

Basic materials research for the development of ubiquitous-energy devices

— Applications to positive electrode materials of Li-ion batteries, electrode catalysts of proton-exchange fuel cells and gold catalysts —

Masanori Kohyama^{1*}, Tomoki Akita¹, Shingo Tanaka¹, Yasushi Maeda¹,
Koji Tanaka¹, Kazuyuki Okazaki² and Jun Kikkawa³

[Translation from *Synthesiology*, Vol.2, No.1, p.42-50 (2009)]

For ubiquitous-energy devices, the development of well-performing functional materials is the key issue. Effective collaboration between development researchers and researchers carrying out basic materials analysis using electron microscopy observations, surface-science observations and theoretical calculations is of great importance. We have previously discussed the role of basic materials research in our discussion of *full research* and have made efforts to carry out a successful collaboration. To this end, we have attained valuable contributions to materials development as well as high-level scientific achievements as substantiated by numerous awards through the development of original observational and calculation techniques relating to the positive electrode material of Li-ion batteries, the electrode catalysts of proton-exchange fuel cells and gold/oxide catalysts.

Keywords : Materials for energy and environmental problems, basic materials research, electron microscope observation, first-principles calculation, lithium-ion battery, fuel-cell electrode, gold catalyst

1 Introduction

With the advent of the ubiquitous information society, lithium ion (Li-ion) batteries and fuel cells are drawing attention as portable power source for cell phones and mobile PC. Portable power sources, which are lightweight, high output, high capacity, highly durable, and environment-friendly, are important for use in robots, various medical devices, and small transportation device such as electric wheelchair, to serve the society with advanced medical welfare. By achieving higher output, they can be applied further as power sources for electric vehicles and hybrid cars, and are expected to have great impact on the environment. Energy storage and hydrogen gas refinement technologies are important to support the power source devices. The development of excellent functional materials for electrode, catalyst, and storage of hydrogen and ions is positioned at the center of the development of such ubiquitous energy device. Since they must clear high hurdles of output/weight ratio, safety, and environmental compatibility, the role of functional material development is extremely significant. In our research institute, R&D is mainly focused on the development of functional materials^{[1][2]}. The Authors have been conducting research on basic material analysis combining nano-structure analysis using transmission electron microscope (TEM) observation and scanning probe microscope (SPM) and theoretical computations such as first-principles calculation^{[3]-[5]}. We can

expect major results by ingeniously combining *Type 1 Basic Research* and material R&D.

However, effective collaboration between material development and basic material analysis is not generally easy, and much effort and trial and error are required. This is a common issue for R&D in other fields also. Our group engaged in discussions to shape our direction, and was able to achieve some success through collaboration between the development and basic analysis. We shall introduce our experience and results in this paper, and share some of the lessons we learned. Particularly, we shall discuss the role and significance of basic material analysis (*Type 1 Basic Research*) in material development.

2 Importance of basic analysis for energy and environmental materials

Many ubiquitous energy devices such as fuel cells, Li-ion batteries, hydrogen storage devices, and devices for production and refinement of hydrogen gases utilize exchange of electrons during the reaction of molecules and absorption/desorption of ions at the electrode, as well as various reactions and absorption/desorption of energy media. While it is believed that unique properties and phenomena of nanoparticles, nanostructures, and surface/interface dominate the function, details of the mechanism have not been clarified.

1. Research Institute for Ubiquitous-Energy Devices, AIST Midorigaoka 1-8-31, Ikeda 563-8577, Japan * E-mail : m-kohyama@aist.go.jp, 2. Department of Mechanical Engineering, Osaka University Yamadaoka 2-1, Suita 565-0871, Japan, 3. School of Engineering Science, Osaka University Machikaneyamacho 1-3, Toyonaka 560-8531, Japan

Received original manuscript October 21,2008, Revisions received December 9,2008, Accepted December 9,2008

From the perspective of material development, it is extremely important to experimentally and theoretically clarify structure, function, and various phenomena of such energy and environment materials using TEM observation and first-principles calculation^{[3]-[5]}. For example, when a material with excellent function is discovered, further improvement, discovery, and development do not follow unless we understand why such excellent function manifests. Particularly, when the correlation between the structure and function of nanostructure is clarified, the possibility of developing excellent materials through design and control of nanostructures broadens dramatically. Also, the performance of functional materials deteriorate after they are used for some time, but measures against deterioration and plans for improvements cannot be made unless we understand what is occurring on the microscopic level. Rather than searching blindly for materials from experience and inspiration, it is much more efficient to search systematically upon understanding the crystal, electronic, and nano structures of the materials. Of course, there are ample examples of serendipity in material development. However, to run into serendipity efficiently or to not miss serendipity, it is essential to simultaneously conduct microscopic analyses.

On the other hand, basic analysis of energy and environment materials has its unique problems. Manifestation of function involves complex reaction process and material transfer of hydrogen (proton) and Li-ions, such as absorption and reaction, electron transfer, oxidation/reduction, and valence fluctuation under gas atmosphere or in electric field. TEM observation is normally conducted under ultrahigh vacuum, and TEM observation of light element such as hydrogen and lithium is not generally easy. First-principles calculation at this point cannot readily handle large-scale reaction system or material and electron transfer. To advance the basic analysis of energy and environment materials, improvements and innovations of the basic analysis method itself is necessary. These are the factors that have delayed the application of basic analysis compared to other materials (such as semiconductor devices).

3 Issues in the collaboration between material development and basic material analysis

There is a mountain of issues that must be clarified through application of basic analysis in the actual practice of R&D of ubiquitous energy device and its functional materials. However, there are several issues and difficulties to realize an efficient and useful collaboration. First, the pace and phase of material development and basic analysis are not necessary in synch. Since basic analysis involves the development of analysis method, it is often necessary to study one topic over long period. Naturally, the topics are studied separately, and flexible collaboration is inhibited. Second, since the actual materials and phenomena are often too complex, application

of basic analysis is not easy. Therefore it becomes necessary to deal with the model material rather than the actual material, and close communication between the people involved in material development and those in basic analysis becomes necessary. Third, the gap in objectives and values, the difference in knowledge and understanding of the issue, and the lack of understanding of each other's research occur between the researchers of material development and basic analysis, and this inhibits close collaboration.

