

[006]九州大学グローバルCOEプログラム新炭素資源 学ニューズレター

<https://hdl.handle.net/2324/1833714>

出版情報 : Novel Carbon Resource Sciences Newsletter. 6, pp.1-, 2011-12. 九州大学グローバルCOE
プログラム拠点「新炭素資源学」事務局
バージョン :
権利関係 :



G-COE PROGRAM KYUSHU UNIVERSITY
NOVEL CARBON RESOURCE SCIENCES
NEWSLETTER

VOL. **6**
2012.1



contents

- 01 **MESSAGE**
 Hiroshi Sasatsu
 Director, Wakamatsu Research Institute, Research and Development Dept., J-POWER
- 02 **Summary of G-COE "NOVEL CARBON RESOURCE SCIENCES" special feature**
- 03 **G-COE Program Researcher Map**
- 05 **Micro Review**
- 09 **Introduction of Research Projects**
- 15 **Introduction of the Group Researches & Research Reports**
- 42 **Symposium & Workshop Report**
- 50 **Research Performance**
- 54 **Research Report from International Partner Institution**

MESSAGE

Director, Wakamatsu Research Institute,
Research and Development Dept., J-POWER

Hiroshi Sasatsu



Expectation for the Global COE “Novel Carbon Resource Sciences”

Since the 3.11 earthquake and subsequent accident of Fukushima Daiichi nuclear power plant, energy and environmental issues have been spiritedly discussed nation-wide in Japan. As global warming subject shows, such issues have to be addressed also beyond national borders under international cooperative framework. As modern society is based on carbon energy, it is needless to say that carbon will play an essential role in energy and environmental issues in the future as well.

I have engaged in development of high-efficiency technology for coal power generation since joining J-POWER. I feel proud that our efforts have made some contribution to enhancement of power generation efficiency and business creation, and thus I hope that we can continue the development in collaboration with all parties concerned.

As coal, one of carbon resources, has advantages of rich reserve, geographically less uneven distribution, and low and stable price, it generates 40 % of the world's electric power today. On the other hand, utilization of coal is restricted mainly to domestic use because of difficulties to handle compared to oil and natural gases since coal is solid and has an inhomogeneous quality. Against such a background, Japan, which has few resources, has promoted utilization of overseas coals in energy security point of view. Development of high-efficiency coal power generation is necessitated for mitigation of electricity cost rise caused by imported coal including transportation fee. Fortunately, as such high-efficiency technology can also be a key to the solution for global warming subject, Japan's leadership and business creation in

this area is being highly expected. Viewed from another side, it can be said that coal's disadvantage of difficulties in handling and usage asked artifices in power generation processes at energy conversion sectors located at the downstream of the value chain and thus this enabled them to fend off price control pressures from upper stream by creating an entry barrier made from accumulated know-how and experiences. Power generation using coal as one of carbon resources can only be managed on such a delicate balance, and several factors such as future changes in supply and demand or environmental constraint may bring a tough situation for related businesses. Therefore, it will be of utmost importance more than ever to continuously seek solution for existing and expected challenges or risks and foster human resources who can take on such tasks.

Kyushu University has made educational materials by summarizing gained knowledge widely and organized experimental lectures in the Human Resource Development Project for Coal and other Fossil Fuels, which was conducted for 3 years from 2007, and launched the Global COE “Novel Carbon Resource Sciences” together with Fukuoka Women's University in 2008. I feel proud that I could contribute to these activities, which is much expected to be able to foster human resources for the tasks referred to above. I hope that excellent talents, who can take initiative with a global perspective in challenging straightforwardly to the increasingly diversified and complicated issue of energy and environment, which is also the key to Japan's national sustainable development, will grow up from this COE, and fruitful discussion on carbon resources will crystallize around the COE to spark a wider public debates and actions.



