International

1st Ertl Symposium on Electrochemistry and Catalysis

11-14 April 2010 **GIST in Gwangju, South Korea**

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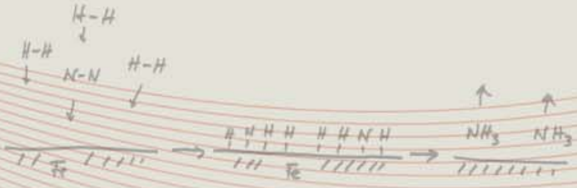

Director

Prof. Dr. Gerhard Ertl

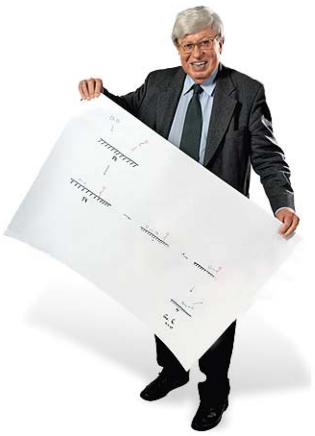
Nobel Laureate 2007

Fritz-Haber-Institut der Max-Planck-Gesellschaft Berlin, Germany

"for his studies of chemical processes on solid surfaces"

Gerhard Ertl

Born in 1936 in Bad Cannstadt, Germany. PhD in Physical Chemistry in 1965 from Technische Universität München, Germany. Prof.Emeritus, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany. Ertl has laid the foundation of a scientific discipline through his enormously systematic and thorough studies. He has often returned to the same problem in surface chemistry decade after decade in order to use new experimental methods to obtain answers to questions posed earlier. His ability to describe in detail how an experiment is to be designed and interpreted has helped him to provide the methodological platform for an entirely new area of research.



Ertl Center

Agenda of the Ertl Center

The first period (2008-2010) ↔	The second period (2011-2014) ↔	The third period (2015-beyond)
- Foundation of the center - 1st Ertl symposium	- Center of excellence (COE) in electochemistry and catalysis reserch	- Continuous research

Role of the Ertl Center

- Bridge between basic research and indestrial applications
- Encouragement of continuous research in Electrochemistry and Catalysis (Surface Science)
- Focused on international collaboration
- Organization of Ertl symposium

Honorary Chair

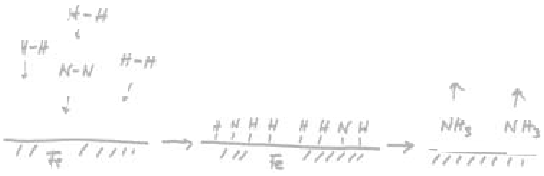
Prof. Dr. Gerhard Ertl (Nobel Laureate 2007)
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany
Ertl Center for Electrochemistry and Catalysis/RISE, GIST, Gwangju 500-712, South Korea

Symposium Chairmen

Prof. Dr. Jaeyoung Lee and **Prof. Seung-Hyeon Moon**
Ertl Center for Electrochemistry and Catalysis/RISE, DESE, GIST, Gwangju 500-712, South Korea
Dr. Markus Eiswirth
Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-14195 Berlin, Germany
Ertl Center for Electrochemistry and Catalysis/RISE, GIST, Gwangju 500-712, South Korea

Key Topics

Electrochemistry for Sustainable Energy & Clean Environments
Electroanalysis
Surface Catalysis
Nanostructured Materials
Nonlinear Dynamics in Electrochemistry



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Yung-Eun Sung (SNU, S. Korea)
Yongsug Tak (Inha Univ., S. Korea)

Invited Speakers

Malte Behrens (FHI der MPG, Germany)
Jason Cheng (UC Riverside, USA)
Salvatore Daniele (Univ. Venice, Italy)
Zhifeng Ding (UW Ontario, Canada)
Markus Eiswirth (FHI der MPG, Germany)
Andreas Friedrich (DLR, Germany)
Gerd Ganteför (Univ. Konstanz, Germany)
Hubert Girault (EPFL, Switzerland)
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Pascal Maire (PSI, Switzerland)
Bongjin Simon Mun (Hanyang Univ., S. Korea)
Suk Woo Nam (KIST, S. Korea)
Kornelius Nielsch (Univ. Hamburg, Germany)
Masatoshi Osawa (Univ. Hokkaido, Japan)
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Carlos Pereira (Univ. Porto, Portugal)
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Rolf Schuster (Univ. Karlsruhe, Germany)
Jens Starke (TU Denmark, Denmark)
Peter Strasser (TU Berlin, Germany)
Hamilton Varela (Univ. Sao Paulo, Brazil)
Seong Ihl Woo (KAIST, S. Korea)
Jong-Sung Yu (Korea Univ., S. Korea)

Abstract submission by 31 January 2010

150-300 words with illustration and pictures in WORD file

E-mail submission: ertl@gist.ac.kr

There is only small number of additional oral presentations. Most contributions will have to be in the form of posters.

Speech time allocated

Opening Speech (OS) : 40 min
Keynote Speech (KS) : 40 min
Invited Speech (IS) : 30 min
Oral Speech (OS) : 20 min

Symposium Secretariat

For further information please contact:
Ertl Center for Electrochemistry and Catalysis, GIST
261 Cheomdan-gwagiro, Buk-gu, Gwangju, 500-712 South Korea

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http://env1.gist.ac.kr/ertl/new/ERTLCenter/

Conference fees (on-site registration only)

▶ Regular participants: €300 ▶ Students: €150 ▶ Accompany person: €90

The symposium registration fee includes a copy of the Book of abstracts, the Welcome reception on Sunday evening, Lunch on Monday, Tuesday and Wednesday, Conference dinner on Tuesday.

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Welcome

At the beginning of the 21st century our world is confronted with serious problems related to climate, energy, and environment. Catalysis and electrochemistry will be of vital importance for the solution of these problems. Considerable progress has recently been made in these fields through the development of novel experimental techniques and theoretical concepts which provide closer insights into the underlying elementary processes. The first ERTL symposium will present an international forum for the discussion of the latest results in this area. I wish all the participants fruitful interactions and an interesting stay.

Gerh. Ertl

Gerhard Ertl

1st Ertl Symposium on Electrochemistry and Catalysis, 11-14 April 2010

OS(Opening Speech, 50 min), KS(Keynote Speech, 40min), IS(Invited Speech, 30 min), OS(Oral Speech, 20min)		Time
	April 11	
16:30 - 18:30	Session 0 : Jaeyoung Lee **Opening of the Symposium** Jaeyoung Lee (Conference Chair) **OS M Eiswirth** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) ▶ Surface Chemistry- Quo Vadis? **IS1 H Varela** (University of São Paulo, Brazil) ▶ The influence of temperature on the oscillatory electro-oxidation of small organic molecules **KS1 H Kim** (Seoul National University, South Korea) ▶ Fuel Cell as a Green Energy Alternative	120
18:30-20:30	Welcome reception	120

1st Ertl Symposium on Electrochemistry and Catalysis, 11-14 April 2010

	April 12	
08:10-08:50	*Registration*	40
08:50 - 10:30	Session 1 : Peter Strasser **KS2 A Friedrich** (German Aerospace Center, Germany) ▶ Fuel Cells for Aircraft Application **IS2 T Homma** (Waseda University, Japan) ▶ Electrochemical approaches for fabrication of micro/ nano scale functional structures and devices **IS3 S Daniele** (University of Venice, Italy) ▶ Investigation of formic acid electrooxidation at mesoporous platinum microelectrodes. The effect of temperature, anion and bismuth ad-atoms	100
10:30-11:00	*Coffee Break*	30
11:00 - 12:40	Session 2 : Masatoshi Osawa **KS3 R Schuster** (Karlsruhe Institute of Technology, Germany) ▶ Electrochemical Microcalorimetry **IS4 P Parmananda** (IIT Bombay, India) ▶ Coupling electrochemical oscillators **IS5 H Jensen** (University of Copenhagen, Denmark) ▶ Electrochemical at ITIES as a Microanalytical Tool for Nanoliter Analyte Detection and Sample Preparation	100
12:40-14:20	*Lunch & Ertl center Visit*	100
14:20 - 15:50	Session 3 : T Homma **KS4 P Plath** (Minir-Chemie-Informatik, Germany) ▶ Battery - Forecast via Synergetics **OS1 JM Lee** (Ertl center, South Korea) ▶ Phase Transformation of Thermoelectric Bismuth Telluride Nanowires as a Result of an Annealing Process **IS6 G Ganteför** (University of Konstanz, Germany) ▶ Chances and Challenges of Cluster Chemistry	90
15:50-16:20	*Coffee Break & Photograph*	30
16:20 - 18:00	Session 4 : Andreas Friedrich **IS7 SI Woo** (KAIST, South Korea) ▶ Reliable Combinatorial method for Fuel cell Electrode and MEA **OS2 JJ Woo** (GIST, South Korea) ▶ Enhanced fuel cell performance under humidified and non-humidified conditions by the structural modification of a polymer electrolyte membrane **IS8 HJ Lee** (Kyungpook National University, South Korea) ▶ Creating ITIES for Ion-selective Sensing and Fuel Cell Applications **OS3 S Haram** (University of Pune, India) ▶ Synergistic Effect of Carbon Nanotubes Support on Electrocatalytic Properties of Silver in the Nitrate Ions Reduction	100
18:00-20:30	**Poster Session (K Nielsch, H Varela, M Behrens, YD Kim, H Jensen)** **Beer & Wine Party**	150

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	April 13	
08:10-08:40	*Registration*	30
08:40 - 10:20	Session 5 : Olaf Magnussen **KS5 E Savinova** (University of Strabourg, Frace) ▶ Interplay of the electrochemical reaction and diffusion in 3D nanoparticle arrays **IS9 BS Mun** (Hanyang University, South Korea) ▶ The study of Pd70Au30(110) surface properties under CO, O_2 and CO+O_2 elevated pressures **IS10 P Maire** (Paul Scherrer Institut, Switzerland) ▶ In situ methods for the investigation of lithium batteries	100
10:20-10:50	*Coffee Break*	30
10:50 - 12:40	Session 6 : Salvatore Daniele **IS11 Z Ding** (The University of Western Ontario, Canada) ▶ Electrochemical Avenue toward Cu(In,Ga)Se2-Based Solar Cells **O4 G-G Park** (Korea Institute of Energy Research, South Korea) ▶ Temperature cycling effects on the durability of polymer electrolyte fuel cells **IS12 K Nielsch** (University of Hamburg, Germany) ▶ Multifunctional Cylindrical Nanoobjects: From ALD Growth towards Physical Model Systems **IS13 JS Yu** (Korea University, South Korea) ▶ Ordered hierarchical nanostructured carbon as a highly efficient catalyst support in low-temperature fuel cell	110
12:40-14:00	*Lunch & Ertl center Visit*	80
14:00 - 15:50	Session 7 : Pascal Maire **IS14 O Magnussen** (University of Kiel, Germany) ▶ In situ Video-STM studies of the surface reconstruction of Cu(100) electrodes during hydrogen evolution_ **IS15 SW Nam** (Korea Institute of Science and Technology, South Korea) ▶ Sulfur-tolerant Ni-based anodes for high-temperature fuel cells **OS5 S Uhm** (Ertl center, South Korea) ▶ Synthesis and Electrochemical Activity of PGM-free Cathode Catalysts in Alkaline Ethanol Fuel Cells **IS16 J Cheng** (University of California Riverside, USA) ▶ Biosensing with SPR-Active Surface: Exploring Cell-Surface Phenomenon in Combination with Electrochemistry and Mass Spectrometry	110
15:50-16:20	*Coffee Break*	30
16:20 - 18:10	Session 8 : Zhifeng Ding **IS17 IS Kim** (GIST, South Korea) ▶ Bioelectricity and biohydrogen production through biocatalyzed electron harvesting from organic compounds in microbial fuel cell-based systems **IS18 M Behrens** (Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany) ▶ Synthesis of high performance Cu-based catalysts active in the conversion of carbon dioxide to methanol **IS19 J Starke** (Technical University of Denmark, Denmark) ▶ Deterministic and stochastic modelling of catalytic surface processes **OS6 J Choi** (Inha University, South Korea) ▶ Potential shock method for through-hole TiO2 nanotubes	110
18:10-20:40	Markus Eiswirth **Poster Award Ceremony (Seung-Hyeon Moon & Jaeyoung Lee)** **Congratulatory Remarks (President of GIST)** **Korean Traditional Music Concerts (MOHO)** **Symposium Dinner**	150

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	April 14	Time
08:10-08:40	*Registration*	30
08:40 - 10:20	Session 9 : Hye Jin Lee **KS6 H Girault** (Ecole Polytechnique Federale de Lausanne, Switzerland) ▶ Molecular electrocatalysis at soft interfaces : Oxygen reduction by amphiphilic porphyrins **IS20 YD Kim** (Sungkyunkwan University, South Korea) ▶ Photocatalytic activity of various TiO2 nanostructures **IS21 C Pereira** (University of Porto, Portugal) ▶ Characterization of catecholamines electrochemical sensors	100
10:20-10:50	*Coffee Break*	30
10:50 - 12:40	Session 10 : JS Yu **KS7 M Koper** (Leiden University, The Netherlands) ▶ Electrocatalysis at gold **IS22 M Osawa** (Hokkaido University, Japan) ▶ Role of bridge-bonded formate in formic acid electrooxidation on Pt : Reaction intermediate or site-blocking spectator? **IS23 P Strasser** (TU Berlin, Germany) ▶ Tuning surface electrocatalytic reactivity using core-shell structural concepts **Close of Symposium (P Strasser)**	110
12:40-13:30	*Lunch*	50
13:30-20:00	**Excursion** Naganeupseong Folk Village & Damyang (30,000won/person)	

List of Oral Presentations

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List of Poster Presentations

List of Poster Presentation

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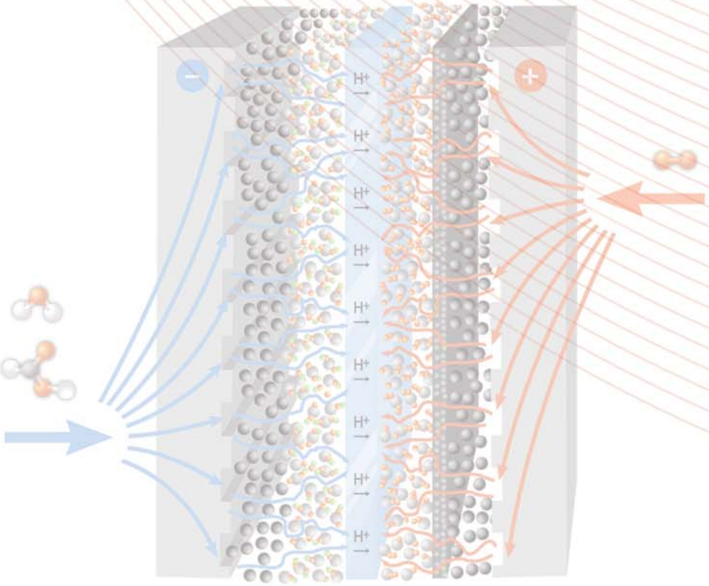
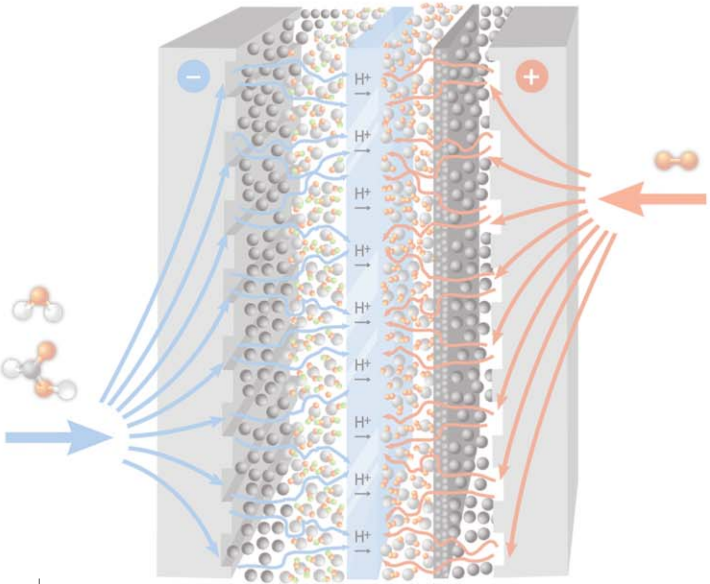
1st Ertl Symposium on
Electrochemistry and Catalysis

Oral Session





Surface chemistry – Quo Vadis?

Markus Eiswirth[*] and Gerhard Ertl

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Chemical reactions on surfaces have been studied for about two centuries, while large-scale industrial applications started with ammonia synthesis about 100 years ago and have grown ever more important since. Surface chemistry does not only play a leading role in the industrial production of chemicals, but is also of great importance in pollution control (cf. Figure). Moreover, electrochemical systems are crucial for energy conversion, i.e. the transformation of electrical in to chemical energy or vice versa (such as in batteries and fuel cells). Because of its crucial importance, the mastering of surface chemistry may well become one of the key technologies of the 21st century.

In recent decades the study of clean surfaces in ultra-high vacuum and the development of more and more sophisticated surface science techniques with increasing spatial and temporal resolution allowed to study surface processes directly and have greatly enhanced our understanding of the underlying mechanisms. The identification of the crucial step(s) of a given process may become helpful for the development of tailor-made materials and consequently enhance the efficiency or selectivity of (electro)chemical reactions. For example, although noble metals still are the most important catalyst and electrode material, multi-component materials, often with a well-defined nanostructure, are being developed with active sites for specific purposes.

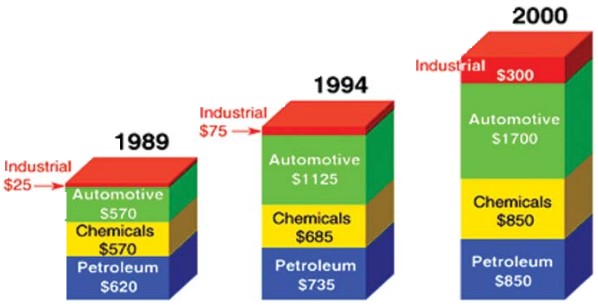

Figure. Development of catalyst market in the US (million $).

The influence of temperature on the oscillatory electro-oxidation of small organic molecules

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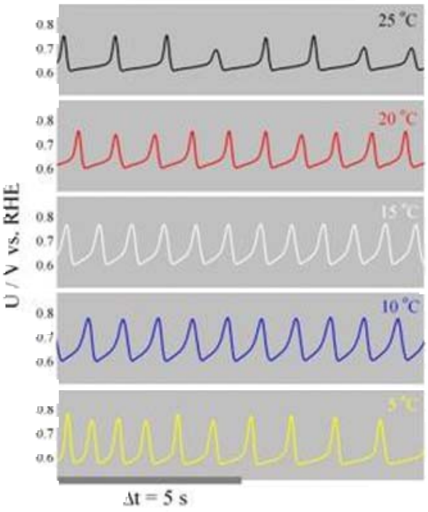
Temperature plays a decisive role on each individual step of a network of coupled chemical reactions, understanding its global influence on the reaction mechanism is often a difficult task. This is especially true for oscillatory systems studied under far from equilibrium conditions. We have recently studied [1-4] the effect of temperature on the catalytic electro-oxidation of some small (C1 and C2) organic molecules on platinum surfaces, under conventional and far from equilibrium conditions. Overall, the apparent activation energies found differs significantly accordingly to the method employed to determined it. In particular for the cases of formic acid in acidic (see Figure) and of ethylene glycol in alkaline electrolyte, the systems were nearly unaffected by temperature within the oscillatory regime. The relative independence of the oscillatory period on temperature is called *temperature compensation* and is one the key features of biological rhythms. Our studies indicate that temperature compensation might occur more often in electrochemical oscillators than in chemical ones. Understanding the way in which coupled reaction steps can cooperate to produce a reaction network which exhibits temperature compensation might be easier for a small number of surface reactions than that in real biological networks. So that, the examples cited can be used as model systems. As an attempt to infer on the mechanistic aspects of the temperature influence on the global kinetics, we have also worked with single crystal surfaces, and were able to rationalize the role of temperature on some specific steps.



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3 C.A. Angelucci, H. Varela, E. Herrero, J.M. Feliu, *J. Phys. Chem. C,* 2009*,* **113,** 18835.
4 E. Sitta, H. Varela, *Electrocatal.* (2010), in press. DOI: 10.1007/s12678-010-0005-2.

Fuel cell as a green energy alternative

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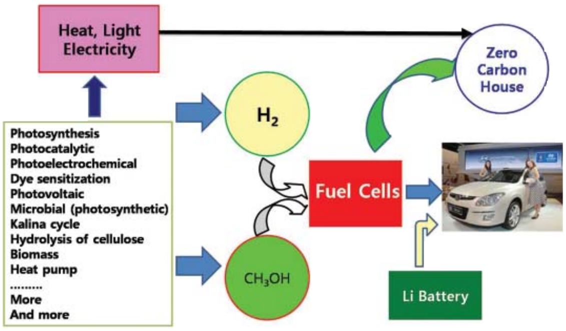
Depletion of fossil fuel and global warming problem derived to find new ways for future energy sources. It is well accepted that hydrogen is the energy for the next centuries. Hydrogen provides such great advantages as abundant supply and clean end product. Additional merit is that no carbon dioxide emission which is believed a major source for the global warming and weather changes. Production cost, however, exceeds other type of fuel cost at the moment. Therefore, interim alternative energy source and efficient use of energy must be considered.

There are several ways to utilize the alternate energy sources; they are solar or/and photo voltaics, wind energy, geothermal energy, biofuel and fuel cells. Of course, use of solar energy is the smartest way of use for alternative energy, but the efficiency needs to be improved as well as the stability problem associated with solar materials.

Fuel cells, on the other hand, have been receiving considerable interests as power sources because they exhibit high energy efficiency and are environmentally benign. Despite these advantages, fuel cells in general need to overcome not only technical, but also economic barriers for wide applications. Catalysts are the core material for fuel cell operation and many attempts have been made to find out the most active, efficient and durable formulae in the MEA preparation step.[1]

In these respects, works performed for fuel cell technology will be summarized, they are preparation of catalysts such as modified impregnation and galvanostatic pulse electrodeposition on Nafion-bonded carbon layer,[2] and effect of carbon supports for catalysts. The effect of carbon substrate was interpreted in terms of surface area and pore sizes.[3] Attempts to increase the triple phase boundaries[4] are explained in detail.



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2 J. Lee, K. Han, Hasuck Kim, *J. Power Sources,* 2006, **163,** 349.

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Fuel cells for aircraft application

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Although air transport is responsible for only about 2 % of all anthropogenic CO_2 emissions, the rapidly increasing volume of air traffic leads to a general concern about the environmental impact of aircrafts. Future aircraft generations have to face enhanced requirements concerning productivity, environmental compatibility and higher operational availability, thus effecting technical, operational and economical aspects of in-flight and on-ground power generation systems. Today's development in aircraft architecture undergoes a trend to a "more electric aircraft" which is characterised by a higher proportion of electrical systems substituting hydraulically or pneumatically driven components, and, thus, increasing the amount of electrical power. Fuel cell systems in this context represent a promising solution regarding the enhancement of the energy efficiency for both cruise and ground operations.

For several years the Institute of Technical Thermodynamics of the German Aerospace Center (Deutsches Zentrum für Luft- und Raumfahrt, DLR) in Stuttgart is engaged in the development of fuel cell systems for aircraft applications. The activities of DLR focus on:

- Identification of fuel cell applications in aircraft in which the properties of fuel cell systems, namely high electric efficiency, low emissions and silent operation, are capitalized for the airplane application.
- Design and modeling of possible system designs.
- Experimental investigations regarding specific aircraft relevant operating conditions,
- Qualification of airworthy fuel cell systems.
- Set up and full scale testing of fuel cell systems for application in research aircraft.

In cooperation with Airbus several fuel cell applications within the aircraft for both ground and cruise operation could be identified. In consequence fuel cell systems capable to support or even replace existing systems were derived. In this context, kerosene tank inertization and electrical cabin power supply including water regeneration represent the most promising application fields. The contribution will present the state of development discussing the following points:

- Modeling of different system architectures and evaluation of promising fuel cell technologies (PEFC vs. SOFC).
- Experimental evaluation of fuel cell systems under relevant conditions (low-pressure, vibrations, reformate operation, etc.).
- Fuel cell system demonstrator Antares DLR-H2 and Hyfish (hydrogen powered model aircraft)
- Fuel cell test in DLR`s research aircraft ATRA (A320) including the test of an emergency system based on hydrogen and oxygen with 20 Kilo Watts (kW) of electrical power.

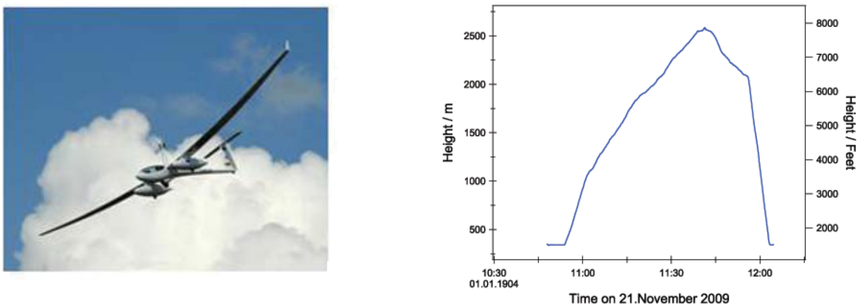

Figure. Motor glider Antares DLR-H2 with two pods for hydrogen tanks and fuel cell system; flight profile on November 21st, 2009.

Electrochemical approaches for fabrication of micro/ nano scale functional structures and devices

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In this paper, the electrochemical fabrication processes for functional nano/microstructures and devices are described. Electrodeposition process has been applied to fabricate the array of ferromagnetic nanodots in combination with the formation of nano-patterned substrates using electron beam lithography (EBL) and nanoimprint lithography (NIL), which is one of the key materials for ultra-high density data storage devices.[1,2] Figure 1 shows representative SEM image of the CoPt nanodots deposited into the nano-patterned substrate fabricated by EBL, showing that the CoPt was successfully deposited into the pores. We also applied the electrodeposition process to fabricate ultra-thin films for the formation of nanogap electrode for molecular electronic devices.[3] For this, enhancement of lateral growth of the electrodeposition has been achieved by modifying the substrate surface by self-assembled monolayers. On the other hand, electrochemical etching process is applied to Si wafer surface and the area-selective fabrication process to form array of high aspect ratio pores was developed, and by modifying this process, various functional microstructures were fabricated.[4, 5]

The author would like to thank the colleagues working for the projects described here. This work was carried out at the "Center for Practical Chemical Wisdom" in the Global-COE Program, MEXT, Japan, and was financially supported in part by Grant-in-Aid for Scientific Research (B) and the grant from the Storage Research Consortium (SRC).

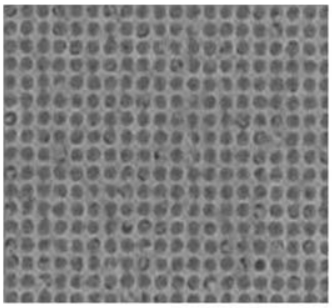

Figure 1. SEM image of electrodeposited CoPt magnetic nanodot arrays.

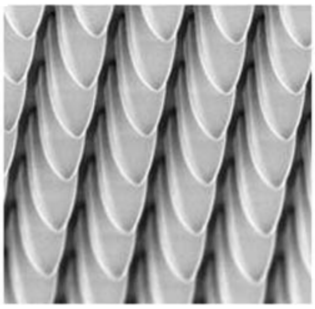

Figure 2. SEM image of the arrayed SiO_2 tubes.

References

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2 T. Ouchi et al., *IEEE Trans. Magn., in press.*
3 C. Kobayashi et al., *Electrochem. Soc. Trans., in press.*
4 H. Sato et al., *Electrochem.Comm., submitted.*

Investigation of formic acid electrooxidation at mesoporous platinum microelectrodes. The effect of temperature, anion and bismuth ad-atoms

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Formic acid, as a fuel for fuel cell applications, has gained special interest recently, because of good power densities and because of its lower crossover rate through the polymer membrane compared with methanol. Moreover, direct formic acid fuel cell has the advantage of displaying high performance at relatively low temperature. The electrooxidation process of formic acid is also highlighted, as this molecule represents a good model compound to understand the catalytic reactions of other small organic molecules (SOMs) such as methanol and ethanol.

Platinum-based catalysts are some of the most efficient material for formic acid oxidation. However, platinum is susceptible to poisons such as CO, which is an intermediate of such reaction process, because it strongly adsorbs onto the electrode surface active sites, resulting in a dramatic decrease in efficiency. A similar negative effect on current density can be caused when the electrolyte medium contains adsorbing anions. Under given conditions, poison effects can be minimised by either using nanostructured platinum electrodes or platinum electrodes modified by foreign metal ad-atoms.

In recent papers mesoporous platinum electrodes with high surface area, prepared by directed templating techniques, have been employed to investigate the electrooxidation processes of SOMs. In particular, nanostructured platinum films with high surface areas and uniform size of pores have been prepared by reduction of platinum salts from the aqueous domain of lyotropic liquid crystalline phases of non-ionic surfactants.

In this paper we present a comprehensive investigation for the electroxidation of formic acid (Figure. a) at mesoporous platinum microelectrodes (**MPtMs**) (Figure. b), prepared by the above templating technique, highlighting the effects of temperature, anions and irreversibly adsorbed bismuth atoms on current density. Both a platinum and gold microelectrode 25 μm diameter is employed as substrates for the deposition of the mesoporous platinum film. These electrodes are advantageous for kinetic investigations, as they allow measurements to be performed at high current densities with negligible effects due to homic drop.

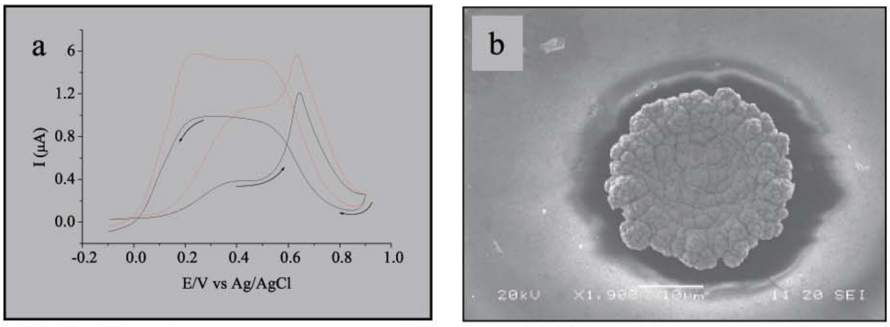

Figure. (a) Cyclic voltammograms recorded at two **MPtMs** with roughness factors (real to geometric surface area ratio) equal to 60 (black line) and 200 (red line) in 0.5 M H_2SO_4 + 0.1 M HCOOH. Scan rate 50 mVs^{-1}. (b) SEM image of a **MPtM.**

Electrochemical microcalorimetry

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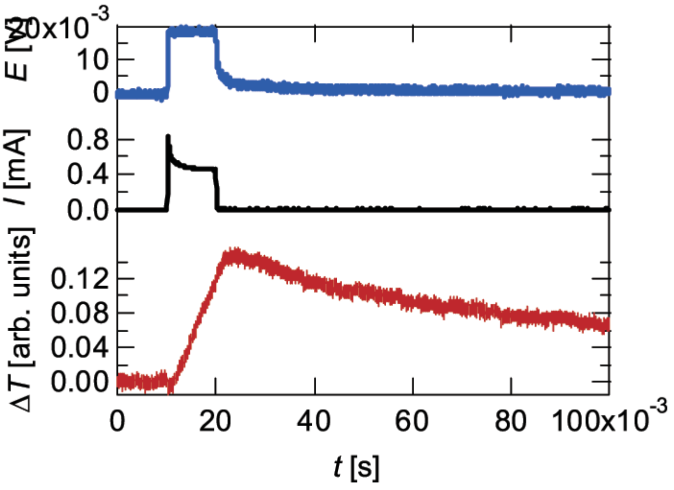
The measurement of heat changes upon electrochemical reactions provides valuable information on the entropy of reaction as well as on possible irreversible reactions accompanying the charge transfer. However, in electrochemical environment calorimetric measurements usually require large conversions, due to the high heat capacity of electrode and electrolyte. Here we present an experimental approach, which allows the investigation of electrochemical reactions with submonolayer conversions. We achieved the high sensitivity by adapting the calorimetric method, introduced by David King's and Charles Campbell's groups for the measurement of heats of adsorption in UHV, to electrochemical systems. Combining the use of a thin electrode-sensor assembly with pulsed electrochemical reactions resulted in sensitivities high enough for measuring heat changes upon conversions of a few percent of a monolayer.

