

Nano and crystal structures of hydrogen storage materials

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Hydrogen storage and transportation are one of the critical issues to realize the hydrogen economy because energy density of hydrogen is only 1/3000 of gasoline. Because hydrogen storage materials absorb hydrogen more than 1000 times of their volume, they are expected to be applied for on board hydrogen storage.

Japan is conducting a few National R & D projects on fundamentals, application and codes & standards of hydrogen storage materials.

Our recent studies revealed that nano structure, crystal structure and defects in the lattice significantly influence the hydrogen storage properties such as hydrogen capacity, hydrogen equilibrium pressure, and the cyclic life.

LaNi₅ showed higher hydrogen absorbing pressure at the first hydrogenation than that of the second and following hydrogenation. Using in-situ X-ray diffraction method, lattice strain and crystallite size were measured during the first hydrogenation and dehydrogenation. Huge lattice strain introduction was observed at the first hydrogenation and the introduced strain remained the lattice in the following hydrogenation/dehydrogenation cycles¹⁾. Yamamoto et al.²⁾ observed significantly dense dislocations in LaNi₅ after repeated hydrogenation by transmission electron micrograph (TEM). The Burgers vector of the lattice strain analyzed by in-situ X-ray diffraction agreed that of dislocation observed by TEM. Positron life time in the lattice of LaNi₅ was measured during hydrogenation³⁾. It was clearly shown that both dislocation and vacancy were introduced into the lattice. We concluded that observed lattice strain by in-situ X-ray diffraction is dislocations introduced by hydrogenation.

If some part of Ni in LaNi₅ is substituted by the third element, defect introduction changed dramatically. When Al is replaced to Ni, around 1/10 of defect to LaNi₅ was introduced into the lattice⁴⁾. In case of Sn substitution, the concentration of defects became around 1/100 of LaNi₅. In addition, the defect introduced in Sn substituted LaNi₅ is reversible; the defect is released with dehydrogenation at room temperature⁵⁾.

In 1996, we reported that Ti based alloys with BCC structure is the potential materials for on board hydrogen storage because the alloys developed have the hydrogen capacity of 2.6 mass % that is almost double to the conventional AB₅ type alloys⁶⁾. One of the authors named these alloys as "Laves phase related BCC solid solution alloys". These alloys have a modulated structure originated from spinodal decomposition. Laves phase related BCC alloys are composed of two BCC phases formed by spinodal decomposition, which means that these phases have slightly different lattice parameters and coherent phase boundary. We assume that physical interaction such as tension through the coherent boundary influences the

hydrogen absorbing properties, especially the hydrogen content.

Recently, local structure around hydrogen in the Laves phase related BCC alloys have been investigated by radial distribution functions of constituting elements including hydrogen using neutron total scattering data⁷⁾. Hydrogen is not located at the center of the interstitial sites composed by transition metals. However, conventional diffraction method can not observe these phenomena because the center of the hydrogen positions is at the center of interstitial sites even though hydrogen does not occupy the center. It has been reported this occurred in the V-H system and this is induced by the strain in the lattice introduced by hydrogenation. It strongly suggests that the local structure that is influenced by the lattice strain is closely related to the cycle life of the alloys.

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Corrosion-resistant sub-stoichiometric titanium oxides as PEMFC catalyst support materials

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Durability of proton exchange membrane fuel cell (PEMFCs) is an important subject before commercialization of the PEMFC power generation systems [1,2]. Although many factors are related to the durability in the actual PEMFC systems, corrosion of carbonaceous catalyst support materials have been recently recognized as one of the factor of performance degradation [3,4]. In particular, rapid carbon corrosion was reported by several groups under repeated start-stop cycles [5,6]. Reiser et al. [5] showed a mechanism of potential excursions of the cathode up to 1.5 V due to a H₂/air boundary in the fuel flow stream, causing carbon corrosion and performance degradation. This H₂/air boundary is likely to arise during start-stop cycling. Therefore, a more oxidation-resistant catalyst support at high potentials is needed for practical fuel cells, especially for automotive applications because 30,000 start-stop cycles is estimated over the life of the vehicle [2].

As alternative catalyst-support materials, some conducting oxides such as sub-stoichiometric titanium oxide [7,8], niobium-doped titanium oxide [8,9], indium tin oxide [10], and sulfonated zirconium oxide [11] have been reported. Sub-stoichiometric titanium oxide of the general formula Ti_nO_{2n-1} (4 < n < 10), which is known as Magnéli phase [12], is an attractive material because of its high electric conductivity. In this series of distinct oxides, the Ti₄O₇ phase exhibits the highest electrical conductivity (ca. 10³ S cm⁻¹) at room temperature, which is comparable to that of graphitized carbon [13]. In this presentation, I will discuss the applicability of Ti₄O₇ as an oxidation-resistant catalyst support, based on its electrochemical properties. Ti₄O₇ catalyst support shows better oxidation-resistance than conventional carbon black support at high potentials > 1.0 V [7]. Nano-sized platinum particles are deposited on Ti₄O₇ support (Pt/Ti₄O₇) and electrochemical properties of the Pt/Ti₄O₇ catalysts were examined under actual PEMFC operation conditions. In particular, effects of high potential holding (1.0 – 1.5 vs. H₂ anode) on the electrochemical activity and stability of Pt/Ti₄O₇ catalyst in comparison to a Pt/C will be discussed.

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Biography

Tsutomu Ioroi received the M.S. and Ph.D. degrees in engineering from the Kyoto University, Japan in 1994 and 1997. His Ph.D. dissertation investigated ideal anode structure and electrode reaction mechanisms on cathode in solid oxide fuel cells. He joined as a Research Scientist in the Osaka National Research Institute in 1997. In 2001, Osaka National Research Institute was re-organized as National Institute of Advanced Industrial Science and Technology (AIST). Since he joined the institute, he explored electrocatalyst materials mainly for PEMFC and unitized regenerative fuel cell (URFC), including CO-tolerant anode catalysts, alternative catalyst support used for cathode catalysts, and bi-functional Pt/Ir catalyst material and structure for O₂ evolution/reduction electrode.

Development of new hydrocarbon membranes

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For fuel cell membranes, perfluorinated sulfonic acid ionomers have been most studied. There is a great demand, however, for non-fluorinated alternative membranes in terms of production cost, environmental friendliness, and high temperature stability. Through the research work on hydrocarbon ionomer membranes, we have developed highly proton conductive polyethers¹ and polyimides² which were durable for 5000 hours in H₂/O₂ fuel cells.^{3,4} In this lecture, we herein report optimization of the chemical structure of sulfonated polyethers (SPEs) for improving proton conductive properties at high temperature and low humidity.⁵

In order to increase the ion exchange capacity (IEC) and thus proton conductivity without sacrificing hydrolytic, oxidative, dimensional, and mechanical stability, we have investigated the effect of methyl substituents on the sulfonated aromatic polyethers (SPE-Me, Fig.1 where R₁-R₅ are CH₃ and A is isopropylidene groups). Methyl group substitution resulted in a higher IEC membrane with substantial chemical and dimensional stability. The SPE-Me membrane showed comparable proton conductivity to Nafion at 20 - 93% RH (Fig. 2). The new membrane was stable in conductivity measurement at 80 and 120 °C for 10000 hours. A fuel cell operated at 20% RH and 90 °C using the SPE-Me ionomer membrane showed better performance than that of Nafion.

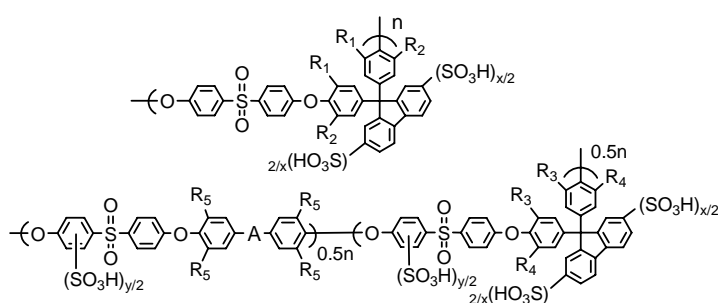


Fig. 1 Chemical structure of SPE-Me.

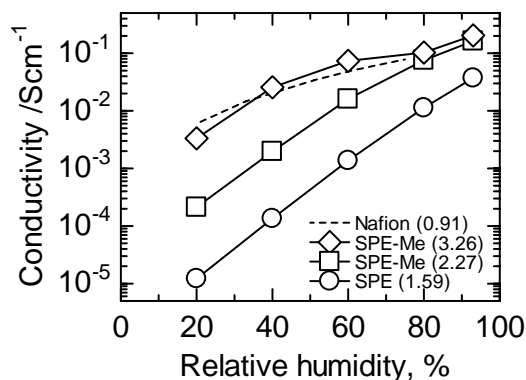


Fig. 2 Humidity dependence of the proton conductivity of SPEs and Nafion at 100 °C with IEC value in parenthesis.

Another strategy we have adopted for improving the membrane properties is to incorporate acid functionalized silica (polysilsesquioxane; SiOPS).⁶ Composite membranes were prepared by in-situ sol-gel processing of a precursor, 3-trihydroxysilyl-1-propanesulfonic acid (THOPS), in the ionomer solution followed by

casting (Figure 3). The composite membranes showed higher water uptake and higher proton conductivity than those of the bare ionomer membranes. Especially, proton conductivity at low humidity was significantly improved. The methodology is likely versatile as confirmed with two different series of polymer electrolytes, although the miscibility with SiOPS depends on the matrix polymer. Other membrane properties will be presented.