Summary of G-COE Program “Novel Carbon Resource Sciences”

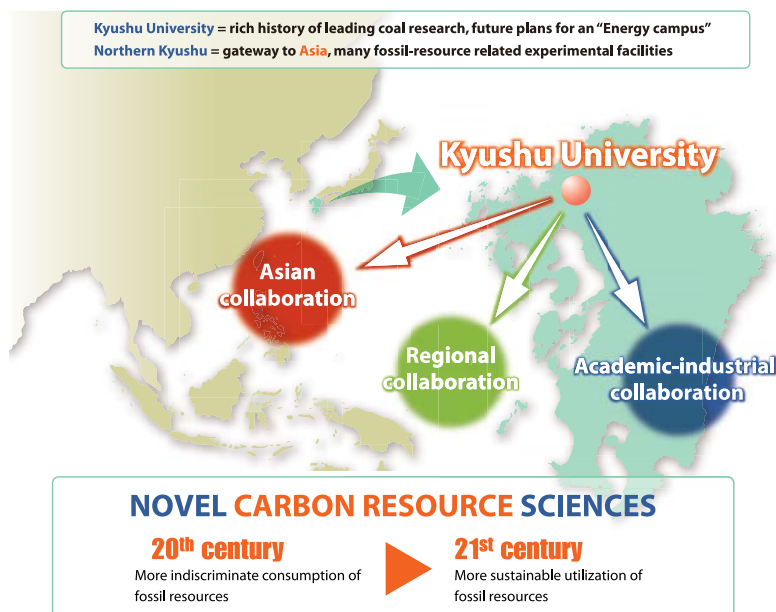
The Global COE program of Novel Carbon Resource Sciences (NCRS) arose from a partnership between Kyushu University and Fukuoka Women's University in FY 2008. Faculty members of 8 departments in the two universities are investigating a new field of science that concentrates on the efficient use of carbon resources and global environmental protection. The education of young researchers is performed from a global perspective through advanced research. Carbon resources such as oil and coal are vital to human life, not only as energy resources, but also as chemical raw materials.

Today people need to approach the issues associated with rapid economic development, such as depletion of resources, environmental pollution and global warming. Carbon resources are indispensable as energy resources or chemical raw materials, but at the same time they have a problem that they produce large amount of CO₂ which in turn causes global warming. How can we produce energy in an effective and environmentally-friendly manner, with a well-balanced approach that allows us to maintain comfortable lives? In order to address this challenge, it is essential to use carbon resources “wisely”, considering a best mix with other energy. In such viewpoints, coal can be called as the symbol of the carbon resources, because it has an advantage that it can be found in many parts of the world with large reserves, whereas we need to overcome the problem of air pollution and massive emission of CO₂ it causes.

As the world is exploring various countermeasures, this COE is striving to solve the issue with the objective of creating environmentally-friendly society for the next generation. We are promoting the development of technology for the maximally efficient use of carbon resources and materials derived from carbon resources to realize a low-energy society, and encouraging the education of young researchers who will be able to help build a future strategy for overcoming practical problems through advanced research.

Three years have passed since its foundation. Last year, our COE underwent an interim assessment of the government, and received a high evaluation in it. The COE, in which more than half of students are from overseas, has been implementing distinctive curriculums including the advanced research on resources, environment and energy, short-term and long-term internships, fieldworks, and the NCRS forums with the cooperation of Asian countries, urging human resource development.

Group Leader, Hideo Nagashima



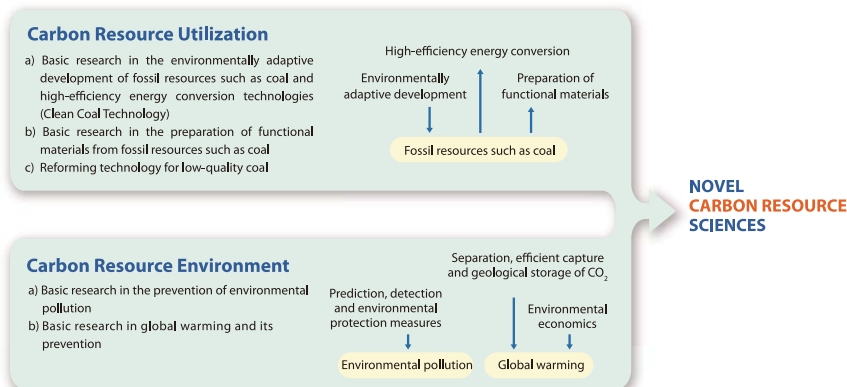
Cooperation with local community and Asian countries

The center takes full advantage of Kyushu University's location in Northern Kyushu, a gateway to Asia. We will be actively engaging in bidirectional exchanges of research and education among universities and institutes in China, Korea, Indonesia, India, Australia and Thailand and so on, and international collaboration on education

with Fukuoka Women's University. Also, we will be sharing intelligence with people in region through public lectures, and promoting regional, nationwide and international joint research between industry and academia.