We will present examples for heat effects upon metal deposition/dissolution, electron transfer reactions on electrodes and the adsorption of SDS. As an example the figure shows the transients of temperature and cell current upon the dissolution of 4 % of a monolayer of Cu from a thick Cu layer by the application of a 10 ms potential pulse. Applications towards the investigation of phase transitions in surface adlayers or reconstruction of surfaces will be discussed.



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Coupling electrochemical oscillators

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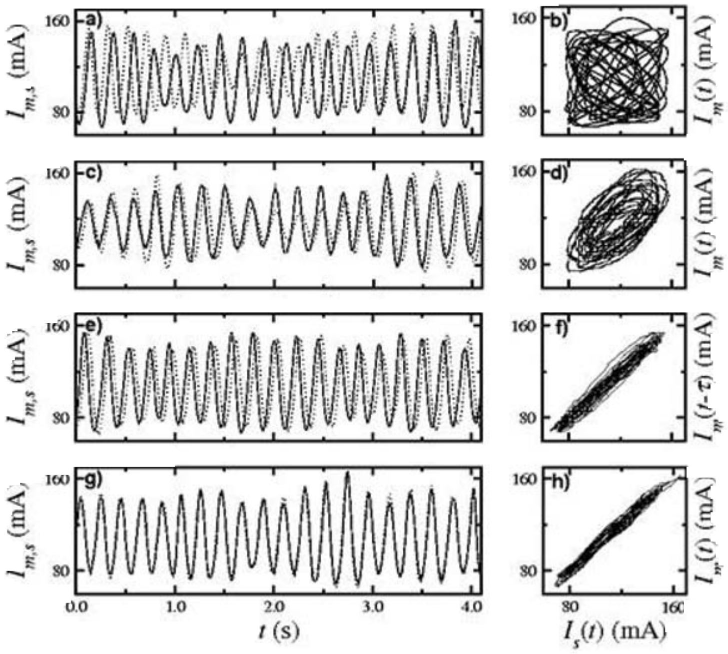
Two electrochemical oscillators are subjected to bidirectional and unidirectional coupling. The system parameters are chosen such that the autonomous dynamics of the oscillators exhibit chaotic behavior. Different domains of chaotic synchronization for this pair of electrochemical oscillators are studied systematically. In the bidirectional scenario, the underlying coupling between the two oscillators is achieved by immersing the two anodes in a common electrolytic solution. The horizontal distance between these two electrodes determines the strength of the coupling constant. As shown in the attached figure, monotonically decreasing the distance between the two anodes, different domains of synchronization are identified. Furthermore, chaotic synchronization is studied when the two electrochemical oscillators are coupled unidirectionally namely the master--slave configuration. Finally, a time delay is introduced in the bidirectional coupling between the two oscillators. When this time delay is varied, a phase--flip transition is observed: the relative phase between the synchronized oscillations changes abruptly from zero to π.



Electrochemical at ITIES as a microanalytical tool for nanoliter analyte detection and sample preparation

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In this work we present new procedures based on electrochemistry at Interfaces between Immiscible Electrolyte Solutions (ITIES) aimed at analyte extraction and detection in nanoliter biological samples. The electrochemical flow cell detector is modeled using finite element simulations using the software COMSOL (Fig 1). The detector response is in good agreement with the numerical simulations (Fig 2). The detector can quantify an analyte present in nanomolar concentration and is easily coupled to a separation system such as e.g. HPLC.

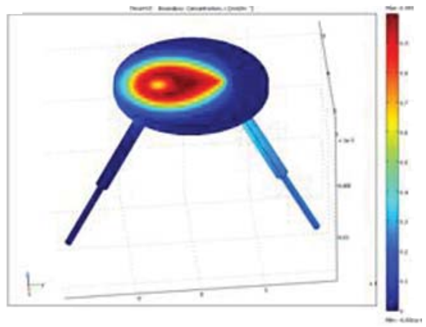

Figure 1. Finite element simulation of a sample Plug in the detector cell chamber.

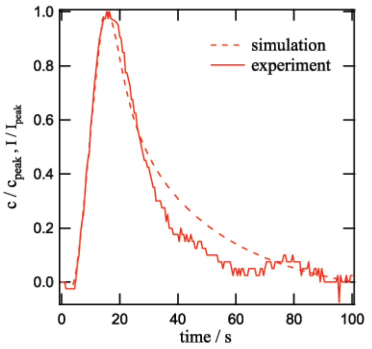

Figure 2. Comparison of simulation and experimental results.

It is also shown that an imposed potential difference is effective for sample preparation as charged analytes can be extracted across an oil phase supported by a hydrophobic membrane. In this example the extracted analyte is recovered in an aqueous acceptor phase making subsequent analysis straightforward. This principle is well-suited for stagnant systems (drop analysis) as well as for flow based systems.

Battery – forecast via synergetics

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A short introduction on synergetics is given using some intuitive experimental examples. Local potential measurements in lead acid batteries are realized in order to find reliable quantities for state of charge SOC and state of health SOH evaluations. It is known, that in lead-acid batteries as an example for strongly coupled non-linear electrochemical systems, spatial inhomogeneities can be found like acid stratification due to inhomogeneous current density distribution. To detect such inhomogeneities in situ, we made spatial resolved potential measurements between the plates of a cell stack under charging / discharging conditions. This spatially resolved potential information from inside the cell stack gives additional information about the driven electro-chemical process of charging and discharging Figure. This information cannot be obtained by potential and current monitoring at the outside poles of the battery and is therefore suitable for developing a reliable prognosis of the battery's service time.

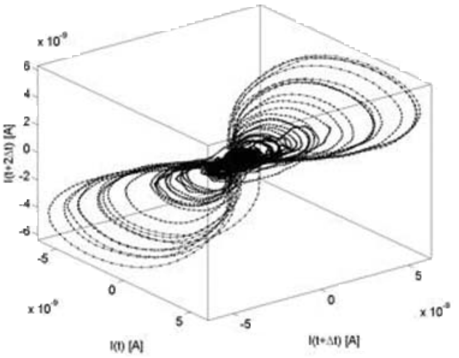

Figure. Chaotic attractor of the time series of the current flow through the lead reference- electrode inside the cell stack.

Delay-time: Δt = 100 ms

In order to achieve a forecast of the capability of the battery without having knowledge on what happens inside, one should imitate the influence of the outside world on the battery. Of course one cannot simulate the total history of an individual battery but one can investigate the responsiveness of the battery on complex signals. The evaluation of the answers of the battery by the methods of synergetics will enable a forecast of life-time and capability without having an insight on the internal processes. As you may imagine, this method is not restricted to lead-acid batteries.

Phase transformation of thermoelectric bismuth telluride nanowires as a result of an annealing process

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P-type thermoelectric bismuth telluride nanowires were fabricated by pulsed electrodeposition in anodic aluminum oxide (AAO) membranes. Subsequently, the nanowires were annealed at 423, 523 and 673 K in an inert atmosphere for 4 hrs. With increasing annealing temperature, it has been observed that the Te compound incongruently sublimates due to its high vapor pressure, leading to a phase transformation (from Bi_2Te_3 to Bi_4Te_3 via Bi_4Te_5). The crystalline structure of the nanowires was investigated by X-ray diffraction (XRD) as well as by selected area electron diffraction (SAED). The composition of nanowires was investigated by energy dispersive X-ray spectroscopy (EDX) attached to a transmission electron microscope (TEM). The crystallinity of the nanowires enhanced with increasing of annealing temperature and in particular the nanowires annealed at 673 K were stably kept as the Bi_4Te_3 phase. Additionally, the Seebeck coefficient has been determined and slightly enhanced thermopower of the nanowires annealed at a temperature of 423 K and significantly suppressed values for annealing temperatures of 523 K and 673 K has been observed.

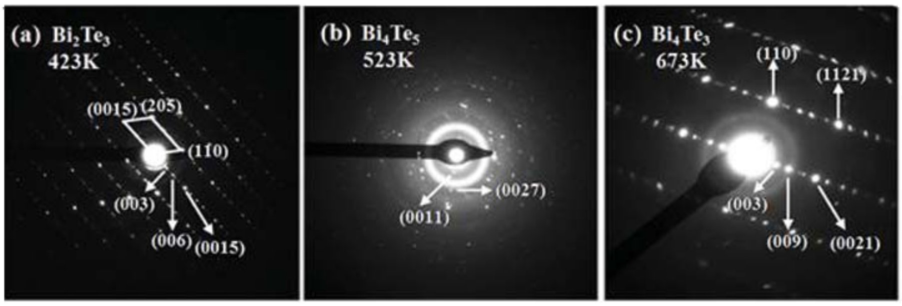

Figure. Selected area electron diffraction patterns (SAED) of annealed nanowires at different temperatures (a) 423 K, (b) 523 K, and (c) 673 K, respectively.

Chances and Challenges of Cluster Chemistry

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A cluster is an aggregate consisting of an adjustable number of atoms. In contrast to molecules, the number and sort of atoms in clusters can be varied. Clusters consist of up to 1000 atoms and with each additional atom their properties might change dramatically (Figure). Cluster science opens the window to new chemistry, because properties such as chemisorption energies, catalytic activities or photodesorption yields vary with size and are different from the ones of the bulk surfaces and the atoms. One famous example is the reactivity of small Au clusters versus oxygen. While a gold surface does not react with O_2, small Au cluster anions with an even number of atoms readily react with O_2. Cluster anions with an odd number of atoms and clusters with more than 20 atoms do not react with O_2.

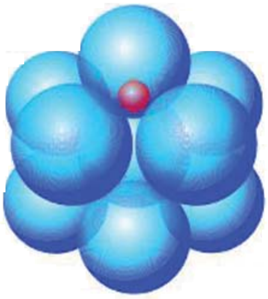

Figure. Structure of an $Al_{13}H$ Cluster. The geometric and electronic structure of this cluster is highly stable and comparable to the one of C_{60}.

This new chemistry of clusters has fascinating possibilities. Using size-selected clusters heterogeneous catalysis gains a new dimension of detailed control at the nano-level. The high quantum yield of photodesorption makes small metal clusters to promising nanodevices converting light energy into chemical energy. Novel cluster-based materials might exhibit a superior performance in specialized applications such as hydrogen storage. However, there are challenges. Already the simple determination of the properties requires experiments on size-selected clusters. Size-selection results in extremely low cluster intensities. In addition, any atom in contact with a cluster alters its properties and experiments need to be conducted at ultra-clean conditions. Hence, experiments on size-selected clusters are difficult and time-consuming.

Enhanced fuel cell performance under humidified and non-humidified conditions by the structural modification of a polymer electrolyte membrane

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One of the most critical issues of polymer electrolyte membrane fuel cells is water management because dehydration of a membrane increases membrane-resistance whereas excessive water flooding at the cathode impedes the gaseous diffusion of oxygen to reaction sites at the wetted catalyst surface. In this study, we have developed a fuctional polymer electrolyte membrane that facilitates water management. The structural modification of membranes strongly affected water management, due primarily to the fact that water must move through a membrane during fuel cell operation. The asymmetric membrane improved transport of water from the cathode to the anode when the hydophilic side of the membrane located to the cathode, thereby enhancing overall fuel cell performance under both fully humidified and non-humidified conditions.

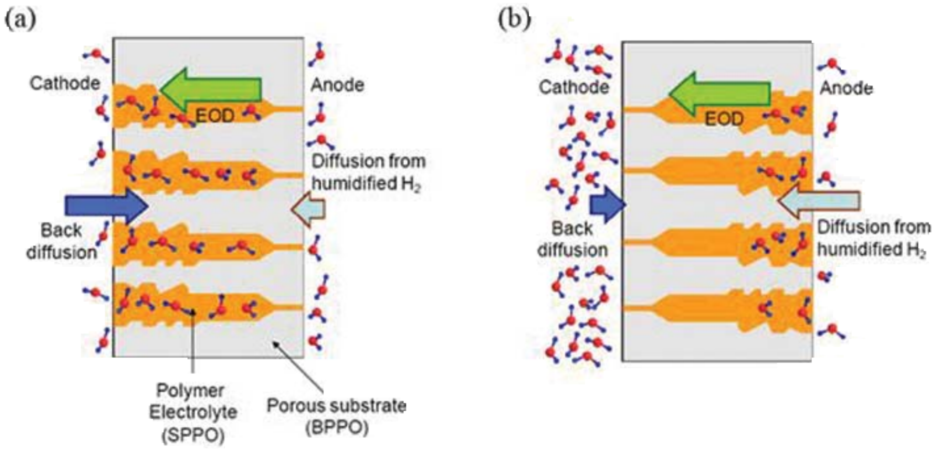

Figure. Schematic of water flux in the asymmetric membrane under HYP_C (a) and HYP_A (b) conditions.

Interplay of the electrochemical reaction and diffusion in 3D nanoparticle arrays

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Microelectrodes and microelectrode arrays have been widely applied in electroanalytical chemistry for sensor purposes, and in physical electrochemistry for studying the kinetics and the mechanisms of electrode reactions.[1] In this presentation we will introduce the concept of three-dimensional (3D) array electrodes (Figure) based on Pt nanoparticles supported on vertically aligned carbon nano-filaments (VACNFs),[2] and discuss their applications to the investigation of the oxygen reduction (ORR), hydrogen oxidation (HOR) and CO oxidation reactions. VACNFs were grafted to a core of a rotating disk electrode by catalytic pyrolysis of toluene in the presence of ferrocene, the latter serving for in situ generation of the growth catalyst.[3] HOR and bulk CO oxidation reaction were studied with the RDE, and ORR – with the RDE and RRDE methods. The interplay of electrochemical reactions and mass transport was mathematically modeled within the diffusion domain approximation[4] using finite element software, Freefem+.

We will demonstrate that utilization of Pt/VACNF layers offers a number of assets for the investigation of the kinetics and the mechanisms of electrocatalytic reactions on nanomaterials. Pt surface area can be varied in a much wider range than either for conventional random 3D layers based on powder Pt/C, or model 2D particle arrays on flat substrates. Application of Pt/VACNFs allows to independently vary the layer thickness L, the Pt coverage, and in perspective the nano-fiber density per unit surface area. High degree of homogeneity and structural order ensures control of the interfacial conditions at nanoparticle surfaces and allows application of actual rather than apparent parameters for the description of the porous layer, namely pore diameter, length and tortuosity factor. This allows direct comparison between the experiment and the modeling and access to such parameters as the penetration depth, Pt utilization, *etc,* the latter will be discussed as a function of the nanofiber length L and Pt coverage. On the other hand, VACNFs may be further applied for the optimization of the catalytic layers for the fuel cell applications.

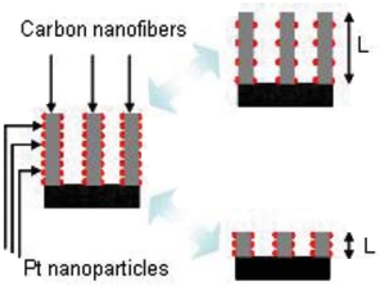

Figure. Schematic representation of 3D nanoparticle arrays.

Acknowledgements
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Reliable combinatorial method for fuel cell electrode and MEA

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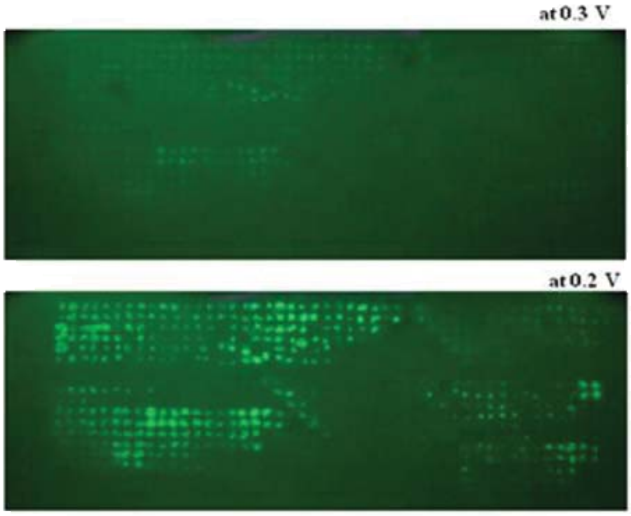
The development of cheap and highly-active electrode for fuel cell is quite crucial to commercialization of fuel cell. The price of electricity produced by fuel cell is ten times as high as than that of electricity prepared by conventional power generation method. Robust combinatorial method for screening ternary PtRuFe and PtRuMo alloy systems will be discussed. Among 121 libraries $Pt_4Ru_3Fe_3$, $Pt_5Ru_4Mo_1$, and $Pt_4Ru_4Mo_2$ compositions (mass ratio) were among the highest,

Methanol crossover is inevitable for DMFC, Hence the best strategy is to develop methanol tolerant ORR catalyst. 645 different compositions composed of 4 of 5 metals among Pt, Ru, Mo, Se, and Fe, were prepared by ink jet printer, Optical screening indicated Pt(50)Ru(20)Fe(10) Se(10)/C is the most methanol tolerant and highly active catalyst superior to Pt/C catalyst

A combinatorial array of membrane-electrode-assembly (MEA) with novel multilayer structure used for direct methanol fuel cell was fabricated. It can be concluded that MEA structure prepared by the optimum concentration gradient of electrocatalyst, Nafion ionomer and PTEE is recommended instead of uniform concentrations of those components.



Synergistic effect of carbon nanotubes support on electrocatalytic properties of silver in the nitrate ions reduction

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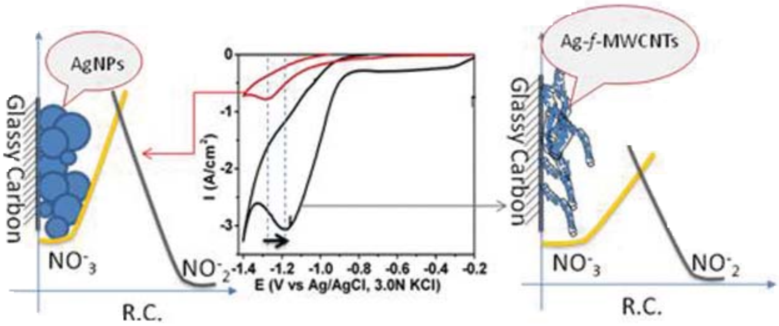

Synergistic effect of carbon nanotubes support on electrocatalytic properties of Ag deposited on –COOH functionalized multiwalled carbon nanotubes (*f*-MWCNTs) is presented. MWCNTs were filled and coated with silver by the electrophoretic dissolution of silver anode in aqueous dispersion of *f*-MWCNTs.[1] All the materials were characterized by XRD, FTIR, Raman and SEM and TEM. For the comparison, the voltammetric investigations were also carried out on the bulk Ag electrode and Ag nanoparticles (AgNPs). For that, the uncapped AgNPs were prepared by anodic dissolution of Ag anode in DMSO.[2] Oxidation of hydroquinone, electroformation and subsequent reduction of Ag_2O and electroreduction of nitrate ion in aqueous solutions were chosen to be model reactions, to investigate the activity of silver in three forms. Detail cyclic voltammetry (CV) analysis on all these cases revealed that the underlying MWCNTs play a vital role in electrocatalytic activity of silver. Carbon nanotubes are known to be electron acceptor and makes Ag electron deficient. This increase in oxophillicity makes the reduction of nitrate ion and oxidation of hydroquinone on Ag-*f*-MWNT, kinetically facile and thermodynamically more favorable. Thus, the electrodes modified with Ag-*f*-MWCNTs composites have been proposed to be a better candidate over the one with silver bulk as well as AgNPs, for the nitrate ion detection.[3]

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3 Mohsin A. Bhat, Pravin P. Ingole, Vijay R. Chaudhari and Santosh K. Haram, *New Journal of Chemistry*, 2009, **33** , 207.

Creating ITIES for ion-selective sensing and fuel cell applications

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) can offer a superb sensing platform for the analysis of non-redox and biological species with an enhanced selectivity given by incorporating target specific ionophores into an organic electrolyte phase. In this talk, we will demonstrate cost-effective amperometric sensors based on measuring current changes associate with ion transfer reactions across a polarized ellipse-shaped single micro-interface between the aqueous phase and the polyvinyl chloride-2-nitrophenyloctylether (PVC-NPOE) gel phase. The micro-hole was fabricated by simple mechanical punching with a sharp needle on a thin PVC film (12 μm thick) commercially available as a food wrapping material (see Figure inset). Both the direct and assisted transfer characteristics of various ionic species across the newly developed single micro-hole interface were studied using cyclic voltammetry (see Figure) and differential pulse stripping voltammetry. As an example, we will introduce an amperometric proton ion selective sensor based on the assisted transfer of protons across the single micro-hole interface by the ionophore, octadecyl isonicotinate, incorporated into the organic gel layer. In addition, we will discuss on creating other type of polymeric ITIES such as biopolymer electrolyte multilayers formed via layer by layer self-assembly of poly-lysine and DNA for biosensing applications as well as for potential usages in direct liquid fuel cells as an alternative Nafion membrane electrolyte.

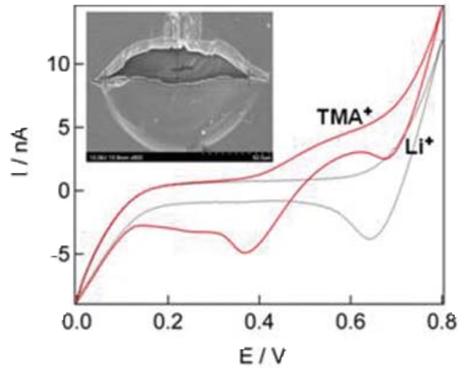

Figure. Representative cyclic voltammograms showing 0.1 mM tetramethylammonium ion transfer across the single microhole interface filled with 3% polyvinyl chloride-2-nitrophenyloctylether gel. 10 mM LiCl was used as a supporting electrolyte in the aqueous phase. Scan rate = 20 mV/s. Inset shows SEM image of the single ellipse shaped micro-hole interface created on a PVC wrapping film.

The study of $Pd_{70}Au_{30}(110)$ surface properties under CO, O_2 and $CO+O_2$ elevated pressures

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In recent years, the development of various *in-situ* high pressure surface-science tools generates many interesting results and opens up a new field of surface science, especially in surface catalysis. Being able to monitor chemical reactions under high pressure condition provides important information for better understanding of surface catalytic properties under realistic condition. The CO oxidation on $Pd_{70}Au_{30}(110)$ surface is investigated with various state-of-the-art *in-situ* surface techniques, including *in-situ* scanning tunneling microscope (STM), polarization modulation Infrared reflection absorption spectroscopy (PM-IRRAS), and ambient pressure x-ray photoemission spectroscopy (AP XPS). The surface of $Pd_{70}Au_{30}(110)$ under UHV conditions exhibits a (1x1) un-reconstructed surface while, under elevated pressure of CO, the surface roughens and a "rice grain" morphology shows up with typical domain sizes around 4 nm and 0.05 nm corrugation which prevails up to 500Torr. PM-IRRAS of CO adsorption on $Pd_{70}Au_{30}(110)$ (at various pressures of CO : 0.02Torr to 100Torr) shows three vibration bands : 2115cm^{-1} (CO top on Au), 2090cm^{-1} (CO top on Pd) and 1980-1990cm^{-1} (bridged CO). With AP XPS, the surface segregation of Pd is observed with increasing CO pressure. Under O_2 pressure (<1 Torr) XPS reveals segregation of Pd to the surface followed by its oxidation, shown in Figure. The O_2 pressure of 500mTorr induces the formation of a bulk-like Pd oxide at T=673K. AP XSP studies revealed the catalytic efficiency of the surface under reaction conditions (CO in high excess of O_2).

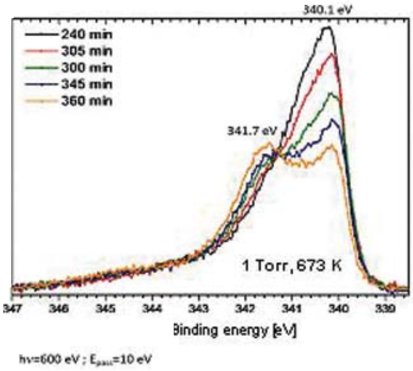

Figure. AP XPS : Pd-$3d_{3/2}$ peak showing the formation of a surface PdO layer (341.7 eV) under pressure of 1 Torr of O_2 at 673 K.

In situ methods for the investigation of lithium batteries

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There is a growing need for efficient electrochemical energy storage systems to power electric vehicles in the future. Lithium-ion batteries are widely used today in consumer electronics due to their high energy density, but capacity fading upon prolonged cycling and safety issues still prevent their widespread use in vehicles. A thorough understanding of the ageing mechanisms will be a key to further development of lithium-ion and other batteries.

In this contribution we describe the use of advanced *in situ* methods to observe changes in battery materials directly while the battery is being cycled. Examples include the use of vibration spectroscopy (IR/Raman), colorimetry, and differential electrochemical mass spectrometry (DEMS).

Electrochemical cells designed for the acquisition of Raman and infrared spectra will be presented, and their application for the characterization of organic cathode materials will be discussed. *In situ* colorimetry is a straightforward method to measure the lithium content in composite graphite electrodes. DEMS was used to investigate electrolyte decomposition reactions in lithium/oxygen batteries. Gases produced in the cell during the charging step were fed into a quadrupol mass spectrometer, and ion-currents of selected mass numbers were plotted vs. current or voltage (Figure). Thereby the formation of carbon dioxide was revealed in addition to the expected oxygen production, suggesting an anodic decomposition of the electrolyte solvents at high potentials.

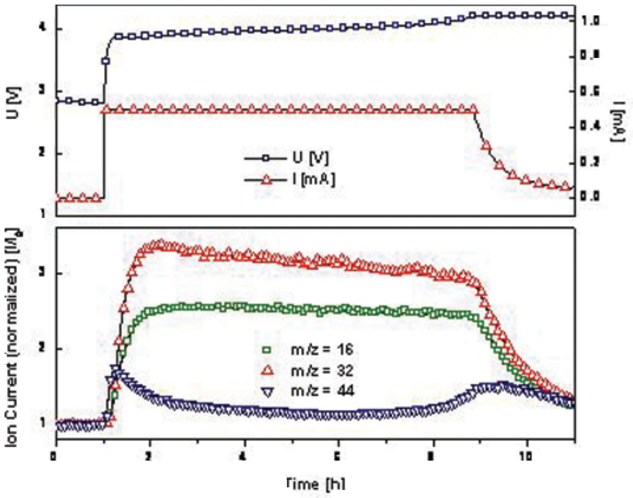

Figure. Differential electrochemical mass spectrometry of a lithium/oxygen cell, relating current (I) and voltage (U) (top graph) to the oxygen gas formation (bottom graph, m/z = 16; 32). Carbon dioxide ions (m/z = 44) result from decomposition of the propylene carbonate electrolyte.

Electrochemical avenue toward $Cu(In,Ga)Se_2$ –Based solar cells

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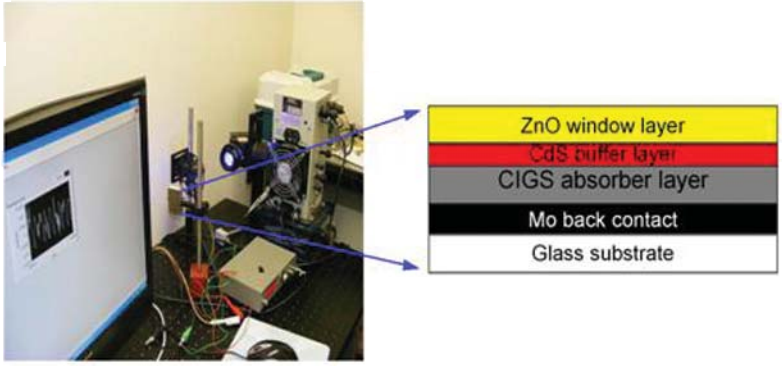
One of the most important challenges for modern sciences and technologies is to develop clean renewable energy resources. Solar cells based on $Cu(In,Ga)Se_2$ (CIGS) as the absorber layers have attracted much attention for highly efficient devices and have reached an efficiency as high as 20% on a laboratory scale.

In this study, sputtered Mo on soda lime glass or ITO/PET was used as the back contact (BC) materials. CIGS thin films were prepared by one-port direct electrochemical deposition in an ionic liquid environment or by annealing CIG precursors at 500 ºC for 30 min in an elemental Se atmosphere in a furnace. The composition, structures and photoreactivity of the prepared thin films were investigated by electron dispersive x-ray (EDX), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman microspectroscopy and scanning photoelectrochemical microscopy.



Solar cells such as ITO/ZnO/CdS/CIGS/Mo/glass and ITO/ZnO/CdS/CIGS/Ag paste were built. Their efficiency was characterized.

Temperature cycling effects on the durability of polymer electrolyte fuel cells

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For the successful commercialization of polymer electrolyte fuel cells (PEFCs), many critical obstacles still remain. Among them, performance, durability and cost problems should be solved in advance. In PEFC systems, water management is an important point to get enhanced durability as well as good performance.

In general, PEFC systems experience various temperatures during operations from room temperature to around 80 ℃. Especially, in winter season, the system can be exposed under 0 ℃. During such temperature cycles, the membrane electrode assembly (MEA) in the stack can be dried and/or wetted resulting in expansion and/or shrinkage of membrane electrolyte. The repeated changes in dimension of membranes can cause the deterioration of fuel cell performance. And at the sub-zero temperature condition, the freezing phenomena can occur accelerating the cell degradation.

In this work, the effect of gas diffusion layers on the life time of PEFCs in the temperature cycling conditions was investigated. For the selected gas diffusion layers, which have the same material, the similar thickness but different bending stiffness, systematic durability analyses were conducted. As a result, the core property of gas diffusion layers to enhance the durability of PEFC systems in the temperature cycling conditions could be suggested.

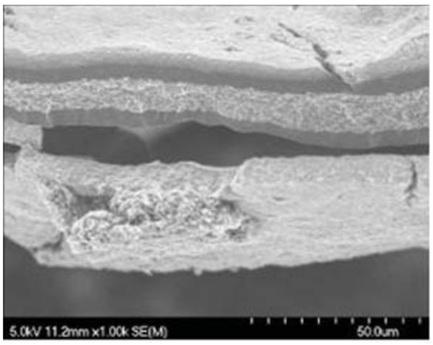

Figure. SEM image of freeze/thaw cycled membrane electrode assembly (MEA).