In the Research Institute for Ubiquitous Energy Devices (established in 2004) of AIST Kansai, a group was formed by researchers who were involved in TEM, SPM, and first-principles calculation since the inception of the Special Division of Green Life Technology in 2001. The group has engaged in discussion of where to position the basic material analysis in the system of *Full Research* and ways to contribute to material development. The reasons are: first, as mentioned earlier, energy and environment materials have potential for dramatic development through design and control provided by basic analysis since nanostructure itself is key to phenomena and functions; and second, we believe there is a creative value in the research methodology for the collaborative effort between basic analysis and development. Of course, as third reason, such collaborative effort is advantageous in obtaining research fund to maintain large apparatus.

Figure 1 is an outline of the collaborative effort from the standpoint of basic analysis. First, for research unit management, we promoted (1) the sharing of objectives between development and basic analysis, and (2) the construction of system where flexible sharing and close communication were possible. These were promoted by holding colloquiums for the whole unit and working groups as well as discussion between unit leaders and groups, and budgetary allowances were provided to promote such activities. The Authors' basic analysis group discussed the role of basic analysis as part of *Full Research*, and defined (1) the clarification and search to overcome the valley of death, and (2) the discovery and generalization/systematization of the potentials. It can be said that both aspects are necessary including the promotion of specific collaboration with development and the continuous effort for systemization by basic analysis. For the latter, we set the objectives of construction and systemization of theories of "metal/inorganic nano-hetero interfaces" that often held the key of function in ubiquitous energy devices^[3]. In the metal-oxide hetero catalyst, exemplified by gold catalysts that will be mentioned later, and the Pt/C catalysts of proton-exchange fuel cells, hetero effect of the interface and the nano-size effect of metal particles are greatly involved in excellent function, but the details are unclear, and there is potential for building generalized design theory and guideline through the construction and systemization of theories. While tackling various topics flexibly from the perspective of (1), the findings

are accumulated and systematized in long-term from the stance of (2). The latter findings must be shared by everyone including the members of the material development group.

As tasks to be achieved by the basic analysis group, we conducted the specification and clarification of issues through collaboration with development group, as well as the establishment of observation technology of the actual materials and system. This involved pioneering the original TEM observation method for the fuel cells and the Li-ion batteries that will be described later. Second, we worked on the review and establishment of first-principles calculation technique of complex structure. Also, we worked on the collaborative analysis technology of theoretical calculation and TEM observation and surface science methods. Such pioneering of the basic analysis technology for energy and environment materials is not easy, but must be tackled simultaneously to solve the issues of various phenomena and functions of the materials.

The three issues described in the beginning of this chapter could not be solved easily. However, when efforts spent while the researchers were fully aware of the issues, improvements and solutions did progress. Specific results will be described in the next chapter, and the lessons learnt from the effort will be discussed in chapter 5.

4 Some examples of significant results

In this research, we obtained several significant results that

were utilized in the development of functional materials, and were highly evaluated academically as demonstrated by reception of various awards. Some examples are explained herein. The example of positive electrode materials for Li-ion batteries was a result that leads directly to new material development, while the examples of Pt/C electrode catalysts for fuel cells and gold/oxide catalysts had great impact on the construction and systematization of theories for metal/inorganic nano-hetero interfaces as well as the improvement and development of materials. Both helped advance the basic analysis technology.

4.1 Mechanism for increasing capacity of positive-electrode materials for Li-ion batteries

A Li-ion battery is a storage cell that uses transition metal oxides including Li for its positive electrode, and carbon or Li metal or alloy for its negative electrode. The capacity and power density in comparison to weight are outstanding compared to conventional storage cells. It is expected to be used widely in automobiles as well as mobile devices, and further increase in capacity and power density, and improvement in durability and safety are necessary. In the charge process, Li ions move from the positive to negative electrodes through electrolytes, and return from the negative to positive electrodes in the discharge process. The development of excellent positive electrode materials that can absorb and release high density of Li ions repeatedly is the most important. Currently, LiCoO₂ is commonly used as the positive electrode material, but a material that is capable of achieving high capacity and high power density without using

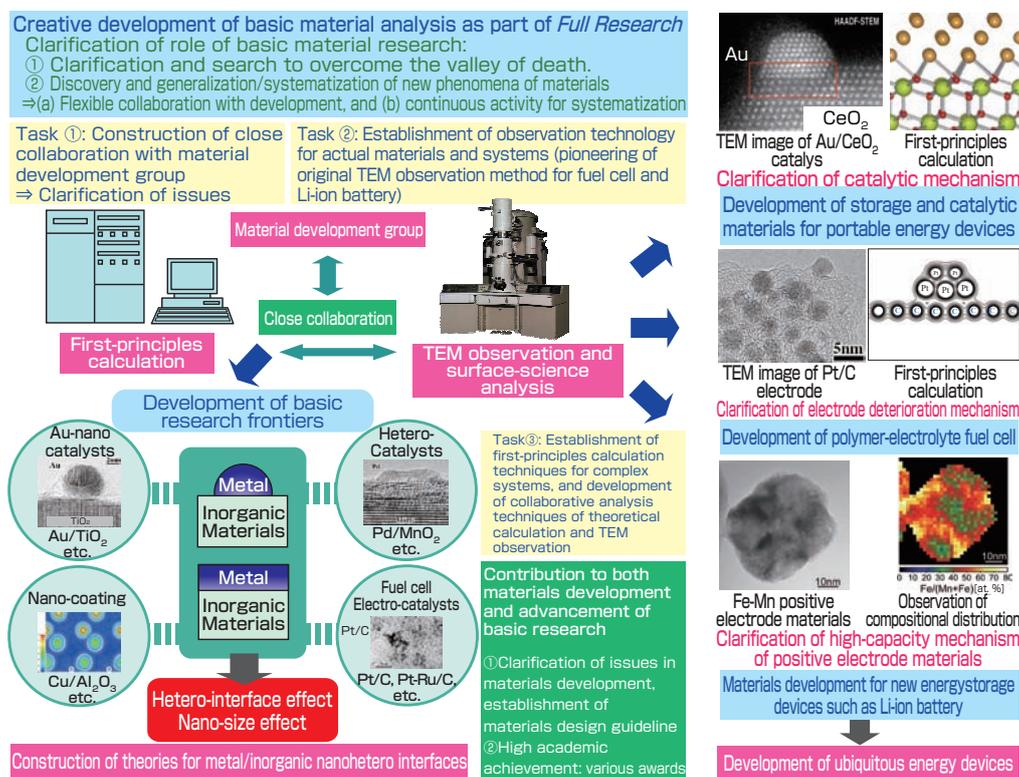


Fig. 1 Outline of research activities of basic material analysis for the development of ubiquitous energy devices.