Development and integration of two research fields

This COE has two research fields. In the field of “Carbon Resource Utilization”, we are pursuing smart use of carbon resources, that is, maximally efficient energy use and energy saving combined by carbon materials, devices and systems. In the field of “Carbon Resource Environment”, we are trying to understand environmental changes and solve them from both standpoints of economics and engineering sciences. This COE's mission is to fuse these two research fields together to establish a new academic field “Novel Carbon Resource Sciences”.



Recruitment of Doctoral Students, Postdoctoral Researchers

The COE calls for Doctoral students, Postdoctoral Researchers from inside and outside of Japan.

See more detail in HP.

URL: <http://ncrs.cm.kyushu-u.ac.jp>

G-COE Program Researcher Map

Program members

Carbon resource utilization cluster

Program members

Carbon resource environment cluster

Program collaborators

Collaborative member

Energy Utilization of Carbon Resources: Development of Environmentally Efficient Technology

Upgrading, conversion and material/ materials production of carbon resource

Tsuyoshi Hirajima

Advanced processing of carbon resources; Biomass utilization

Isao Mochida

Coal gasification; Carbon materials; Carbon nanofibers

Seong-Ho Yoon

Carbon nanofibers; Reaction engineering of carbon materials

Yasutake Teraoka

Functional inorganic materials; Environmental catalytic chemistry

► P25

Jun Fukai

Thermal analysis of coal conversion; Energy saving utilization of carbon fibers

Yuichi Fujioka

Coal gasification; CO₂ capture

► P5

Jun-ichiro Hayashi

Sustainable carbon cycle chemistry; Coproduction

Yohsuke Matsushita

Numerical analysis of reacting thermo-fluid dynamics; Analysis of coal combustion and gasification

Koyo Norinaga

Chemical reaction engineering for carbonaceous resource conversion; Detailed simulation of chemically reacting flows

Katsuki Kusakabe

Inorganic separation membrane; Separation of environmental pollutant

Collaborative Projects on Innovative Coal Gasification & Combined Cycle Power Generation

Central Research Institute of Electric Power Industry; National Institute of Advanced Industrial Science and Technology; Other Universities (Akita University, Ehime University, Kyoto University, Gunma University, the University of Tokyo)

International Joint Research; Industrial-Academic Cooperation in Human Resource Development

Research and Education Center of Carbon Resources, Kyushu University; Japan Coal Energy Center; Foreign Research Institutes

Kyushu society of low-carbon system

Kyushu University; Domestic Companies; Kyushu Bureau of Economy, Trade and Industry; Other Universities & Research Institutes

Advanced Technological Development for Low Energy Consuming Society

Basic chemistry

Katsuhiko Tomooka

Organic synthetic chemistry; Efficient oxidation reaction

Minoru Nishida

Transmission electron microscopy; Structure control in crystalline materials

Haruo Honjo

Nonlinear physics; Fractal physics

Seigi Mizuno

Structural analysis of solid surfaces; Graphite films on vicinal SiC

Yoshiaki Takahashi

Polymer chemistry; Analysis and control of soft matters

Environmental material development

Hideo Nagashima

Environmentally benign chemistry; Efficient metal complex catalysts

Seong-Ho Yoon

Carbon nanofibers; Reaction engineering of carbon materials

Advanced electronic material development

Shiyoshi Yokoyama

Device applications of carbon resources; Polymer photonic materials

Hiroki Ago

Carbon electronics; Synthesis and applications of carbon nanotubes and graphene films

Katsuhiko Fujita

Organic photovoltaic cells; Organic EL device

Energy material development

Michitaka Ohtaki

Thermoelectric device; Heat energy recovery

Shigeto Okada

Energy active materials and storage technology for next generation rechargeable lithium battery