Multifunctional cylindrical nanoobjects: From ALD growth towards physical model systems

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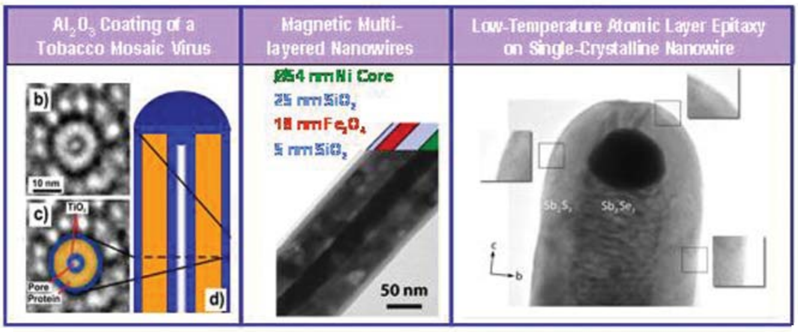
A broad range of potential applications of magnetic nanostructures have been developed in the recent years. Magnetic data storage, microelectronics, or biomedical uses such as cell separation or biosensing present a special interest among these applications. Atomic layer deposition (ALD) is a very suitable method for the conformal deposition of magnetic thin films in pore structures of high aspect ratio, while offering the precise tuning of the layer thickness and high uniformity.[1]

By ALD coating of self-ordered Al_2O_3 membranes, arrays of magnetic nanotubes with diameters down to 20 nm and wall thicknesses of less than 5 nm have been achieved.[2] The magnetic properties of the nanotube arrays as a function of wall thickness and tube diameter have been studied by using SQUID magnetometry and compared with magnetic simulations. We will discuss the properties of magnetic multi-layered nanotubes (core-shell) and the application of conformal magnetic coatings of other template systems and 3D nanostructures.

Furthermore, thermoelectric materials might play an increasing role for the efficient use of energy resources and waste heat recovery in the future. We have grown nanowires of V-VI semiconductors by cyclic vapour liquid solid growth mode.[3] The synthesized Sb_2Se_3 and Sb_2S_3 nanowires have been applied successfully as three dimensional substrates for epitaxial atomic layer deposition at low temperatures starting at 90 °C. The presentation will be completed by the presentation of selected results on template-based synthesis of magnetic and oxides nanostructures by atomic layer deposition.



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Ordered hierarchical nanostructured carbon as a highly efficient catalyst support in low-temperature fuel cell

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Proton exchange membrane fuel cell (PEMFC) as a low-temperature fuel cell has attracted much attention as future energy sources. Catalyst support technology has been proved as an important approach to enhance the utilization of the platinum[1]. Carbon black Vulcan XC-72 (VC) has been usually used as a catalyst support for low-temperature fuel cells[2]. However, VC contains some primary pores with the size being less than 1.0 nm which are inaccessible to the electrolyte polymer, and the catalyst nanoparticles engulfed in the pores do not contribute to the electrochemical reactions due to lack of the three-phase boundary.

In this study, ordered hierarchical nanostructured carbon (OHNC) has been fabricated through inverse replication of silica template[3] and explored to support high loading of Pt and PtRu nanoparticles as electrocatalysts in PEMFC. The superb characteristics such as ordered hierarchical nanostructure consisting of ordered macropores of 300 nm and interconnected mesopores of 10 - 20 nm, large surface area and mesopore volume enable the OHNC to support high loading (60 wt%) of Pt-based nanoparticles with uniform dispersion and small particle size. The OHNC-supported Pt(50)-Ru(50) anode catalyst has demonstrated great improvement in electrocatalytic activity toward hydrogen oxidation and much higher power density (an enhancement ~ 70 %) than the commercial carbon black Vulcan XC-72-supported Pt-Ru in PEMFC application. In addition, compared to carbon black Vulcan XC-72 (VC)-supported Pt (60 wt%), the OHNC-supported one has exhibited greatly enhanced catalytic activity toward oxygen reduction reaction and considerably improved PEMFC performance.

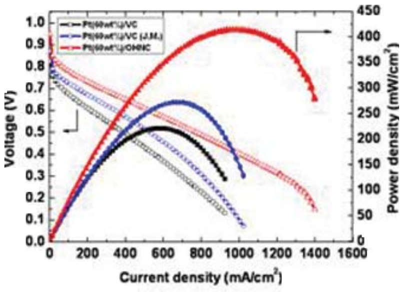

Figure. Polarization and power density plots at 60 °C for PEMFCs using the VC- or the OHNC-supported Pt (60 wt%) catalyst cathodes, catalyst loading in the cathodes: 0.2mgPt/cm^2.

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In situ Video-STM studies of the surface reconstruction of Cu(100) electrodes during hydrogen evolution

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Although the hydrogen evolution reaction (HER) is one of the most important electrochemical processes very little is known on the structure of electrode surfaces during this reaction. Studies of hydrogen adsorption from the gas phase on single crystal transition metal surfaces by UHV surface science and theoretical methods indicate that hydrogen can induce reconstructions of the surface layer, often involving hydrogen in subsurface sites.

In this study we present high-resolution *in situ* scanning tunneling microscopy (STM) results on the Cu(100) surface structure in the hydrogen evolution regime and supplementary electrochemical data, which unambiguously demonstrate that hydrogen-induced reconstructions can also occur at electrochemical interfaces and have a pronounced influence on the electrode reactivity.[1] Specifically, the rapid formation of stripes, formed by two elevated rows of Cu atoms in the surface layer, is observed on the electrode surface after lowering the potential into the HER regime. The structural details suggest a local quasi-hexagonal distortion of the Cu surface layer within the elevated atomic rows. With decreasing potential the density of these stripes increases, saturating at distances of 4 Cu lattice spacings. At even lower potentials an additional long-range moiré modulation along the stripes is found, indicating a ≈20% expansion of the surface lattice in this direction. The latter is also supported by changes in the Cu surface morphology during the reversible transitions between reconstructed and unreconstructed surface. In analogy to related (but not identical) structural data for the hydrogen-induced reconstruction of Cu(100) under UHV conditions, incorporation of hydrogen in subsurface sites is suggested as the driving force for the formation of this novel reconstruction. Using potential step experiments the reactivity of the reconstructed and unreconstructed Cu(100) electrode could be investigated, indicating an enhanced electrocatalytic activity of the more open reconstructed Cu lattice as well as a change in the reaction mechanism.

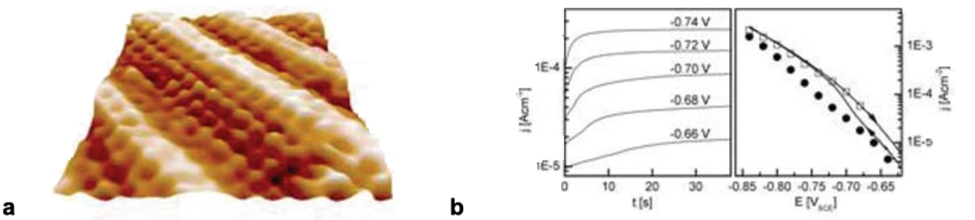

Figure. (a) *In situ* Video-STM image of Cu(100) in 0.1 M $HClO_4$ solution at -0.65 V_{SCE}. (b) current transients during potential steps from -0.54 V_{SCE} (left) and resulting Tafel plots for the unreconstructed (full circles) and reconstructed (open squares) Cu(100) electrode surface. The solid line shows the current density during a cyclic voltammogram at 2 mV/s potential sweep rate (after ref. 1).

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Sulfur-tolerant Ni-based anodes for high-temperature fuel cells

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Energy from biomass/waste is expected to play a quite significant role in changing the present fossil fuel-based energy systems. Importantly, biogas containing high quantity of methane is promising as a fuel for high-temperature fuel cells since internal reforming operation is possible within the fuel cell stack. The contaminant levels in biogas, however, are often unacceptable and fluctuate over wide ranges, hindering long-term stability of the fuel cell stack and increasing the system liability due to extensive gas clean-up processes. To be able to profit from the characteristic advantages of high-temperature fuel cell combined with biogas utilization, it is thus essential to develop fuel cell components tolerant to residual contaminants in the biogas. Among the contaminants in the biogas, the most harmful components are sulfur compounds because of their abundances (~ several hundreds ppm) as well as concentration fluctuation (up to several thousands ppm). Ni-based anodes are widely used in high-temperature fuel cells, but these anodes usually react with sulfur compounds such as H_2S contained within the biogas at operating temperature of the fuel cells, leading to the degradation of fuel cell performance. Various techniques to enhance sulfur tolerance of Ni-based anodes have been developed and one method was to apply ceria coating on pore surface of the anode (Figure.). In this talk, effect of ceria coating on H_2S tolerance of molten carbonate fuel cell and solid oxide fuel cell will be thoroughly reviewed.

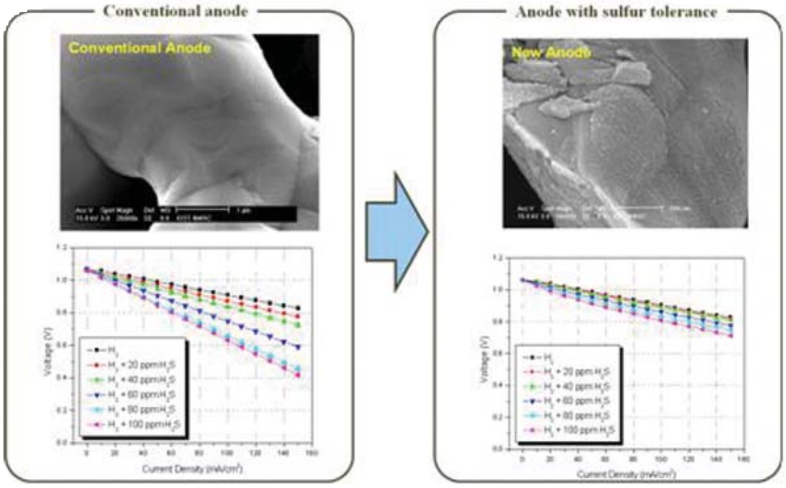

Figure. Effect of ceria coating on H_2S tolerance of porous Ni-10wt%Cr anode.

Synthesis and electrochemical activity of PGM-free cathode catalysts in alkaline ethanol fuel cells

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While platinum is the most effective catalyst for polymer electrolyte fuel cells, its cost and availability limits commercial applications using current technology. Complete replacing platinum will require the development of platinum alternatives, which is very hard challenge to achieve. Recently alkaline fuel cell system has been enhancing their presence because of increased possibility of platinum group metal (PGM)-free catalysts and low overpotentials at cathode reaction furthermore. Additionally, several studies have been carried out on the ethanol oxidation in alkaline media due to a possible use of this alcohol as a fuel in alkaline fuel cells because ethanol is not only the most environmentally friendly liquid fuel but also can offer many of advantages in terms of mass production from agricultural products as well as fermentation of biomass. However, for commercialization aspects of ethanol fuel cells, one of the big technical challenges is to reduce the material cost, mostly Pt based precious metal electrocatalysts.

In this study, we report on our approach, which are based on electrospinning and pyrolysis, to prepare PGM-free catalysts to enhance the electrocatalytic activity for oxygen reduction reaction as well as ethanol oxidation in alkaline media. Furthermore, the electrochemical and morphological nature of the catalysts was characterized together with electronic state of surface region.

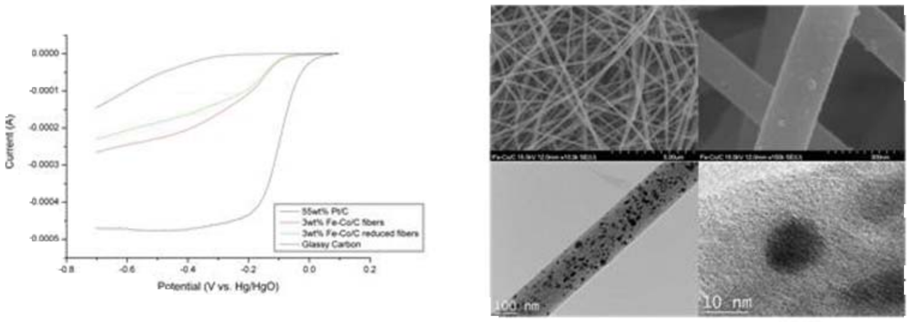

Figure. Current voltage polarization curves of oxygen reduction reaction (left) and FE-SEM & TEM images (right) of Fe-Co-N in carbon nanofiber prepared by electrospinning and subsequent pyrolysis.

Biosensing with SPR-active surface: Exploring cell-surface phenomenon in combination with electrochemistry and mass spectrometry

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Cell membrane, exemplifying an ordered and dynamic supramolecular system, is critical to many biological processes, including signal transduction, energy metabolism, and cell division and adhesion. The specific molecular recognition at the cell surface plays an extremely important role for these processes. This seminar discusses our recent research efforts in the exploration and understanding of molecular recognition –based cell surface phenomenon with a supported lipid membrane interface in combination with surface plasmon resonance (SPR) spectroscopy and electrochemistry. Stress will be placed on micropatterning of lipid layers for obtaining a high degree control of the membrane structure and creation of hydrophilic "patches" into which specific membrane components are introduced in a spatially defined manner for electrochemical characterization. Two examples, ligand-protein interaction and transmembrane pore formation with bacterial toxins, will be discussed in details. Analytical implication of the systems for ultra-sensitive detection of proteins by electrochemical methods will be presented. In addition, the development of nanoscale calcinated silicate layers on a gold substrate and their application in biosensing will be discussed. This method generates a glass-like surface suitable for preparation of supported bilayer membranes, allowing convenient characterization of molecular interactions on the membrane by SPR. Use of photolithographic techniques to pattern the silica layers will be demonstrated for building nanoscale 3D microarrays on the hybrid chips for analysis with imaging SPR. Finally, a new method that combines SPR and laser desorption/ionization mass spectrometry on the calcinated chips will be presented for protein analysis with high sensitivity.

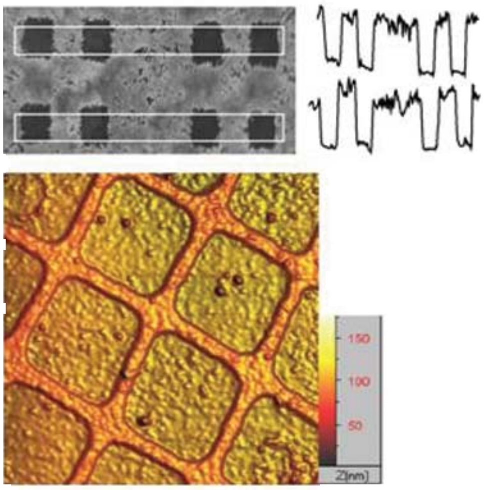

Figure. Top: SPR image and reflectivity profile of an array of 200µm x200µm wells. Bottom: AFM image of 30-layer calcinated film etched with 0.1M HF. A 1000-mesh TEM grid was used as the photomask.

Bioelectricity and biohydrogen production through biocatalyzed electron harvesting from organic compounds in microbial fuel cell-based systems

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Global warming, pollution, and energy challenges are becoming major concerns as an inevitable consequence of the increasing energy demand for fossil fuels. This has encouraged the production of hydrogen, a clean and efficient energy carrier, as an alternative to fossil fuels. A microbial fuel cell can supply bioelectricity or even biohydrogen in a promising way. The MFC is a device that converts organic compounds to bioelectricity with the assistance of a biocatalyst. The specific biocatalysts on the anode, such as exoelectrogens capable of producing an electrical current, use organic compounds as electron donors and an insoluble electrode as an electron acceptor to produce electricity. The MFC can be modified to produce hydrogen instead of bioelectricity by boosting the electrochemical potential achieved by anode bacteria with a small voltage addition. This modified MFC is termed to be a microbial electrolysis cell (MEC).

This paper deals with biocatalytic reactions on the anode, such as an exocellular electron transfer, representative exoelectrogen species, and cathodic proton reduction to hydrogen with and without catalyst assistance. MECs typically use both external bias and Platinum as a cathode catalyst to reduce high overpotential for proton reduction. This is a major disadvantage of conventional MECs. Therefore, this work also shows a dye sensitized solar cell (DSSC)-powered MEC without a Pt catalyst on the cathode. Ruthenium-based DSSCs were used to harvest light energy for use as an external power, instead of using fossil fuel-based electricity (Figure).

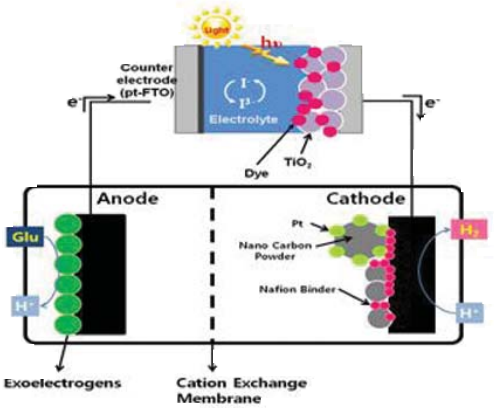

Figure. A schematic diagram of a dye sensitized solar cell (DSSC)-powered MEC with a non-catalysed cathode electrode.

Synthesis of high performance Cu-based catalysts active in the conversion of carbon dioxide to methanol

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Cu-based catalysts, e.g. the well-known Cu/ZnO/Al_2O_3 system, are active in industrial methanol synthesis, which ranges among the top ten most important processes in chemical industry. It has been pointed out by Olah[1] that methanol, moreover, may play an important role in the future as a CO_2-neutral chemical storage molecule for hydrogen via the methanol steam reforming and CO_2 hydrogenation reactions.

These new fields of application and further efficiency optimization of the industrial methanol synthesis require continuous and knowledge based improvement of the already empirically highly optimized Cu/ZnO/(Al_2O_3) system. In this contribution the technically applied way of catalyst synthesis is described and a concept is discussed[2], which identifies the key role of the carbonate precursor material and helps rationalizing the success of this particular multi-step preparation route (Figure. a).

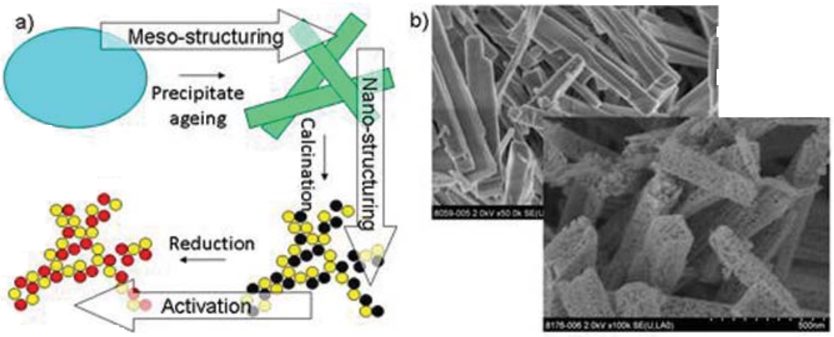

Figure. (a) Schematic representation of the general catalyst preparation comprising precipitate, precursor, calcined and reduced material – (b) SEM of a formate derived sample on the stage of precursor and calcined material with hierachial porosity.

Based on this insight, alternative novel precursor compounds for high performance Cu/ZnO/(Al_2O_3) catalysts are presented, such as hydrotacite-like compounds[3], mixed formates (Figure. b) or spinell phases. These precursors result in catalysts of unique microstructure, small copper nano-particles and interesting catalytic activities.

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Deterministic and stochastic modelling of catalytic surface processes

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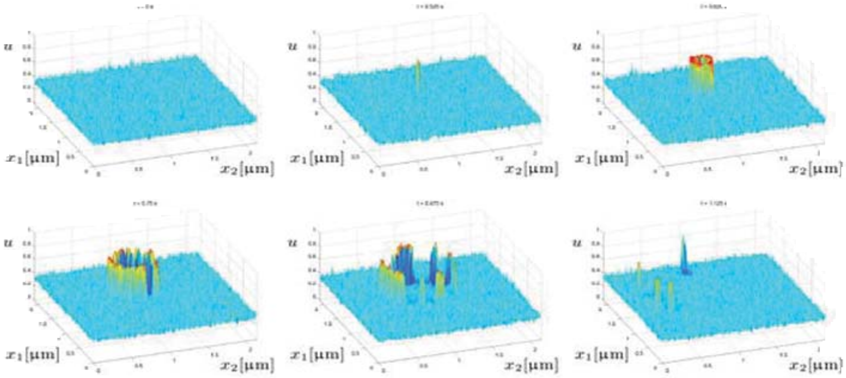
Three levels of modelling, the microscopic, the mesoscopic and the macroscopic level are discussed for the CO oxidation on low-index platinum single crystal surfaces. The introduced models on the microscopic and mesoscopic level are stochastic while the model on the macroscopic level is deterministic. The macroscopic description can be derived rigorously for low pressure conditions as limit of the stochastic many particle model for large particle numbers. This is in correspondence with the successful description of experiments under low pressure conditions by deterministic reaction-diffusion equations while for intermediate pressures phenomena of stochastic origin can be observed in experiments. The introduced models include a new approach for the platinum phase transition which allows for a unification of existing models for Pt(100) and Pt(110). The rich nonlinear dynamical behaviour of the macroscopic reaction kinetics is investigated and shows good agreement with low pressure experiments. Furthermore, for intermediate pressures, noise-induced pattern formation, so-called raindrop patterns which are not captured by earlier models, can be reproduced and are shown in simulations.

This is joint work with M. Eiswirth, K. Oelschlaeger and C. Reichert.



Potential shock method for through-hole TiO_2 nanotubes

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Herein, we describe an electrochemical potential shock method to prepare through-hole nanotubular membranes of anodic TiO_2 on the basis of the removal of the barrier layer (Figure.). Pores in the barrier layer can be homogenously opened by the abrupt increase in the potential within 10 s. The pore opening corresponds to the breakdown of the center of the barrier layer through the massive diffusion of the F^-ions, which are triggered by the significantly high potential (here, > 80 V). The potential shock voltage and time are optimized based on the breakdown mechanism. The shape of the opened pores is likely a truncated cone, where the outlet is larger than the inlet. These results correlate well to the anion movement, which is confirmed by the XPS data. The method described in this work exhibits very rapid and homogenous pore opening in the barrier layer of anodic titanium oxide, resulting in the facile formation of a uniform through-hole membrane.

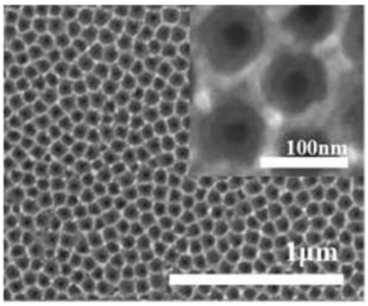

Figure. Homogenously opened TiO_2 pores by the potential shock method.

Molecular electrocatalysis at soft interfaces: Oxygen reduction by amphiphilic porphyrins

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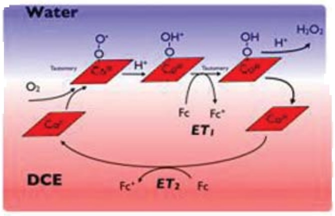
When a molecular catalyst is adsorbed at polarised liquid-liquid interfaces, it is possible to vary the interfacial polarisation to drive catalytic reactions. This defines molecular electrocatalysis.

Within a European COST program, our groups have studied oxygen reduction at polarised interfaces between an aqueous solution containing protons and an organic solution in 1,2-DCE containing electron donors such as metallocenes.

Here, we shall report the synthesis of amphiphilic porphyrins such as cobalt 2,8,13,17-tetraethyl-3,7,12,18-tetramethyl-5-*p*-amino-phenylporphyrin (CoAP) and the free base analog H_2FAP. We have characterised the adsorption properties of these amphiphilic molecules by surface tension and capacitances measurements.

We shall report how both the metallated and free base porphyrins catalyse oxygen reduction as studied by voltammetry and by biphasic reactions with analysis of the products. In particular, we shall discuss the catalytic reaction mechanisms and show how the reaction is electrocatalytic as its rate depends on the applied Galvani potential difference between the two phases



Preliminary studies of molecular electrocatalysis at the water/supercritical CO_2 interface will also be presented.

References

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Photocatalytic activity of various TiO_2 nanostructures

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Activities of various TiO_2 nanostructures in photocatalytic decomposition of methylene blue and toluene were determined in order to shed light on the relationship between structures and photocatalytic activity. Commercially available P-25 samples were used in the present work. In addition, TiO_2 nanostructures were synthesized using atomic layer deposition (ALD). We show that change in the surface structure of TiO_2 upon variois surface treatments results in variation in photocatalytic activity. In particular, increase in the number of OH groups on the surface leads to the enhancement in photocatalytc activity. Surface OH groups increases adsorption reactivity of organic reactants, thereby increasing activity in photocatalytic decomposition of methylene blue and toluene.

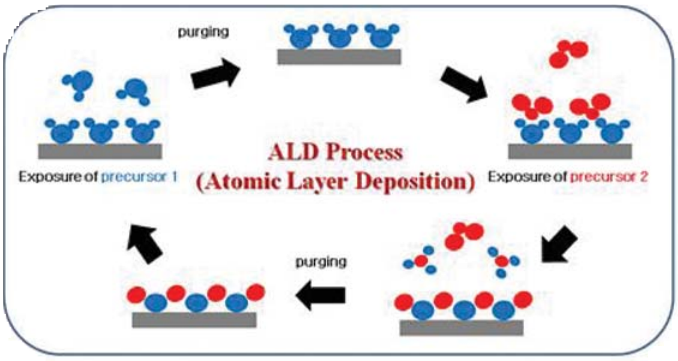

Figure. Schematic description of the ALD process.

Charecterization of catecholamines electrochemical sensors

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Catecholamines and among them adrenaline (A), noradrenaline (NA), and dopamine (DA) are of the greatest biological importance[1] playing an important role in living organisms. The development of novel drugs and treatments for neurodegenerative diseases relies on the analysis of cathecolamines often by chromatographic separations with electrochemical detection.[2] Electrochemical sensors could play a relevant role on the in-situ monitoring of catecholamines release from tissues or cells, however, one of the main problems in electrochemical catecholamines determination is the strong effect of the pH on the electrochemical behaviour of the catecholamines (see figure) and the modification of the working electrode by a polymeric film formed by the oxidation of the catecholamines resulting in a degradation of the analytical performance of the sensor. Results will be presented and measurement strategies will be discussed in order to improve the determination of catechoamines in buffer solutions.

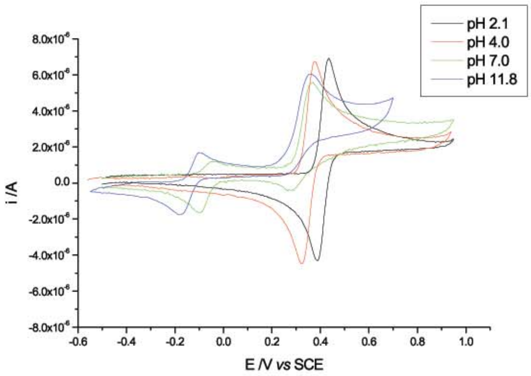

Figure. Effect of pH on dopamine electrochemical behavior. (gold working electrode, scan rate: 50 mV/s).

Acknowledgments:
The authors are grateful to FCT and FEDER under project PTDC/QUI/69685/2006 for financial support. J.A. Ribeiro acknowledges FCT for a PhD grant SFRH/BD/45492/2008.

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Electrocatalysis at gold

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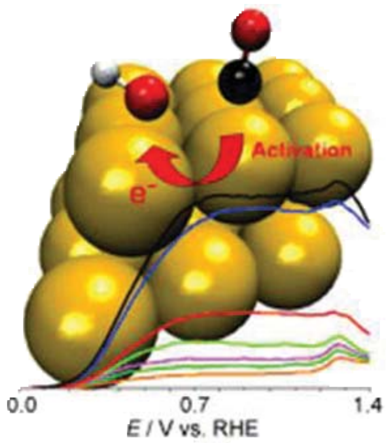
Although gold is known as the most noble of all metal electrodes, and therefore typically not active as an electrocatalyst, under certain circumstances gold is able to catalyze various electrochemical reactions, even those normally assumed to involve strongly adsorbed intermediates. In this talk, I will summarize some of our recent observations of gold electrocatalysis, with special attention to the oxidation of carbon monoxide, for which gold appears to be the most active catalyst in alkaline media. Some possible explanations will also be discussed, in particular our recent self-promotion model for gold electrocatalysis.[1]



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Role of bridge-bonded formate in formic acid electrooxidation on Pt: Reaction intermediate or site-blocking spectator?

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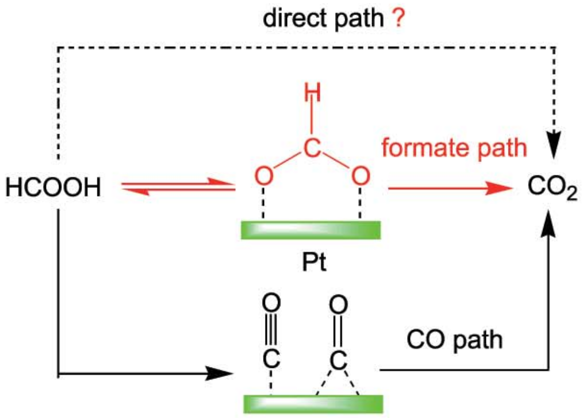
Electrocatalytic oxidation of formic acid to CO_2 on Pt has been studied extensively as a model electrocatalytic reaction. Now it is generally believed that formic acid is oxidized via the so-called dual path mechanism; one path though a reactive intermediate and the other through a poisoning species, adsorbed CO formed by dehydration of formic acid (CO-path). However, the reactive intermediate in the former path (non-CO path) has not been determined definitely.

Samjeské et al.[1-3] suggested that bridge-bonded formate is a reaction intermediate in the oxidation (formate-path), while Chen et al.[4] claimed in the follow-up work that adsorbed formate is a site-blocking spectator rather than the reactive intermediate and proposed that formic acid is directly oxidized via weakly adsorbed molecular formic acid (direct-path). In this paper, we will discuss that the formate-path is the main contributor and the direct-path does not work if any.



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Tuning surface electrocatalytic reactivity using core-shell structural concepts

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Core-shell architectures are attractive structural concepts for the rational design of improved catalysts for surface electrochemical reactions. For instance, core-shell catalysts showed improved reactivity combined with drastically reduced Pt content for oxygen electroreduction, hydrogen electrooxidation or carbon monoxide electrooxidation – all key reactions in the area of electrochemical energy conversion and storage. Given the number of electrochemically active elements, bimetallic core-shell architectures alone should offer a large number of catalysts with distinct geometric and electronic surface structures. Since surface electronic structure controls the chemisorption properties and, thus, ultimately the catalytic reactivity of surfaces, bimetallic core shell catalyst offer in principle a rational way to tune surface catalytic activity, limited only by our synthetic capabilities and the stability of the targeted structures.

Here, we will discuss recent progress in the area of core-shell electrocatalysis for fuel cell relevant electrocatalytic reactions. We will compare and contrast the two prominent and promising “monolayer ” and “skin’ core-shell concepts (Figure. b,c), and will critically discuss multi-layer shell catalyst architectures obtained by deliberate dealloying of precursor materials (Figure. d,e). In recent work we have greatly improved our atomic-scale understanding of the origin of the improved activity of such dealloyed core shell catalyst materials.

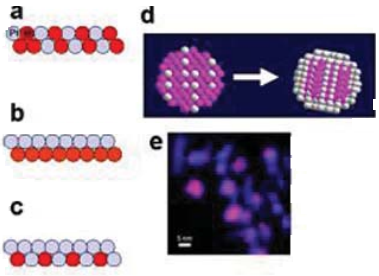

Figure. Bimetallic core shell structural concepts for electrochemical catalysis. a) ideal non-core shell (uniform) bimetallic catalyst b) “Monolayer” catalyst c) “Skin” catalyst. Shown are the top two surface layers of the catalyst. d) schematic illustration of the formation of core shell nanoparticle catalysts by preferential electrochemical dissolution (dealloying); e) STEM EDX of dealloyed Pt core shell catalyst (red=Cu, Blue=Pt). Scale bar 5nm.