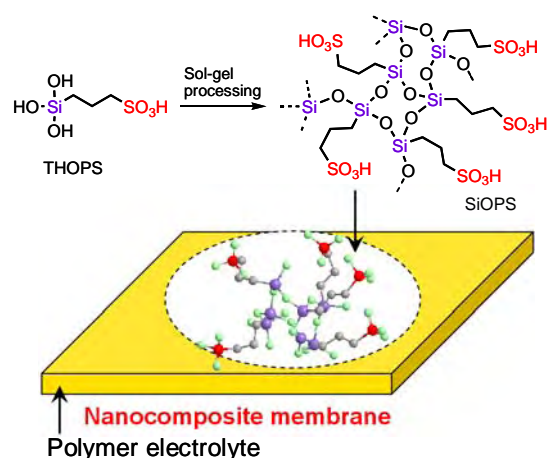


Fig. 3 Preparation of SPE and SiOPS composite membrane.

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Dr. Kenji Miyatake received his PhD degree in Polymer Chemistry from Waseda University under the supervision of Prof. Eishun Tsuchida in 1996. He worked at McGill University (Canada) as a postdoctoral fellow with Prof. Allan S. Hay until 2001 supported by JSPS. He is currently an Associate Professor at University of Yamanashi. His research interest involves design, synthesis, and characterization of new functional polymers especially for polymer electrolyte fuel cell applications.

Highly Durable MEAs for PEM Fuel Cells

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Over the past few years the durability of the membranes has been one of the most important issues in the development of polymer electrolyte membrane (PEM) fuel cells.

For automotive use, in particular, durability under severe operating conditions, such as high temperatures of 110-120°C and low humidity, is required.

Perfluorosulfonic acid (PFSA) polymers have been widely used for membranes in PEM fuel cells because PFSA polymers have considerably higher chemical stability than hydrocarbon-based polymers.

However, a membrane electrode assembly (MEA) can be degraded by the attack of hydroxyl radicals under low humidity conditions¹ even though it employs a PFSA polymer whose glass transition temperature is around 80°C. In addition, a critical breakdown of the membrane occurs when an MEA is operated at high temperatures. Operating conditions for PEM fuel cells are, therefore, limited to low temperatures (below 80°C) and high humidity conditions (ca.100% RH).

In 2004 we announced the success in developing the world's first highly durable PFSA polymer-based MEA which operated under high temperatures and low humidity conditions.^{2,3,4} The newly developed MEA using a new polymer composite (NPC) membrane was able to operate for more than 4,000 hours under the severe conditions of 120°C and 50% RH.

Fig.1 indicates the result of MEA durability testing operated at 0.2A/cm², 120°C, 50%RH and 200 kPa_{abs}. The control MEA with a conventional PFSA membrane failed within 100 hours of operation, releasing a high amount of fluoride ion; meanwhile, NPC MEA-I showed excellent durability for more than 4,000 hours.

Although NPC MEA-I gave the fluoride ion release rate as small as 1% of the control MEA, its degradation rate was approximately 75μV/hr during the 4,000 hours of operation, which was still not satisfactory for practical use.

Intensive postmortem analysis of the MEA showed that the degradation was mainly due to the damage of the cathode catalyst layer. Based on the analytical results, we have been working on the improvement of catalyst layers as well as membranes.

Fig.2 shows the durability of our state-of-the-art MEA, NPC MEA-VII, which employs our original cathode catalyst. The operating conditions are the same as shown in Fig.1.

The MEA has an excellent degradation rate; below 3μV/hr during the 6,000 hours of operation. My presentation will cover the degradation mechanism of the conventional membrane and MEAs, and also more detailed performance of the NPC MEA.

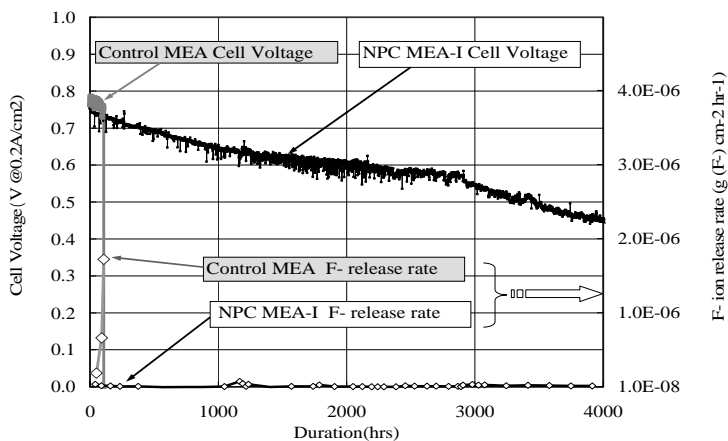


Fig.1 Durability of Control MEA and NPC MEA-I

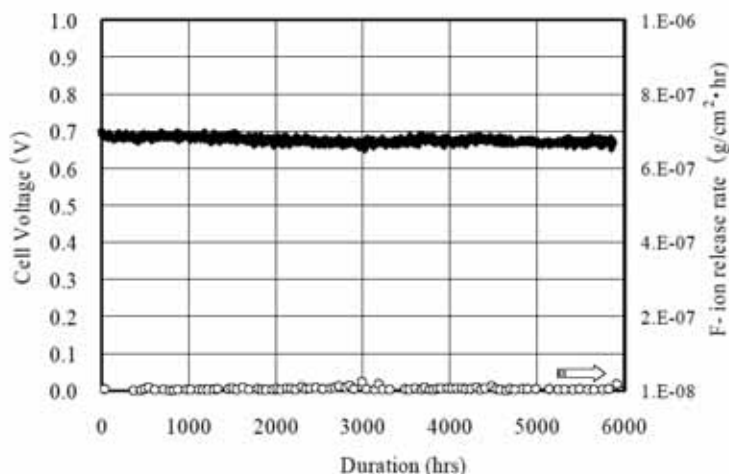


Fig.2 Durability of NPC MEA-VII

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Biography



Hideki Nakagawa received an M.S. degree in chemistry from Kyoto University in 1986, completing his thesis on photochemical reaction mechanism of amino acid derivatives in the presence of singlet oxygen. He joined Asahi Glass at the research center in that year and developed novel composite polymers for electronic devices etc. for 11 years. From 1997 to 2002, he worked on new business development focused on energy and environment fields at the technology planning division in headquarters. In 2002, he moved to the Fuel Cell Project and has been involved in a variety of MEA design and marketing activities as a technical leader for the past few years. He is currently the senior manager for MEA technology and business development.

New alloy foils for fuel reforming and hydrogen purification

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Hydrogen storage alloys or compounds, which are representative metallic materials for hydrogen energy applications, require quick hydrogen absorption and desorption. So they need high surface area and short distance for hydrogen diffusion, thus they are used in crashed or pulverized state. Brittleness of the alloy is even preferred.

While, metallic membrane materials for hydrogen purification have to keep their monolithic membrane structure under certain hydrogen pressure, to assure impurity gas molecules never permeate the membrane. As long as the membrane is free from pinholes or small cracks, hydrogen atoms can only easily permeate the membrane by lattice diffusion. The materials need a resilient structural feature, instead of embrittlement in hydrogen.

Here I introduce the recent development of metallic foil materials for two purposes in hydrogen energy applications: hydrogen purification and fuel reforming. It is well known that hydrogen diffusivity is faster in bcc metals than in fcc metals. The most typical example is PdCu. Hydrogen diffusion coefficient for bcc (B2) structure is larger than that in quenched fcc structure at the same composition, in four orders of magnitude at room temperature.¹ So, the main target materials are bcc alloys, vanadium^{2,3} or niobium⁴, for hydrogen purification membranes.

At NIMS, we have continued to ductilize the brittle Ni₃Al intermetallic compound. Recently we have succeeded in fabricating a thin foil of Ni₃Al to a thickness of 20 μm.⁵ We have also found a catalytic activity of the Ni₃Al foil for methanol decomposition⁶ or methane reforming.⁷ The foil is well deformable and weldable, and expected to be applied in reactor materials at high temperature for fuel reforming reactions to produce hydrogen.

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Biography

Dr. C. Nishimura received the M.S. and Ph.D. degrees in materials science from Waseda University, Tokyo, Japan in 1984 and 1996. His Ph.D. dissertation investigated environmental embrittlement in $L1_2$ -ordered $(\text{Co,Fe})_3\text{V}$ and Ni_3Al at room temperature. He started his research career in National Research Institute for Metals (NRIM), Japan. There he investigated combustion synthesis of hydrogen storage alloys, hydrogen diffusion behaviors in alloys, hydrogen embrittlement of intermetallics. From 1990 to 1991, he was with the Oak Ridge National Laboratory, Tennessee, USA, as a Visiting Scientist, exploring the moisture-induced hydrogen embrittlement in $L1_2$ -ordered $(\text{Co,Fe})_3\text{V}$ and reaction sintering of Ni_3Al . In 2001, NRIM turned to be National Institute for Materials Science (NIMS), the only one Independent Administrative Institution for Materials Science in Japan. Since 2006, he has been with the Fuel Cell Materials Center, NIMS, as the Managing Director of the Center and as the Group Leader of Hydrogen Purification Materials Group, mainly involved in the investigation of the vanadium-based alloy membranes for producing highly pure hydrogen for the fuel of PEFC.

Oxidation of carbon materials – Reaction of HOPG deposited with nano-Pt catalyst

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PEMFC is attracting much attention not only of researchers and engineers but also even of investors and politicians because of its potential to solve issues of energy and environment. Some of large problems for PEMC remaining to be solved are its durability and cost. Carbonaceous materials play important roles in PEMFC such as catalyst support, GDL layer, and separator. Carbonaceous materials are not always stable under conditions of PEMC operation. The low stability of carbon materials causes some serious problems such as flooding and catalyst degradation. In this work, oxidation of carbon was investigated using HOPG with and without deposited nano-platinum particles as a model of Pt/C electrode under conditions of potential holding and potential cycling in 1 M H₂SO₄.