rare metal Co is desired. Tabuchi *et al* of AIST developed the high-capacity complex oxide $\text{Li}_2\text{MnO}_3\text{-LiFeO}_2$ ($x\text{Li}_2\text{MnO}_3\text{-(1-x)LiFeO}_2$) (capacity > 200 mAh/g) containing Fe and Mn^[6]. Li_2MnO_3 and LiFeO_2 that comprise this material are inactive materials that do not absorb or release the Li ions in individual bulk. Superior materials may be developed by clarifying the mechanism of how they are activated to achieve high capacity when they are in complex form.

Therefore, we began working on this material using TEM observation under close collaboration with the development group. First, we discovered that each particle of the material had structure with Fe-rich (LiFeO_2 -like) and Mn-rich (Li_2MnO_3 -like) chemical nano-domain under common oxygen lattice, using the STEM-EELS (scanning transmission electron microscope - electron energy loss spectroscopy) spectrum imaging method (method of quantifying and imaging the element concentration distribution by accumulating EELS data at every scan position of the electron beam^[7]) and the nano-beam analysis method (Fig. 2)^{[8][9]}. The nano-scale domain structure without clear grain boundaries or interfaces was a new discovery. It is thought that the difference of lattice constants was small between the two phases and there was mixing at the atomic level in the interface region. In conventional x-ray diffraction observations, it was estimated from average information that the LiFeO_2 -like and Li_2MnO_3 -like phases might exist, but the existence in the form of chemical nano-domain structure was finding far beyond expectation.

To investigate the mechanism whereby chemical nano-domain structure produces high capacity, it is necessary to investigate the absorption and release of Li ions in each phase by charge and discharge. Therefore, we developed a new method to visualize the concentration distribution of Li ions in real space using the STEM-EELS spectrum imaging method. Conventionally, analysis of EELS data for Li was not easy, and quantitative analysis of Li concentration distribution was in fact impossible. If the thickness of the sample was sufficiently thin, the strength of the secondary differential peak strength of the EELS spectrum was deemed

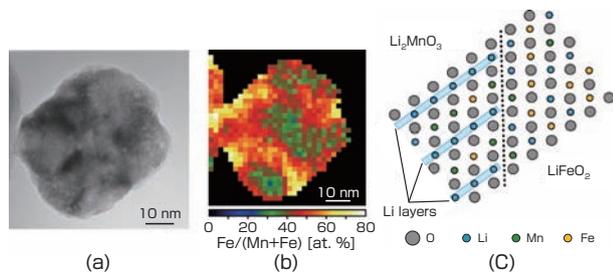


Fig. 2 (a) Transmission EM image of a $\text{Li}_2\text{MnO}_3\text{-LiFeO}_2$ particle as positive electrode materials for high-capacity Li-ion batteries. (b) Concentration distribution of transition-metal elements observed by the STEM-EELS spectrum imaging method. (c) Conceptual diagram of the chemical nano-domain structure.

to be in proportion with concentration, and therefore, we succeeded in quantitative visualization of Li concentration distribution by devising a data analysis method^[10]. This method was first in the world to investigate the real space distribution of Li ions.

As shown in Fig. 3, by applying the new method to the positive electrode material in the processes of charge and discharge in a battery cell, it was found that the Li ions are extracted first from the Fe-rich domain in the charge process and then extracted from the Mn-rich domain. Li returned after discharge, but there were unevenness in recovered concentration in certain places in correspondence to decreased capacity^[10]. As shown in Fig. 4, it is clear that in nano-domain structure, Fe-rich domain that is inactive

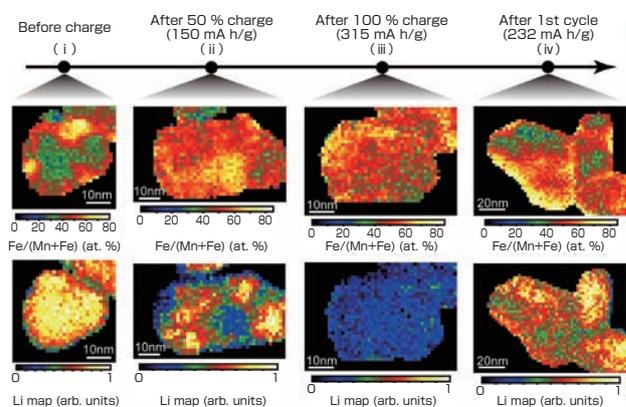


Fig. 3 Concentration distributions of transition-metal elements (upper) and of Li (lower) in $\text{Li}_2\text{MnO}_3\text{-LiFeO}_2$ particles as positive electrode materials for high-capacity Li-ion batteries, observed during the charge and discharge processes.

- (i) In a sample before charging, each particle reveals chemical nano-domain structure consisting of Li_2MnO_3 -like (green, blue) and LiFeO_2 -like (yellow) domains (upper figure), where Li ions are distributed throughout the particle (lower figure).
- (ii) In a 50 %-charged sample, there is a match between the blue domains for the concentration distribution of Li (lower figure) and the yellow domains for the concentration distribution of transition metal elements (upper figure), which clearly indicates the preferential Li-ion extraction from the LiFeO_2 -like domains in the early stage of charging.
- (iii) In a 100 %-charged sample, Li ions are desorbed from the entire region of each particle (lower figure).
- (iv) In a sample after discharge, Li ions are recovered throughout the particle (lower figure). However, the recovery does not seem to be perfect, because slight decreases of Li-ion concentration are detected locally.