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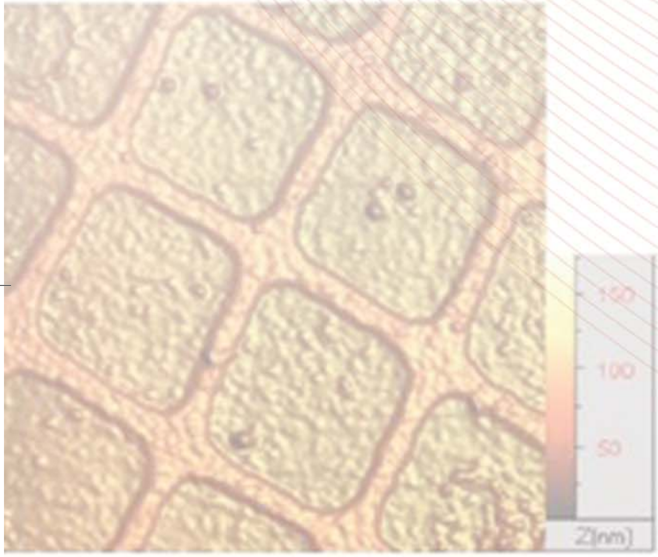

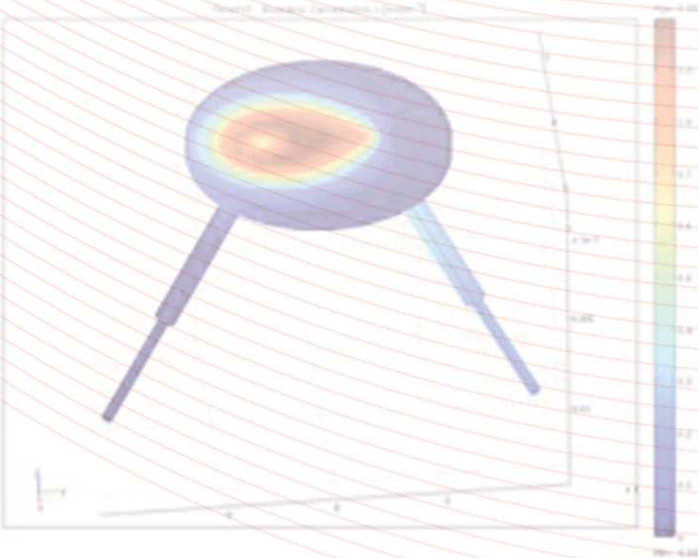

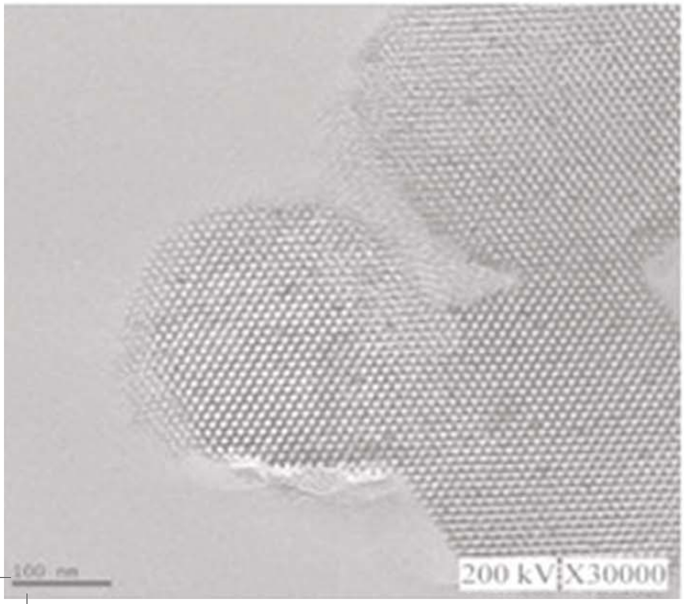

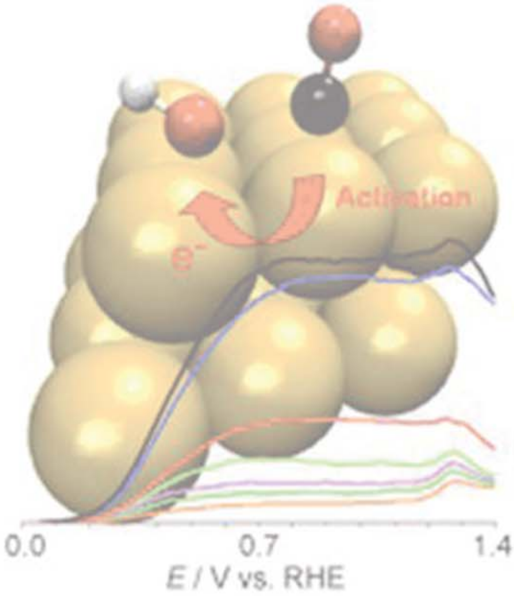

PtRu alloy catalysts on carbon aerogel for DMFC application

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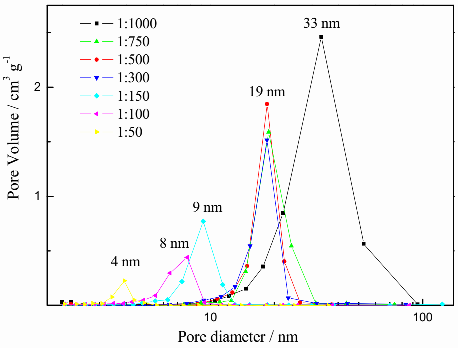
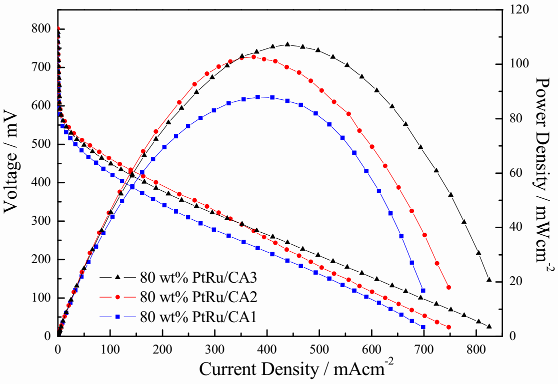
Carbon aerogel is a very useful supporting material for DMFC. It has advantages of large surface area, good conductivity, great meso-porous volume and continuous porosities and these properties are necessary for DMFC application.

We focused on high-loading catalyst (80 wt%) supported on carbon aerogels with different meso-pore sizes. It is important to have meso-pores because methanol can penetrate easily and carbon dioxide goes out through the channel. So, it is expected to improve mass transport and, thus, improves overall performance of a unit cell.

We synthesized carbon aerogels having several pore sizes and prepared high-loading PtRu catalyst on each carbon aerogel.

PtRu catalysts on carbon aerogel were examined by HR-TEM for morphology, and they were very uniformly dispersed throughout all carbon support. In addition, they exhibited better overall performance compared with catalysts supported on different carbons in unit cell and CV. It is interesting to know that the particle size was larger that that on conventional carbon supports calculated from the Scherrer equation. Details of experiments and results will be discussed.





Shape dependent electro-catalytic activity of nano-gold

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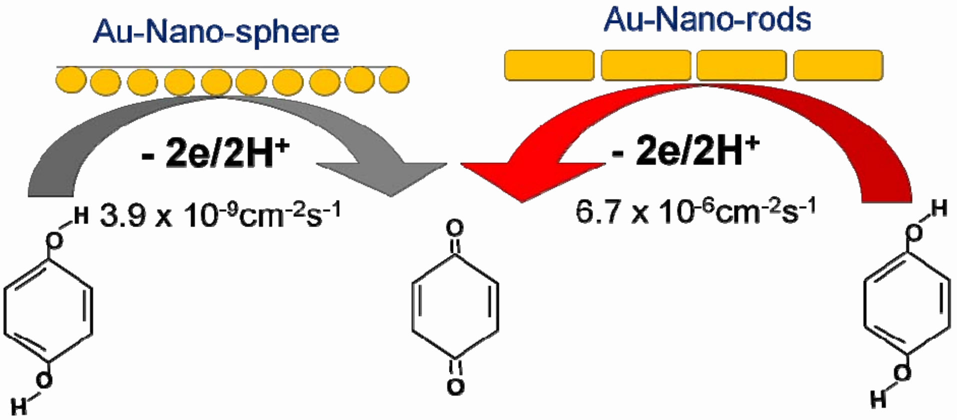

The shape dependent electrocatalytic activity of gold in nanosize regime (AuNPs) for quinone/hydroquinone (Q/HQ) redox system is described. spherical and rod shaped AuNPs stabilized with CTAB were synthesized for this purpose. The AuNPs modified electrodes were prepared by using 3-mercaptopropionic acid (MPA) as a linker. The surface structure of AuNPs was characterized by the under potential deposition of Pb^{2+} method, which revealed significant variation in surface structure as function of shape. The electro-catalytic activity of spherical and rod shape AuNPs toward HQ redox reactions was investigated, using a cyclic voltammetry. The heterogeneous electron transfer rate constant (k_s) and transfer coefficients (a) were evaluated using Nicholson's method. In case of spheres, k_s was found to be three orders of magnitude lower than that of rod as well as bulk gold, which suggested the significantly different in the surface structure of spheres than rods/ bulk.

Enhanced open-circuit voltage by hydrophilic ionic liquids as buffer layer in conjugated polymer - Nanoporous titania hybrid solar cells

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The porous titanium dioxide (TiO_2) network structure was synthesized using a poly (stylene-block-poly 4-vinylpyridine) (PS-b-P4VP) diblock copolymer template and influence of molecular weight of PS-b-P4VP on the nanoporous structure of TiO_2 was studied. We have fabricated a hybrid solar cells based on nanoporous TiO_2 (NP-TiO_2) and poly (2-methoxy-5-(2’-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV). The effect of hydrophilic ionic liquids (ILs) layer, 1-butyl-3-methylimidazolium tetrafluoroborate (bmim-BF_4) and 1-benzyl-3-methylimidazolium chloride (benmim-Cl), as a function of concentration between the MEH-PPV layer and TiO_2 layer on the solar cell performance was investigated. The device with bmim-BF_4 and benmim-Cl IL layer showed enhanced open-circuit voltage (V_{oc}) of 1.05 V and 0.91 V, respectively, while reference device without IL layer exhibited V_{oc} of 0.60 V. Significantly improved V_{oc} can be attributed to tuning of internal electric field by interfacial dipole between MEH-PPV and TiO_2 layer in the presence of the IL buffer layer.

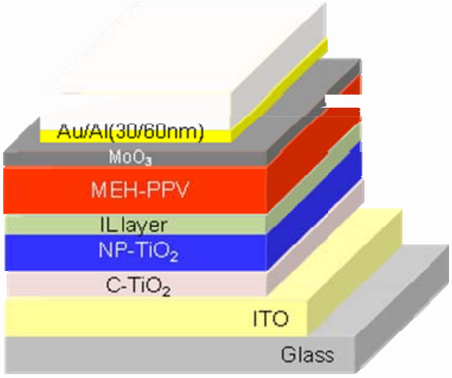

Figure 1. Device structure of MEH-PPV:NP- TiO_2 hybrid solar cells with IL layer.

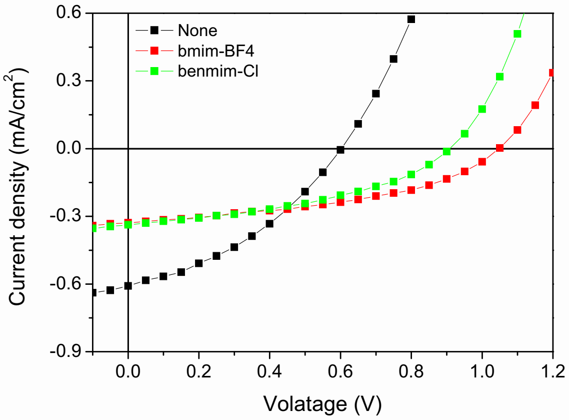

Figure 2. Current – voltage characteristics of MEH-PPV:NP- TiO_2 hybrid solar cells with IL layer.

Method for improving catalytic activity of pure ruthenium for oxygen reduction in polymer electrolyte fuel cells

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The development of well-performing inexpensive and easily accessible non-platinum catalysts has become a major challenge for PEFCs. In addition, platinum-based cathode catalysts have an additional disadvantage of being methanol-tolerant, which leads to the performance and efficiency losses due to the formation of a mixed potential. Unlike Pt, several classes of alternative oxygen reduction reaction (ORR) catalysts promise to be either fully or partially methanol-tolerant, thus providing additional benefits for DMFCs, particularly for mixed-reactant DMFC design. Of such materials, the most promising materials are transition metal chalcogenide, pyrolyzed macrocyclic compounds and various composite materials. Unfortunately, no catalyst alternative to platinum has reached the level of ORR activity and performance stability of platinum and platinum-based alloys.

In this presentation, we demonstrate that respectable performance enhancement of pure ruthenium cathode can be achieved by electrochemical reduction. Figure shows H_2-air fuel cell performance for Ru cathodes before and after the electrochemical reduction at 80°C. The performance of hydrogen-air fuel cell with as-received Ru cathode was relatively poor because commercial Ru black consisted of lots of ruthenium oxides which are not favorable to oxygen reduction. After the electrochemical reduction of as-received Ru, the performance of reduced Ru cathode was greatly improved, compared to as-received Ru.

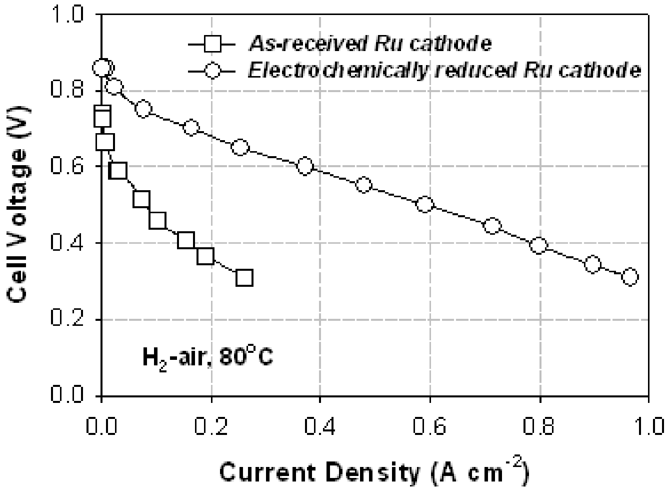

Figure. Performance test of Ru cathodes in a hydrogen-air polymer-electrolyte fuel cell. Cell temperature 80°C; H_2 flow 300 sccm; anode backpressure: 30 psig; air flow 466 sccm; cathode backpressure 30 psig.

Synthesis and Characterization of PtRuMoO_x/C for Direct Methanol Fuel Cells

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Degree of methanol oxidation reaction in anode is mainly decided by the performance of direct methanol fuel cell (DMFC). Generally, Pt was used as an anode catalyst in old days due to its' high catalytic activity but there were some drawbacks of Pt. High cost of Pt and CO poisoning of Pt were the drawbacks. To overcome these problems PtRu is prevailing as an anode catalyst. It is well known that Pt and Ru have bifunctional effect which promotes the elimination of CO adsorbed on Pt. However, PtRu catalyst may still have some limits to be commercialized in the industry. In order to improve the methanol oxidation reaction of the DMFC without losing performance or increasing cost searching for ternary catalyst is required. In addition, ternary catalysts need to be stable in acid condition and resistant to changes in surface properties. Therefore, MoO_x is appropriate material for the third component to aid Ru with CO oxidation or to reduce CO adsorption on Pt without surface changes.

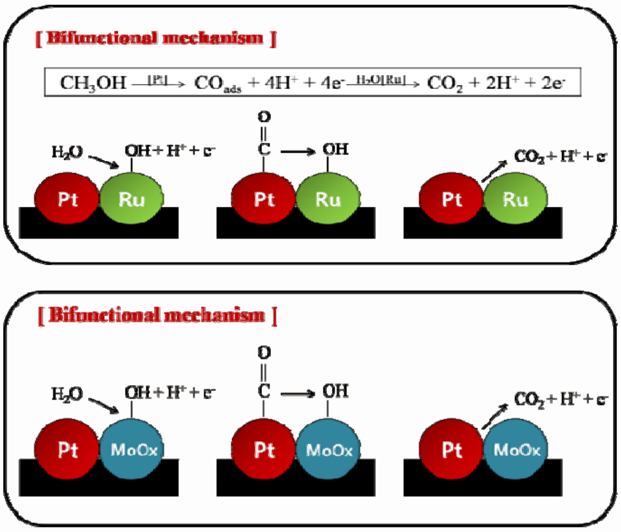

Figure. (a) Bifunctional mechanism of Pt and Ru (b) Bifunctional mechanism of Pt and MoOx.

Synthesis and characterization of high loaded Pt on functionalized graphene sheets for methanol oxidation

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Graphene sheets, mono-layers of sp^2 bonded carbon atoms arranged in a honeycomb network, are basic building block for graphitic materials, such as carbon nanotubes (CNT), buckyballs (C_{60}), and graphite. Also, these are promising candidates for catalyst supports of fuel cells due to its high specific surface area (theoretically, ca. 2620 m^2/g) and high conductivity, as long as they can be prepared through viable manufacturing process and provide high dispersion of Pt nanoparticles.

In this work, graphene-supported Pt catalyst was prepared via impregnation method of Pt precursor on functionalized graphene sheets that are synthesized by hydrothermal expansion of graphite oxide. The structure and morphology of the Pt nanoparticles on graphene characterized by X-ray diffraction (XRD: Figure. 1) and transmission electron microscopy (TEM: Figure. 2), revealing a uniform diameter of ca. 2.1 nm with fine dispersion. The graphene supported Pt catalyst (80 wt.% Pt/G) showed the better electrochemical mass activities over the methanol electro-oxidation than amorphous carbon supported Pt catalyst (20 wt.% Pt/C) and unsupported Pt catalyst (Pt black). This enhancement could be rationalized by unique structural and electrical properties of graphene, such as high specific surface area and high conductivity.

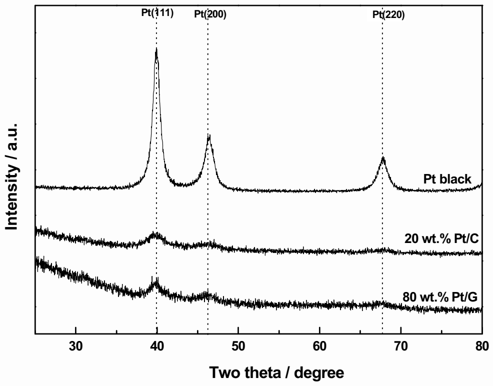

Figure 1. XRD patterns of Pt black, 20 wt.% Pt/C, and 80 wt.% Pt/G.

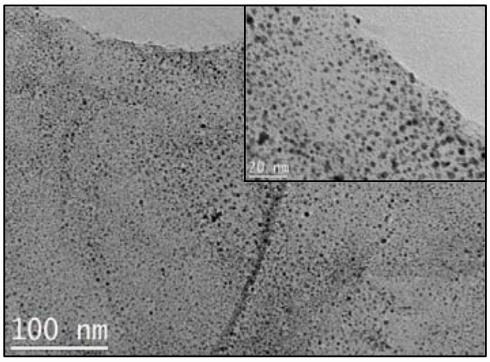

Figure 2. Representative TEM image of the 80 wt.% Pt/G.

Acknowledgments

This work was supported by the Korea Science and Engineering Foundation (KOSEF) NCRC grant funded from the Korean Government (MEST) (No. R01-2008-006-03002-0), by New & Renewable Energy R&D program (20093020030020-11-1-000) under the Ministry of Knowledge Economy, Korea.

Organic/inorganic composite membranes for high temperature proton exchange membrane fuel cells

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Recently, many researches have concentrated on the polymer electrolyte fuel cells (PEFCs) for a wide variety of their promising applications such as stationary power supply, electric vehicle, power sources in space and military. The commercialization of PEFCs, however, is being hampered by several serious obstacles such as the difficulty of water and temperature control, necessity of a large amount of expensive Pt catalyst, and its poisoning by carbon monoxide (CO). Nafion® membranes have been most widely studied and used in PEFCs because of their excellent chemical, physical, and electrical properties. The major drawback of the Nafion® membranes, however, is that the conductivity drops at temperatures higher than 100 °C due to the evaporation of water. The low thermal stability at high temperatures is also disadvantages of Nafion® for PEFC applications. In order to solve these problems, novel hydrocarbon polymer electrolyte membranes impregnated with sulfated ZrO_2 in the range of 1 – 10 wt% were developed for the application to high temperature proton exchange membrane fuel cells under the low relative humidification in this research. The thermal and morphological properties of the prepared membranes were characterized by TGA, DSC, SEM and TEM. The prepared membrane conductivities were also estimated with the various conditions of temperature and relative humidification. Finally the cell performance using an optimal one of the prepared membranes was evaluated at 120 °C with 50% relative humidification.

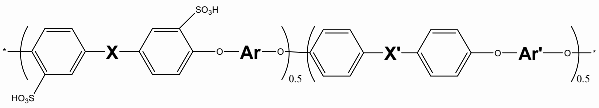

Figure 1. Synthesized sulfonated poly(arylene ether) sulfone.

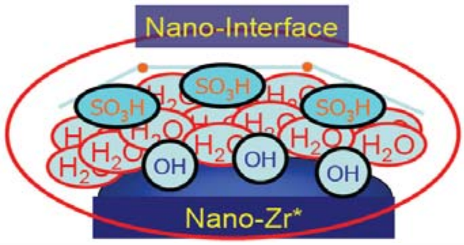

Figure 2. The schematic illustration of a nano interface between s-ZrO2 & SPES.

Preparation and characterization of anion exchange polymer electrolytes for solid alkaline fuel cell

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Anion exchange polymer electrolytes consisting of the whole hydrocarbon materials were prepared by photo polymerization with various quaternary ammonium cationic monomers and characterized with specific thermal and chemical analyses. They were also applied to pore-filling membranes and ionomers as the binder in the catalyst coated electrodes, anode and cathode, for solid alkaline fuel cells (SAFC).

In this study, the prepared anion exchange polymer electrolytes were synthesized without an amination process which is generally used for preparing anion exchange polymers. Hydrocarbon porous substrates such as polyethylene were used for the preparation of the pore-filling membranes. Furthermore, alkaline cell performances were evaluated using the membrane electrode assemblies prepared by these pore-filling membranes and ionomer binders.

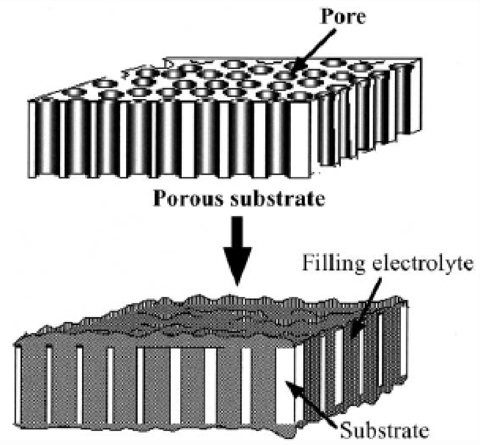

Figure 1. The concept of a pore filling membrane.

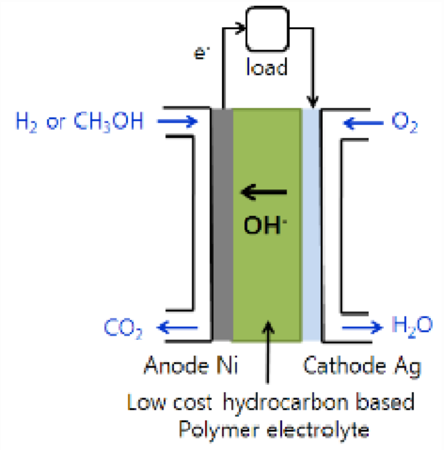

Figure 2. Solid alkaline fuel cell system.

Double layer in room temperature ionic liquids: Influence of temperature and ionic size on the differential capacitance and electrocapillary curves

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Ionic liquids provide a class of environment – friendly and safe solvents composed only by ions, one alternative that has been attracting much attention.[1,2] Little is known about the interfacial structure of these liquids at electrode interface.

Differential capacity – potential curves were obtained from electrochemical impedance spectra (12kHz-2Hz) for the interfaces between Hg and a series of alkyl imidazolium based room temperature ionic liquids having the same anion bis(trifluoromethylsulfonyl)imide [Tf_2N]: 1-Ethyl-3-methylimidazolium [EMIM][Tf_2N], 1-Butyl-3-methylimidazolium [BMIM][Tf_2N], 1-Hexyl-3-methylimidazolium [HMIM][Tf_2N]. The electrocapillary curves were obtained from drop time measurements and the values of the potential of zero charge (PZC) were calculated. The effect of temperature on the capacitance, drop time electrocapillary curve and on the PZC was also obtained. The PZC apparently becomes more negative as the imidazolium alkyl chain length increases.

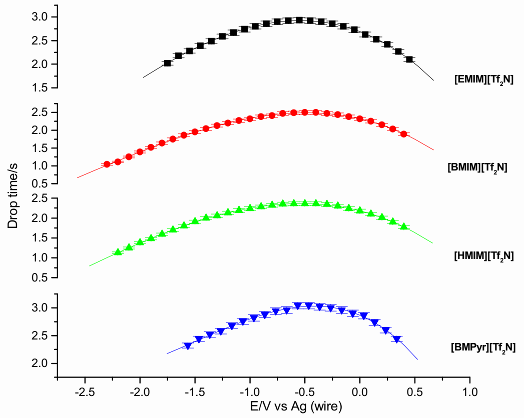

Figure. Electrocapillary curves measured at Hg/RTIL´s interface (20ºC).

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Real-time fuel monitoring sensors for direct formic acid fuel cells

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Formic acid is one of emerging liquid fuels for direct liquid fuel cells (DLFCs) due to its high efficiency on energy generation and relatively low toxicity towards our ecology. Implementation of fuel sensors, which control fuel concentrations in real time, into DLFCs could enhance fuel cell performance and efficiency.

In this presentation, we demonstrate two different types of fuel monitoring sensors for direct formic acid fuel cells; (i) Amperometric proton selective sensors based on assisted ion transfer reaction by proton selective ionophores across the micro-hole interface between the aqueous phase and the polyvinyl chloride-2-nitrophenyloctylether (PVC-NPOE) gel phase. Proton sensing properties of two different proton selective ionophores (i.e. dibenzo-18-crown-6 and ETH 1778) were studied using cyclic voltammetry (see Figure a) and differential pulse stripping voltammetry. (ii) Miniaturized surface plasmon resonance sensors measuring reflectivity changes upon the adsorption of fuels onto the thin gold film modified with -amine or carboxylic or hydroxyl functionalized alkane-thiol monolayers (see Figure. b). Both sensing platforms show good sensitivity and excellent reproducibility for measuring commonly used concentration ranges of formic acid.

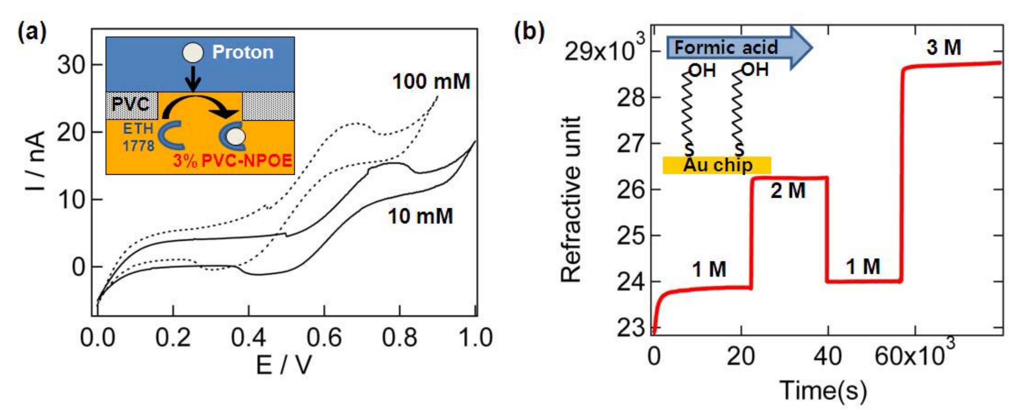

Figure. (a) Cyclic voltammograms for the assisted transfer of 10 and 100 mM H^+ ions by 10 mM ETH 1778 in the PVC-NPOE gel containing 10 mM BTPPATPBCl as a supporting electrolyte. Scan rate was 20 mV/s. (b) Real-time SPR detection signals for continuous monitoring of different concentrations of formic acid ranging from 1 M to 3 M.

Interfacial complexes between a protein and lipophilic anions at an oil-water interface

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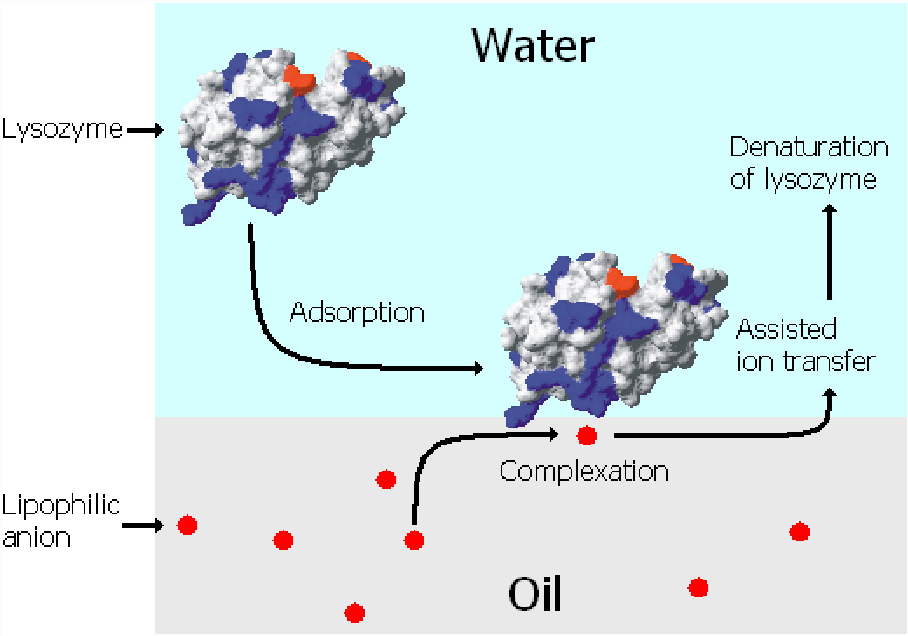

The interaction between an intact protein (lysozyme) and two organic ions an oil-water interface has been investigated using cyclic voltammetry, impedance based techniques and a newly developed method in which the biphasic oil-water system is analyzed using an electrospray ionization mass spectrometer (BESI-MS). It is found that the protein forms interfacial complexes with the lipophilic ions and that it specifically requires the presence of the oil-water interface to be formed under the experimental conditions. Furthermore, impedance based techniques and BESI-MS with a common ion to polarize the interface indicated that the Galvani potential difference across the oil water interface significantly influences the interfacial complexation degree. The ability to investigate protein-ligand complexes formed at polarized liquid-liquid interfaces is thus a new analytical method for assessing potential dependent interfacial complexation using a structure elucidating detection principle.