► P12

Green process development

Shigeru Koyama

Heat energy conversion system; Heat transfer characteristics of CO₂

Yoshio Iwai

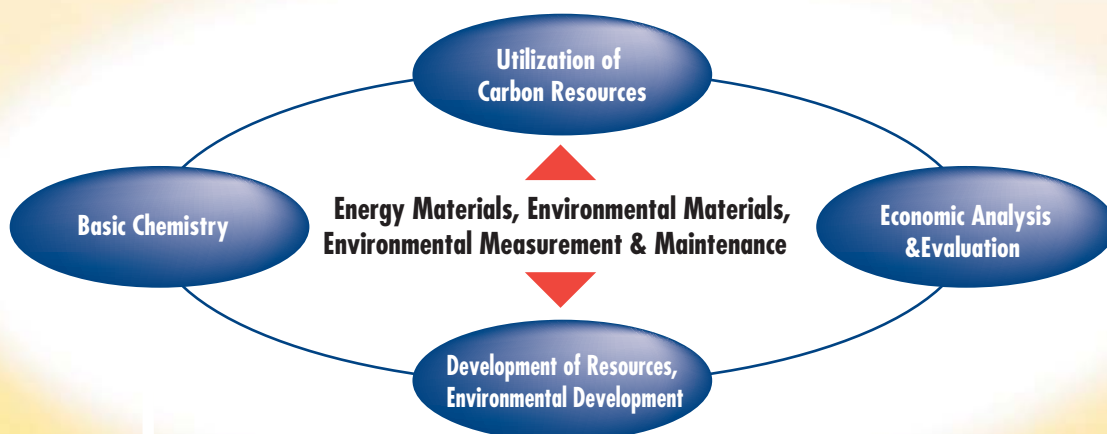
Separation technology; Supercritical fluid technology

Toshihisa Kajiwara

Polymer processing; Computer simulation

Yoshifumi Tsuge

Large scale process management; Process support system



Technology for Development of Carbon Resources

Technology for Utilization of Carbon Resources

Technology for resource development below the earth

Tsuyoshi Hirajima

Advanced processing of carbon resources; Biomass utilization

Kyuro Sasaki

CO₂ storage; CO₂-ECBM; CO₂-EOR

Kikuo Matsui

Environmental restoration associated with resource development; Coal mining development and environmental issues

Hideki Shimada

Low impact mining; Coal ash utilization

Environmental restoration technology

Koichiro Watanabe

Geoscience database; Environmental impact by resources development

Ryuichi Itoi

Development of geothermal energy; Development of fossil fuel resource

Keiko Sasaki

Remediation of groundwaters and soils; Reactive materials for environmental remediation

Technology for resource development in the ocean

Masahiko Nakamura

Marine-viewing vehicle; Positional controls of marine constructions

Yusaku Kyojuka

Utilization of ocean energies; Simulation of marine environments

Changhong Hu

Sea keeping performance of ship in actual seas; Simulation of ships

CO₂ Capture and storage (CCS)

Kyuro Sasaki

CO₂ storage; CO₂-ECBM; CO₂-EOR

Economic analysis

Nobuhiro Hori

Economic development and coal industry; China's coal and power industry

Basic chemistry

Akira Harata

Ultrasensitive environmental analysis; Laser spectroscopic analysis

Separation, removal of pollution

Yasutake Teraoka

Functional inorganic materials; Environmental catalytic chemistry

Masaki Minemoto

Analysis of flow and transport phenomena; Upgrade of various types of plants

Functional devices and materials for environmental concerns

Norio Miura

Sensors for environmental concerns; Electrochemical devices

Kengo Shimano

Design of gas sensors; Development of high performance electrocatalyst

Economic analysis

Toshiyuki Fujita

Environmental economics; Analyses of global environmental issues

Environmental measurement

Itsushi Uno

Numerical simulation of transborder air pollution; Aerial environmental modelling in Asia

Thoshihiko Takemura

Global scale simulation of aerosol

Kazuhide Ito

Chemical pollution of life environments; Indoor and environmental chemistry

Tetsuo Hayashi

Analysis of urban thermal environment; Prediction of energy consumption in residential buildings

Tadakatsu Ohnaka

Physiological and psychological features and life environment; Research on thermo-environment and aero-environment condition

Chang-Jin Ma

Global scale air pollution; Properties of Asian dust storm particles

Proposal of Adsorption Heat Pump for Generating Steam from Waste Water at Low Temperatures