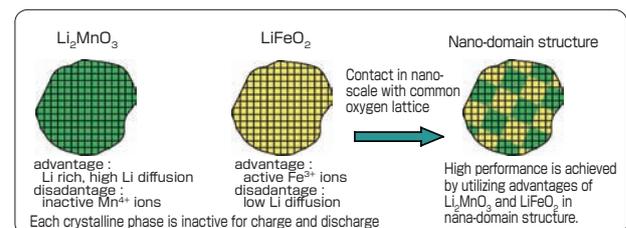


Fig. 4 Conceptual diagram of the generation of excellent performance in $\text{Li}_2\text{MnO}_3\text{-LiFeO}_2$ positive electrode material through the chemical nano-domain structure.

in bulk is activated by being surrounded by the layered Mn-rich domain that is advantageous for diffusion of Li ions, and then when Li becomes depleted in the Fe-rich domain, the Li ions are extracted even from the Mn-rich domain. It is thought that oxygen provides charge compensation in Li extraction from the Li_2MnO_3 domain composed of tetravalent Mn. Decrease of capacity is thought to occur due to the desorption of neutral oxygen by charge compensation, and the actual reduction in oxygen concentration was observed in the STEM-EELS spectrum imaging.

It was possible to clarify the mechanism of increased capacity where the chemical nano-domain structure activated each component material, by discovering the chemical nano-domain structure utilizing the TEM technology and by developing the visualization technology for quantitative distribution of Li-ion concentration. It is greatly significant to clarify the specific involvement of the nanostructure in the performance of positive electrode materials. Currently, material performance is being improved from the perspective of optimal control of such chemical nano-domain structure. The essential factor that enabled the above results was the

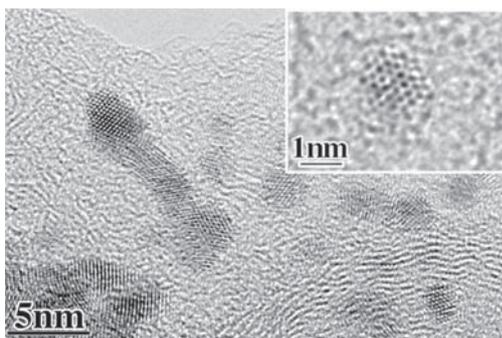


Fig. 5 High-resolution TEM image of PtRu/C electrode catalysts.

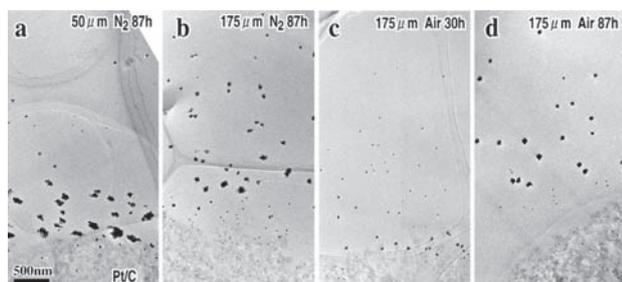


Fig. 6 TEM images of the precipitation and growth of Pt particles inside the electrolyte film, caused by Pt dissolution from the Pt/C positive electrode in various testing conditions.

(a) Nitrogen was supplied to the Pt/C electrode with an electrolyte film of thickness 50 μm , under the potential for 87 h. (b) Nitrogen was supplied to the electrode with an electrolyte film of thickness 175 μm , under the potential for 87 h. (c) Air was supplied to the electrode with an electrolyte film of thickness 175 μm , under the potential for 30 h. (d) Air was supplied to the electrode with an electrolyte film of thickness 175 μm , under the potential for 87 h. The features of the precipitation and growth of Pt particles depend on the thickness of the electrolyte film, supplied gasses, and the time of potential charge.

research conducted through daily communication of issues, topics, and experimental observation plan through close collaboration with the Li_2MnO_3 - LiFeO_2 development group.

4.2 Microscopic structure and deterioration mechanism of electrode catalysts in fuel cells

In a polymer-electrolyte fuel cell, electrons are extracted by the dissociation and oxidation of a fuel hydrogen molecule at the Pt particle of the negative electrode ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) by using the structure in which Pt particles are supported by carbon material (Pt/C electrode) as electrode catalysts, and proton H^+ transfers to the positive electrode through the polymer electrolyte. Similarly, water is produced by reaction of proton and oxygen on the Pt particle at the positive electrode ($1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$). At this moment, electrons from the negative electrode are used through the carbon and the conductor. Since CO often mixed in the hydrogen gas suppresses the catalytic activity of Pt particles at the negative electrode (CO poisoning), Pt-Ru alloy particles are used. It is important to increase the reaction efficiency while reducing the amount of rare metal Pt by controlling the electrode composition as well as the size and dispersion of Pt particles and Pt alloy particles.

Deterioration through use is an issue for the Pt/C electrode, and the clarification of that mechanism is demanded. Under close collaboration with the group conducting the development of electrode catalysts and deterioration testing, we attempted clarification through TEM observation^{[11]-[13]}. The TEM observation of the electrode catalysts of fuel cells was extremely rare. Electrolyte-electrode catalyst assembly was sliced using ultra-microtome to prepare the TEM samples, and optimal observation conditions were sought by trial and error. Figure 5 shows the typical high-resolution transmission electron microscope (HRTEM) image of the PtRu/C electrode catalysts. The lattice image of the fine particles of the catalyst could be seen clearly, indicating that excellent high-resolution observation was possible.

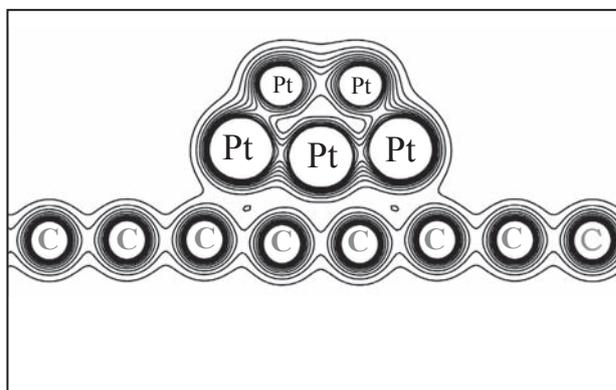


Fig. 7 First-principles calculation of a Pt_{10} cluster/graphene system.

Valence-electron charge distribution of the relaxed configuration indicates little electron transfer or orbital hybridization at the interface.