HOPG surface is not so stable as expected and is oxidized to form some surface functional group containing oxygen even without deposition of nano-platinum catalyst during potential cycling and potential holding. The oxidized layer grows at the initial stage of exposure to the operating conditions, up to 20 h at 0.6 – 1.0 V, and the oxidized layer is fairly weak. The oxidized layer at high potential contains C=O and C(O)O group. shows redox current on CVs assigned to quinon / hydroquinon couple. The current increased with oxidation together with increase in charging current of surface double layer. The introduction of functional group containing oxygen on the surface by the oxidation process decreases hydrophobicity of the HOPG surface gradually, which can lead to flooding.

Surface is weakly oxidized during potential holding at 1.0 V and some hillocks or swells are observed on the HOPG surface. The prolonged exposure extends the oxidation and leads to the formation of some pits on the surface.

Potential cycling beyond 0.6 V causes oxidation of HOPG surface. Upper and lower limits potential limit during cycling give influences on the surface oxidation. Potential cycling beyond 0.8 V accelerates the surface oxidation. Surface oxidation during potential cycling is more remarkable between 1.0 V and

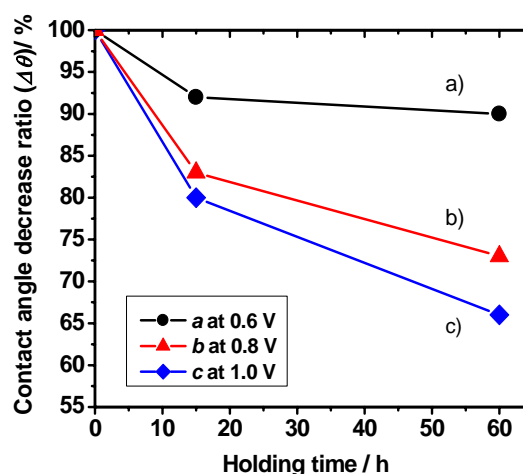


Fig. 1 Contact angle after holding at fixed potential without Pt

0.2 V than 1.0 V and 0.5 V.

Platinum deposition accelerates the oxidation as shown in Fig. 2 and surface roughness estimated from double layer capacitance increased more than the case without Pt loading.

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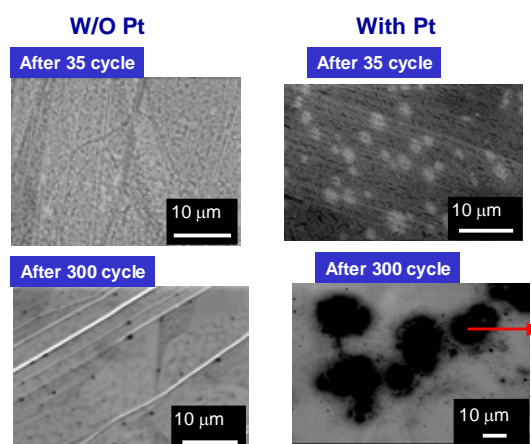


Fig. 2 HOPG surface after potential cycling 0.2—0.8 V with & W.O Pt without Pt

Dr. Z. Ogumi has graduated from Department of Industrial Chemistry, Faculty of Engineering, Kyoto University in 1968 and has received the M.S. and Ph.D. degrees in Engineering from Kyoto University in 1970 and 1979. His Ph.D. dissertation investigated “Electro-initiated polymerization of acryl amide”. He worked for one year as a Research Scientist in Fritz-Haber Institute of Max-Planck Foundation in West Berlin in Germany before he became an Assistant Professor with Kyoto University in 1981. During his professorship he explored organic electrochemistry, Solid Polymer Electrolyte (SPE) Electrolyzer, plasma CVD for preparation of ionically conductive thin film, SOFC, PEMFC, and lithium ion batteries. He is now the President of the Electrochemical Society of Japan.



Non Platinum Cathode for Polymer Electrolyte Fuel Cell

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Introduction

Polymer electrolyte fuel cells (PEFCs) are expected as power sources for residential and transportation applications due to their high theoretical efficiency of energy conversion, high power density and low operating temperature. However, PEFCs have some serious problems to be solved before a wide commercialization. In particular, the large overpotential of oxygen reduction reaction (ORR) must be reduced in order to obtain high energy efficiency. Although Pt is generally used as a cathode catalyst in the present PEFCs, its catalytic activity for the ORR is insufficient. Other issues regarding the Pt usage are its high cost and limited resources. Considering the application to FC vehicles, the natural source of Pt is insufficient. Therefore, the development of a stable non-platinum catalyst is strongly required

In this study, non-platinum materials such as transition metal oxynitrides and oxides have been tried to apply to the ORR catalysts without Pt. Tantalum oxynitride (TaON) [1, 2], zirconium oxide (ZrO_{2-x}) [3, 4], titanium oxide (TiO_{2-x}) [5], zirconium oxynitride (ZrON) [6], and partially oxidized TaCN [7] were prepared using various methods and evaluated as new cathode catalysts.

Results and Discussion

Table 1. Solubility of new ceramics for non-Pt cathode in 0.1 M H_2SO_4 at 30°C under atmospheric condition.

Catalysts	Preparation	Solubility / $\mu mol dm^{-3}$
TaO _x N _y (Powder)	Nitridation of Ta ₂ O ₅ with NH ₃	0.33
TaO _x N _y (Film)	Reactive sputtering	0.20
ZrO _x N _y (Film)	Reactive sputtering	0.04
TiO _{2-x} (Plate)	Heat treatment	0.36
Pt (Powder)		0.56

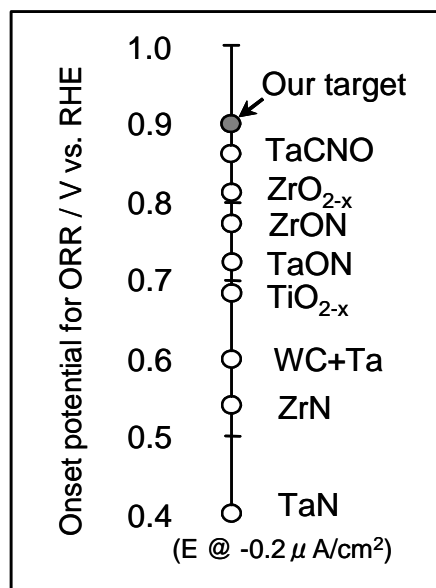


Fig.1 Comparison of the onset potential for the ORR of non-platinum catalysts. (0.1 M H_2SO_4 , 30°C)

We believe that a high stability is initially needed because the cathode catalysts are

exposed to an acidic and oxidative atmosphere, namely, a strong corrosive environment. Since the group 4 and 5 metal oxides have high chemical stabilities and are well known valve metals, they are expected to be stable under an acidic and oxidative atmosphere. The solubility of new ceramics for non-Pt cathode in 0.1 M H₂SO₄ at 30°C under atmospheric condition was summarized in Table 1. Compared to the solubility of the platinum powder, the solubility of these materials was enough small to apply to the cathode catalysts.

These non-platinum materials had a definite catalytic activity for the ORR. The catalytic activity was compared with the electrode potential at $-0.2 \mu\text{Acm}^{-2}$ for the ORR current density (the onset potential for the ORR) as shown in Fig.1. Among these materials, partially oxidized tantalum carbonitride (TaCNO) had highest catalytic activity. Its onset potential for the ORR was ca. 0.88 V. Our tentative target value was ca. 0.90 V and TaCNO became close to this performance.

Conclusions

To develop a non-platinum cathode catalyst of polymer electrolyte fuel cells, the group 4 and 5 metal oxides and oxynitrides were tried to apply to the ORR catalysts without Pt. These materials had a high stability in an acid electrolyte and a definite catalytic activity for the ORR. In particular, the onset potential for the ORR of the partially oxidized tantalum carbonitride was ca. 0.88 V. These materials might have the possibility to be substitute materials for the platinum cathode of polymer electrolyte fuel cells.

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Degradation of Membrane Electrode Assembly for Fuel Cell Vehicle

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Nissan's current FCV model, the Nissan 05 X-Trail, is providing driving and riding opportunities to the customers through leasing, regular test drive events, and world first hired taxi in business, etc. But to commercialize the FCV, cost reduction with sufficient durability should be achieved. Many different types of phenomena that can lead to MEA degradation occur under the diverse operating conditions of vehicles. In addition, with the present level of fuel cell technology, the volume (weight) of the stack and auxiliary units is too large relative to an internal combustion engine and a large quantity of Pt must also be used. Accordingly, there are issues related to cost and supply of the required resources that must also be addressed to facilitate practical use of fuel cells on vehicles. One pressing issue in particular is to improve stack durability, in addition to securing acceptable MEA cost and performance levels. Taking MEA degradation as a typical example, this paper presents an analysis of degradation phenomena and some proposed measures for mitigating degradation, based on what is generally known at present.

Table 1 lists typical fuel cell operating modes under actual vehicle operating conditions along with various types and causes of degradation observed.^{1,2} Characteristic fuel cell operating modes corresponding to vehicle operating conditions can be broadly classified as start-stop (stack start-up/shut-down), load cycling (acceleration/deceleration while driving), high-load operation (steady high-speed driving), and low-load operation (continued idling). Another important degradation factor is the atmospheric environment of the area where a vehicle is driven.

Typical examples of degradation phenomena include carbon support oxidation/corrosion, Pt dissolution/agglomeration, chemical degradation of the electrolyte membrane and three-dimensional structural changes in the electrocatalyst layers, among others. These phenomena do not occur individually, but rather simultaneously and in a compound manner.