Adoption of Magnéli phase titanium oxides for the electro-catalyst of membrane electrode assembly in fuel cells

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For the commercialization of polymer electrolyte fuel cells (PEFCs), the durability is one of the key issues. The electro-catalysts have been thought as a core component for improving the durability of membrane electrode assembly (MEA) in PEFC research fields. The corrosion phenomena of conventional carbon-based supporting materials, i.e. Vulcan XC 72, were revealed as a main cause of MEA degradation. To overcome this problem, several research groups have focused on the development of noble supporting materials. In recent, metal oxides are getting much attention for their high corrosion resistivity even in a high cell potential condition. Among them, Magnéli phase titanium oxide (MPTO) showed a high possibility for the supporting material of electro-catalysts for its good electron conductivity as well as high corrosion resistivity. However, there is a restricted number of reports on the application of MPTO for the MEA of PEFCs.

This work aims at investigating the fuel cell performance of MEAs consisting of Pt/MPTO electro-catalysts. MEAs which have various Pt/MPTO electrode structures were evaluated by several electrochemical analyses such as I-V measurement, cyclic voltammetry, and ac-impedance spectroscopy, etc. Post-analyses for the tested MEAs were also conducted to check the changes in electrodes by SEM, TEM, XRD and so on. From the results, the MPTO showed a potential as a corrosion resistive support material for the fuel cell applications.

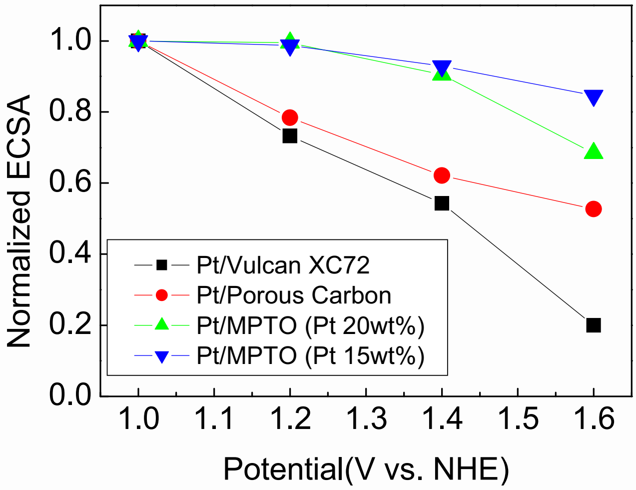

Figure. Comparison of electrochemical surface area (ECSA) changes of prepared catalysts.

Bacterial controls on the abundance of nano-sized mercury in semi-enclosed coastal waters

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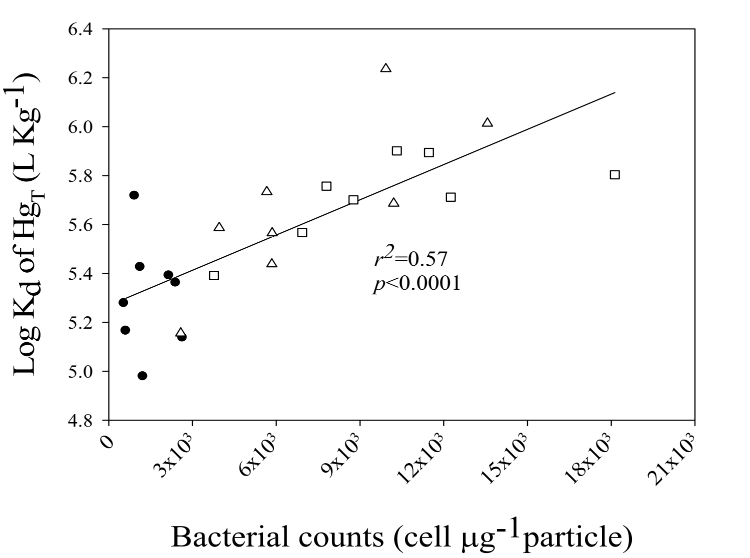
Mercury (Hg) cycling in coastal waters is known to be affected by the abundance of nano-sized (colloidal) particles; however, the role played by living organic particles in Hg cycling is not yet thoroughly understood. In the present study, we hypothesized that an abundance of living organic particles (i.e., marine bacteria and phytoplankton) would be associated with the abundance of nano-sized particles and the particle-water partitioning of Hg in coastal waters. Surface water samples were collected from 8 stations in Gwangyang Bay, Korea, in the wet (July 2009) and dry seasons (April and November 2009) for determination of Hg concentrations in unfiltered and filtered waters, concentrations of suspended particulate matter and chlorophyll-a, and bacterial abundance. A particle concentration effect – a negative linear relationship between log K_d (particle-water partition coefficient) and particle concentration – was demonstrated under low chlorophyll-a and high bacterial abundances, indicating that bacterial abundance is associated with the presence of nano-sized particulate Hg. In addition, mercury solubility decreased while bacterial abundance in total particle concentration increased, which was likely the result of the increased surface area of suspended particles associated with bacterial abundance. Overall, microbial abundance appears to be associated with the formation of nano-sized particulate Hg in surface coastal waters.



On the origin of reactive Pd catalyst in an electrooxidation of formic acid

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Direct formic acid fuel cells (DFAFCs) have been widely investigated since early 21st century due to their suitable properties such as high energy density, fast oxidation kinetics, and safety of liquid formic acid (HCOOH) for portable power sources. Pt and Pt-based catalysts have been intensively studied for anode catalysts. However, problems Pt-based catalysts associated with low activity due to CO poisoning and high cost constitute one of the main obstacles to using this material in DFAFC. Recently, Pd catalyst is being recognized as an alternative to Pt catalyst due to high activity and low cost. In spite of these advantages, deactivation of Pd-based catalysts was found to be much faster than Pt-based catalysts. Nevertheless, mechanism of this fast activity loss is still unclear.

In this work, we investigated regeneration of Pd, which electrodeposited on the carbon fiber substrate for the use of anode in DFAFC system. Surface study revealed that surface composition of Pd catalyst is significantly different at an active and a passive state. On the basis of analysis results, we show a simple method for regeneration of Pd catalyst and this method retards deactivation rate of Pd catalyst significantly.

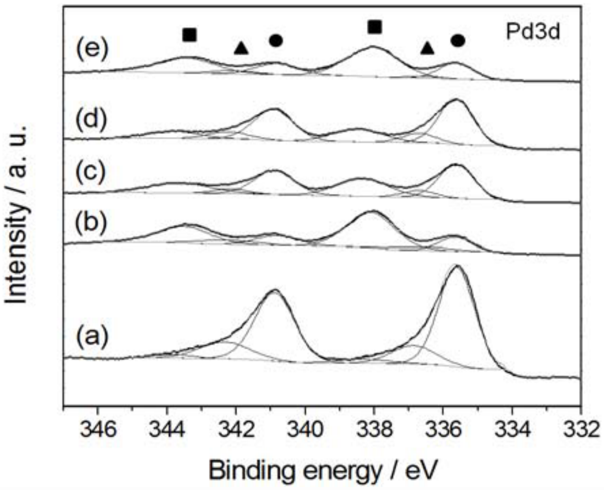

Figure. Pd_{3d} narrow scan spectra of the (a) as-prepared Pd, (b) after contact with formic acid at OCV, (c) after one cycle in formic acid, (d) after ten cycle in formic acid, and (e) after regeneration (●: Pd, ▲: PdO, and ■: PdO_2).

Size-oxophilicity relationships of carbon-supported Pt nanoparticles for oxygen reduction reaction

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It has been discovered that as the size of metal nanoparticles decreases, its oxophilicity increases.[1] This phenomenon is directly related to the shift of the redox potential with cluster size in colloid chemistry.[2] The increased oxophilicity originates from the decrease in the number of nearest neighbors of a Pt atom. The decrease in the coordination number of Pt atoms causes the further narrowing of d-band of surface Pt atoms and the substantial increase in the binding energy with the oxygen-containing species such as the important intermediates during oxygen reduction reaction (ORR), *i.e.*, O, OH, OOH, and O_2. This results in higher overpotential for ORR.[3]

X-ray absorption near-edge structure (XANES) analysis generally shows that the white-line intensity increases with smaller particle size. It means that the smaller particle has the lower fractional d-band occupancy. From experimental results including X-ray absorption spectroscopy (XAS), the particle size effect should be still an issue for electrocatalysis. This study is, therefore, aimed for elucidating the particle size effect on the ORR and the oxidation state of Pt nanoparticles.

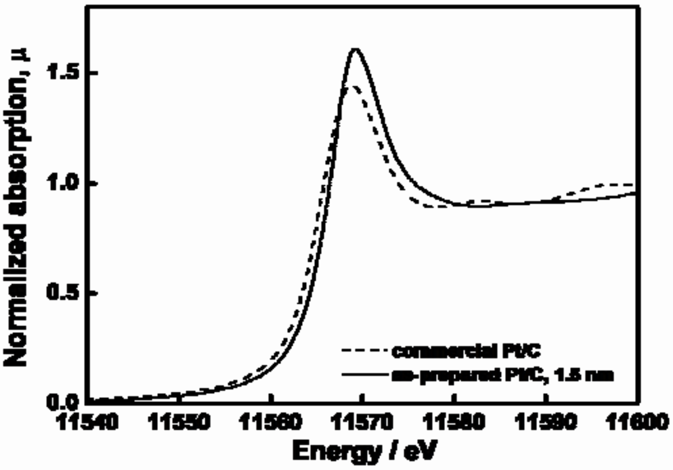

Figure. XANES spectra of Pt L_{III} edge for Pt nanoparticles with different mean sizes.

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Carbon anode thin films for all-solid-state thin film batteries

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Much attention have been paid to the rechargeable thin film lithium ion batteries, which have great potential for application in smart cards, integrated power circuits and RF sensors etc. Lithium thin film, which is originally used as anode materials for its highest specific capacity(3.86 Ah/g) and good cyclability, need special packaging layer to protect from moisture in atmospheric conditions. One of simple packaging is to encapsulate the lithium using metal or ceramic pouch by special adhesives, but it can not protect side attack through the polymer based adhesives. The advanced packaging is to coat the organic/inorganic multi-layers. However, it also has difficulties in perfect sealing when it can not fully cover the large particles or cause pin-holes. Thus, it is necessary to substitute lithium metal for other proper anode materials. Carbon can reversibly intercalate or de-intercalate lithium ions without significant swelling under prolonged cycling unlike other lithium metal alloys which show several hundred percent volume expansions. It can deliver many advantages of no dendrite formation, process compatibility and relatively low packaging regulations. Carbon is refractory, hard vaporized material condensing in amorphous state(onto low substrate temperature), and its anode properties depend on the condensation conditions.

In this work, we made an effort to use simple DC sputtering method for variation of chamber pressure and post-annealing temperatures. To analyze the film structures, Raman and XPS were also used. Figure 1 shows the potential profiles of the carbon thin films which were deposited at 16mTorr and room temperature. Test condition was at a 1/10C rate from 2V to 0V(vs.Li/Li$^+$) range. There was initial irreversible capacity loss but it was stabilized to a discharge capacity of 100uAh/cm^2-um after 2 cycles. From this result, we understood that carbon thin films are very promising alternatives for conventional lithium in a thin film batteries.

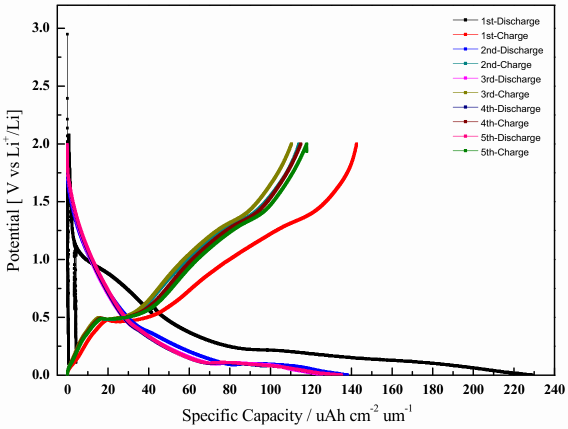

Figure. The charge and discharge curves of the carbon thin film during 5 cycles.

Preparation of electrospun manganese oxide/carbon nanofibers composite electrodes for electrochemical capacitors

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Manganese(II) oxide (MnO)-embedded activated carbon nanofibers (ACNF) composite electrodes for electrochemical capacitors were synthesized by stabilizing and activating after electrospinning the composite solution of manganese nitrate and PAN in N, N–dimethylformamide (DMF). In this study, the MnO-free carbon nanofiber electrode is defined as a CN electrode. The 1.67, 4.16, 6.80 and 10.04 wt % MnO-embedded carbon nanofiber electrodes are defined as the MnO-CN1, MnO-CN2, MnO-CN3, and MnO-CN4 electrodes, respectively. The MnO particles were well dispersed within ACNF, and the MnO particles were distributed ranging from 5 to 25 nm with increasing the contents of MnO. The specific capacitance of MnO-free ACNF was 140 F/g, while that of 10.04 wt % MnO-embedded ACNF increased to 276 F/g as the improvement of 197 %. Eventually, the above results lead to the enhancement of electrochemical performance by inducing the synergic effect of both electrical double capacitance (EDLC) and pseudocapacitance (PC). Finally, the structure changes of MnO within ACNF after 1000cycle was investigated with the Extened X-ray Absorption Fine Structure(EXAFS).

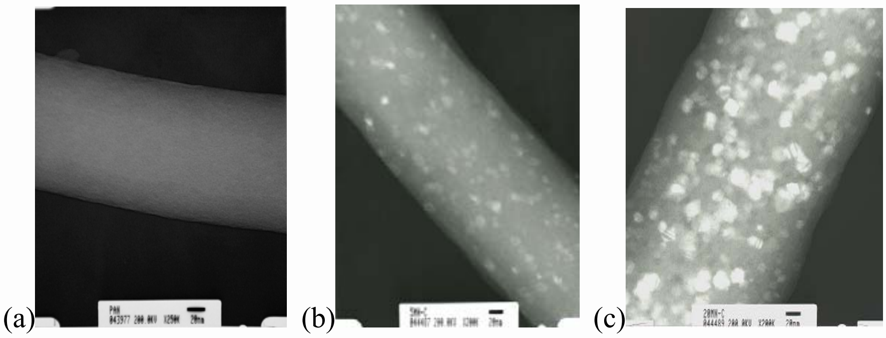

Figure. TEM images of (a) CN, (b) MnO -CN1 and (c) MnO-CN4.

Facile method for the fabrication of nickel oxalate nanostructures and their supercapacitor applications

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Herein, the facile method to produce nickel oxalate nanostructures is described based on chemical reaction of oxalic acid and a nickel foil in various organic solvents and water. The chemical reaction in all solvents leads to produce grass-like structures consisting of nickel oxalate 30 min. Interestingly, nickel oxalate nanowires can be produced by the addition of small amount of water in certain solvents. The contents of water increases, the diameter of formed nickel oxalate nanowires becomes large since absolute amount of H^+ and OH^- increases. The H^+ and OH^- promote dissolution of nickel, making free nickel ions in the solution. Self-complex of nickel oxalate, which is the source for the precipitation, is formed in a solution containing nickel ions and oxalate ions. As a result, directionally grown nanowires are prepared by preferential precipitation. Nickel oxide structures can be produced by the annealing of nickel oxalate structures under optimize conditions. Compositions of the nanostructures are investigated by TEM and FT-IR analysis. In addition, supercapacitance of nickel oxalate nanostructures is characterized, showing that it is superior to that of nickel oxide nanostructures.

Figure. Nickel oxalate nanowires prepared by the immersion of a nickel foil in ethanol solvent containing oxalic acid.

Effect of catalyst ink preparation on catalyst layer structure for direct methanol fuel cells

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The problem such as mixed potential by the methanol crossover should be solved for DMFC to be commercialized. Methanol is transported from anode catalyst layers to cathode catalyst layers through a polymer membrane and reacts in the cathode together with oxygen. Some of the catalyst surfaces in the cathode may be occupied by methanol instead of oxygen, and Pt utilization for the oxygen reduction reaction (ORR) could be decreased. Accordingly, more excessive Pt catalysts in the cathode are needed to overcome the methanol crossover effect as well as the poor kinetics of the ORR in the cathode.

To mitigate the methanol crossover effect and to decrease Pt loading in the cathode, a MEA with improved cathode electrode structure is fabricated by new catalyst ink preparation method in order to maximize Pt catalyst utilization for the ORR in cathode despite methanol crossover. A two-step ink preparation is conducted to regulate the solvent polarity in the catalyst ink solution, which results in the structural changes of the cathode catalyst layer. Consequently, the MEA exhibits higher performance at low and high methanol concentrations, and has larger electrochemical active surface (EAS) than traditional MEA.

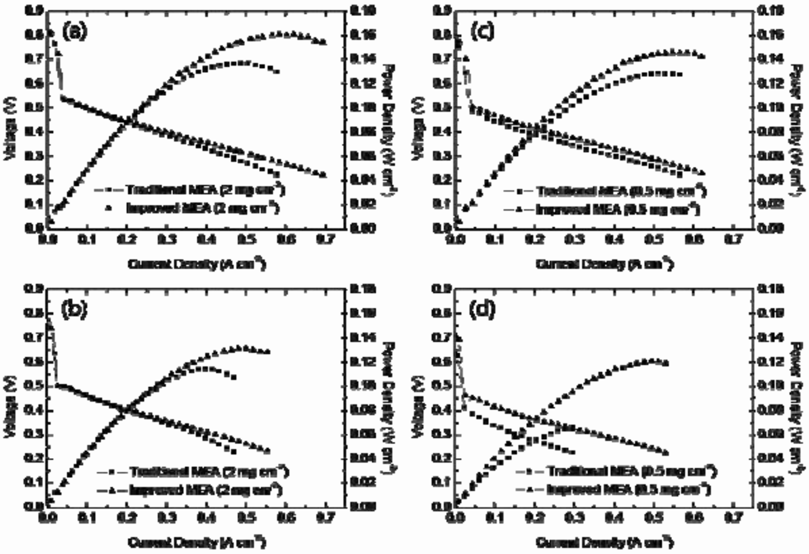

Figure. Polarization curves of MEAs with Pt loading of 2 mg cm^{-2} in cathode at methanol concentrations of (a) 1 M and (b) 3 M. Those with Pt loading of 0.5 mg cm^{-2} in cathode at methanol concentrations of (c) 1 M and (d) 3 M.

Synthesis and electrochemical properties of IT-SOFC unit cell using ScSZ-based electrolyte powder via co-precipitation

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Scandium-doped zirconium, ScSZ-based electrolyte, provides higher oxygen conductivity than YSZ, and nano-based electrolyte materials are ideal for fabricating thin film electrolyte membrane of SOFC unit cell. In this report, CeScSZ powders were prepared via the co-precipitation process, then fabricated using the tape-casting and co-sintering techniques as an anode-supported electrolyte with a thin (6-µm) electrolyte layer which is applied to anode and cathode as well as electrolyte as ionic conductor. The characteristic of the powders was analyzed by X-ray diffraction and thermal analysis. Also, its particle size, surface area and morphology of the powders were observed by BET, SEM and TEM. The open-circuit voltage (OCV) of the unit cell was 1.05 V at 800°C, indicating the negligible leakage of fuel through the electrolyte layer. The operating voltages of the SOFC unit cell at the current density of 1.5 A/cm^2 were 0.4, 0.60, 0.62, and 0.80 V at 700, 750, 800, and 900°C, respectively as Figure. The electrolyte of the SOFC unit cell with a thin layer and good conductivity exhibits good performance due to the drastic reduction of the ohmic and polarization resistances.

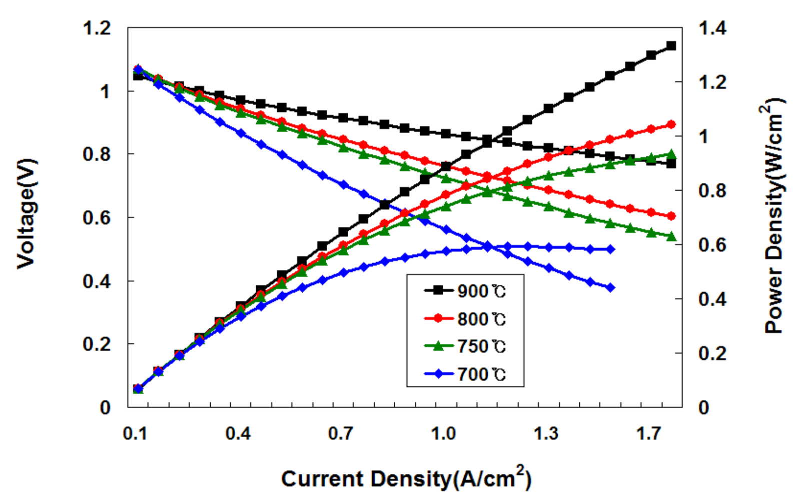

Figure. *I-V* characteristics of SOFC unit cell with ScSZ-based powder using the co-precipitation synthesis.

Mitigation of methanol crossover by using blocking layer on anode in direct methanol fuel cells

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In Direct methanol fuel cell(DMFC), the methanol crossover is one of the major problem for commercialization of DMFC. When methanol crossover occurs, the cathode performance decreases seriously because of mixed potential from methanol oxidation. To mitigate methanol crossover, we design new type catalyst layer using blocking layer. This layer locates between anode catalyst layer and Nafion membrane. By introducing this layer, methanol crossover will be minimized and we can use less platinum catalyst on cathode electrode. And blocking layer is expected to raise residential time of methanol on anode for electrochemical oxidation, so we can achieve better DMFC performance using less platinum catalyst on anode.

Blocking layer consists of fine carbon particle with Nafion ionomer. Carbon will block methanol molecules physically. But if only carbon is exist in blocking layer, this layer maybe performs the resistance for proton movement to cathode. So, appropriate Nafion ionomer must be inside this layer to maintain proton conductivity.

We fabricate single cells made by two MEAs(Membrane Electrode Assembly) w/ and w/o blocking layer to find out the effect of this layer. To prove the effect of blocking layer, single cell performance test, methanol crossover will be checked. Also, We will optimize the quantity of carbon and Nafion ionomer and the layer thickness to find optimal condition of layer for better single cell performance.

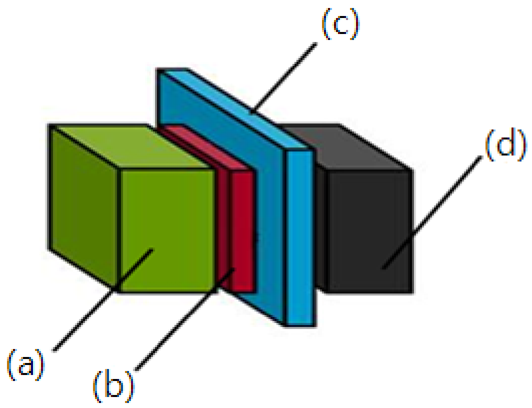

Figure. MEA structure. (a) Anode catalyst layer, (b) Blocking layer, (c) Nafion membrane, (d) Cathode catalyst layer.

Carbon monoxide oxidation, fixation and further conversion to electricity by biocatalysts

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Carbon monoxide can be converted to electricity by two kinds of biocatalysts: acetogens and electrochemically active bacteria (EABs). Acetogens are the microbes that oxidize CO to CO_2 and subsequently convert it to fatty acids and alcohols, chemolithoautotrophically; while EABs are the microbes that oxidize organic compounds and facilitate electron transfer to anode electrode of microbial fuel cell (MFC). The major end product of acetogenesis is an acetic acid, and our previous researches verified that it can be converted to electricity by MFC. Hence, we combined acetogenic fermentation and MFC technology to harvest electricity from CO. Successful operation of the combined process confirmed that microbes are able to generate electricity from CO. However, the conversion yield from CO to electricity was ca. 2.32%. It was mainly due to low coulombic yield of MFC (ca. 5.03%). Therefore, we developed MFC part to generate electricity at high efficient. We were able to increase the coulombic yield up to 65% at MFC part. Our results imply that biocatalysts enable the CO to be converted to electricity.

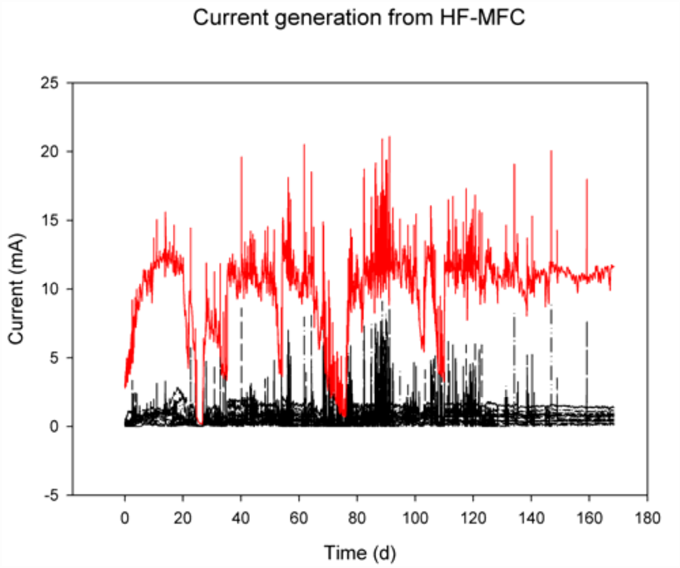

Figure. Current generation from the microbial fuel cell. Black lines at the bottom are the current generation of each of eighteen electrodes, and a red line at the top is their numerical sum.

Carbon dioxide reforming of methane (CRM) by nickel catalysts

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We designed a new experimental set-up for measuring activity of heterogeneously catalyzed reactions. Using this set-up, we studied reduction of carbon dioxide by carbon dioxide reforming of methane (CRM) using nickel powder as catalyst. The properties of the catalysts were characterized by X-ray diffraction (XRD), Brunauer, Emmett & Teller (BET) surface area and X-ray photoelectron spectroscopy (XPS) techniques. The reactivity experiments were performed in the temperature range of 300 - 500 ℃. At reactivity experiment, result showed consumption of CO_2 and CH_4 with a 1:1 stoichiometry. At the same time, carbon monoxide and hydrogen were produced, which could be used for synthesizing fuels such as methanol. During the reaction, deposition of carbon on Ni was observed, which caused deactivation of the catalyst. Surface structure of catalyst after deactivation was studied using X-ray Photoelectron Spectroscopy, and the results will be demonstrated.

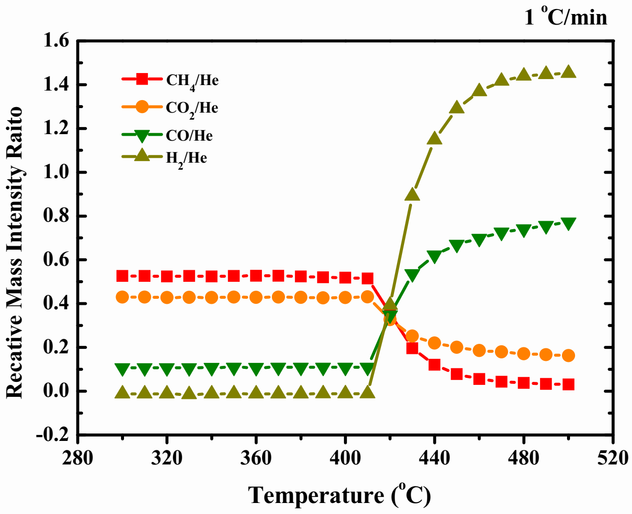

Figure. Change in the gas composition in the reactor during CO_2 reforming of methane using Ni catalysts.

Fabrication and characterization of high performance cathode materials for SOFC

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LSM is widely used as a cathode material in SOFC, because of its excellent mechanical, thermal and chemical stability at a high temperature. In order to reduce the resistance as well as the operating temperature of SOFC system, the cathode materials of LSCF is one of the most suitable electrode materials because of its high mixed ionic and electronic conductivity. LSCF is synthesized as the cathode material for solid oxide fuel cell using pechini type-polymerizable complex method. The particle size, surface area, crystal structure and morphology of the oxide powder were investigated by SEM XRD, and BET, etc. Moreover, in order to investigate electrochemical properties of the synthesized powder for cathode materials, slurry mixture with the synthesized powder was coated by screen-printing process on the anode-supported electrolyte, which was prepared by a tape casting method and co-sintering. Finally, electrochemical studies of the SOFC unit cell, including measurements such as power density and impedance, were performed.

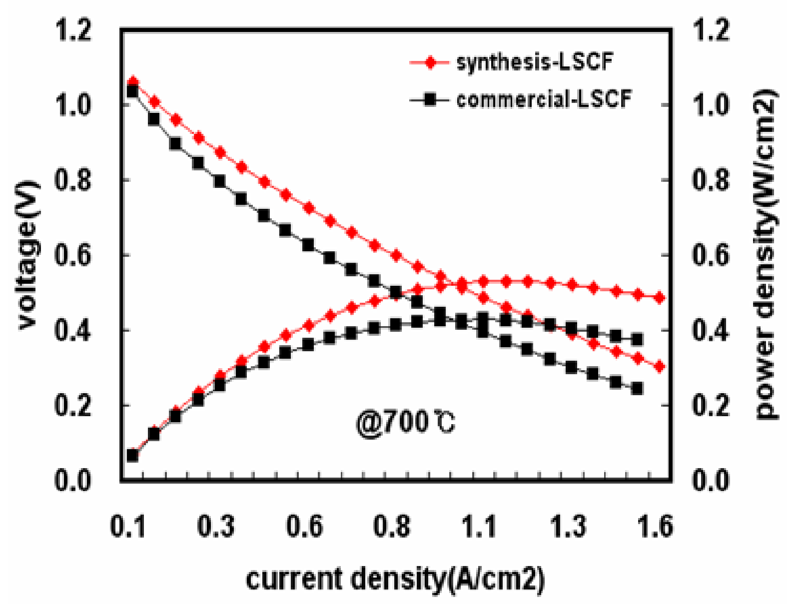

Figure. Performance test of unit cell at intermediate temperature 700℃.

Development of nonlinear dynamic models for a PEMFC hydrogen recirculation system

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In case of the automotive fuel cell, the stable recirculation of the unused hydrogen is one of the important factors to keep the desired utilization and good performance during a load following driving. However, the performance of both an ejector and a blower is so changeable according to the output power of fuel cell that the single usage of an ejector or a blower is not acceptable for a hydrogen recirculation system of an automotive PEMFC. As the practical solution, the ejector and blower hybrid system has been recently proposed for the hydrogen recirculation system of the automotive PEMFC. Unused hydrogen is designed to be mainly recirculated by the ejector and the blower supports to recirculate the rest amount of hydrogen when the ejector can not recirculate sufficient hydrogen. At that case, there are some control problems such as the blower on/off control and deciding the amount of hydrogen recirculated by blower.

In this paper, the dynamic modeling and interpretation for an ejector/blower hybrid hydrogen recirculation system including fuel cell stack, balance of plants, control systems, etc are developed to solve the mentioned control problems. In case of ejector, experimental data based empirical model is used to estimate the ejector entrainment ratio with respect to the fuel cell load change. As the result of the modeling, firstly the dynamic behaviors about pressures and flow rates for the recirculation system are estimated according to the change of the fuel cell power duty. And thereby we can predict the system stability in terms of hydrogen supplement and pressure. Secondly, the parasitic power consumed by the blower is also estimated to calculate the efficiency of the hydrogen recirculation system. Furthermore, the proposed dynamic models can be used to monitor and analyze the performance of the automotive fuel cell system.