The deterioration test was conducted by activating the fuel cell under various conditions. By TEM, the increase of the diameter of the catalyst metal particles was observed, the preference dissolution of Ru from the Pt-Ru particles was detected, and the precipitation and growth of catalyst metal particles within the electrolyte film far from the electrode was observed, depending on the test condition (Fig. 6). The particle diameter distribution and particle space distribution changed by altering the type of gas supplied to the negative and positive electrodes and by changing the thickness of the electrolyte film. It was clarified for the first time, that such dissolution and precipitation behaviors of the catalyst metal particles were factors of the deterioration phenomena, along with oxidation of carbon material. The TEM observation of microscopic structures and deterioration of the electrode catalyst of a polymer-electrolyte fuel cell was done for the first time in the world (Table 1).

On the other hand, first-principles calculation is important in understanding the function and nanostructure of the Pt/C electrode. We are working on first-principles calculations of basic interface reactions for various forms of Pt metals or clusters deposited on carbon (graphene sheet) (Fig. 7)^[14]. The reactivity of the π bond surface of the graphene sheet is small. The interactive (bonding) energy between Pt-C reaches maximum for single Pt atom, then decreases as the coordination number and size increase for Pt clusters, and reaches minimum for the crystal surface. Using this calculation data, it is possible to simulate the mesoscale structure of the Pt/C electrode. We obtained comparable results in the TEM observation, and this is important as theory of metal/inorganic nano-hetero interfaces^[15].

The above results were only possible with daily collaborations and discussions with the group that was actually creating the electrode catalyst for fuel cells and conducting the deterioration test.

4.3 Mechanism of gold/oxide nano-hetero catalysts

Gold is generally inactive, but shows distinctive catalytic activities such as CO low temperature oxidation and water gas shift reaction (reaction to remove CO from hydrogen gas,

$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) when it is supported on the surface of oxides such as TiO_2 and CeO_2 in nano-particle form^[16]. To clarify the mechanism of how inactive gold is activated should contribute to the development of designing technology of novel metal/inorganic nano-hetero catalysts. We have been engaging in the basic analysis combining TEM observation, surface science, and first-principles calculation, under close collaboration with the catalyst development group.

In the Au/ TiO_2 system, the strong interaction between Au and TiO_2 could be inferred since there is preferred orientation relationship at the interface observed by TEM. From surface science experiments such as SPM observation, it was found that the Au- TiO_2 interaction is stronger in the reduced surface (Ti-rich surface) with oxygen deficiency compared to the normal stoichiometric surface of TiO_2 (surface with equal amount of anion and cation). On the other hand, it was indicated from the first-principles calculation that the interfacial bond becomes much stronger when the interface is non-stoichiometric as Ti-rich or O-rich, revealing stronger orbital hybridization and electron transfer between Au and TiO_2 , which would affect the catalyst activities^{[17][18]}. For further investigation, we conducted detailed observation of atomic arrangement at the interface using the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (a method for obtaining the image of atomic column through high-angle scattered wave from atoms by scanning with focused electron beam), and succeeded for the first time in detailed observation that allowed the identification of the atomic columns. On the other hand, from the first-principles calculation of atomic and electronic structures of the interface based on such observation model, it was clarified that Ti-rich or O-rich interfaces might be stabilized according to the atmosphere, and that Ti-rich or O-rich interfaces have unique electronic states.

Table 1 Recent awards from academic societies and conferences.

FY 2004	Satoshi Ichikawa, Japan Institute of Metals 2004 Fall Meeting, Best Poster Award (EM) Tomoki Akita, MRS 2004 Fall Meeting Poster Award (EM) Satoshi Ichikawa, MRS 2004 Fall Meeting Poster Award (EM) Shingo Tanaka, MRS-J 2004 Symposium Encouragement Award (Computation)
FY 2005	Tomoki Akita, Catalysis Society of Japan Poster Award (EM) Shingo Tanaka, MRS-J 2005 Symposium Encouragement Award (Computation)
FY 2006	Tomoki Akita, International Federation of Societies for Microscopy ICM-16 Poster Award (EM) Tomoki Akita, IUMRS-ICA 2006 Best Paper Award (EM)
FY 2007	Koji Tanaka, Japan Institute of Metals, Metallographic Contest in Division B 1st Prize(EM)
FY 2008	Jun Kikkawa, The 63th Annual Meeting of the Japanese Society of Microscopy, Poster Award (EM) Jun Kikkawa, The 14th International Meeting on Lithium Batteries, Most Excellent Poster Paper Award (EM) Tomoki Akita, ICC-14 Pre-Symposium, Best Poster Presentation Award (EM)

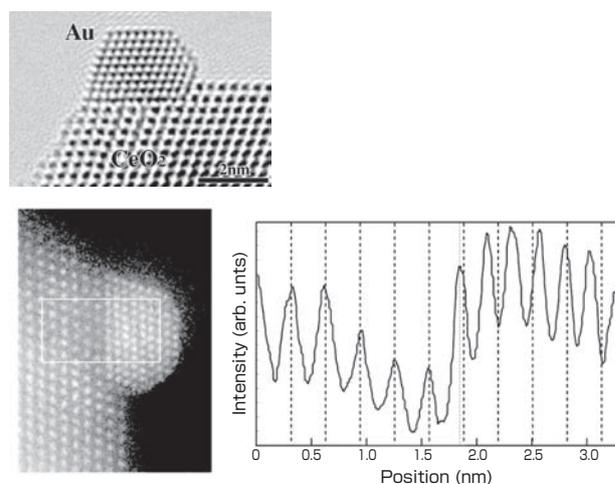


Fig. 8 TEM observation of a Au/ CeO_2 catalyst system.

Upper: High-resolution TEM image of a Au nano-particle bonded on CeO_2 . Lower, left: HAADF-STEM observation of the same structure. Lower, Right: Analysis of inter-layer distances by the profile of integrated HAADF-STEM image intensity along each atomic layer.