Naturally, the durability level demanded of the MEA will vary depending on the stack operating conditions and operating modes. Accordingly, analyses of the factors causing degradation phenomena and estimates of degradation rates are especially important parameters in designing stack durability. That makes it essential to analyze degradation phenomena thoroughly and to devise measures for controlling degradation rates. At present,

there are virtually no standard test procedures that have been clearly defined for accurately simulating degradation modes, so such methods must also be developed.

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Table 1. Fuel cell operating modes and major types of degradation.

Operation mode	Degradation	Cause
Start-stop	•Cathode catalyst surface area loss	Catalyst particle agglomeration due to carbon support corrosion
	•Catalyst layer water accumulation	Catalyst layer morphology change due to carbon support corrosion
	•Membrane pinhole formation	Mechanical stress by hydration/dehydration
Load cycling	•Cathode catalyst surface area loss	Catalyst dissolution by potential cycle
	•Membrane pinhole formation	Mechanical stress by hydration, pressure and thermal cycle
Idling	•Membrane pinhole formation	Chemical decomposition by peroxide attack
	•Membrane proton conductivity loss	Chemical decomposition by peroxide attack
	•Catalyst activity loss	Poisoning by membrane fragments
High load	•Catalyst surface area loss	Catalyst particle ripening at higher temperature
Severe	•Catalyst activity loss	Poisoning by air/fuel impurities
environmental condition	•Membrane proton conductivity loss	Cation contaminants exchanged with protons
	•GDL gas permeability loss	Gas flow blocked by dust accumulation



Biography

Dr. K. Shinohara received the M.S. degrees in applied physics in 1981 and Dr.of Materials Science 1993 from the Tokyo Institute of Technology Japan.

1981. Materials Research Labs. Nissan Motor

1988-1990 Applied Physics Stanford University : Visiting Researcher

Fields: Superconductor and Superconducting Oxides, Semiconductor, Energy conversion materials such as Thermoelectric devices and Fuel Cells.

Currently I am in charge of MEA research and development for FCV

Development of highly dispersed alloy catalysts and their performances

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The PtRu/C catalyst can be considered as one of the most promising candidates for the anode catalyst in PEFCs and DMFCs, owing to its high CO-tolerance and methanol oxidation activity.¹ However, the activity of the PtRu/C alloy catalyst is still inadequate for many commercial applications. Thus, more advanced and intricate catalysts are being widely considered, including ternary and quaternary alloys as well as metal-metal oxide systems. The development of new advanced characterization methods has contributed a great deal to the understanding of the anodic reactions, although fundamental aspects of the reaction mechanism still need to be clarified. In addition to catalyst poisoning, the degradation of the catalyst due to dissolution and aggregation has also been recognized as a major concern. Researchers in the field of electrocatalyst thus face a challenging task of increasing the precious metal utilization (enhance intrinsic activity, decrease loading, etc) while at the same time worry about dissolution and aggregation.

The fundamental understanding of the CO and CH₃OH oxidation reactions with emphasis on the structure-property relation has been a long-time subject. We and others have evaluated related anodic reactions using Pt/GC model electrodes as well as carbon supported Pt and Pt alloys using various metal loadings and supports. It has been shown that the choice of precursor and thermal reduction temperatures are some of the key factors for preparing well-alloyed carbon supported PtRu alloys by impregnation methods, and that the Pt:Ru=1:1 alloy exhibits the highest activity.^{2,3} Based on our data, if the surface area of the carbon support or the metal loading is changed, a maximum in catalytic activity is obtained for PtRu alloys with particle size near 4 nm.⁴ Similar results have been reported by others, using different supports.⁵ We have also systematically monitored the CO and CH₃OH oxidation reactions by various methods, including stripping voltammetry and electrochemical impedance, to further understand the role of Ru as well as the effect of cell temperature on the oxidation reactions.^{6,7} The promotional role of Ru is often discussed based on the so-called “bifunctional mechanism” or the “ligand effect mechanism”. Both mechanism rely on the chemical or electronic characteristic of the alloying second or third metal. In an attempt to enhance the catalytic activity by altering the electronic state of the alloy, a series of well-alloyed fcc PtRuRh/C catalysts with various compositions was prepared, which exhibited higher activity than the most popular Pt₁Ru₁/C.⁸ In another attempt to enhance the catalytic activity, Pt/C was modified with ruthenium oxide nanosheets. The modified catalyst showed enhanced CO-tolerance and methanol oxidation properties.⁹ Perhaps the most interesting property of the RuO₂ nanosheet-Pt/C nanocomposite is that it showed better

durability than Pt/C against potential cycling tests.¹⁰

My presentation will cover in particular such aspect of the preparation of well-alloyed catalysts by impregnation methods, and the role of the additive metal or metal oxide to the anode performance.

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Biography

Dr. W. Sugimoto received his M.S. degree in applied chemistry from Waseda University, Japan in 1995. After working for Toshiba Corp. for one year, he returned to Waseda University in 1996, and received his PhD in 1999. During this period, he obtained knowledge on the field of synthesis, characterization, and chemistry of layered compounds, and received a research fellowship from Japan Society for the Promotion of Science (JSPS). He joined the group of Professor Yoshio Takasu at Shinshu University as a Research Associate after finishing his PhD. He currently holds a position as Associate Professor, mainly involved in electrode materials for electrochemical energy storage and conversion; namely, fuel cell catalysts and supercapacitor electrodes. Materials of interest are, nanoparticulate metals, metal oxides and oxide nanosheets. He has received a number of awards from academic societies, including the Sano Prize of The Electrochemical Society of Japan for Young Researchers in 2004, Oronzio De Nora Foundation Prize of the International Society of Electrochemistry on Electrochemical Energy Conversion in 2005, etc.

Hydrogen production by steam reforming of hydrocarbons over trace noble metal-doped Ni/Mg(Al)O catalysts - High activity and high sustainability due to self-regeneration of nano-sized Ni metal particles -

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Hydrogen production for polymer electrolyte fuel cells (PEFCs) is a research area of urgent importance in addressing global warming. Steam reforming of hydrocarbons, especially of methane, is the most widespread and generally the most economical way to make hydrogen. This process still requires further advances in the preparation of superior reforming catalysts, however. We previously reported that Ni/Mg(Al)O catalyst derived from hydrotalcite (HT)-like compounds produced highly dispersed and stable Ni metal particles on the surface and have been successfully applied in the steam reforming and oxidative reforming of CH₄.^{1,2} In contrast to the large-scale use of reformers in the industry under stationary operating conditions, temperature varied frequently by daily start-up and shut-down (DSS) operation under purging by steam for hydrogen production of PEFC in domestic use. The Ni/Mg(Al)O catalysts showed a high resistance against coking, but were quickly deactivated due to the oxidation of Ni metal not only by oxygen gas but also by steam when applied in the DSS operation of steam reforming of methane.³ The combination of trace noble metals and the Ni/Mg(Al)O catalysts has been found to be effective for suppressing the Ni oxidation during the DSS operation.⁴⁻⁷ Moreover a high resistance against sintering of metallic Ni particles was observed; Ni/Mg(Al)O catalysts doped with trace noble metals such as Ru, Rh and Pt showed a self-regenerative activity during the DSS operation of steam reforming of methane.⁸ Formation of Ni-noble metal alloy in the surface layer of fine Ni metal particles on the catalysts was strongly suggested by EXAFS, XRD and TPR measurements. The self-regeneration of the noble metal-Ni/Mg(Al)O catalysts can be achieved by the continuous rebirth of nano-sized active Ni metal species assisted cooperatively by both reduction from Ni²⁺ to Ni⁰ by hydrogen-spillover *via* trace noble metal or Ni-noble metal alloy and reversible reduction-oxidation between Ni⁰ and Ni²⁺ through Mg(Ni,Al)O periclase.

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Biography



Prof. K. Takehira received the M. Eng. and D. Eng. degrees in chemical engineering from the Hiroshima University and Tokyo Institute of Technology, Japan in 1967 and 1981. His Ph.D. dissertation investigated homogeneous-heterogeneous catalytic phenomena of mixed metal oxides for the oxidation of hydrocarbons in liquid phase. He worked for 10 years as a Research Engineer in the Governmental Chemical Laboratory for Industry in Tokyo, MITI, Japan and then stayed in the Institut Français du Pétrole, Rueil Malmaison, France for one year. He became the Head of Department of Surface Chemistry, National Chemical Laboratory for Industry in Tsukuba Japan in 1993 and then moved to Hiroshima University as a Professor of Department of Chemistry and Chemical Engineering in 1997. During his stay in Tsukuba he mainly explored various types of catalytic system for the conversion of hydrocarbons. Since 1995 he has been engaged in the catalysis research work for the hydrogen production for PEFCs using perovskite materials and then now by using the hydrotalcite-derived materials as the nano-sized supported metal catalysts for the reforming of hydrocarbons.

Temperature Dependence of Oxygen Reduction Activity at Nafion-Coated Pt–Co Alloy/Carbon Black Catalysts Prepared by Nanocapsule Method

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Development of highly active electrocatalysts for the oxygen reduction reaction (ORR) is one of the most important subjects to increase the efficiency of PEFC. Enhanced ORR activities at the planar electrodes of Pt alloyed with non-precious metals (Fe, Co, Ni, Cr, etc.) have been reported.^{1–3} In order to obtain high mass activity of Pt, it is essential to disperse such Pt alloy nanoparticles on high surface area supports. While various binary and ternary Pt-based alloys supported on carbon black (CB) have been prepared, the ORR activities of these supported catalysts are not always consistent with those evaluated for bulk alloys. One of the reasons could be ascribed to non-uniform chemical composition among the whole alloy nanoparticles. Recently, we have developed nanocapsule method to prepare monodispersed Pt–M (M = V, Cr, Fe, Co, and Ni) alloy particles supported on CB with well-controlled composition.⁴ In the present paper, we report the temperature dependencies of the real ORR activities (apparent rate constant per real active surface area, k_{app}) and H₂O₂ yield, $P(\text{H}_2\text{O}_2)$, at Nafion-coated Pt_xCo/CB (atomic ratio X = 1, 2, and 3) prepared by the nanocapsule method.