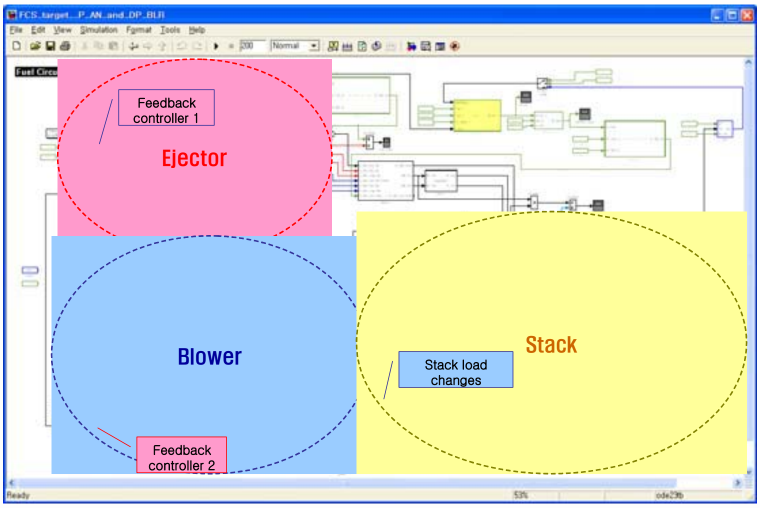

Figure. Fuel circuit dynamic models including controllers.

Development of the 1 kW residential fuel cell cogeneration system based on the computer-aided simulation

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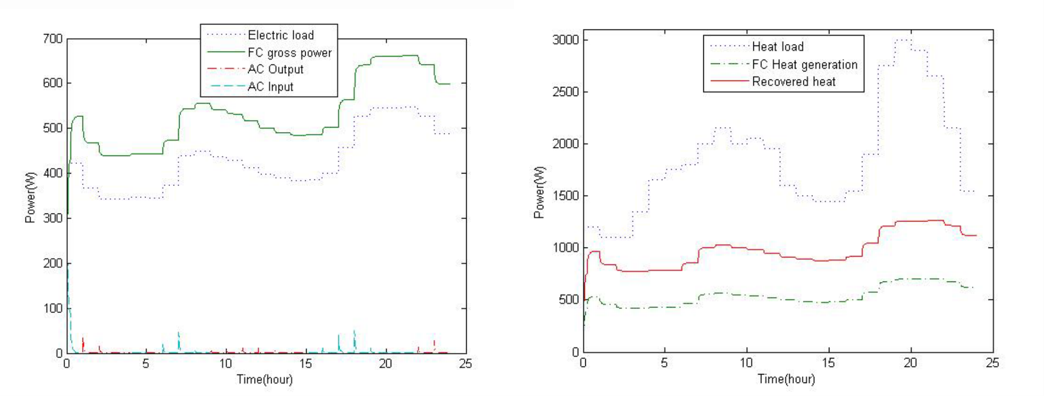
The residential power generator (RPG) has been focused as one of the highly efficient new generators lately. Since the RPG based on a fuel cell stack supply not only electric energy but also heat energy, its overall energy efficiency is more than 80 %. However the efficiency of the RPG can be changed by 10 %. The major factors effect the efficiency of the RPG are as followings: 1) efficiency of the components such as an air blower, a water pump, a power management system and so on; 2) the change of heat and power demand which should be followed by the fuel cell system; and 3) the control strategies to manage power between the fuel cell system and a grid as well as heat between a sub-boiler and a cooling system. In order to effectively operate the RPG, the computer-aided simulation is necessary because the simulation can estimate the RPG efficiency based on the various conditions of the efficiency control factors mentioned above. In order to improve the RPG efficiency, so many trials should be conducted and thereby the much cost and time are wasted. If we have the RPG simulation program, the operational efficiency can be effectively enhanced with lower cost and time. In this study, the computer-aided simulation for a 1 kW RPG using PEMFC stack is introduced. My group made the 1 kW RPG based on PEMFC by ourselves and used the RPG to verify the accuracy of the proposed simulation program. This developed simulation is expected to be applied to the real-time optimization of the RPG according to the highly dynamic changes of heat and power demands.



(a) (b)

Figure. Simulation results using a power oriented control : load & supply For (a) power and (b) heat.

Incorporating hierarchical nanostructured carbon counter electrode into metal-free organic dye-sensitized solar cell

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The counter electrode is an important component of DSSC, and FTO loaded with platinum has been frequently used as the counter electrode.[1,2] However, cost consideration necessitates the development of alternative material. Hierarchical nanostructured hollow macroporous core/mesoporous shell carbon (HCMSC) with a core of ca. 60 nm in diameter and a shell of 30 nm in thickness has been explored as counter electrode in metal-free organic DSSC. Compared with other porous carbon counterparts such as activated carbon (AC) and ordered mesoporous carbon CMK-3 and Pt counter electrode, the superior structural characteristics including large specific surface area and mesoporous volume particularly the unique hierarchical macroporous core/mesoporous shell nanostructure gurantee fast mass transport in HCMSC and enable HCMSC to have highly enhanced catalytic activity towards the reduction of I_3^-, and accordingly cosiderably improved photovoltaic performance. HCMSC exhibits a V_{oc} of 0.74 V, which is 20 mV higher than that (i.e., 0.72 V) of Pt. In addition, it also demonstrates a fill factor of 0.65 and a power conversion efficiency of 7.56%, which are markedly higher than that of its carbon counterparts and comparable to that of Pt.

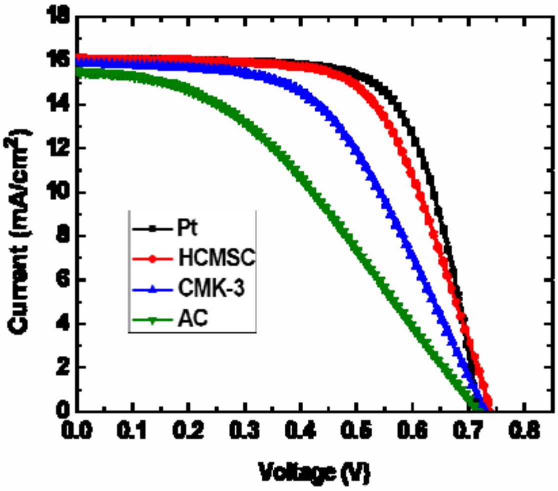

Figure. J-V curves of the solar cells using various counter electrode materials. Anode: 10 µm thick TiO_2 on FTO glass, Dye: (JK2)-ethanol solution (0.3 mM) containing 3a,7a-dihydroxy-5b-cholic acid (10 mM), Electrolyte: 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, 0.05 M I_2, 0.1 M LiI, and 0.5 M 4-tert-butylpyridine in acetonitrile.

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XAFS characterization of exceptionally dispersive and stable platinum catalysts supported on the metal oxide-incorporated silica

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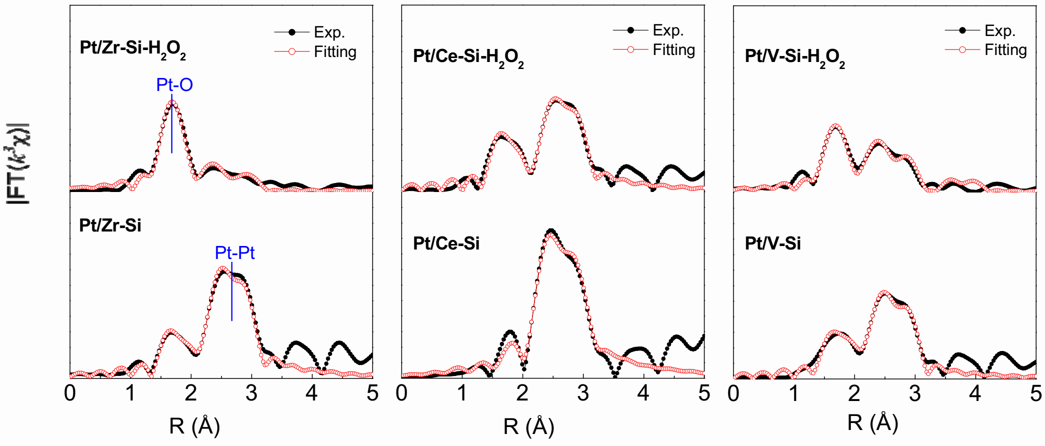
Exceptionally dispersive and stable platinum catalysts supported on silica were prepared by incorporating layer of titania, zirconia, ceria or vanadia and treating subsequently subsequent treatment with hydrogen peroxide. The strong metal-support interaction between platinum and transition metal oxide layer incorporated stabilized platinum dispersed on them and the treatment of platinum precursor impregnated with hydrogen peroxide retained the oxidized state of platinum. The Pt L_{III}-edge EXAFS technique is one of the most effective tool for the confirmation of platinum dispersion because the average coordination number of platinum estimated from the EXAFS spectra corresponds to the average platinum particle size. The platinum catalysts supported on metal oxide-incorporated silica followed by treating with hydrogen peroxide showed very small peaks attributed to Pt-Pt atomic pair, indicating the high dispersion of platinum atoms. XANES and EXAFS results of platinum catalysts supported on the transition metal oxide-incorporated silica indicated the presence of titania, zirconia, ceria and vanadia. They were dispersed on silica as oxide layers and interacted with platinum. EXAFS spectra of the platinum catalysts strongly suggested the formation of Pt-O-M(M =Ti, Zr, Ce, V) bond between platinum and metal oxides at the outer circle of platinum particles. The presence of Pt-O-M bonds suppresses the agglomeration of platinum at higher temperatures above 700 °C even at reduced temperature. The adsorption of hydrogen and carbon monoxide also supported the high dispersion of platinum. The platinum catalysts prepared on the metal oxide-incorporated silica treated with hydrogen peroxide showed high catalytic activity in the oxidation of carbon monoxide.



(a) (b) (c)

Figure Fourier transformed radial distributions of platinum obtained from the Pt L_{III}-edge EXAFS spectra of platinum catalysts; (upper) with and (lower) without hydrogen peroxide treatment.

The interaction of oxygen with Pt (111) surface studied with angle resolved photoelectron spectroscopy

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The absorbed oxygen state and the interaction between absorbed oxygen and Pt(111) surface is investigated by using angle resolved photoelectron spectroscopy. Oxygen dosing (~30 L) is performed at 30 K and immediately intense synchrotron radiation light is applied to measure the XPS at various temperatures. The LEED pattern and XPS analysis of O and Pt core level results indicate that two kinds of oxygen species are produced on the Pt(111) surface at the low temperature (30–50 K). The formation of dissociated atomic oxygen and PtO on the Pt surface even at low temperature can be attributable to the inelastic scatterings of photoelectrons generated from intense undulator beam.

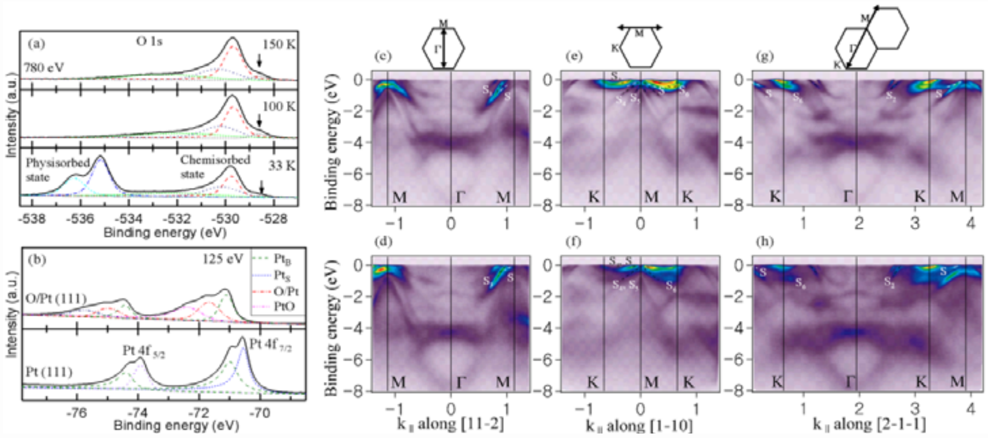

Figure. (a) and (b) XPS core level spectra of O 1s and Pt 4f (c)–(h) Energy-momentum dispersion along ΓM, KM and ΓKM direction.

The reversible temperature dependence of binding energy of oxygen core level shows thermally activated transition from physisorbed to chemisorbed state at around 40 K. Constant energy maps at the Fermi level and energy-momentum dispersion of Pt (111) and O/Pt (111) clearly shows that one of the surface state of Pt contribute to weak donor-acceptor interaction resulting in upward band shifting. Our results will provide a bridge of understanding to the real system, which has oxygen, hydroxyl and water on the catalyst surface.

Crosslinking density effect of fluorinated aromatic polyethers on transport properties

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Novel sulfonated poly(arylene ether) copolymers containing crosslinking moiety and fluorine atoms were prepared for proton exchange membranes of fuel cells. The copolymers were synthesized using potassium-2,5-dihydroxybenzenesulfonate (SHQ), 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA), decafluorobiphenyl (DFBP), and 1-ethynyl-2,4-difluorobenzeneand (CM) as a crosslinking moiety through polycondensation. Crosslinked membranes are obtained by thermal curing of the crosslinkable copolymers. The proton conductivity and methanol permeability of the membranes decreased with increasing crosslinking moiety (CM). The SFPE90-CM20 membrane in particular showed low water uptake (37.5 %), high proton conductivity (0.091 S/cm), and low methanol permeability (37 × 10^{-8} cm^2/s). The selectivities of all the crosslinked membranes, that is, the ratio of proton conductivity to methanol permeability, fell in the range of 122 × 10^3 – 587 × 10^3 $S{\cdot}s/cm^3$, and they were thus also much higher than the selectivity of Nafion 212 (56 × 10^3 $S{\cdot}s/cm^3$).

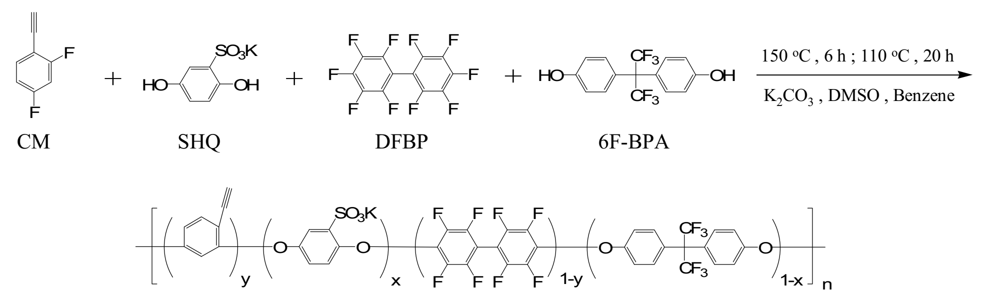

Figure. Sulfonated poly(arylene ether) copolymers containing crosslinking moiety.

Fabrication and characterization of ScSZ-based electrolyte powder for IT-SOFC unit cell using hydrothermal process

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Scandium-doped zirconia provides higher oxygen conductivity than YSZ electrolyte and nanoscale electrolyte materials are ideal for fabricating thin film electrolyte layer for SOFC unit cell. In this study, nanoscale ScSZ-based electrolyte powder was prepared by hydrothermal synthesis method. The synthesis characteristics of powder such as particle crystallite, morphology of the powder surface and surface area were observed by XRD, SEM and BET. As a result, the powder shows a uniform morphology of nano particle, which has crystallite size of 5-10nm level with a high surface area of 300m^2/g after synthesis as Figure. Moreover thin film electrolyte of under 10 ㎛ was fabricated by tape casting using the synthesized ScSZ-based powders. The ionic conductivity and gas permeability of electrolyte film were evaluated. Finally, the SOFC unit cell with a nanoscale ScSZ-based powder was fabricated by a tape casting method and co-sintering. Electrochemical evaluations of the SOFC unit cell including measurements such as power density and impedance were performed and analyzed.

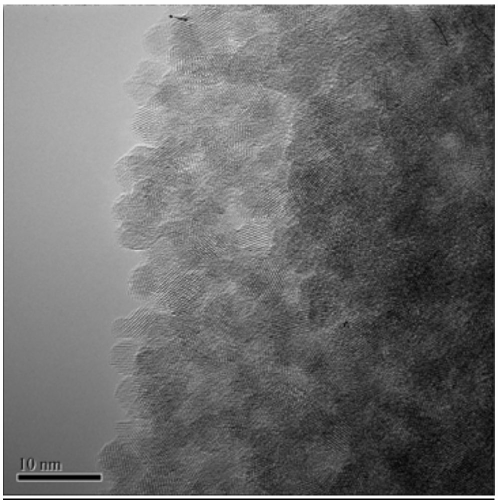

Figure. TEM morphology of ScSZ-based powder using the hydrothermal synthesis.

Platinum nanostructure electrodes supported by tungsten carbide and oxide in methanol electrooxidation

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Direct methanol fuel cells (DMFCs) have attracted considerable interest because of a variety of merits such as low operating temperatures, ease of handling a liquid fuel, the high energy density of methanol, and applications to micro-sized fuel cells. The excellent catalytic activity of platinum for methanol oxidation, especially, at low temperatures makes this metal electrocatalyst ideal for use as an anode in DMFCs.

We report nanostructure electrodes for methanol electrooxidation by means of co-sputtering deposition method. The two-phase electrodes formed by two sputtering targets consist of Pt metallic nano-phase and WC or WO_3 phase. Furthermore, the Pt-WC-WO_3 three-phase electrode formed by three sputtering targets exhibits Pt nano-phases dispersed with the WC and WO_3 phase.

For methanol electrooxidation, the Pt-WC-WO_3 electrode indicates higher I_f/I_b and current density i.e. improved electrocatalytic activity compared to pure Pt and two-phase electrodes. It is likely that such an excellent electrocatalytic activity of the Pt-WC-WO_3 may be attributed to synergy effect of tungsten carbide and oxide.

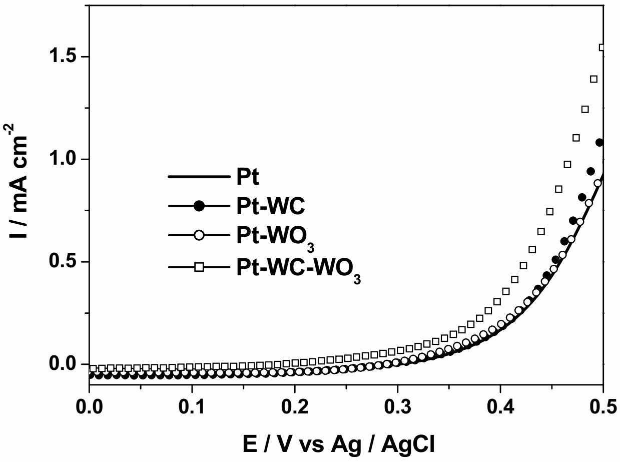

Figure. *I-V* characteristic curves of electrodes for methanol electrooxidation in 2.0 M CH_3OH + 0.5 M H_2SO_4.

Cu,Zn,Al hydrotalcite-like compounds as precursors for copper catalysts in methanol chemistry

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Cu,Zn,Al hydrotalcite-like compounds (or layered double hydroxides, LDH) are formed as a by-phase during the synthesis of the precursors of Cu/ZnO/Al_2O_3 catalysts for methanol synthesis. They can be obtained in a phase pure, Cu-rich form by co-precipitation with NaOH/Na_2CO_3.[1] These phase-pure LDH precursors are a promising initial point for activity-property-correlations, as they have a perfect distribution of all three metal species on an atomic scale, and are expected to yield catalysts of homogeneous microstructure. In our work we will present the application of the microemulsion (ME) technique for the synthesis of Cu,Zn,Al hydrotalcite (Cu:Zn:Al = 50:17:33) in comparison to co-precipitation route as well as the characterization of both products and the resulting Cu catalysts.

The hydrotalcite (ME-LDH) was formed within the water droplets by constant dosing of the Cu^{2+}/Zn^{2+}/Al^{3+} nitrate solution. A reference catalyst (co-LDH) was prepared by conventional co-precipitation without microemulsion under analogous conditions (temperature, concentrations, drying). Both co-precipitation as well as microemulsion technique result in a phase-pure Cu,Zn,Al hydrotalcite (Figure. 1), where ME-LDH has the higher BET surface area. After calcination in air at 330°C both products were converted into nearly amorphous, carbonate containing mixed oxides. Reduction in hydrogen results in the final Cu-based (Cu^0) catalysts. By TEM small Cu particles (average diameter ~8nm) which are embedded within the oxide matrix where found for both samples, whereas the ME sample has a significant higher Cu surface area. Both catalysts are active in steam reforming of methanol.

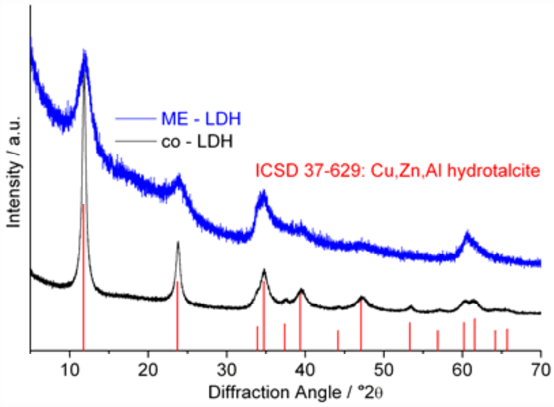

Figure. X-ray diffraction pattern of ME-LDH and co-LDH.

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High throughput DNA separation with functionalized magnetic silica nanoparticles

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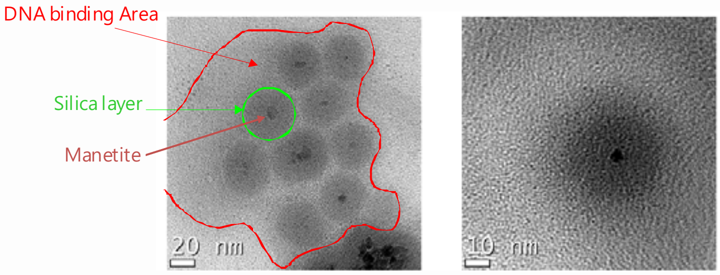
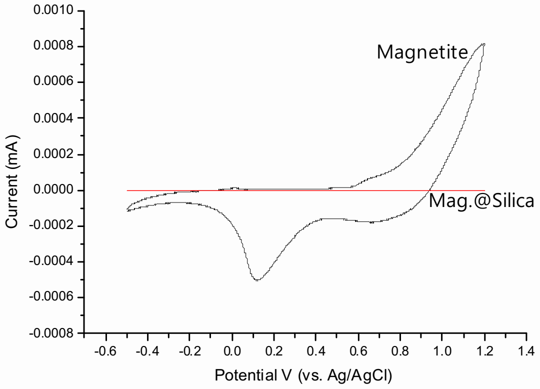
Work presented here describes a simple and convenient process to highly efficient and direct DNA separation with functionalized silica-coated magnetic nanoparticles. Iron oxide magnetic nanoparticles and silica-coated magnetic nano-particles were obtained uniformly and the silica coating thickness could be easily controlled in a range from 10 to 50 nm by changing the concentration of silica precursor (TEOS) including the controlled magnetic strength and particle size. A change in the surface hydrophilicity on the nanoparticles was introduced by aminosilanization to enhance the selective DNA separation resulting from electrostatic interaction. The efficiency of the DNA separation was explored via the function of the amino-group numbers, particle size, the amount of the nanoparticles used, and the concentration of NaCl salt. The DNA adsorption yields were high in terms of the amount of triaminofunctionalized nano-particles used, and the average particle size was 35 nm. The adsorption efficiency of amino-functionalized nanoparticles was the 4-5 times (80-100%) higher compared to silica-coated nano-particles only (10-20%). DNA desorption efficiency showed an optimum level of over 0.7 M of the NaCl concentration.





Tin oxide nanowires created by chemical anodization

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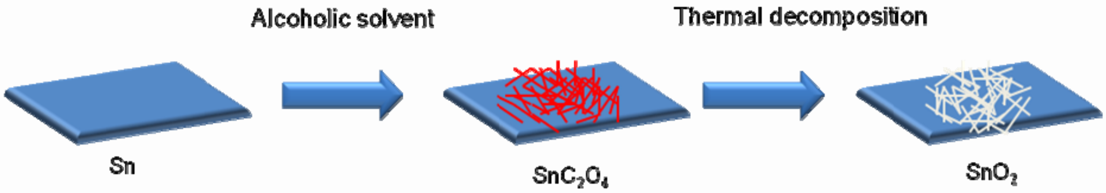
We report on simple approach to create spontaneous growth of SnO_2 nanowires via chemical anodization followed by annealing process. First, chemical oxidation of tin metal is applied for the formation of tin oxalate nanowires and it is considered as a precursor of tin oxide having one dimensional nanostructure. The density and the shape of tin oxalates on tin surface are strongly dependent of the solubility of oxalic acid and ion transfer of proton and oxalate anion. Then, thermal decomposition is performed to convert tin oxalate to tin oxide under oxygen atmosphere. Each step of the sample is extensively compared by SEM and XPS analysis.



Effective elimination of carbon monoxide by Fe-impregnated ordered mesoporous silica

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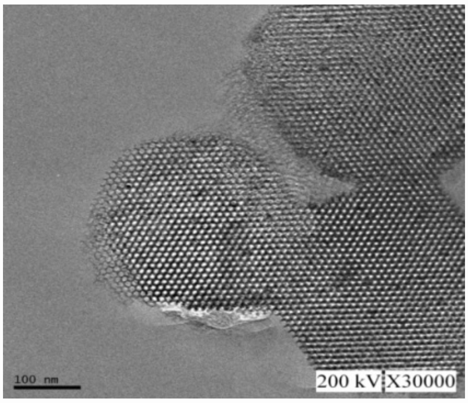
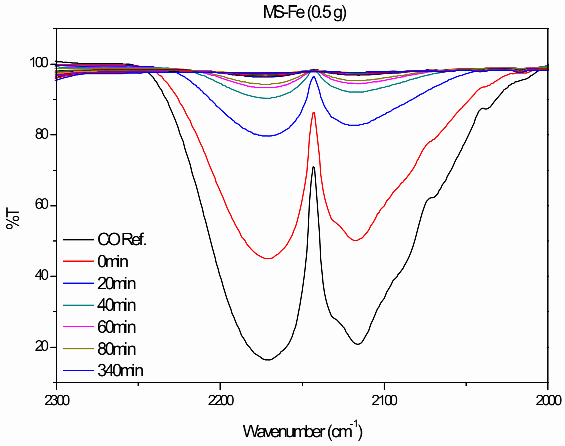
This work describes the innovative development of effective elimination of carbon monoxide using a Fe-impregnated mesoporous silicas (MS-Fe). The mesoporous silicas were prepared by sol-gel process and Fe-nanocluster was formed after impregnation and reduction process. The characterization of the materials was achieved by SAXS, TEM with SEM analysis, solid-state ^{29}Si-NMR, XPS, FT-IR(ATR-method), and BET. As a result, the catalytic efficiency was demonstrated as a function of the catalyst amounts and time. Consequently, the carbon monoxide was effectively removed over 80% at room temperature. Moreover, this work reported the catalytic efficiency as a function of the catalyst amounts and time.





Hybrid electrokinetic processes for the remediation of metal contaminated soil

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In the present study, heavy metal contaminated soil, mainly by Pb, Cu, and Zn, was collected from a military shooting range located in the Civilian Control Line of Korea. Acid-enhanced electrokinetic soil process showed good performance on the removal of multiple heavy metals from field soil. For the hybrid electrokinetics, bioleaching processes including bioaugumentation (injection of S oxidizing bacteria, *Acidithiobacillus thiooxidans*) were evaluated as the pre-treatment step. These were sequentially integrated with electrokinetic soil processes which include acid-enhanced process using HNO_3 and chelating-enhanced process using EDTA. Although the S oxidizing bacteria, *A. thiooxidans*, enhanced the mobility of heavy metals in soil, the byproduct of S oxidation, sulfate, could easily make metal complexes when the concentration was extremely high in the pore water. It could affect negatively on the electrokinetic soil process. On the other hand, the method by application of electrokinetic EDTA injection made a great combination with bacterial pre-treatment. All the heavy metals were removed below the criteria of soil contamination, and the residual heavy metals in soil after the process were environmentally stable. This study demonstrate the applicability of the electrokinetic and hybrid electrokinetic processes on the metal contaminated field site.

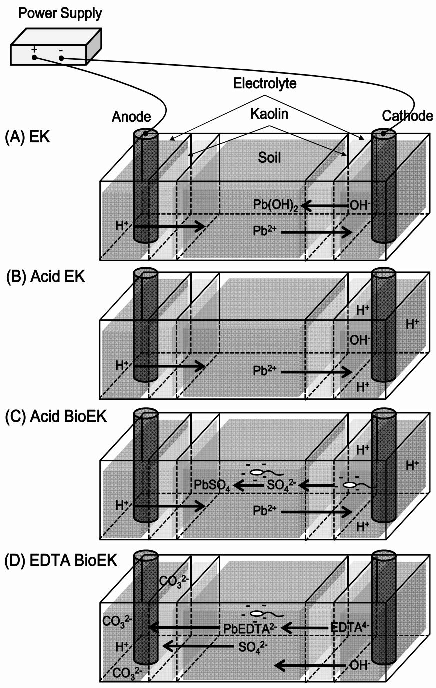

Figure. Schematic diagram of major reactions and transportations in (hybrid)electrokinetic soil processes.

Synthesis of octahedral Pt-Pd alloy nanoparticles: Structural and electrochemical properties

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Pt-based nanoparticles (NPs) have been well known as the most effective catalysts for methanol electrooxidation of in acid solutions. However, a critical problem with Pt-based catalysts is poisoning by CO-species as a by-product during methanol electrooxidation in acid medium. Thus, many recent efforts have been made to overcome the CO poisoning effect and enhance the oxidation rate of methanol on metallic catalysts by alloying Pt with other metals. Among them, palladium shows relatively low cost, excellent catalytic activity, and CO-tolerance. The alloy nanoparticles are expected to be a single-component material with particular functionalities compared to pure Pt.

In this paper, the alloy catalyst was obtained by means of reduction of metal ions using glycerol as a reducing agent and poly (vinyl pyrrolidone) as a stabilizer in aqueous solution. The crystal structure octahedral Pt-Pd alloy nanoparticle has dominant (111) plane compared to commercial Pt/C. In an electrochemical measurement for methanol and formic acid electrooxidation, the octahedral Pt-Pd alloy catalyst shows an excellent catalytic activity, CO-tolerant, and much higher stability compared to commercial Pt/C catalyst.

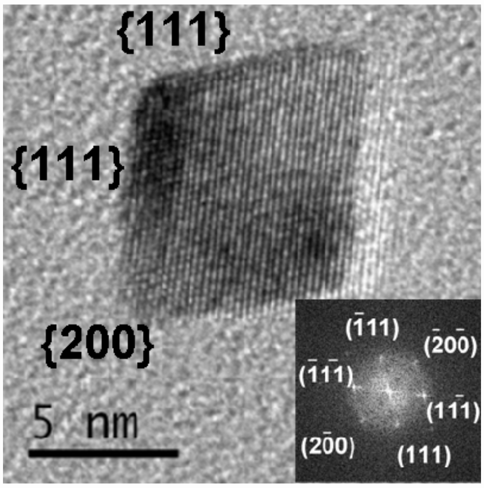

Figure. The octahedral Pt-Pd alloy nanoparticle.