For the Au/CeO₂ system, we discovered the novel phenomena that (i) Au nano-particles supported on CeO₂ disappeared during TEM observation, as layer-by-layer with only the Au first layer at the interface remained, and that (ii) the Au nano-particles recovered at the same places when the electron beam was stopped and left in the chamber^{[19][20]}. Such atmosphere-dependent structural changes should be related to the catalytic property, and the clarification of mechanism is important. It could be inferred that the effect of oxygen deficiency on CeO₂ surfaces is important since the Au particle growth on CeO₂ at high temperature could be controlled in the H₂ atmosphere. We succeeded in obtaining a detailed image of the interface atomic arrangement for the first time using the HAADF-STEM method (Fig. 8)^[21]. The interface is steep and the distance between the Au and Ce atomic layers can be measured. By comparing this observation with the first-principles calculation, it could be concluded that a Ce-terminated interface is formed. The series of phenomena could be explained from the theoretical analysis including the chemical potential depending on the atmosphere, where the Au-atom trapping by oxygen vacancies in CeO₂ surfaces and bulk and the strong bonding at the Ce-terminate interface are involved.

At this point, the mechanism of the catalytic activity of the Au/TiO₂ and Au/CeO₂ systems are not completely clarified, but there have been no other cases where the interface structures of metal/oxide hetero catalysts are revealed at this resolution, as proved by many awards (Table 1). From the first-principles calculated based on this observation, it is strongly implied that the key of function is held by the stoichiometry of the interface and its control by atmosphere. As next step, the TEM observation in gas atmosphere and the first-principles calculation of molecular absorption and reaction path of the real interface and peripheral models are in progress.

The above results were made possible by effectively setting topics and plans through continuous collaboration and close information exchange with the catalyst production groups inside and outside the unit.

4.4 Recent awards

The above research activities have won several awards. Table 1 shows the recent awards. The results of basic material analysis through close collaboration with the material development have drawn much attention, and our activities have been acclaimed highly as basic science. The reasons for receiving the awards are as follows: (1) the construction of high level basic analysis technologies and new methods, (2) the pioneering work advancing the frontier of the clarification of the energy and environment materials and the metal/inorganic nano-hetero interfaces, and (3) the results of basic analysis highly expected to be used in real material development and improvement. Of course, rather than pure basic research, the awards were probably given to the results and expectations from the developmental viewpoint.

5 Discussion and summary

In general, there are still no solid methodology or guideline for the development of new materials, and this is a grave fact. From the perspective of device development (*Type 2 Basic Research*), various findings must be pursued (results of *Type 1 Basic Research* and experience from *Type 2 Basic Research*) and the development and search of the materials must be done by trial and error. However, since the process (of making the material in various ways) deals with nature (matter), we often run into novel mysterious phenomena that no one has experienced before. In seeking novel materials, this cannot be avoided. When that happens, we cannot wait for someone else to solve the issue for us (with *Type 1 Basic Research*). The developer and group of developers must attempt clarification by investigating the phenomena by themselves. Therefore, it is necessary to utilize the *Type 1 Basic Research* available within the same research organization and to closely collaborate with such researchers. This is the way of materials development as *Full Research*. On the other hand, to make such collaborative activity effective, the researchers involved in *Type 1 Basic Research* bear mission to work hard on analysis method and to pioneer and refine the new methods. For dramatic materials development, it is important to strike balance and efficiency of “specialized” and “collaborative” researches between the development (*Type 2 Basic Research*) and the analysis (*Type 1 Basic Research*).

The experience of the Authors is limited, and not all issues are solved. Some areas are dependent on individual ability. The lessons and significance at this point can be summarized as follows. First, it is important to have an organization and management policy where the development and basic analysis groups can collaborate through daily information exchange on the same floor or at close proximity. Second, the priority topic in actual development often deals with new phenomenon or interdisciplinary phenomenon that are valuable in terms of basic science. Basic research in collaboration with actual development raises the level of basic research. Of course, the researchers must spend more effort to establish new analysis technology. Such efforts may lead to the creation of new disciplines (for example, electrochemistry and catalyst chemistry at the atomic and electronic level). Third, the cooperation of development and basic research provides plans and ideas for material design and development from new perspective to the development side. Of course, continuous efforts are necessary for such ideas to be truly utilized in dramatic development. Fourth, we believe the continuous accumulation and systemization of experience and knowledge in the collaboration of such materials development and basic research, as well as the education of human resources that are capable to handle them, is the “core competence” that must be carried on and developed in a research institution.

Acknowledgements

The case study described in this paper was conducted in cooperation with the researchers of the material development group. For the positive electrode materials in Li-ion batteries, we thank Dr. Mitsuharu Tabuchi, Dr. Masahiro Shikano, and Dr. Kuniaki Tatsumi (Research Institute for Ubiquitous Energy Devices, AIST); for the electrode in fuel cells, Dr. Kazuaki Yasuda (Research Institute for Ubiquitous Energy Devices, AIST); for the gold catalyst, Professor Masatake Haruta (formerly of Research Institute for Green Technology, currently Tokyo Metropolitan University), and Dr. Tadahiro Fujitani (Research Institute for Innovation in Sustainable Chemistry, AIST). We received the support of the New Energy and Industrial Technology Development Organization (NEDO) for the researches of the positive electrode materials in Li-ion batteries and the electrode in fuel cells; the Japan Science and Technology Agency (JST) for the calculation of fuel cell electrodes; and Grant-in-Aid for Scientific Research and JST for the study of gold catalysts. We are grateful to all the people and sections involved.