All the Pt_xCo/CB (50wt% metal loading) catalysts prepared were heat-treated at 230 °C for 4 h in a flow of N₂ to remove organic moieties used in the synthesis.⁴ The XRD peak positions for the Pt_xCo/CB shifted to higher angle than those of Pt/CB. No extra peaks assigned to metallic Co and the oxides as well as the Pt–Co ordered alloys were identified, indicating the formation of the solid solution with fcc structure. As shown in Fig. 1, Pt–Co alloy nanoparticles were uniformly dispersed on CB and their size distribution was fairly narrow. It was found that the analyzed values of the loading level and the composition of all the catalysts agreed well with the starting values used for the preparation.

Figure 2 shows Arrhenius plots of k_{app} for the ORR at Nafion-coated Pt_xCo/CB evaluated by a channel flow double electrode method.^{5, 6} In the low temperature region (≤ 60 °C for PtCo/CB, ≤ 70 °C for Pt₂Co/CB, and ≤ 80 °C for Pt₃Co/CB), linear relationships between $\log k_{app}$ and $1/T$ are observed. The value of k_{app} on Pt₃Co/CB is the largest, by a factor of 2.2 compared with that of Pt/CB (50wt%-Pt, $d = 2.6$ nm), *i.e.*, the mass activity of Pt is expected to be enhanced by 3.0 times due to an

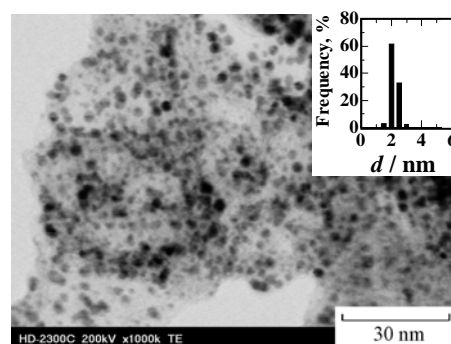


Fig. 1. Typical TEM image of Pt₃Co/CB and the size distribution for 500 particles, $d = 1.9 \pm 0.3$ nm.

advantage of higher specific surface area with the smaller d (factor of 2.6/1.9). The apparent activation energy on each alloy was found to be ca. 40 kJ/mol, which is almost comparable to that on the Pt/CB, indicating that the high ORR activities at the alloys are ascribed to a large pre-exponential factor in the rate constant.⁵ The modified electronic state at the Pt skin layer formed on the alloy may increase the coverage of adsorbed oxygen species.^{1, 5}

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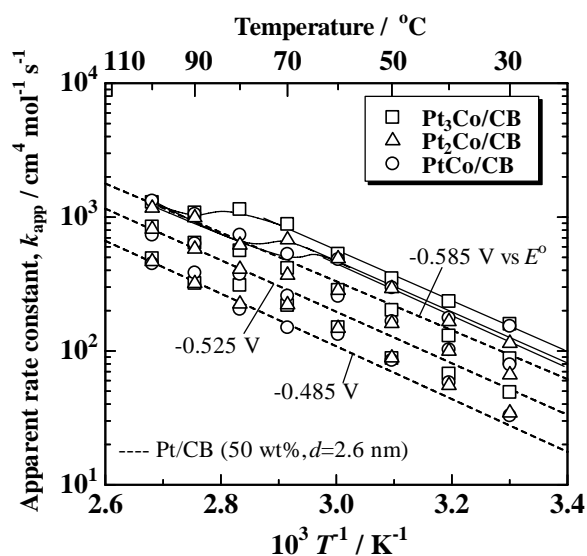


Fig. 2. Arrhenius plots of the ORR rate constants k_{app} . The applied potential of -0.485 , -0.525 , and -0.585 V vs. E^0 correspond to 0.80, 0.76, and 0.70 V vs. RHE at 30 °C, respectively.



Biography

Dr. H. Uchida received the M.S. degree in applied chemistry from Osaka University in 1979 and Ph.D. from Kyoto University in 1984. His Ph.D. dissertation investigated high temperature proton conducting solid electrolyte based on SrCeO₃. He worked for ten years as a Research Assistant with Tottori University and 4 years as Assistant Professor with Osaka University, before he joined with Prof. M. Watanabe's group of Yamanashi University (presently University of Yamanashi) as an Associate Professor in 1993. He was promoted to Professor in 2001. He engaged in fuel cell research work since 1979. In University of Yamanashi, he has been performing R&D of materials for SOFC and PEFC based on electrochemistry. Recent achievements are 1) high-performance mixed conducting electrodes with metal nanocatalysts for medium-temperature reversible SOFC, 2) evaluation of real ORR and HOR activities by using channel flow electrode method, 3) 3D-TEM observation of ionomers in catalyst layer, 4) preparation of highly dispersed alloy catalysts by nanocapsule method, etc.

Challenges in the design of active and durable nano-electrocatalysts for fuel cells

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Metal nanoparticles used as electrocatalysts in fuel cells are expected to provide the necessary activity and stability such that the fuel cell performance is minimally affected by catalytic decay. In particular, the slow kinetics of the oxygen reduction cathode reaction and the cost and scarcity of platinum -so far the best catalyst for this reaction- has motivated a very intense multidisciplinary field of research especially oriented to finding the best alloy nanomaterials.[1,2] In this talk we discuss challenges associated with the design of efficient alloy nano-electrocatalysts, especially those due to the nano regime and to the harsh chemical environment where these electrocatalysts work.

Producing nanoparticles with a robust and sustained catalytic activity –one of such challenges- is tightly related to understanding the mechanisms by which nanoparticles are fabricated, with the goal of reaching a better control over nanoparticle composition, shape, and size. Although the development of nanoparticle synthesis techniques has been spectacular in recent years, some of the new techniques even offering the ability to modify composition and structure,[3] microscopic details of the synthesis mechanisms are not known. Regarding the objective of gaining control over surface composition there is another important challenge especially concerning alloys: it is associated with the stability of the particle to surface segregation and phase separation. A few models have been proposed[4] but the development of phase diagrams for alloy nanoparticles and their dependence on particle size are still far from being understood. Furthermore, the dynamics of the nanoparticle[5] and its connection with the particle-substrate interactions, especially at the real catalytic conditions is another fundamental aspect that deserves careful investigations. And certainly, in connection to fuel cells, one of the most interesting problems is associated with the electrochemical dissolution of metal atoms from nanoparticles in acid medium, [6-9] and the role of alloys in stabilizing or destabilizing the precious platinum sites.

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Biography

Dr. Perla B. Balbuena received the MSc degree from the University of Pennsylvania and the Ph.D. degree from the University of Texas at Austin, both in chemical engineering. Her PhD dissertation investigated the effects of water as a solvent at high pressures and temperatures on chemical reactions, using molecular simulations techniques. Dr. Balbuena was an Assistant Professor from 1997 to 2002 and an Associate Professor from 2002 to 2004 at the University of South Carolina, Department of Chemical Engineering. Since 2004, she is Professor of Chemical Engineering, and Professor of the Materials Science and Engineering Program at Texas A&M University. Her research focuses on first-principles computational design of materials and processes. In recent years, she has been active in the field of materials design for catalysis and surface phenomena with applications to electrolytes and electrodes of lithium-ion batteries and fuel cells, catalyzed growth of single-wall carbon nanotubes, and hydrogen storage. She has published ninety seven peer-reviewed articles and has been co-editor of three books in her fields of specialization in recent years.

Surface science of the oxygen reduction reactions

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Abstract

The need to understand the key structure/composition relationships governing the electrocatalytic behavior of metal surfaces continues to motivate fundamental studies of surface processes at the solid-liquid interfaces. To this end, systematic variation of surface crystallography and or surface composition has been employed to delineate very important electrocatalytic trends. Although the field is still in its infancy, a great deal has already been learned and trends are beginning to emerge that give new insight into the true relationship between the surface structure/composition and electrocatalytic activity.

In order to give an overview of the field, this presentation will provide a carefully balanced selection of results for the oxygen reduction reaction (ORR) on monometallic (Pt, Au and Ag) and bimetallic (Pt_3M ; $\text{M}=\text{Ni}$, Co, Cr, Fe, V and Ti) surfaces. As a background for discussion, ex-situ UHV and in-situ SXS, STM studies in combination with the RDE method will be used in order to probe the influence of the surface structure and composition on the electrochemical reactivity. The presentation will attempt to discuss four important issues: (i) nature and stability of active sites; (ii) the effect of surface segregation on catalytic activity; (iii) the relationship between the *surface* electronic structure and the rate of the reaction; and (iv) the relationship between the catalytic activities on single crystal surfaces and real nanoparticles. In this presentation, we demonstrate that the ability to make a controlled and well-characterized arrangement of two elements in electrode surface and even near the surface region presages a new era of advances in our knowledge of creating new materials that can solve challenging problems of clean energy production and conversion. .

