compositions of PtTe (primary phase) and small amount of Pt_3Te_4 (secondary phase) and highly-oriented single-crystalline growth along c-axis, leading to the nanorod-shaped single crystalline PtTe. This PtTe nanorods behaves an efficient electrocatalyst for hydrogen production via electrochemical water splitting with a low overpotential of -0.164 V and a small tafel slope of 68.71 mV/dec, which have never reported before. Our study demonstrates a facile electrochemical synthetic method of bimetallic electrocatalyst for efficient hydrogen production.

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*Corresponding author	Suyeon Cho
Affiliation	Ewha Womans University
E-mail address	chosuyeon@gmail.com

06-3791

Nano-porous Ag grown on metallic tungsten ditelluride single crystal for active hydrogen evolution

Hagyeong Kwon[1], Dongyeon Bae[1], Byungdo Ji[2], Heejun Yang[2], Suyeon Cho[1*]
[1]*Ewha Womans University, Korea*
[2]*Sungkyunkwan University, Korea*

Recently, hydrogen energy, one of the renewable and eco-friendly energies, becomes spotlighted due to fossil energy depletion and global environmental pollution problem. Platinum(Pt) catalyst, currently used in hydrogen production, has high catalytic hydrogen evolution reaction(HER) activity with a low over-potential and a Tafel slope around 30 mV/dec, but it is expensive. For effective and inexpensive hydrogen production to satisfy the growing demands, highly active and earth-abundant electro-catalysts are desired. Semi-metallic transition-metal dichalcogenide(TMD)s have many active sites on the basal plane. However, their HER performance is not good due to their low electron transfer. On the other hands, bulk silver(Ag) is highly electro-conductive, but inactive for hydrogen evolution due to high Gibbs energy. Here, we develop a high performance hybrid catalyst with metallic TMDs and Ag nanoparticles as good as Pt electro-catalyst for hydrogen evolution. The hybrid catalyst is prepared by electrochemical deposition of Ag on single crystalline WTe_2 and nano-porously grown Ag on WTe_2surface is catalytically activated for hydrogen evolution with Tafel slope of 47 mV/dec and overpotential of 0.035V. This nano-porous Ag on WTe_2 exhibits abundant active sites and high electrical conductivity resulting in improved HER activities. This study provides a new insight into the possibility of nano-porous Ag grown on TMD as non-precious catalyst for HER.

*Corresponding author Suyeon Cho
Affiliation Ewha Womans University
E-mail address s.cho@ewha.ac.kr

06-3831

Enhanced activity and durability of Pt catalyst supported on reduced graphene oxide for oxygen reduction of proton exchange membrane fuel cells.

Jemin Kim[1], Seung Geun Jo[1], Yeon Wook Jung[1], Taeseob Lim[1], Hae-in Moon[1], Young Won Kim[1], Duck Hyun Lee[2*], Jung Woo Lee[1*]

[1]Department of Materials Science and Engineering, Pusan National University, Busan, 46241, Korea

[2]Green Materials and Processes Group, Korea Institute of Industrial Technology, Ulsan, 44413, Korea

Proton exchange membrane fuel cells (PEMFCs) are mainly used as a power source of hydrogen fuel cell vehicles and the activity and durability of the Pt catalyst for oxygen reduction reaction is important because they operate at high voltage and strong acidic conditions. In this research, we studied the characteristics at Pt catalysts supported on graphene oxide (GO), partially reduced graphene oxide (GO-r), and reduced graphene oxide (rGO) to investigate the enhancement of the activity and durability of oxygen reduction catalysts for PEMFCs. Pt catalysts supported on carbonaceous materials were synthesized through a facile polyol method, and the characteristics of the synthesized catalysts were analyzed with transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectroscopy, cyclic voltammetry, and Raman spectroscopy analysis. The results proved that the rGO was superior to the carbon black support in oxygen reduction activity and long-term durability. Here, the reduced concentration of oxygen related functional groups on the graphene support was a key factor to enhance the oxygen reduction activity and long-term durability of Pt/rGO catalyst.

*Corresponding author 1	Duck Hyun Lee
Affiliation	Green Materials and Processes Group, Korea Institute of Industrial Technology, Ulsan, 44413
E-mail address	dulee@kitech.re.kr
*Corresponding author 2	Jung Woo Lee
Affiliation	Department of Materials Science and Engineering, Pusan National University, Busan, 46241
E-mail address	jungwoolee@pusan.ac.kr

06-4118

Atomically Dispersed Electrocatalysts for Fuel Cell and Water Electrolysis

Jinwoo Lee*

Korea Advanced Institute of Science and Technology, Korea

It is of great importance to reduce the amount of noble metals in the chemical industry. In this sense, single atom or atomically dispersed catalysts have attracted much attention due to high metal utilization and unique catalytic property. In this presentation, we will show a combination of density functional theory (DFT) and experimental approaches to explore the stability and electrocatalyic activity of a wide range of metal single atoms on a TiC support. We also tuned and enhanced the activity of Fe-N-C, atomically dispersed electrocatalyst, by givign the effect of electron withdrawing/donating functionalities.

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