References

- [1] T. Sakai and T. Kobayashi (eds.): *Yubikitasuenerugi no saishin gijutsu (Latest Technology of Ubiquitous Energy Devices)*, CMC Publishing (2006) (in Japanese).
- [2] K. Oguro: Research strategy for ubiquitous-energy device technology, *Materials Integration*, 21(2), 1 (2008) (in Japanese).
- [3] M. Kohyama, S. Tanaka, K. Okazaki-Maeda and T. Akita: Theoretical studies of the atomic and electronic structure of nano-hetero metal/inorganic material interfaces in collaboration with electron microscopy observations, *Mater. Trans.*, 48, 675-683 (2007).
- [4] M. Kohyama, S. Tanaka, K. Maeda, T. Akita and K. Tanaka: First-principles calculations of atomic and electronic structures of materials interfaces – approach through collaboration with TEM observation, *Kenbikyo*, 41(3), 178-184 (2006) (in Japanese).
- [5] T. Akita, J. Kikkawa and M. Kohyama: Structural analysis of ubiquitous-energy materials using analytical electron microscope, *Materials Integration*, 21(2), 45-51 (2008) (in Japanese).
- [6] M. Tabuchi, Y. Nabeshima, M. Shikano, K. Ado, H. Kageyama and K. Tatsumi: Optimizing chemical composition and preparation conditions for Fe-substituted Li_2MnO_3 positive electrode material, *J. Electrochem. Soc.*, 154, A638-648 (2007).
- [7] C. Colliex: New trends in STEM-based nano-EELS analysis, *J. Electron Microsc.*, 45, 44-50 (1996).
- [8] J. Kikkawa, T. Akita, M. Tabuchi, M. Shikano, K. Tatsumi and M. Kohyama: Fe-rich and Mn-rich nanodomains in $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ positive electrode materials for Li-ion batteries, *Appl. Phys. Lett.*, 91, 054103 (2007).
- [9] J. Kikkawa, T. Akita, M. Tabuchi, M. Shikano, K. Tatsumi and M. Kohyama: Coexistence of layered and cubic rocksalt structures with a common oxygen sub-lattice in $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ particles: A transmission electron microscopy study, *J. Appl. Phys.*, 103, 104911 (2008).
- [10] J. Kikkawa, T. Akita, M. Tabuchi, M. Shikano, K. Tatsumi and M. Kohyama: Real-space observation of Li extraction/insertion in $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ positive electrode material for Li-ion batteries, *Electrochem. Solid-State Lett.*, 11, A183-A186 (2008).
- [11] A. Taniguchi, T. Akita, K. Yasuda and Y. Miyazaki: Analysis of electrocatalyst degradation in PEMFC caused by cell reversal during fuel starvation, *J. Power Sources*, 130, 42-49 (2004).
- [12] K. Yasuda, A. Taniguchi, T. Akita, T. Ioroi and Z. Siroma: Platinum dissolution and deposition in the polymer electrolyte membrane of a PEM fuel cell as studied by potential cycling, *Phys. Chem. Chem. Phys.*, 8, 746-752 (2006).
- [13] T. Akita, A. Taniguchi, J. Maekawa, Z. Siroma, K. Tanaka, M. Kohyama and K. Yasuda: Analytical TEM study of Pt particle deposition in the proton-exchange membrane of a membrane-electrode-assembly, *J. Power Sources*, 159, 461-467 (2006).
- [14] K. Okazaki, S. Yamakawa, R. Morikawa, T. Akita, S. Tanaka and M. Kohyama: Simulation of growth process of Pt-particle - first-principles calculations, *J. Physics: Conference Series*, 100, 72044 (2008).
- [15] S. Yamakawa, K. Okazaki, M. Kohyama and S. Hyodo: Phase-field model for deposition of platinum nanoparticle on graphite, *J. Physics: Conference Series*, 100, 72042 (2008).
- [16] M. Haruta: Size- and support-dependency in the catalysis of gold, *Catal. Today*, 36, 153-166 (1997).
- [17] K. Okazaki, S. Ichikawa, Y. Maeda, M. Haruta and M. Kohyama: Electronic structures of Au supported on TiO_2 , *Appl. Catal. A*, 291, 45-54 (2005).
- [18] T. Okazawa, M. Fujiwara, T. Nishimura, T. Akita, M. Kohyama and Y. Kido: Growth mode and electronic structure of Au nano-clusters on NiO (001) and TiO_2 (110), *Surf. Sci.*, 600, 1331-1338 (2006).
- [19] T. Akita, M. Okumura, K. Tanaka, M. Kohyama and M. Haruta: Analytical TEM observation of Au nano-particles on cerium oxide, *Catal. Today*, 117, 62-68 (2006).
- [20] T. Akita, K. Tanaka, M. Kohyama and M. Haruta: Analytical TEM study on structural changes of Au particles on cerium oxide using a heating holder, *Catal. Today*, 122, 233-238 (2007).
- [21] T. Akita, K. Tanaka and M. Kohyama: TEM and HAADF-STEM study of the structure of Au nano-particles on CeO_2 , *J. Mater. Sci.*, 43, 3917-3922 (2008).

Authors

Masanori Kohyama

Principal Scientist in Research Institute for Ubiquitous Energy Devices (UBIQEN) of AIST. He graduated from the master's course of the University of Tokyo in 1984, and received Doctor of Engineering in 1992 from the University of Tokyo. He joined Government Industrial Research Institute, Osaka, Agency of Industrial Science and Technology (current AIST) in 1985. He became Leader of Interface Science Research Group in Special Division of Green Life Technology, AIST in 2001, and Leader of Material Science Research Group in UBIQEN, AIST in 2004. He is engaged in first-principles calculations of materials interfaces and the development of computer programs of first-principles calculations and collaboration technology between TEM observation and theoretical calculations. For this paper, he leads the discussions on the overall direction of research and conducts the practical research planning and

results. He received Distinguished Achievement Award of the Japan Institute of Metals in 2001, and became Fellow of the Institute of Physics (UK) in 2004.

Tomoki Akita

Senior Researcher of Materials Science Research Group of UBIQEN, AIST. He received his PhD (engineering) in Applied Physics from Graduate School of Engineering, Osaka University in 1998. After post-doctoral research in Osaka National Research Institute (current AIST), he joined Osaka National Research Institute in 1999. In 2001, he became a researcher of Interface Science Research Group, Special Division for Green Life Technology, AIST, and joined the present research group in 2004. He is engaged in structural analysis of functional materials (metal/inorganic hetero catalysts, fuel cells, Li-ion batteries, etc.) using the analytical TEM method. He received a lot of awards as listed in Table 1. For this paper, the TEM observation was mainly performed by him.

Shingo Tanaka

Researcher of Materials Science Research Group of UBIQEN, AIST. He received Doctor of Science at Graduate School of Science, Osaka Prefecture University in 1998. He joined Osaka National Research Institute (current AIST) in 1998, became a researcher of Interface Science Research Group, Special Division of Green Life Technology, AIST in 2001, and joined the present research group in 2004. He is engaged in computational materials science. He is dealing with first-principles calculations of metal/inorganic hetero interfaces (metal/ceramics interfaces, hetero catalysts, etc.) and development of computer programs of first-principles calculations. For this paper, he worked on first-principles calculations of gold/oxide interfaces.