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Nenad Markovic is a Senior Scientist in the Material Sciences Division Argonne National Laboratory. He was a Staff scientist at Lawrence Berkeley Laboratory from 1991 to 2005, and a Group Leader at the Institute of Electrochemistry at the University of Belgrade from 1986-1991. He did his graduate work at the University of Belgrade and a postdoctoral fellow under Professor Ernest Yeager at Case Western Reserve University. Dr. Markovic's research interests are in the areas physical chemistry of the electrified metal-solution interface and new materials for energy storage and conversion. He has over 165 refereed publications to his credit.



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Processing Considerations in Tailoring the Nanostructure of Perfluorosulfonate Ionomer Membranes for Enhanced Performance and Durability in PEM Fuel Cell Applications

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Recently, we have probed the molecular and morphological origins of the dynamic behavior of Nafion[®] using a wide spectrum of analytical methods including dynamic mechanical analysis (DMA), small-angle (synchrotron) x-ray and neutron scattering (SAXS and QENS), solid-state ¹⁹F NMR spectroscopy, and dielectric spectroscopy.¹⁻⁴ Through the use of these complimentary analytical tools, we are now discovering the precise origins of the principle relaxations in these membrane materials.^{1, 4} Moreover, we have recently discovered the true glass transition temperature for Nafion[®] in the H⁺-form⁴ – a fundamental property of great importance in PEMFC applications. Based on our recent studies of the chain dynamics in these important polymers, we are now exploring the impact of various processing parameters on the morphology, properties, and performance of the ionomer component in proton exchange membrane fuel cell (PEMFC) systems. For example, the nanoscale organization of the ionic domains may be tailored by manipulating electrostatic interactions with variable counterions during membrane processing.⁵⁻⁷ In addition, variations in solvent-polymer interactions and thermal treatments during solvent evaporation can have a significant effect on the crystalline component of solvent-cast ionomer membranes.⁸⁻¹⁰ Thus, through controlled processing, we are particularly interested in the development of tailored morphologies of the ionomer in both the membrane and the catalyst layers for enhanced membrane electrode assembly (MEA) performance. In this presentation, we will explore the current state of understanding related to morphology-property relationships in PFSIs¹¹ with specific attention to the nano-scale organization of the ionic and crystalline domains and how a variety of processing parameters affect the morphological development of these complex features for enhancements in performance and durability.

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Biography Dr. Robert B. Moore is a Professor of Chemistry at Virginia Polytechnic Institute and State University (Virginia Tech). He received the Ph.D. in Analytical Chemistry from Texas A&M University in 1988 under the direction of Professor Charles R. Martin, followed by a Postdoctoral Fellowship in the Department of Chemistry at McGill University in Montreal, Quebec under the direction of Professor Adi Eisenberg. In January of 1991, he joined the faculty of the Department of Polymer Science at The University of Southern Mississippi and currently holds an appointment there as Adjunct Professor. In August of 2007, he joined the faculty in the Department of Chemistry at Virginia Tech. Professor Moore's current research interests include: morphological characterization and physical property modifications of ion-containing polymers, control of morphology-transport property relationships in PEM fuel cell systems via tailored processing procedures, characterization and control of actuation behavior in nanostructured ionic polymer metal composite (IPMC) artificial muscles, and the use of small-angle x-ray and neutron scattering methods for the characterization of morphology and dynamics in nanostructured materials and polymer-based nanocomposites.

Molecular Level Understanding of Interfacial Phenomenon in PEMFCs

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Abstract

This presentation will provide an introduction to materials considerations as it pertains to design of electrocatalysts for Polymer Electrolyte Fuel Cells (PEMFCs). New insights on structure property correlation for electrocatalysts and their interactions with the solid polymer electrolyte will be presented in the context of the unique environment afforded by these nano-phase composite structures. The relatively high overpotential for cathodic oxygen reduction will be discussed in terms of interplay of molecular oxygen adsorption and water activation pathways on Pt and Pt alloys^{1,2} as well as the more complex reaction environment in chalcogenides³ and enzymatic mimics. Some new insight on the effect of electrocatalyst morphology and kinetics of direct methanol oxidation will be presented⁴, together with the effect of Ru dissolution and migration⁵. In these systems the role of the reaction center will be presented in light of new data from synchrotron based *in situ* X-ray absorption spectroscopy measurements which are more specifically tailored towards elucidation of surface adsorption modes. This new methodology referred to as the Delta μ -Technique uses recently developed code (FEFF-8) to simulate multi-electron scattering from XAS to simulate the near edge part of the spectra called x-ray absorption near edge structure (XANES)⁶⁻⁸. This in conjunction with the extended part of the spectra, referred to as extended x-ray absorption fine structure (EXAFS) is used to generate a complete map of the electronic and structural changes on the transition metal reaction center as a function of reactant composition, interfacial water activity as well as electrode potentials. A combination of theory and experiment (classical electrochemistry and synchrotron based *in situ* x-ray absorption spectroscopy), will show specific pathways for electrocatalysis as a function of overpotential. Besides this, free radical initiated chemical attack at the electrocatalyst-electrode interface will also be shown, wherein the degradation mode of the surrounding ionomer will be discussed in the context of peroxide generation. The theoretical contribution will be based on an ab-initio charge self-consistent method for predicting redox reaction energies and electron transfer activation energies for reactant and products solvated in bulk solution.

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About the Principal Investigator

The Principal Investigator is a Professor in the Department of Chemistry and Chemical Biology; where he has been since September of 1998. He also heads the newly created center for Energy Studies at Northeastern University and its subset the Laboratory



for Electrochemical Advanced Power (LEAP). His research on charge transfer dynamics at both two and three dimensional electrochemical interfaces encompasses materials development, in situ synchrotron spectroscopy and electro-analytical methods. In addition new computational initiatives are in progress involving both molecular modeling and simulation of multiple electron scattering in the context of in situ synchrotron XANES method. The latter is in collaboration with George

Washington University. The current projects in the group include materials development for new electrocatalysts, polymer electrolyte membranes and high energy density (and capacity) cathode materials for aqueous and non aqueous storage cells. Fundamental understanding of structure property relationships are in concert with applications. In this context two startup companies, Encite Corp, Burlington, MA and Protonex Corp., Westboro, MA are notable with ongoing sponsored projects in the lab. In addition partnership with De Nora, for which we are a research hub in North America, is involved in developing a number of fuel cell and electrolyzer technologies. Further, Industrial support from BASF-Fuel Cells, W. L. Gore and Cabot-Superior Micro-powders are gratefully acknowledged. Federal funding comes from the Army Research Office, Department of Energy, National Science Foundation and National Institute of Technology-Advanced Technology Program.

FIRST PRINCIPLES ELUCIDATION AND DESIGN OF ELECTROCATALYTIC MATERIALS

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An atomic scale understanding of the sites that control catalytic behavior of electrocatalytic systems and their local nanoscale reaction environment could lead to tremendous breakthroughs in our ability to design more active electrocatalytic materials. While the intrinsic chemical bonds that are formed and broken as part of the operative electrocatalytic cycle are critical, the presence of defect surface sites, alloy composition and surface structure, polymer electrolyte, applied potential, coadsorbed intermediates, and carbon support can be just as important in controlling the overall electrocatalytic behavior. The atomic scale features that comprise the active sites and their environment are dictated by catalyst synthesis procedures. An understanding how these features form and their subsequent influence on the reaction kinetics could ultimately be used to aid the design of next generation materials with improved electrocatalytic catalytic performance.

Ab initio quantum mechanical methods have reached the stage where they can be used to model the atomic structure along with the local molecular topography about proposed active sites and establish the influence of their environment on their catalytic reactivity. In addition, the combination of theory and atomic scale simulation can be used to ultimately track individual transformations of molecules over catalytic substrates thus connecting catalytic structure with performance. This allows for an "in-silico" approach to tailor these structural features toward the design of more active materials. Theory and simulation have thus become invaluable partners with experiment in the elucidation and design of active sites. In this talk, we will describe the application of theory and simulation to the design of alloys for the electrocatalytic oxidation of methanol, CO and formic acid.

Multi-scale modeling of Proton Exchange Membranes

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Although a large number of strategies [1] have emerged in the design of proton exchange membranes (PEMs) that meet the requirements of high proton conductivity ($> 10^{-2} \text{ Scm}^{-1}$) under low humidity conditions, long-time thermal and chemical stability (including resistance to oxidation and degradation by reactive species) at temperatures above 100 °C, state-of-the-art electrolytes in current PEM fuel cells still utilize perfluorosulfonic acid (PFSA) ionomers such as Nafion®. Both experiments and modeling have shown that the transport of water and hydrated protons within PFSA is dependent upon: the characteristic dimensions of the phase-separated hydrated polymer morphology; acidity, density, and distribution of the sulfonic acid groups; and the external conditions including humidity, temperature, and pressure [2-4]. A complete understanding of how all these factors may be used in a synergetic fashion in the engineering of a novel high performance material remains forth-coming. This talk will describe some of our ongoing efforts [5-9] in securing a fundamental molecular-level understanding of the chemical and physical processes governing the *transfer, hydration, and diffusion* of protons in PEMs through multi-scale modeling over long and short length and time scales.

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Biography



Stephen J. Paddison received a B.Sc.(Honours) in Chemical Physics and a Ph.D. (1996) in Physical/Theoretical Chemistry from the University of Calgary, Canada. He was, subsequently, a postdoctoral fellow and staff member in the Materials Science Division at Los Alamos National Laboratory where he undertook both experimental and theoretical investigations of sulfonic acid based polymer electrolyte membranes. This work was continued while he was part of Motorola's Computational Materials Group in Los Alamos, NM. He took up his first academic position in the Department of Chemistry and Materials Science at the University of Alabama in Huntsville in 2004. In August of 2007 he moved to the University of Tennessee (Knoxville) as an associate professor in the Department of Chemical and Biomolecular Engineering. He was a guest scientist at

the Max Planck Institute for Solid State Research in Stuttgart during the summer of 2004 and a Visiting Fellow of Fitzwilliam College at the University of Cambridge, UK in 2003.