Carbon aerogel prepared from phloroglucinol and HMF: Relationship between their structural/chemical characteristics and electrochemical double-layer capacitance

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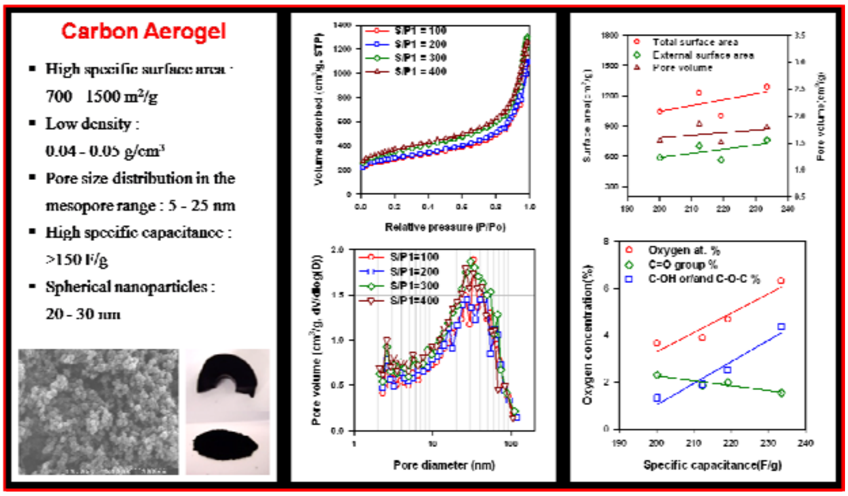
Typically, carbon aerogels have been synthesized by aqueous polycondensation of O- or N-containing cyclic compounds (e.g., resorcinol, melamine, etc.) with formaldehyde, and followed by a low-temperature supercritical drying with CO_2. On account of the asymmetry of conjugated ring structures involving oxygen or nitrogen species as functionality of monomers, a superior specific capacitance can be observed in carbon aerogels. Herein, we utilized phloroglucinol (P) and 5-hydroxymethyl furfural (HMF) as carbon monomers to prepare carbon aerogels which was named as PHMF.

In the synthesis of alcogels, several preparation variables such as the pH, the aging time, the P/solvent, P/HNO_3 (catalyst) and P/HMF ratios, and the carbonization temperature were varied, and the textural and surface chemical properties of the produced carbon aerogels were obtained by N_2 physisorption at 77 K and XPS, respectively. Finally, the gravimetric capacitance (C_g) of PHMF carbon aerogel in the unit of Fg^{-1} was determined by cyclic voltammetry (CV) measurement in 0.5 M H_2SO_4.

In the correlation of C_g with the textural properties of PHMF carbon aerogels, the gravimetric capacitance was in a linear relationship with S_{total} and the external surface area (S_{ext}), but not with the micropore surface area (S_{micro}), where the contribution of S_{total} depends in that of S_{ext}. In determining the surface functional groups, C_g turned out to be dependent on the total surface oxygen atomic content (O_{surf}) and the C–O groups ($O_{C–O}$) concentration.

We are now investigating which of the structural and the chemical contribution is a more dominant factor in enhancing the capacitance of PHMF carbon aerogels, which will be posted on-site.



Carbon Aerogel

- High specific surface area : 700 1500 m²/g
- Low density : 0.04 - 0.05 g/cm³
- Pore size distribution in the mesopore range : 5 - 25 nm
- High specific capacitance : >150 F/g
- Spherical nanoparticles : 20 - 30 nm

Enhanced durability of Pd catalyst composited with polythiophene

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Polymer electrolyte membrane fuel cell (PEMFC) has attempted to develop a class of platinum-free catalyst demanding high activity as well as enhanced durability since the Pt metal itself increases the fuel cell stack cost to an economically unacceptable level. Therefore, development of Pt-free catalyst appears to be essential, but unfortunately, any pure or composited catalyst based on the common transition metals unlikely stable in the acid condition because of its thermodynamical and electrochemical vulnerability at low pH and high potential region. We propose that polythiophene (PTh) could stabilize the Pd metal, which may be one candidate for the Pt-free electrocatalysts. The Pd-PTh composite shows an improved stability and activity for hydrogen oxidation compared to the electrodeposited bare Pd. Such catalytic stability and activity of Pd-PTh are demonstrated by half-cell test and cyclic voltammetry test together with physico-chemical characterization. While the bare Pd shows a poor stability on the hydrogen oxidation performance, the Pd-PTh composite catalyst maintains the activity up to 500 cycles. It seems that the conducting polymer of the polythiophene layer effectively prevents the active Pd catalyst from undergoing oxidative dissolution, allowing the high electrocatalytic activity of Pd to be maintained under the acidic conditions[1]. This should enable a new strategy for electrocatalyst development through the stabilization of highly reactive but otherwise unstable non-noble metal catalysts.

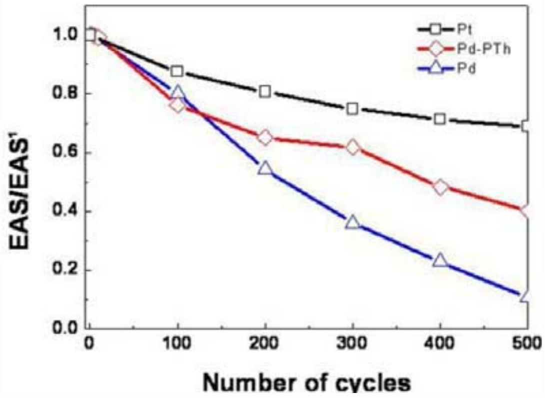

Figure. Long term accelerate test of Pt(□), Pd- PTh(◇) and Pd(△) and in 0.5M H_2SO_4 at scan rate of 50mV/S at room temperature. Equivalent quantity of metal was deposited and tested.(PTh: Polythiophene).

Acknowledgement
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This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology (R15-2008-006-03002-0)
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This work was supported by the Program for Integrated Molecular Systems (PIMS/GIST).

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Multimodal porous carbon with hierarchical nanostructure as an efficient anode material in Li ion battery

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Rechargeable lithium ion batteries are becoming a key-enabling technology and have potential applications in electric and hybrid vehicles due to their high energy density, high voltage, and long lifespan.[1] However, their rate capability which is dominated by the diffusion rate of lithium ions and the electron transport in electrode materials, needs to be improved greatly.[2] Recently, much attention has been paid to high surface area porous carbons with various nanostructures due to the expected reduced diffusion length of lithium ions and rapid charge transfer.[3]

In this study, ordered hierarchical nanostructured carbon (OHNC) with multimodal porosities ranging from macro- to meso-/micropores was explored as anode material in Li ion battery. Compared with other porous carbon counterparts such as activated carbon and ordered mesoporous carbon CMK-3, OHNC has demonstrated a larger Li ion storage capacity (ca. 770 mAh/g at 200 mA/g) and better rate capability which are mainly attributable to its fantastic structural characteristics such as large specific surface area and mesoporous volume, particularly well-developed 3D interconnected ordered macropore framework with open mesopores embedded in the macropore walls, facilitating fast mass transport and electron transfer.

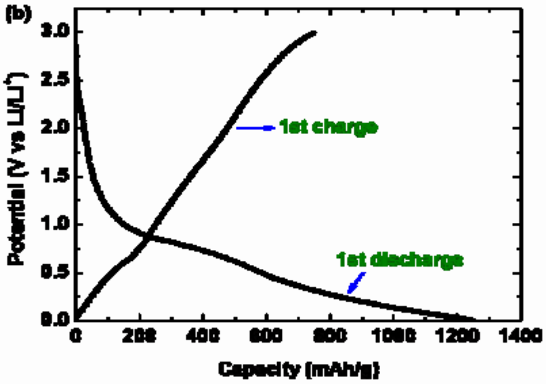

Figure. Constant-current charge-discharge for OHNC at 200 mA/g, electrolyte: 1M $LiClO_4$ in EC-DEC.

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Ceria-coated bulk nickel catalysts for the water-gas shift reaction

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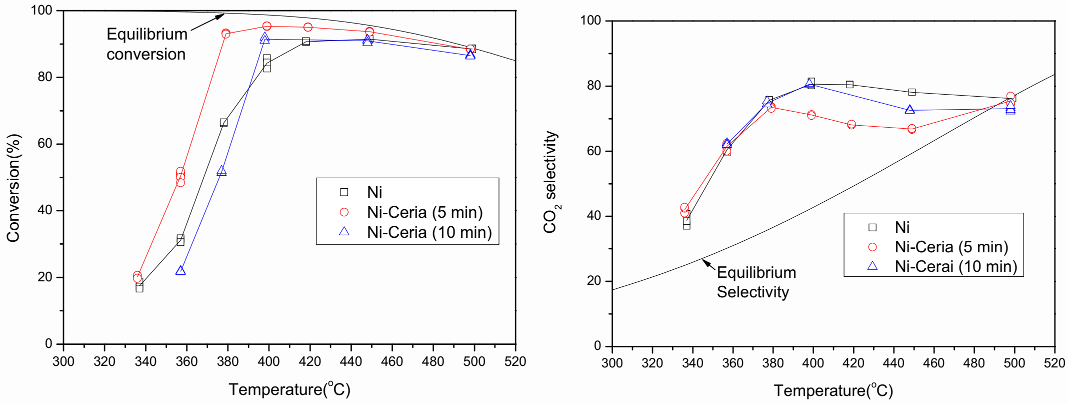
Bulk nickel catalysts were examined for the water gas shift (WGS) reaction. The effects of ceria coating on the activity of the catalysts were thoroughly investigated. Ceria was deposited on the nickel surface by an immersion method which was known to form crystalline ceria films on nickel substrates. Nickel catalysts in the form of either granules or porous plates were employed in this study. Nickel granules, which were prepared by oxidizing and crushing porous nickel plates, were coated with ceria by being immersed into the aqueous solution of cerium nitrate at 30℃. The activity test results showed that there seemed to be the optimum immersing time in terms of activity. Appropriate coating enhanced the activity while the selectivity was not significantly affected by ceria coating below 400℃, where the conversion was limited by reaction rates. The result indicates that ceria promotes both the water gas shift reaction and methanation reaction. The enhanced activity may be attributed to redox reaction mechanism caused by introducing ceria on nickel surface. Impedance of a symmetric cell using the catalysts and molten carbonate electrolyte is being analyzed to clarify effects of ceria coating and applied potential on catalytic activity.



(a) (b)

Figure. CO conversion(a) and CO_2 selectivity(b) of a nickel and coated nickel catalysts (immersing times of the coating in parentheses). 50,000 mℓ/h g_{cat} (STP), 4.7% CO, 13.6% H_2, 18.9% H_2O, N_2 balance.

Photocatalytic decomposition of toluene vapor by bare and TiO_2 coated carbon fibers

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Photocatalytic decomposition of toluene vapor by bare and TiO_2-coated carbon fibers was studied. For TiO_2 coating, atomic layer deposition (ALD) was used. We show that the photocatalytic activity of bare carbon fiber was comparable with those of TiO_2 films, which are known to be good photocatalysts, under our conditions. The origin of the high photocatalytic activity of bare carbon fiber will be discussed.

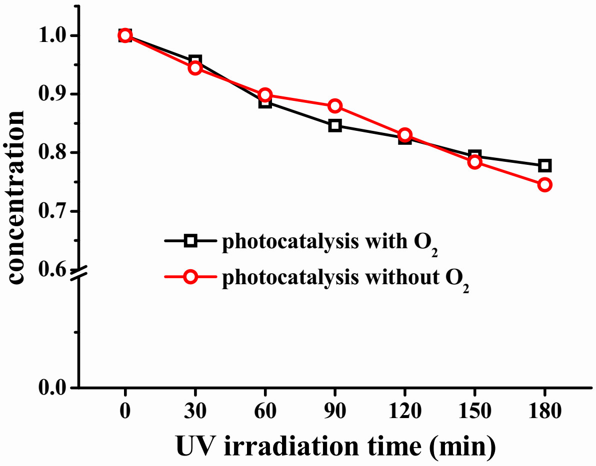

Figure. Photocatalytic removal of toluene by carbon fibers in the presence and absence of O_2.

In-situ dynamics of CO oxidation on Pt(110) with ambient pressure XPS

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Considering the recent increasing demands of improved catalytic materials in energy industry, the understanding clear mechanism of catalytic reactions at an atomic scale level has become more critical. Especially, the formations of oxide on transition metal surface have been actively studied due to its importance in fundamental understanding of heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxide on Pt [110] received much attention due to its unique surface reconstruction under high pressure reaction conditions. Previously, with the combinations of high pressure STM and in-situ x-ray diffraction, the formation of surface Pt oxide is observed when the reaction rate is enhanced, and showed the surface oxide formed is stable with carbonate species. In this work, using combination of the ambient pressure XPS (AP XPS) and mass spectrometer, the in-situ dynamics of CO oxidation on Pt [110] surface are presented. Under the reaction conditions with the pressure of CO and O gases at 450 mTorr in the AP XPS chamber, the experimental results clearly show that a) the chemisorbed oxygen is not stable under the reaction conditions, which desorbs immediately, b) there is no sign of the formation of surface oxide on Pt surface from the inspection of Pt, O, and C core level XPS spectra, and c) consequently the CO oxidation process is most likely following Langmuir-Hinselwood type reaction mechanism. This provides the important information between the pressure gap.

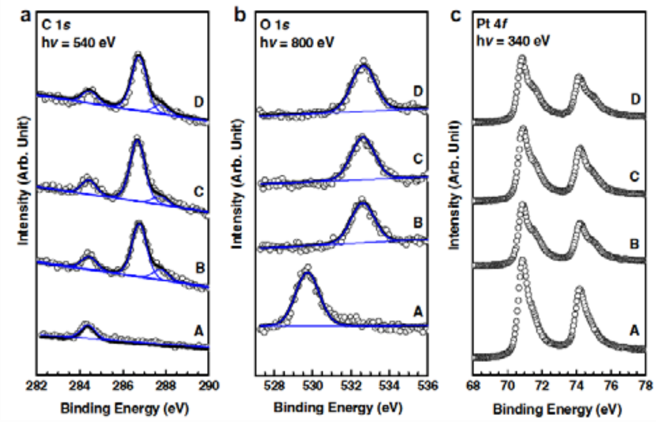

Figure. XPS spectra at each region: (a) C1s spectra taken at 540 eV; (b) O1s spectra taken at 800 eV; (c) Pf4f taken at 340 eV.

Stabilizing experimental oscillatory time-series

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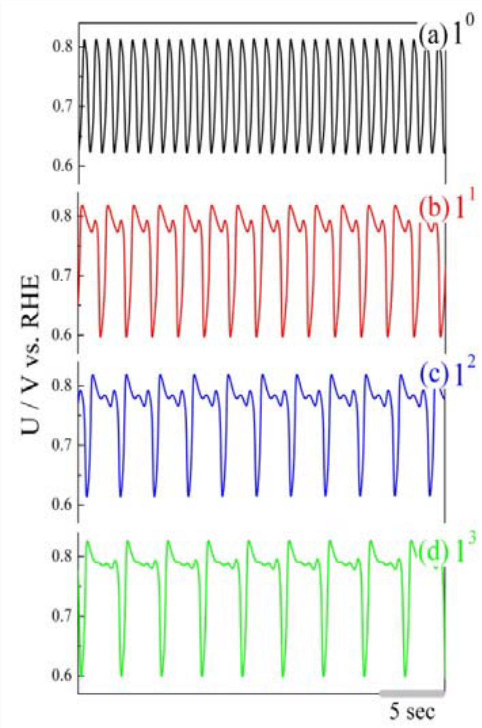

Most of the time-series obtained for electrochemical systems are associated to spontaneous transitions among different patterns, in spite of the fact that all controllable parameters are kept constant. Those transitions are in principle connected to surface processes rather than transport of bulk effects. Herein we present a simple empirical method to stabilize experimental time-series. The method consists of slowing decrease the applied current in order to account for the continuous surface population change, and it was tested for the oscillatory electro-oxidation of methanol on platinum. For a wide range of applied currents, the base system presents spontaneous transitions from quasi-harmonic to mixed mode oscillations in the sequence: $1^0 \rightarrow 1^1 \rightarrow 1^2 \rightarrow 1^3 \rightarrow 1^n$ (L^S: L large and S small amplitude oscillations). Each of the temporal pattern was stabilized by a negative galvanodynamic sweep (NGS), at different rates, -dj/dt, stabilized patterns are given in the Figure. Typical stabilizations of about four times for the 1^3 state and of more than twenty times for the 1^0 pattern were observed for optimum rate of NGS with respect to the base system. In the absence of any NGS, the mean electrode potential was found to increase, suggesting that the surface process underlying the continuous drift or the time-dependent bifurcation parameter, would be associated to the accumulation of adsorbed oxygenated species. In this way, the NGS compensates the decrease of the effective electrode area, by decreasing the imposed rate of the electro-oxidation process, or the externally applied current density. The optimum rate of NGS informs about the time-scale of the, slow, poisoning process. Extending this approach to other systems might be useful not only from the stabilization point of view, but also for mechanistic studies of the poisoning process that usually accompanies the electro-oxidation of small organic molecules.

Layer by layer self-assembly of biopolymers as membrane electrolytes in liquid fuel cells

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In this presentation, we present a simple layer by layer (LbL) self-assembly method to create biopolymeric membrane electrolytes for liquid fuel cell applications. Biopolymeric LbL electrolyte membranes were formed via electrostatically sequential adsorption of oppositely charged layers, mainly poly-lysine as a positive layer and double stranded DNA from salmon testes as a negative layer. Ion conductivities of different thickness of biopolymer membranes both in the presence (see Figure.) and the absence of Nafion film were investigated. The methanol and formic acid cross-over were then measured and their performance was compared to that of using Nafion membrane electrolytes. We envision that the biopolymer membrane could be potentially employed as a membrane electrolyte or could be utilized in conjunction with Nafion membrane in methanol, formic acid and ascorbic acid fuel cells.

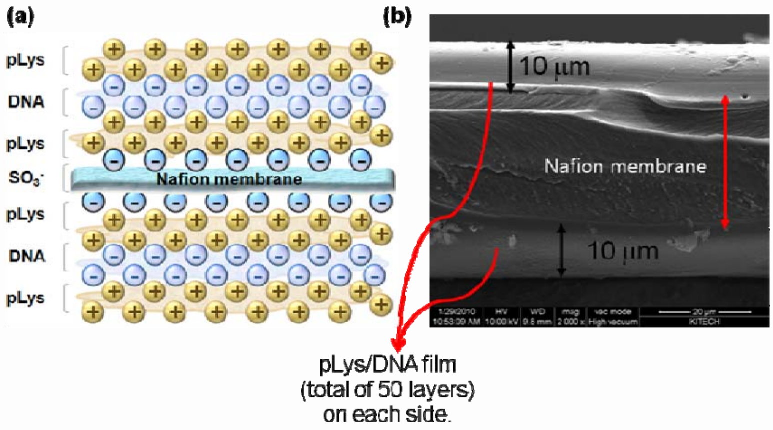

Figure. (a) A schematic showing LbL formation of pLys/dsDNA membrane electrolytes created on an acid treated Nafion membrane. (b) Representative SEM data for the pLys/dsDNA film formed on both sides of a Nafion membrane after the methanol cross-over experiment. Total of 50 layers of the pLys/dsDNA film were formed on each side of Nafion membrane.

Pt/TiO$_2$ nanostructure electrode for methanol electrooxidation

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For best performance, the DMFC electrode should consist of two or more phases, such as a nanosized catalyst and a porous material as a support for the catalyst. The general requirements of support materials for their applications to platinum-based electrocatalyst are a high surface area for a high level of dispersion of nanosized catalysts, a pore structure suitable for maximum fuel contact and by-product release, and good interactions between the catalyst nanoparticles and the support.

In particular, oxide supports are widely used in heterogeneous catalysis and have an excellent stability in oxidizing environments. Until now, TiO$_2$ has been potentially attractive as supports due to strong catalyst-support interaction, stability in fuel cell operation atmosphere, low cost, commercial availability, and the ease to control size and structure. In general, semiconductor materials with a large band gap (~ 3.2 eV) such as TiO$_2$ show an effective photo-catalysis under UV illumination.

In this paper, we fabricated Pt/TiO$_2$ branched nanostructure electrode consisting of nanosized-Pt and TiO$_2$ branched nanostructure for methanol fuel cell and described an improved methanol oxidation of the electrode under UV illumination. The structural and electrochemical properties of the nanostructure electrode were characterized by means of transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), and Cyclic voltammogram (CV).

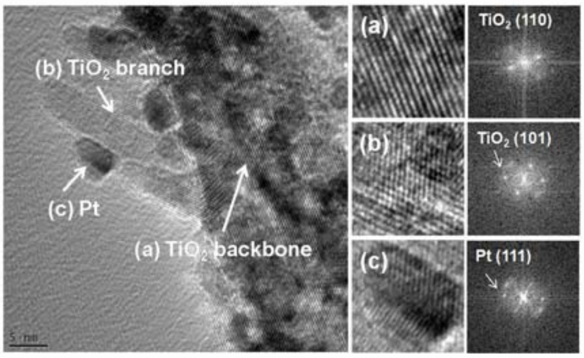

Figure. The Pt/TiO$_2$-branched nanostructure electrode.

Spatiotemporal phenomena during electro-oxidation of formic acid at different conductivities

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Potential oscillations and spatiotemporal pattern formation during the oxidation of formic acid were investigated under potentiostatic conditions on a platinum ring electrode in the presence of bismuth ad-atoms (Figure 1). The conductivity was manipulated by varying the amount of supporting electrolyte Na_2SO_4, in the solution containing 0.1 M HCOOH + x M Na_2SO_4 + 10^{-6} M Bi^{3+}, from 1.8 mS to 17 mS (pH 2.5). Cyclic voltammetry and current transient measurements were carried out. For not too high conductivity κ the passivation at high voltage occurred in three distinct steps. For low κ weakly oscillating domains appeared (Figure 2). At intermediate κ standing waves and travelling pulses were obtained, while at high again domain structures formed adjacent to travelling patterns.

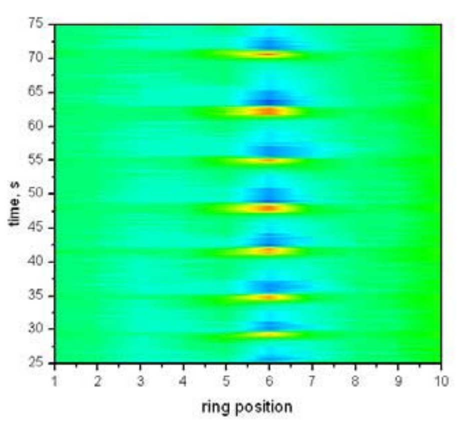

Figure 1. Experimental array of working, counter and reference electrodes, for local potential measurements on a polycrystalline Pt ring electrode.

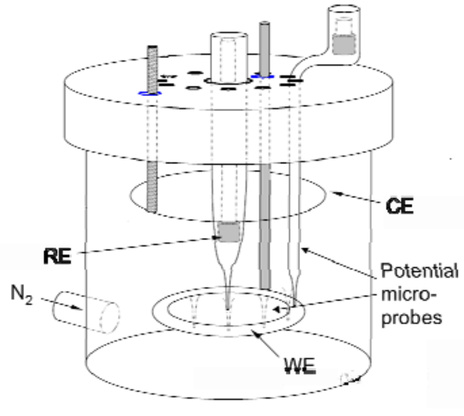

Figure 2. Potential distribution during current oscillations at *U*= 703 m*V*,in the absence of Na_2SO_4,κ=1.84 m*S*.

Corrosion resistive Magnéli phase titanium oxide for the support material of electro-catalyst in polymer electrolyte fuel cells

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Platinum based catalysts supported on carbon materials have been mainly applied in polymer electrolyte fuel cells (PEFCs) for their excellent performance and physico-chemical stability. However, corrosion of the carbon supports, especially at higher voltage range, was observed during cell operations. The severe oxidation of carbon support was considered as a main cause of electro-catalyst degradations. To overcome the catalyst corrosion problem, electric conductive ceramic materials such as TiC, TiN, WC, ITO and titanium oxides (Ti_4O_7) are getting interests for the support of electro-catalysts.

In this study, a titanium oxide with a Magnéli phase structure was used as a supporter of platinum particles. The Pt loaded Magnéli phase titanium oxide (MPTO) electro-catalysts were characterized by various electrochemical analysis to investigate the performance as well as durability. Additionally, TEM, XRD, ICP, BET analyses were conducted to understand the physico-chemical properties of Pt/MPTO catalysts.

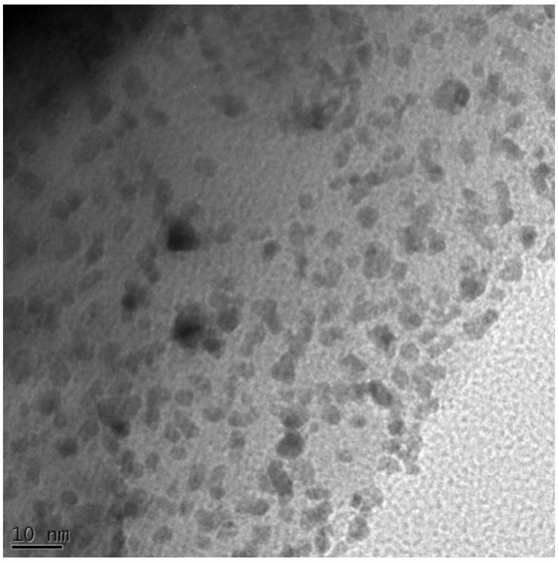

Figure. TEM image of 15 wt% Pt/MPTO electro-catalyst.

Phase separated morphology of supported liquid membranes containing aprotic ionic liquids by small-angle X-ray scattering

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The polymeric membranes containing aprotic ionic liquids (ILs) in replacement of water have been prepared to investigate their nanostructure evolution. Effects of the type and amount of ionic liquids and polymeric membranes on morphology have been studies by small-angle X-ray scattering (SAXS). Room temperature ionic liquids (ILs) are good candidates since they show good ionic conductivity, electrochemical/thermal stability and high boiling point. Understanding on the correlation between morphology and properties of polymer electrolyte membranes containing various ILs is necessary to improve their design for applications in PEMFCs at high temperature (120~180 °C) and anhydrous conditions. In general, proton conductivity of hydrated membranes is very dependent on the structure and morphology of the membranes. In order to explain and understand the mechanism of proton conduction at those conditions, many studies on the morphology of hydrated membranes was carried out by SAXS. The SAXS spectra of hydrated membranes based perfluorinated sulfonic acid polymers (i.e., Nafion^{TM}, Dupont, USA) generally exhibit typical characteristics: i) ionomer peak representing scattering maximum at q value above 0.1 Å^{-1} which is associated with aggregation of individual ionic groups; ii) matrix peak representing scattering maximum at q value around 0.04 Å^{-1} which is associated with crystalline regions; iii) an upturn in intensity at very low q region below 0.01 Å^{-1} which is generally associated with large scale heterogeneities. As a result, the SAXS scattering maximum (ionomer peaks) has been observed in the recast Nafion membranes, whereas it was absent in the membranes based on sulfonated poly(aryl ether ketone)-6F (SPAEK-6F) since SPAEK−6F copolymers has very short ionic group attached on backbone. The size of individual ion aggregate calculated by q values for ionomer peaks is dependent on the amount and type of ILs in membranes, temperature and the type of polymers.

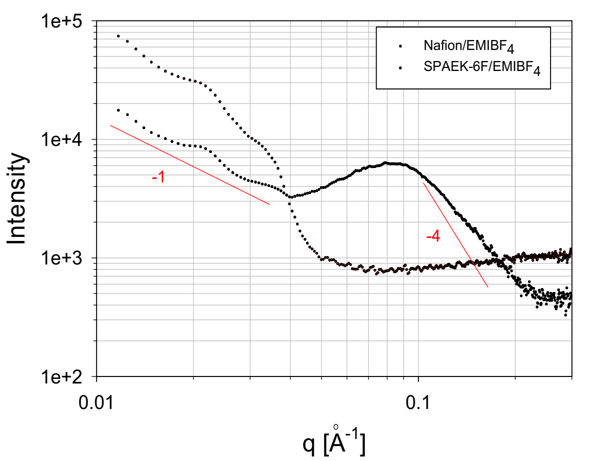

Figure. SAXS spectra of Nafion and SPAEK-6F based membranes containing 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF$_4$).

Characterization of membrane electrode assemblies (MEAs) containing ionic liquids for high temperature fuel cells

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In general, proton conducting membranes have been used in polymer electrolyte fuel cells (PEFCs) as an electrolyte. It is also known that the protons which produced by catalyst reaction of hydrogen passing through water channels in proton conducting polymers. Thus, it is important that sufficient water should exist in the polymer matrix for high proton conductivity. However, under the high temperature operation of the PEFCs, the proton conductivity decreases drastically due to the dehydration of water in the polymer. Therefore, proton conducting polymers require new materials which can play a role as water in the proton conducting polymers. Ionic liquids (ILs), which have superior properties such as wide temperature range, high thermal stability and high ionic conductivity, are focused on a good candidate for the substitution of water in the polymer. We have prepared the membrane electrode assemblies (MEAs) containing the various content of ILs in a catalyst layer. The electrochemical properties of the prepared MEAs were investigated by measurement of cyclic voltamogram and single cell performances.

➢ **Single Cell Test**

➢ **Test Condition**

Cell Temperature : 120 °C
Humidifier Temperature : 98 °C
Active area of electrode : 25 cm^2
Fuel utilization : H_2/Air = 70%/40 %
Pressure : H_2/Air= 0 psig/0 psig

Figure. Single cell performance using a MEA containing the specific contents of ILs.

Efficient removal of toluene vapor by TiO_2 films on carbon fibers

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Using a novel deposition technique, which can be described as pulsed chemical vapor deposition (CVD), TiO_2 thin films were synthesized on carbon fibers. We show that these films can exhibit extraordinarily high absorption capacities of toluene vapor. Such an absorption phenomenon of toluene at room temperature was not found for other TiO_2 samples. We expect that the TiO_2 thin films prepared herein can be used for removing volatile organic compounds from an indoor atmosphere. By X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM), a high concentration of OH species and a unique layered structure were found for the TiO_2 films and these could be related to their high absorption capacity of toluene.

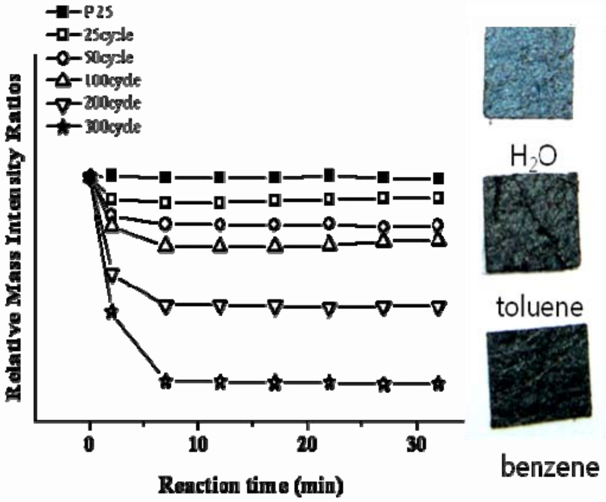

Figure. Change in the relative partial pressure of toluene as a function of time corresponding to the amount of toluene absorbed by the TiO_2 films. The absorption capacities of the TiO_2 films with various thicknesses as well as that of the P-25 sample are compared. Also, the change in the color of the TiO_2-coated carbon papers by exposing to water, toluene and benzene vapors under atmospheric conditions is illustrated.