Yasushi Maeda

Researcher of Materials Science Research Group of UBIQEN, AIST. He received Doctor of Science at Graduate School of Science, Osaka University in 2000, and joined Osaka National Research Institute (current AIST) in 2000. He became a researcher of Interface Science Research Group, Special Division of Green Life Technology, AIST in 2001, and joined the present research group in 2007. He is engaged in surface-science analysis of atomic and electronic structures of nano-hetero catalysts and functional materials. For this paper, he performed SPM observation of gold/oxide systems.

Koji Tanaka

Senior Researcher of Materials Science Research Group of UBIQEN, AIST. He received Doctor of Engineering at Graduate School of Engineering, the University of Tokyo in 1991. After postdoctoral research in US awarded by the Japan Society for Promotion of Science, he joined Osaka National Research Institute (current AIST) in 1994, became a researcher of Interface Science Research Group, Special Division of Green Life Technology, AIST in 2001, and joined the present research group in 2004. He is engaged in investigation of micro and nano-structures of materials using TEM so as to develop a material design theory by clarifying the relationship between structures and properties of materials. For this paper, he provided various support for TEM observation.

Kazuyuki Okazaki

Associate Professor for mechanical engineering at Graduate

School of Engineering, Osaka University. He received Doctor of Science at Graduate School of Science, Osaka Prefecture University in 2000. He joined Osaka National Research Institute (current AIST) as JST Major Research Support Cooperative Member in 2000, and joined Material Science Research Group, UBIQEN, AIST as JST-CREST researcher in 2005. He moved to Osaka University in 2008. He is engaged in basic research on the atomic and electronic structures and reactivity of metal/inorganic hetero systems such as gold/oxide catalysts and Pt/C electrode catalysts of fuel cells, using first-principles calculations. For this paper, he performed first-principles calculations of gold/oxide interfaces and Pt/C interfaces.

Jun Kikkawa

Assistant Professor of Department of Systems Innovation, Graduate School of Engineering Science, Osaka University. He received Doctor of Science in physics at Graduate School of Science, Osaka University in 2006, and joined Material Science Research Group, UBIQEN, AIST as postdoctoral researcher in 2006. He moved to Osaka University in October 2008. He is engaged in basic research on the structure and properties of various nano-systems using TEM observation. For this paper, he performed TEM observation of positive electrode materials of Li-ion batteries.

Discussion with Reviewers

1 Expectation for the management

Question and comment (Kazuo Igarashi)

You mentioned in this paper that it is possible to conduct dramatic material development by taking an effective balance of “specialized” and “collaborative” researches by organizing the groups (human resource) that engage in development (*Type 2 Basic Research*) and analysis (*Type 1 Basic Research*) in the same research unit, and I certainly approve of this idea. I ask you one question related to this. I understand that in this paper, the research was conducted through the consensus of the research unit, but I also think the role of the leader who brings the organization together to formulate the consensus is important. Therefore, what kind of management do you expect from a leader of an organization, in general, to reach a consensus?

Answer (Masanori Kohyama)

In our unit, one of our objectives from its inception was to propagate the research dramatically through effective collaboration of “development” and “basic analysis” and to establish a methodology for that purpose. This is the desire of the research unit leader, and it was understood as a challenging and significant issue through discussions by the members in the course of designing the unit. As discussed in the beginning of chapter 3, there are several inhibitory factors in the collaboration of “development” and “analysis”: (1) pace and phase of the researches of the two groups often are out of synch, (2) consistent effort is necessary since analysis of actual complex materials is not easy, and (3) there are gaps in values and consciousness of the researchers. I think the leader of the organization must understand this situation, listen to the difficulties and complaints of the researchers, patiently provide support, and emphasize the importance of achieving results from the collaboration.

2 Organization and system most suitable for developing new materials

Question and comment (Norimitsu Murayama)

Can you comment on the ideal organization and system when viewing the process from search of material to module creation? The

paper indicates the effectiveness of conducting research by having the measurement/analysis group and the material development group in the same place. Yet on the other hand, research over distance using the Internet or other communication methods has become practical. Please provide your view on the ideal organization and system, for example, organization within AIST in which the Authors work, as well as collaboration among the universities, public research institutions like AIST, and corporations.

Answer (Masanori Kohyama)

In general, it is possible to realize effective collaboration using various communication methods even if the joint research does not take place in the same ground. Also, in case of long-term, deeply involved research, the development and analysis groups can conduct research in different places and occasionally meet for discussion. In fact, we do conduct that type of joint research. However, for working on urgent or concentrated problem solving, and from the perspective of efficiently executing *Full Research* as a research organization, I think there is great advantage for an organization that enables daily exchanges between the development and analysis groups, like us. For example, the inhibitory factors mentioned above can be better moderated through daily discussions within the same unit. Particularly for the basic research group, the desire to challenge new or difficult topics in response to the technological and social demands of the development side is born from the sense of mission of “being part of *Full Research*” by sharing the greater objective as a research organization, without settling into our own little world.

3 Collaboration with analytical instrument industry

Question and comment (Norimitsu Murayama)

I understood very well from this paper about the great contribution that can be made to materials development by the study of assessment and analysis. I think the study of assessment and analysis will promote development of new measurement technologies and instruments, and contribute to the progress of analytical instrument industry industry. Please comment on this point.

Answer (Masanori Kohyama)

The development of measurement technologies and devices can progress further by linking up with actual practice of materials development. In the research of positive electrode materials for Li-ion batteries described in this paper, we originally developed the technology to observe the real space distribution of Li-ion concentration. Also, in various catalyst researches, we are involved in the actual development of technology for “on-site observation under real environment” for catalytic reaction in gas atmosphere. Of course, we ourselves cannot develop the measurement devices, but we are considering joint developments with other research groups and companies.

The companies that develop measurement technologies and devices cannot engage in effective development unless they have thorough knowledge of the complex phenomena of materials and substances handled by the engineers and researchers who would be actually working with the device. This is more substantial as the research becomes more advanced, as in measurement and assessment at atomic and electronic levels. Therefore, the exchanges of researches and human resources between the research groups for basic analysis and measurement assessment and the groups for materials development and energy and environment technology are expected to be extremely useful.