During the past decade his research work has been primarily concerning with obtaining fundamental molecular-level understanding of proton conduction in polymer electrolyte membranes (PEMs) commonly employed in low temperature (< 120 °C) through both *ab initio* and statistical mechanical based theoretical modeling and through high frequency dielectric spectroscopy. He continues to employ a number of methodologies including high level (DFT) electronic structure calculations, *ab initio* molecular dynamics (AIMD), classical molecular dynamics, quantum mechanics/molecular mechanics (QM/MM) and equilibrium and nonequilibrium statistical mechanics. Current collaboration include the group of Klaus-Dieter Kreuer at the Max Planck Institute für Festkörperforschung in Stuttgart, the group of James A. Elliott in the Materials Science Department at the University of Cambridge, and most recently Prof. Mark E. Tuckerman in the Chemistry Department at New York University.

The Electronic Structure and Electrocatalytic Activity of Pt Nanoparticles

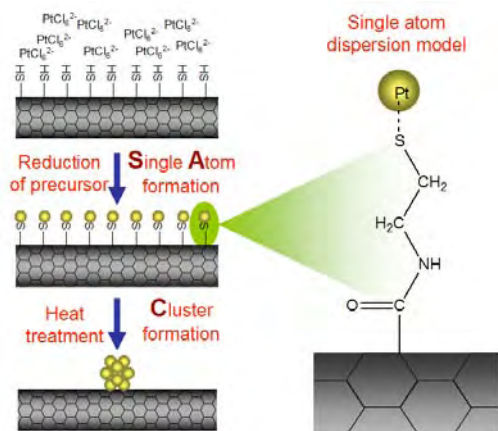
Seung Woo Lee¹, Yong-Tae Kim^{1,2,#}, W.C. Sheng¹, S. Chen¹, Tadaoki Mitani², Yang Shao-Horn¹

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INTRODUCTION

The particle size effect of carbon-supported Pt nanoparticles on the electrocatalytic activity has been a controversial issue for both the oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) in fuel cell applications. From previous reports^{1,2,3}, the electrocatalytic activity of Pt appears to depend on geometric effect (density of edge and kink sites), electronic effect (d band center energy with respect to the Fermi level) and carbon support effect. The discrepancies can be caused by the different amount of Pt loading on carbon support as well as the complex pore structure of activated carbon⁴. To elucidate this controversial issue, we have approached it with our unique single atoms to clusters (SAC) approach (Figure 1), which can control Pt particle size (1nm to 5nm) using constant amount of Pt on flat multi-wall carbon nanotubes⁵. Spectroscopy measurements show that the work

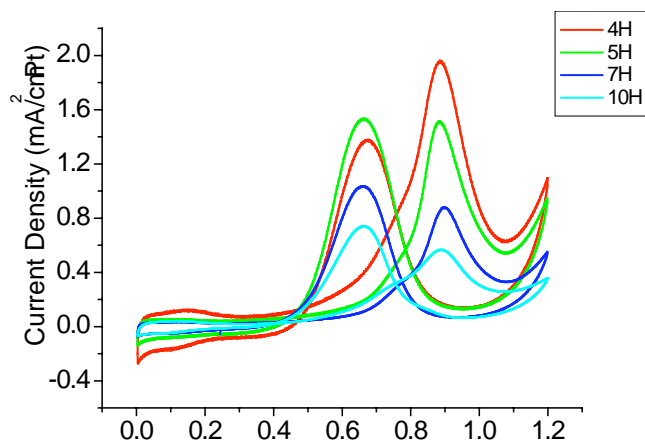


function and valence band of Pt nanoparticles change considerably with decreasing particle sizes. In this paper, we will discuss in detail whether the d-band center approach is applicable to the observed, size-dependent electrocatalytic activity of Pt nanoparticles.

RESULTS AND DISCUSSIONS

The sizes of Pt nanoparticles supported on multi-wall carbon nanotubes are controlled using a two-step process: single atoms formation and size-controlled (1nm to 5nm) particle formation upon heating, as shown in Figure 1. The results of Hard X-ray Photo-Electron Spectroscopy indicate that d-band center energy with respect to the Fermi level decreases

considerably with decreasing particle size. The physical reason of decrease of the d-band center energy of small Pt particle may be related with the reduction of its nearest neighbor distance. Since chemisorption strength between adsorbate and metal depends on the degree of filling of the antibonding states of coupling orbital⁶, the change of d-band center energy of Pt can make an effect on both OH⁷ and CO adsorption strength on metal surface. The size-dependent activity for methanol oxidation is shown in



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Figure 2 (Cyclic voltammograms of different Pt particle sizes supported on MWCNTs in 0.5M H₂SO₄ + 2M CH₃OH. Scan rate: 50mVs⁻¹), where Pt nanoparticle sizes decrease from 10H to 4H. The high specific activity of small Pt might be due to low d-band center energy relative to the Fermi level, which can decrease adsorbate binding strength on Pt. In this paper, we will report ORR and MOR results and discuss the origin of the electrocatalytic activity of Pt nanoparticles in the base of electronic structure.

ACKNOWLEDGEMENT

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Bio: Yang Shao-Horn is Associate Professor in Mechanical Engineering at MIT. Her research in the Electrochemical Energy Laboratory focuses on fundamental understanding in atomic and electronic structures necessary to design materials and material surface/interface for lithium storage and electrocatalysis of small molecules of energy consequence. She obtained her Ph.D. in Metallurgical and Materials Engineering from Michigan Tech. in 1998 and then worked as a staff scientist at Eveready Battery Company. Select honors include Invited Professorship at the Institut des Matériaux Jean Rouxel, Université de Nantes 2007, Dupont Young Faculty Award 2006, MIT Presidential Energy Research Council 2005-2006, invited Professorship at the University of Bordeaux I 2004, the Office of Naval Research Young Investigator Award 2003; NSF International Research Fellow Award 2000-2002, and Norman Hackerman Young Author Award of The Electrochemical Society 1999.

Structure, Size Dynamics, and Strain effects of new ORR Pt alloy electrocatalysts

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Understanding and controlling the electrocatalytic reactivity of surfaces represent key drivers of fuel cell catalysis research. Controlling surface catalytic reactivity requires deliberate modification of the chemisorption energies of surface intermediates and/or transition states. To achieve this, three fundamental effects - electronic, geometric, and ensemble effects – can be leveraged. Bi- and multimetallic alloy surfaces/subsurfaces^[1-3], with their atomic proximity of different metals, are an effective strategy to control reactivity, through a convolution of all three effects. Separate investigation of each of the three controlling effects is very difficult to achieve on surface or subsurface alloys.

Recently, our group has been developing a voltammetric dealloying synthesis techniques that enabled us to prepare core-shell catalysts consisting of a multilayer Pt rich shell surrounding a base metal rich alloy core^[4-8]. Due to the reduced lattice parameters in the alloy core, the shells exhibit controlled amounts of compressive lattice strain. Lattice-strained Pt shells offer the opportunity for a separate investigation of geometric effects on catalytic reactivity. Since surface and subsurface atoms are identical, charge transfer and ensemble effects are absent. Reactivity studies of strained core-shell nanoparticles for fuel cell catalytic reactions, such as the electroreduction of oxygen, suggests that chemisorption energies of intermediate can be controlled by the amount of lattice strain in the catalyst shells. A deliberate control of reactivity based on purely geometric effects has become possible.

In this presentation, we will share recent progress of our work on voltammetrically dealloyed lattice-strained Pt core-shell alloy catalysts. We will discuss the de-alloying synthesis method and discuss structure-activity-stability relationships of the electrocatalysts including microscopic and X-ray based methods. We will compare our experimental results with recent DFT computational modeling results^[9] regarding the control of electrocatalytic surface reactivity using lattice strained Pt surfaces. Experimental and Computation volcano curves will be contrasted. We will also discuss some recent synchrotron based geometric and structural characterization of our catalysts.

On a technological note, we will show how the in-situ electrochemical dealloying synthesis can be implemented to prepare core-shell cathode catalysts in realistic Membrane Electrode Assemblies^[8]. We discuss the impact of the dealloying process on the MEA structure and demonstrate that the dealloying synthesis lends itself well to conventional PEMFCs.

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Biography

Professor Dr. Peter Strasser received his Ph.D. in Physical and Electrochemistry at the 'Fritz-Haber-Institute of the Max-Planck-Society', Berlin, Germany, under the direction of Professor Gerhard Ertl following the completion of his B.S. and M.S. in Chemistry from the University of Tuebingen, Germany, Stanford University, USA, and the University of Pisa, Italy in 1995. His experimental and computational Ph.D. dissertation work investigated the mechanistic origins of self-organized periodic and chaotic spatiotemporal oscillations in electrocatalytic surface reactions. His thesis earned him the 'Otto-Hahn Research Medal' for the 'best dissertation in the year 1999' by the Max-Planck Society. During his Ph.D., in 1996, Dr. Strasser spent one year as 'Visiting Scientist' with Sony Central Research, Yokohama, Japan.

After completing postdoctoral work at Symyx Technologies, Santa Clara, CA, with Prof. W. H. Weinberg, he worked as Senior Staff Scientist at Symyx Technologies on the design and utilization of combinatorial and high throughput screening tools and strategies for the discovery and development of novel hydrogen production and clean-up catalysts as well as hydrogen fuel cell electrode electrocatalysts.