Carbon supported Pd nanoparticles composited by polypyrrole for polymer electrolyte fuel cell (PEMFC)

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Development of Pt-free electrocatalyst is the most important issue in polymer electrolyte fuel cells because the high price with a limited supply of Pt is an obstacle to successful commercialization of the fuel cells in the near future[1]. In previous works, we have reported a new Pt-free electrocatalyst of conjugated polymer-composted palladium catalyst as an alternative catalyst to platinum in low temperature fuel cells[2]. A significant stability enhancement of Pd by compositing electropolymerized polypyrrole was observed in acidic condition[2]. However, the study investigated over a bulk phase of Pd-PPy electrocatalyst, leading to a low electrochemical active surface area (EAS) of with a relatively low performance in the H_2-O_2 fuel cell condition when compared with a highly dispersed Pt catalyst supported on carbon.

For further studies, in this work, Pd nanoparticles on carbon supports were electrochemically or chemically modified by conjugated polymer. The accelerated tests of the catalysts in severe condition and redox properties of the polymer on Pd were studied using cyclic voltammetry(CV) with three-electrode cell as well as physico-chemical studies by FESEM, EDS , TEM and XPS analysis.

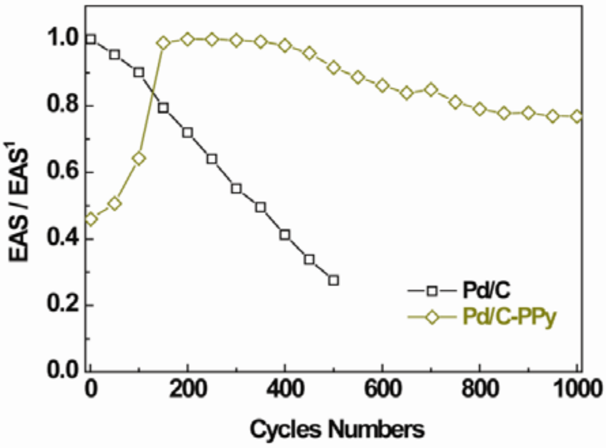

Figure. Long-term accelerated cycle tests of Pd/C (square) and Pd/C-PPy (diamond) electrodes using the three-electrode half-cell systems in 0.1M $HClO_4$ solution at 50 mV/s at room temperature.

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Influence of outer ionomer on the admittance of an MEA and its correlation with the PEMFC performance

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Interfacial resistances between a polymer electrolyte membrane (PEM) and catalyst layer (CL) in membrane-electrode assemblies (MEAs) were quantitatively examined to enhance the PEMFC performance. The outer ionomer was added to vary the interfacial resistance. The total resistance for proton transport (R_{tot}) in MEAs was measured by symmetrical impedance mode (SM) under hydrogen environment. As a result, the improved interface reduced the R_{tot} to 50% of the initial resistance; thus fuel cell performance increased from 0.47 to 1.42 A cm^{-2} at 0.6 V with the outer ionomer content of 0.30 mg cm^{-2}. Particularly, a novel linear correlation between the impedance data and cell performance was attained by introducing the admittance ($1/R_{tot}$) under the same catalyst loading. The admittance mainly exhibits conductance for proton transport through MEAs from anode to cathode by eliminating the resistance for oxygen reduction reaction (ORR). Therefore it is concluded that performance of an MEA in PEMFC can be reasonably predicted from the admittance of proton transport.

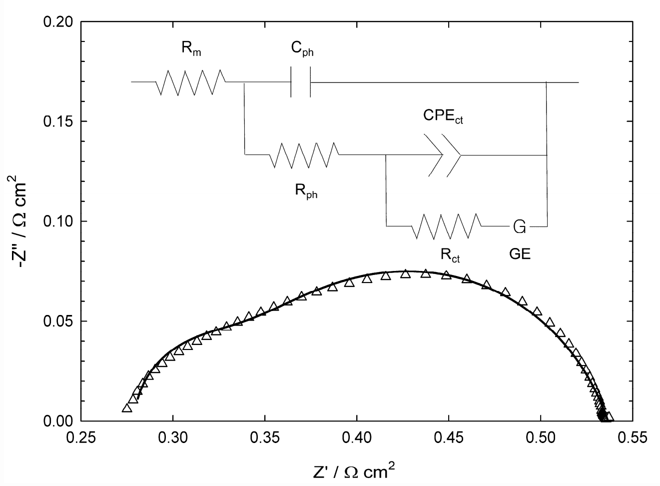

Figure. The impedance spectrum of the symmetrical mode (H_2/H_2) and fitted result according to the equivalent circuit.

Preperation of an amperometric tyrosinase biosensor using gold nanowires synthesized by peptide for detecting pesticide

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Amperometric enzyme-based biosensors have been considered to be the most suitable device for detecting contaminants. To improve the performance of the biosensors, a possible approach is to introduce conducting nanomaterials for the modification of the enzyme electrodes. The gold nanocomposites have some advantages including high chemical stability, large surface area and good biocompatibility. Especially, the gold nonowires (AuNWs) synthesized by a peptide have micron size, well defined morphology and high purity in contrast with other chemical synthesis methods of inorganic nanostructures. We are here concerned with a preparation method of an enzyme-based biosensor using the AuNWs synthesized by a dodecapeptide Midas-11. Ultrasonic dispersion of the AuNWs into N, N-dimethyl formamide (DMF) or nafion solution was carried out. The AuNWs were attached on screen-printed carbon elelctrodes (SPCEs) and modified with formation of self-assembled monolayer (SAM). An oxidoreductase, tyrosinase (Tyr) was immobilized on the AuNW-SPCE by covalent binding. The prepared electrode showed the enzyme-substrate reactions in the catechol solution. The Tyr catalyzes oxidation of catechol in presence of oxygen to produce o-quinone, which can be electrochemically reduced at low potential. The enzyme electrode was also examined to detect pesticides such as parathion and carbaryl. The reduction current of the product (o-quinone) was decreased by the pesticide inhibition of the enzyme activity. The newly designed gold nanocomposite successfully applied in the preparation of the Tyr electrode using SPE for a pesticide detecting biosensor.

Key words: amperometric biosensor, gold nanowires, peptide, tyrosinase, pesticides

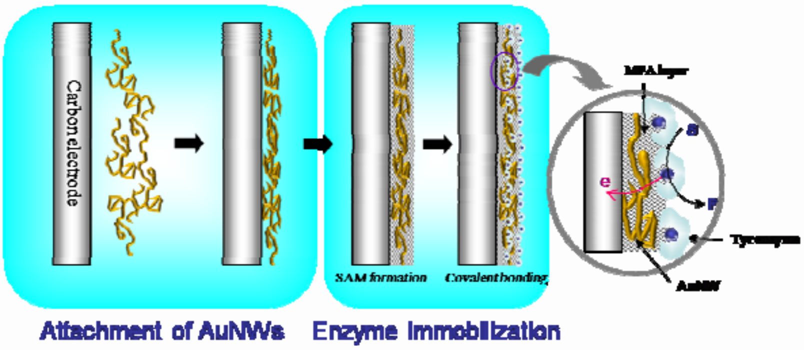

Figure. Preparation of enzyme electrode.

Oscillatory dynamics during the electro-oxidation of ethylene glycol

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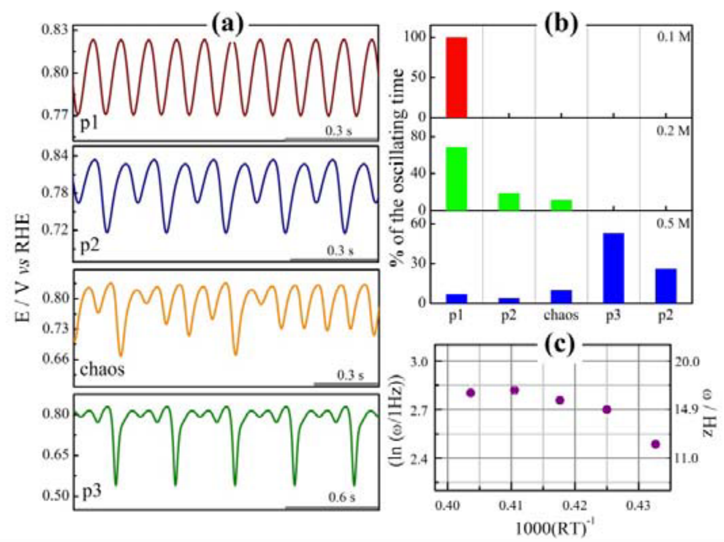
Oscillatory dynamics is commonly observed during the electro-oxidation of small organic molecules. In spite of the considerable number of reported in this direction, there are just few systematic studies, and those are mostly concentrated in formic acid, formaldehyde and methanol. We report in this work the experimental investigation of the electro-oxidation of ethylene glycol (EG) on platinum and in alkaline media. The effect of parameters such as EG concentration and temperature was investigated. Low EG concentration favors period-one, low amplitude states, whereas increasing [EG] results in higher period and chaotic, large amplitude patters, cf. plates (a) and (b). Oscillatory frequencies as high 17 Hz were obtained. Those beta oscillations[1] are at least one order of magnitude higher than most of electro-oxidation of small organic molecules. At lower pHs the oscillatory frequency is considerably smaller, evidencing the role of oxygenated species on the resulting dynamics. Moreover, the system was considerably independent on the temperature, see plate (b). Under regular, non-oscillatory conditions, however, the system shows Arrhenius dependence on the temperature with activation energies around 40 kJ/mol. [2] This show that the reaction is not just insensitive to temperature but that it results from de combination among different steps that compensate each other under oscillatory regime.



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The coolant thermal management effects on membrane conductivity of a PEMFC

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Relative humidity, membrane conductivity and water activity are critical parameters of proton exchange membrane fuel cells (PEMFC) for high performance and reliability. These parameters are closely related with temperature. Moreover, the ideal values of these parameters are not always identical along the channels. Therefore, the cooling channel design and its operating condition should be well optimized along the all location of the channels. In the present study, we have performed a numerical investigation on the effects of cooling channels on performance of a PEMFC. Three-dimensional Navier-Stokes equations are solved with the energy equation including heat generated by the electrochemical reactions in the fuel cell. The present numerical model includes the gas diffusion layers (GDL) and serpentine channels for both anode and cathode gas flows, as well as cooling channels. To accurately predict the water transport across the membrane, the distribution of water content in the membrane is calculated by solving a nonlinear differential equation with a nonlinear coefficient, i.e., the water diffusivity which is a function of water content as well as temperature. Main emphasis is placed on the heat transfer between the solid bipolar plate and coolant flow. The present results show that local current density is affected by cooling channels due to the change of the oxygen concentration and the membrane conductivity as well as the water content. It is also found that the relative humidity is influenced by the generated water and the gas temperature and thus it affects the distribution of fuel concentration and the conductivity of the membrane, ultimately fuel cell performance. Unit-cell experiments are also carried out to validate the numerical models. The performance curves between the models and experiments show reasonable results.

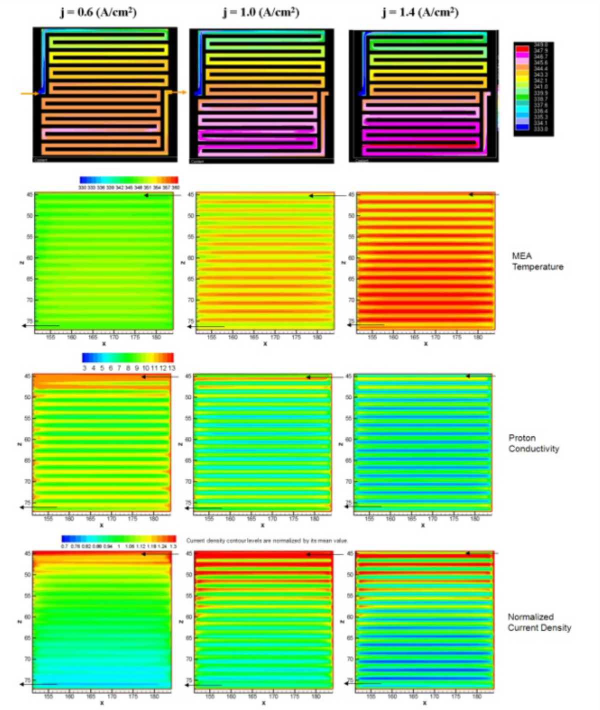

Figure. The analysis result of the operating parameters; coolant and MEA temperature, proton conductivity and density.

Adsorption and photocatalytic decomposition of toluene on TiO_2 surfaces

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Adsorption of toluene and its photodecomposition by TiO_2 surfaces under UV irradiation was studied using P-25 samples with two different treatments. In order to shed light on the elementary steps of the photocatalytic decomposition of toluene, in-situ X-ray Photoelectron Spectroscopy (XPS) was employed. Evidence is provided that a higher population of the surface OH-group of TiO_2 increased the adsorption reactivity and initial rate of the photodecomposition of toluene. A more efficient accumulation of toluene on the surface of TiO_2 with a high concentration of the OH-groups was also identified by the in-situ XPS.

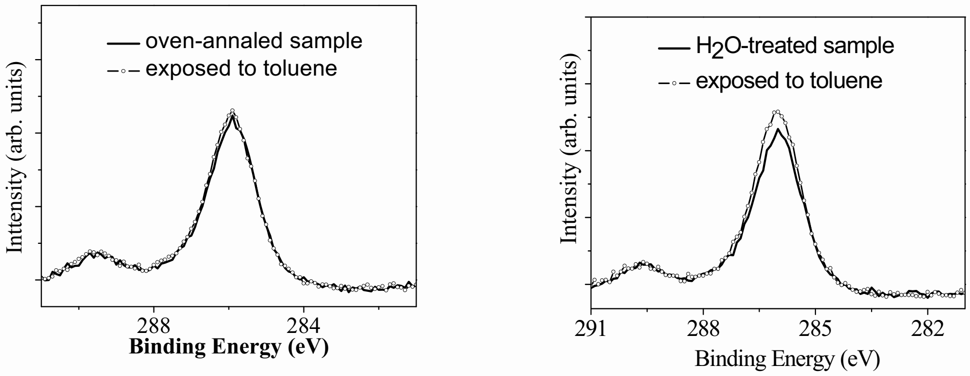

Figure. C 1 spectra taken after various treatment in the preparation chamber. Left: The H_2O-treated sample was exposed to toluene (4 mtorr, 3hr) in the absence and presence of UV light. Right : The oven-annealed sample was exposed to toluene (4 mtorr, 3hr) in the absence and presence of UV light.

Mechanism of hydrogen evolution reaction catalyzed by 4,4'-bipyridine adsorbed on metal electrodes: A combined electrochemical and infrared study

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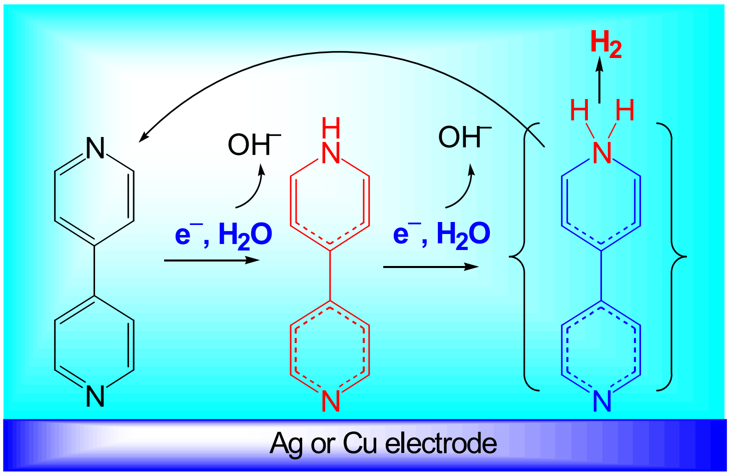
It is well known that addition of some organic molecules containing N atoms into aqueous solution enhances hydrogen evolution reaction (HER) on metal electrodes. However, its mechanism is still unclear. Recently, we found that 4,4'-bipyridine (BiPy) significantly enhances HER on Ag electrodes in neutral and basic aqueous solutions, and proposed that the proton-coupled redox of adsorbed BiPy catalyzes the HER[1]. In the present poster, we will discuss further details of the mechanism through a comparison with the measurements on Cu, Au, and Pt electrodes.



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Electrochemical deposition of Pt-Co catalysts for PEMFC

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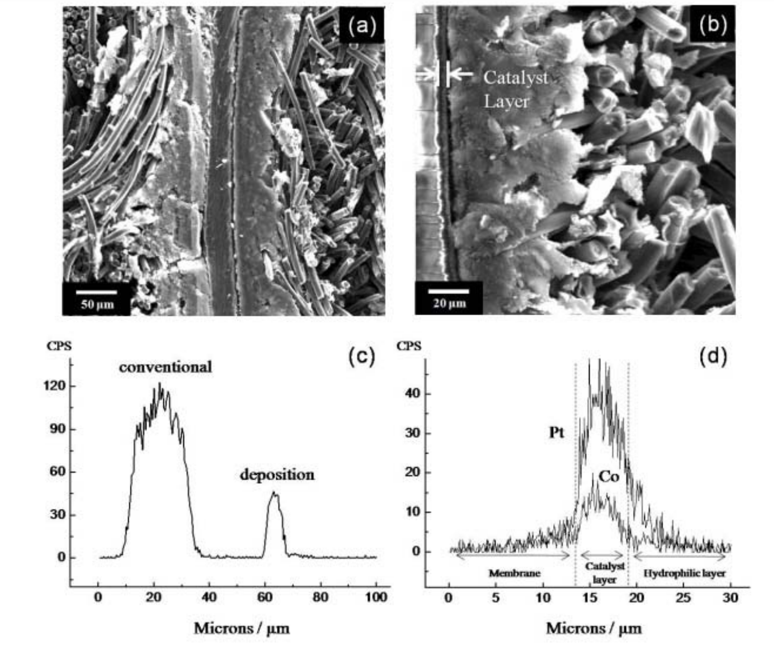
One of the key issues for the wide application of fuel cells is overcoming the economic barrier. In order to reduce the cost, many attempts have been tried, especially to reduce the amount of precious metal used in the catalysts. In this respect, low loading platinum-cobalt (Pt-Co) electrodes were prepared by using galvanostatic pulse technique to show advantages of the electrodeposition for high utilization of catalysts of PEMFC.[1,2] We confirmed that Pt-Co catalysts mainly exist on the surface of carbon layer and the thickness of the catalyst layer was about 5.8 μm measured by SEM coupled with EPMA. Therefore, the electrodeposition can increase the number of triple-phase boundaries where reactant molecules are in contact with catalysts and ionomers. The particle size of the pulse electrodeposited Pt-Co catalysts was measured by HR-TEM, and XRD patterns confirmed the prepared Pt-Co electrode in alloy state. Particle size of the alloyed particles was 3-4 nm. Electrocatalytic activity of Pt-Co catalysts was measured. The Pt-Co catalysts with 3.2 : 1 were found to provide the highest single cell performance among the compositions studied. Pt-Co catalysts showed higher performances than Pt/C. Details of the experimental procedures and results will be discussed.



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Photocatalytic characteristics of Ag-deposited TiO_2 nanoparticles encapsulated with titanium oxide shells (Ag-TiO_2@TiOx)

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In this research, we present the encapsulation of Ag-deposited titanium dioxide with titanium oxide shell (Ag-TiO_2@TiO_x) via the ultrasonic-assisted sol-gel process that is optimized in terms of silver precursor, amounts of ammonia and TEOT, and ultrasonic power. Ag-TiO_2@TiO_x with optimized shell thickness exhibited the higher photocatalytic activity than those of the pristine TiO_2 and Ag-deposited TiO_2 (Ag-TiO_2). The PL spectra of Ag-TiO_2@TiO_x were lower than that of the pristine TiO_2, indicating the increased separation efficiency of electron-hole pairs. The excessive encapsulation of TiO_x overlayer, however, induced the decrease of photocatalytic activity of Ag-TiO_2 nanocomposites owing to the formation of amorphous phases through the ultrasonic-assisted sol-gel reaction. The annealed nanocomposites at 500 ^{o}C for 2 hrs exhibited enhanced photocatalytic activity as compared to non-annealed nanocomposites, probably due to the partial transformation of amorphous phases into crystalline phase of TiO_2.

Key words: Ag-TiO_2, titanium oxide shell, ultrasonic, sol-gel, photocatalytic activity

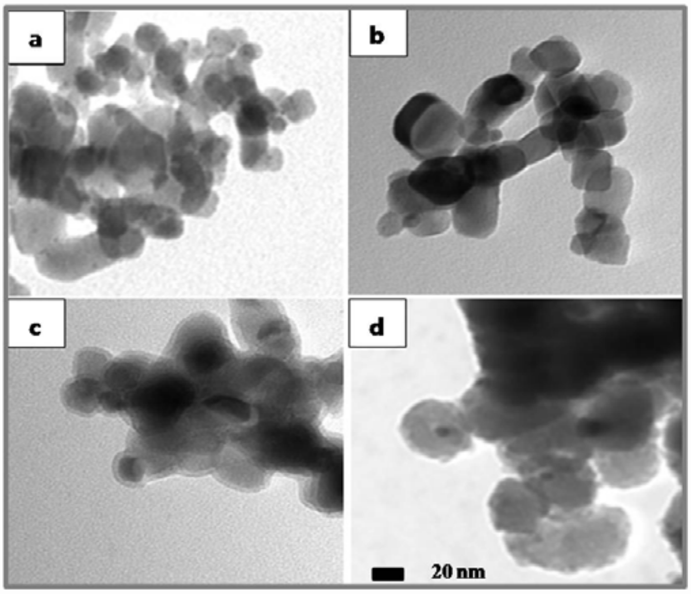

Figure. Ag-deposited TiO_2 prepared by the sonochemical reduction with different loading amounts of silver precursors: (a) Ag-TiO_2 (0.2 ml of 1.0 wt% $AgNO_3$), (b) non-annealed Ag-TiO_2@TiO_x (0.042 ml of TEOT), (c) non-annealed Ag-TiO_2@TiO_x (0.085 ml of TEOT), (d) non-annealed Ag-TiO_2@TiO_x (0.85 ml of TEOT). The scale bar indicates 20 nm.

Electrodeposited nanoporous Ni electrode for water electrolysis and ethanol oxidation in alkaline media

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Nickel is currently considered a suitable electrocatalyst for anodic reaction in water electrolysis and organic molecules oxidation in alkaline media due to its surface oxidation properties. In addition to being a relatively low cost, nickel has better corrosion resistance in the alkaline media than other transition metals. However, it has the problems of low performance compared to noble metals and anodic degradation due to progressive oxidation.

In this study, a nanoporous Ni electrode was fabricated by electrodeposition into alumina template. During the electrodeposition, the gas evolution was intentionally induced in a Ni sulfamate bath without boric acid which acts as a pH buffering agent. The resulting structure shown in Fig. is highly porous like foam.

The fabricated nanoporous Ni electrode was applied to oxygen evolution reaction for water electrolysis and ethanol oxidation in alkaline media. The nickel oxide formed by the redox process on the nickel surface accompanies oxygen evolution in water electrolysis and promotes the dehydrogenation during ethanol oxidation.

The structure and nature of the porous Ni were characterized by SEM, TEM and XRD. The electrocatalytic activity for oxygen evolution and ethanol oxidation was measured using linear sweep voltammetry, cyclic voltammetry and chronoamperometry. In order to evaluate its performance, it was compared to the Ni nanowire electrodeposited in a conventional sulfamate bath containing boric acid.

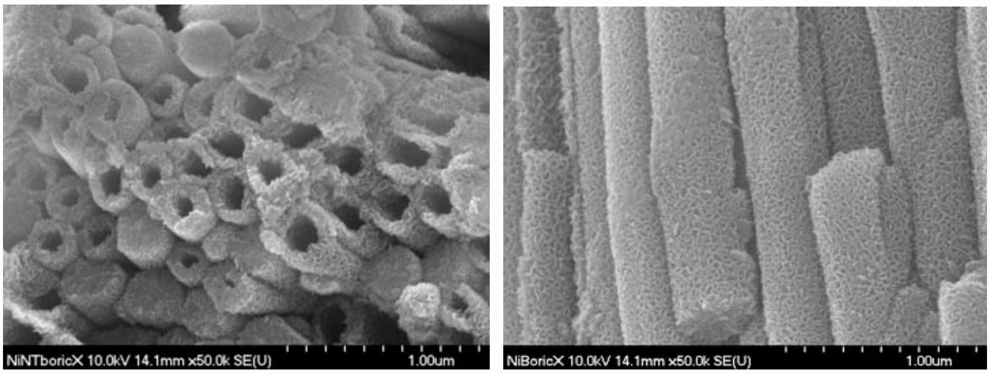

Figure. SEM images of the nanoporous Ni electrode electrodeposited without boric acid at -10mA/cm^2 for 600s.

Surfactant-assisted anodization for nanoporous niobium oxide

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In this presentation, we describe the preparation of nanoporous niobium oxide film with a thickness of 520 nm by anodization of niobium in a mixture of 0.1 M HF, 1 M H_3PO_4, and small amount of SDS surfactant (Figure. 1). We found that a pore depth and surface pattern were strongly affected by the concentration of SDS and temperature in solution. The addition of SDS surfactant improves chemical resistance of niobium oxide during anodization, leading to the formation of pores with a longer length compared to that prepared without SDS surfactant. It can be in part ascribed to protection of surface by the physical adsorption of SDS on the surface due to charge-charge interaction and be in part attributed to the formation of Nb=O bonding on the outermost oxide layer by SDS.

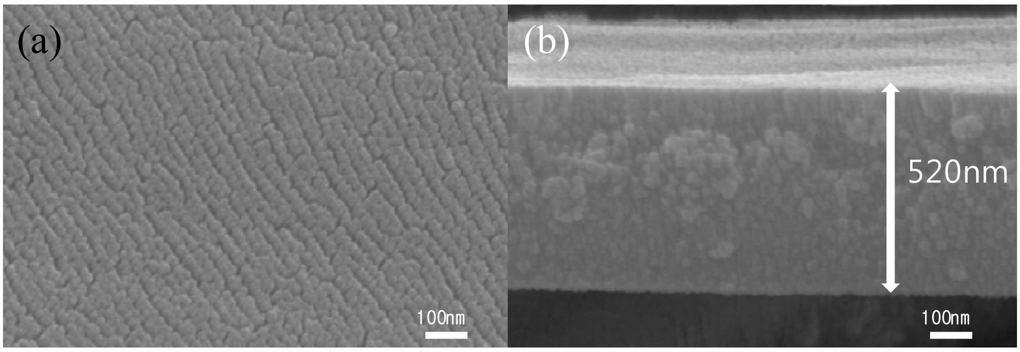

Figure. Anodic niobium oxide prepared by anodization of a niobium foil in a mixture of 0.1 M HF and 1 M H_3PO_4 with the addition of sodium dodecyl sulfate (SDS) surfactant. Anodization was carried out at 5 ℃ for 2 h. Usually, anodic niobium oxide with a thickness of less than 180 nm was obtained at 5 ℃ for 2 h in a mixture of 0.1 M HF and 1 M H_3PO_4 without SDS.

Effects of particle size on surface electronic and electrocatalytic properties of Pt/TiO$_2$ and PtRu/TiO$_2$ nanocatalysts

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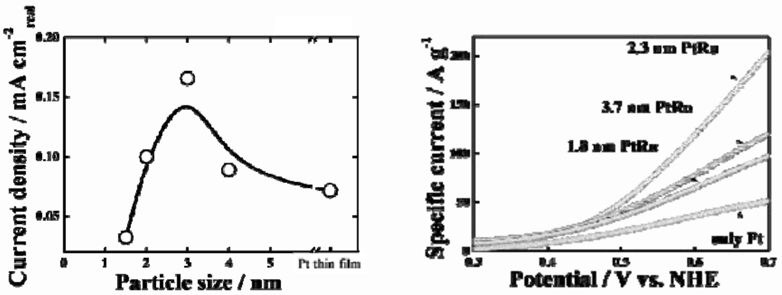
The reaction of Pt particles can be promoted by a TiO$_2$ support, which can lower the adsorption energy of CO. The adsorption of OH on TiO$_2$ can also facilitate the conversion of the poisonous CO into CO$_2$.[1] Despite the extensive efforts that have recently been made to elucidate this extraordinary catalytic behaviour, the correlation of the interfacial properties between the catalyst and solution and the effects of the particle size remain obscure. Herein, we present a new view of supported metal catalysts, which allows them to be much more carefully defined, and illustrate its use in addressing the origin of the size effects.



(a)
(b)

Figure. (a) Specific activity of Pt/TiO$_2$ nanocatalysts and Pt thin films electrodes. (b) Polarization curves for the oxidation of methanol on the 1.8 nm ~ 3.7 nm PtRu/TiO$_2$ nanocatalysts.

In this study, we investigated the oxidation of methanol on Pt/TiO$_2$ and PtRu/TiO$_2$ nanocatalyst electrodes with various sizes compared with that obtained on a pure Pt electrode by using a potential of zero total charge (PZTC) system to analyze the degree of oxophilicity and an in situ X-ray absorption near-edge structure (XANES) system to analyze the electronic states. We focused on the surface electronic structures at the metal-solution-interface of the Pt/TiO$_2$ and PtRu/TiO$_2$ nanocatalysts. To clarify these effects, we introduced a correlation between the values of the PZTC and the in situ XANES on the size-controlled Pt or PtRu induced by the TiO$_2$ support and the methanol oxidation reaction (MOR) activity. The results obtained in this study unambiguously indicate that the specific activities of the MOR are dependent on the particle size, which is in complete agreement with the variation of the oxophilicity, that is, the coverage of the catalyst with oxygenated species.

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RuO_2-Carbon composites as a hybrid capacitor

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Supercapacitors such as electrochemical double layer capacitors (EDLCs), pseudo-capacitors, and hybrid capacitors can store large amounts of electrical charge in atoms-thick layers of the electrodes, theoretically resulting in an indefinite circulation current.[1] During a charging process in energy storage for supercapacitors, the electrically charged ions from the electrolyte migrate towards electrodes of an opposite polarity created by an external potential.[2] In addition, since a chemical reaction is merely involved in supercapacitors, the effect is easily reversible with respect to minimal degradation and rapid charge/discharge. For this reason, supercapacitors can be applied to hybrid power systems that involve batteries and an effective short duration peak power boost.[2] Although pseudo-capacitors composed of metal oxides (i.e., RuO_2) have been demonstrated to have a specific capacitance of about 720 F g^{-1}, which is higher than EDLCs (ca. 300 F g^{-1}),[3,4] economic efficiency should be taken into account. Thus, the use of other less expensive materials for hybrid capacitors has been examined with the promise of developing devices with both high performance and low cost.

In this study, we synthesized RuO_2 composites with various carbons including carbon aerogel, alginate and hierarchical porous graphite carbon for electrode materials in hybrid capacitors. Then, the specific capacitance of each materials was determined using a half cell test in 1 M H_2SO_4 solution with the 3-electrode cell, as well as using a single cell test in the coin cell fabricated by a paste rolling method. Additionally, the prepared RuO_2 composite materials were characterized by TGA, BET, XRD and XPS.

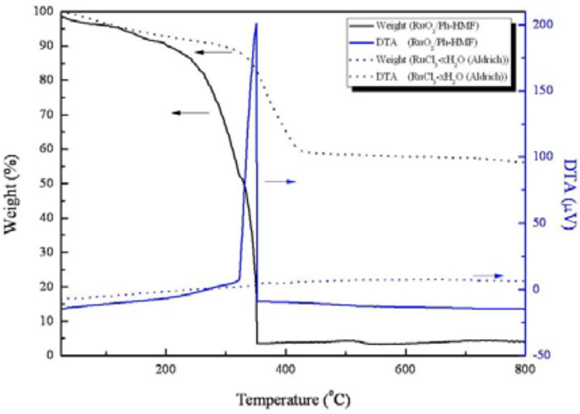

Figure. TGA-DTA of RuO_2 carbon aerogel and $RuCl_3$-xH_2O.

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