He joined the Department of Chemical and Biomolecular Engineering at the University of Houston in 2005. His current research interests include synthesis, structural and catalytic characterization of nanoparticle catalysts for gas-phase and electrochemical surface reactions. He is also developing new techniques for the in-situ characterization of catalytic nanoparticles using synchrotron-based X-ray methods.

Nanostructured Catalysts for Hydrogen Production

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Increasing demands for hydrogen to power fuel cells, produce fertilizers and process poorer quality crude oils into transportation fuels has spurred efforts to discover and develop more effective catalysts for the production of hydrogen. Our research focuses on catalysts that incorporate “active” supports, that is, supports that contribute chemically to the activities and selectivities of the catalysts. We are particularly interested in reducible oxide supported palladium methanol steam reforming catalysts, carbide and nitride supported methanol steam reforming and water gas shift catalysts, and reducible oxide supported gold water gas shift catalysts.

Methanol steam reforming and water gas shift are typically carried out using copper based catalysts, however, these materials are unstable at temperatures in excess of ~300 °C and tend to deactivate on exposure to condensed water. Reduced Cu/Zn/Al catalysts are also pyrophoric which makes them less attractive for consumer applications. Zinc oxide supported Pd catalysts have been reported by several groups to exhibit high activities and CO₂ selectivities for methanol steam reforming, and non-pyrophoric. The high selectivities have been attributed to the formation of Pd-Zn alloys following high temperature reduction [1]. We have produced highly selective catalysts that do not require high temperature reduction and do not appear to contain Pd-Zn alloys. Diffuse reflectance infrared spectroscopic and surface titration results suggest that the enhanced selectivity is associated with acidity of the support. This observation provides some direction for improving the catalytic properties of Pd-based methanol steam reforming catalysts.

Like other highly reduced materials, nanostructured carbides are pyrophoric and have to be passivated. Their use as catalyst supports has typically resulted in deposition of the metals on an oxide or oxycarbide overlayer. We recently developed a method to deposit metals and other species directly onto surfaces of the carbides. For some of the resulting materials there was a synergy between sites on the metal, and sites of the carbides [2]. The acidity and basicity of the carbide surface appeared to play an important role. In addition to characterizing the structural and chemical properties of these materials, we are using combinatorial and high-through-put screening methods to discover new, highly efficient formulations.

Nanostructured gold catalysts are among the most active water gas shift catalysts known, however, these materials can be highly susceptible to deactivation [3]. Using a combination of high resolution transmission electron microscopy, x-ray photoelectron spectroscopy, infrared spectroscopy and thermal desorption spectroscopies, we concluded that the deactivation of a series of ceria supported gold catalysts was due to the formation of carbonates and formates near cationic gold sites. By modifying chemical and structural properties of the support to enhance the mobility of oxygen, materials with better activity maintenance have been demonstrated.

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Biographical Statement



Professor Thompson is Richard E. Balzhiser Professor of Chemical Engineering. Professor of Mechanical Engineering and Director of the Hydrogen Energy Technology Laboratory. He earned his B.ChE. from the University of Delaware, and M.S.E. degrees in Chemical Engineering and Nuclear Engineering, and a Ph.D. in Chemical Engineering from the University of Michigan. Research in his group focuses primarily on the design, characterization and development of nanostructured catalytic, electrocatalytic and adsorbent materials. In addition, his group is using micromachining and self-assembly methods to fabricate fuel processors, fuel cells and batteries. From 2001 to 2005, he served as Associate Dean for Undergraduate Education in the College of Engineering and presently is Director of the Michigan-Louis Stokes Alliance for Minority Participation. Professor Thompson is recipient of a 2006 Michiganiaan of the Year Award for his research, entrepreneurship, and recruitment and mentoring of minority students, National Science Foundation Presidential Young Investigator Award, Engineering Society of Detroit Gold Award, Union Carbide Innovation Recognition Award and Dow Chemical Good Teaching Award. He is also co-founder, with his wife, of T/J Technologies, a developer of nanomaterials for advanced batteries and subsidiary of A123Systems. Professor Thompson is Consulting Editor for the *AICHE Journal*, and member of the External Advisory Committee for the Center of Advanced Materials for Purification of Water with Systems (NSF Science and Technology Center at the University of Illinois), National Academy's Chemical Sciences Roundtable, and *AICHE Chemical Engineering Technology Operating Council*.

Recent Advances in Chemical Hydrogen Storage

William Tumas

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On-board storage of hydrogen represents a critical technical barrier for realizing hydrogen-based transportation and the widespread use of fuel cell vehicles. The DOE Center of Excellence for Chemical Hydrogen Storage which comprises seven universities, four companies, and two national laboratories aims to identify, research, develop, and validate chemical hydrogen storage systems to meet DOE's 2010 goals for cost-effective, energy efficient, on-board hydrogen storage. Key elements include computation and modeling, the design, synthesis, and testing of structures and compositions to control the thermochemistry and kinetics of hydrogen release and spent fuel regeneration, and engineering assessment of concepts and experimental results. Our project structure enables the close coupling of experimental and computational R&D with engineering assessment to facilitate the transition from discovery of new concepts through development to implementation.

Chemical hydrogen storage involves hydrogen stored in chemical bonds that is released by an on-board chemical reaction. Chemical hydrogen storage offers a number of potential advantages including the opportunity for a liquid or solid fuel infrastructure instead of hydrogen delivery and fueling stations or handling of hydrogen directly by the consumer. Off-board regeneration could directly use energy to make the storage material rather than hydrogen itself, so one could envision a hydrogen-based transportation system where hydrogen *could only appear transiently at a fuel cell anode when needed*.

The overall approach of the Center is to develop materials and catalytic processes for high capacity hydrogen release and energy efficient regeneration of spent fuel. We are carrying out research in three general areas, all of which have the potential to meet the goals on volumetric storage capacity and regeneration energy efficiency:

- 1) Conversion of borate-to-borohydride (B-OH to B-H) to enable the use of sodium borohydride (MCEL ref); 2)
- 2) Alternative boron-based chemistry to avoid thermodynamic sinks using polyhedral boranes (B_xH_y) or amine-boranes.
- 3) Concepts using coupled endo/exothermic reactions, nanomaterials, and heteroatom substitution in organic systems for thermodynamic control.

A number of advances have been made on developing catalytic processes for hydrogen release from systems with high hydrogen storage capacity, e.g. ammonia-boranes. We have demonstrated catalyzed dehydrogenations of amine-boranes including the first examples of

non-precious metal catalysts for AB dehydrogenation. We have also shown that alternative reaction media can open up new reaction pathways. New reaction pathways are being delineated and mechanisms are being studied. The energy efficiency of regeneration of spent material, likely to be off-board, will be critical to developing a viable hydrogen storage system. We are investigating routes to regeneration of several systems and have developed concepts for regenerating spent BNHx storage materials including new methods for generating B-H bonds that have the potential to meet DOE targets.

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Biography

Bill Tumas received a B.A. in Chemistry from Ithaca College in 1980 and his Ph.D. in Organic Chemistry from Stanford University in 1985 as a NSF Graduate Fellow and a Hertz Foundation Fellow where he studied the dynamics and reaction mechanisms of gas phase negative ions. After a postdoctoral fellowship at Caltech, he worked at DuPont Central Research as a research chemist, then a project leader in environmental and oxidation catalysis from 1987 to 1993. Bill joined Los Alamos National Laboratory in 1993 where he is now the Program Director for Alternative Energy and Infrastructure (SPO-AEI) at Los Alamos National Laboratory, responsible for applied energy programs in renewable energy, infrastructure, and energy efficiency. From 2005-2007, he was also the lead principal investigator of the DOE Center of Excellence for Chemical Hydrogen Storage. Since 2004, he has been the Institute Director of the Los Alamos Institute for Hydrogen and Fuel Cell Research. He was the group leader of the inorganic chemistry group which consisted of over 60 technical staff from 1994 to 2005. His research activities have included chemical hydrogen storage, homogeneous and phase-separable catalysis, catalytic transformations and chemical processing in supercritical fluids, green chemistry, and waste treatment technology development and assessment.

Degradation of PFSA Membranes in PEM Fuel Cells

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The durability of PEM fuel cells has come under intense scrutiny lately as fuel cells come increasingly close to commercialization. A wide array of failure mechanisms has been identified, ranging from catalyst dissolution to membrane pinhole formation. Underlying mechanisms for these processes are sought. In this talk, we will focus on membrane-related degradation and associated processes.

It is by now well-known that a slow release of fluoride ions occurs in operating PFSA-based fuel cells. The correlation of this phenomenon to fuel cell failure, on the one hand, and to chemical degradation mechanisms on the other is complex. First, membranes such as Nafion are based on chemical structures that are widely considered to be highly stable. The degradation of these materials requires an appropriately active species. Peroxide generated in the cells is thought to be the source of such species. Second, there can also be significant mechanical contributions to pinhole formation.

We will describe work in our labs related to several aspects of chemical degradation of membranes, including:

- Model compounds and whole membrane studies
- Elucidation of peroxide sources
- Studies of peroxide redistribution, decomposition and reaction

Finally, some comments on the mechanical aspects of the problem and on mitigation approaches will complete the discussion.

Thomas Zawodzinski

Thomas Zawodzinski is the F. Alex Nason professor of Engineering, the Ohio Eminent Scholar for Fuel Cells, and the Director of the Case Advance Power Institute at Case Western Reserve University. He was a staff scientist and served in leadership roles at Los Alamos National Laboratory from 1991-2002. His undergraduate and graduate studies took place at SUNY/Buffalo. Dr. Zawodzinski's research interests are in understanding fundamental processes of transport through ionomers and reactions and transport at electrolyte-catalyst interfaces, especially within complex multi-phase structures within PEM fuel cells.