Jun Fukai

Faculty of Engineering, Kyushu University

More reduction in energy consumption is requested for the industry section because a large quantity of waste water at low temperatures is released in the industrial processes. It has potency and possibility for contribution in the energy saving if the waste water can be regenerated to be steam again. To recover waste heat at a low temperature from hot water, adsorption heat pump system can be used as of its advantages. Though most of existing heat pump is indirect heat exchange type, it has some problems such as low heat exchange rates and high capacities of heat exchanger. In this study, the direct heat exchange type which took out heat by contacting directly zeolite and water is proposed. The adsorption heat pump using zeolite-water is theoretically investigated based on adsorption isobar curves. As a result, the ratio of the amount of recovered steam of 140°C to input waste water of 80°C is more than 0.55 when adsorption process is only considered. On the other hand, the ratio is 0.038 when desorption process is also considered as heat source. From these calculations, the heat pump system has potential to reduce the energy of 1.4 million ton of crude oil especially for the field of ironworks.

1. Introduction

More efforts for energy conservation are requested because of the limitation of fossil fuel reserves and the environmental issue of global warming. In spite of the oil crisis, the industry sector consumes the most of all energy and almost does not make an improvement¹⁾. Therefore, more reduction in energy consumption is requested for industry sector.

The iron and steel industry is the largest energy-consuming manufacturing industry. Focusing in the iron and steel industry, a temperature range of 60–90°C is found in the outlet of the cooling water used on hoods of converters, molding of continuous casting equipment and iron heating furnace skids as the waste heat. These waste heats are not utilized because of the difficulty for recovering. The iron and steel industry releases the waste hot water about 1000–2000 t/h at the crude iron/steel production capacity of 10 million-t/year. NEDO promotes COURSE50 (CO₂ Ultimate Reduction in Steelmaking process by innovative technology for cool Earth 50) as one of the big strategic projects to look for the innovation of utilization technology. On the other hand, in the general amine process, the heat source is required for heating up about 120°C in producing amine liquid. To achieve the COURSE50 goals for reducing more 10% CO₂ by CO₂ separation, it is necessary to separate 2 million tons CO₂ per year from the iron and steel industry with the capacity scale of 10 million-t/year²⁾. Meanwhile, the heat source required regularly in the amine process for providing the steam at 140°C is equivalent to 1.8 million-t steam/year. This amount of steam almost equals to the total steam used in the iron and steel industry now. Improvement in the energy efficiency of iron and steel production is one option to counteract the increasing demands for energy. The domestic iron and steelmaking industries have already tried the possibility of the potential for energy efficiency improvement by recovering the waste heat. However, using the current technologies are still impossible to recover the waste heat and secure the amount of CO₂ separation.

In addition, after sequence of the energy consumption in the iron and steel industry, the petrochemical industry is estimated to be 53% of the total energy consumption in chemical industry. CO₂ emission from the petrochemical industry totally reaches

6% of the whole³⁾. However, with the aim of achieving the highest level energy efficiency, the development of technology for innovative energy conversion becomes important. According to eco-innovation promotion project of NEDO in fiscal year 2009 "Research for exploring on innovative energy conversion in petrochemical industry"⁴⁾, the energy for producing steam at temperatures higher than 143°C in the petrochemical plants is extremely large. Based on the temperature levels of the waste hot water and the calorific values of gas released in the petrochemical industry, the unused heat mostly consists of waste water (at 30–50°C) and gas (at 80–150°C). Moreover, 74% of the steam energy are released during the manufacturing process when the reference temperatures of the released water and gas are assumed to be 30°C and 80°C, respectively.

From the above-mentioned current condition, the technology for utilizing waste heat of hot water in temperature range of 50–100°C to generate steam more than 150°C, ideally up to 180°C, is extremely required. In this paper, the current existing technology for steam generation is firstly described. Then, the authors provides the brief overview of the proposed adsorption heat pump for stem generation. After that, the performance of the proposed system for generating steam more than 150°C from hot water less than 100°C is estimated and analyzed. Finally, the advantages of the proposed system on the energy conservation in the iron and steel industry are presented.

2. Existing Technology for Steam Generation

Boiler is a general existing technology for steam generation. However, boiler has a low energy saving (COP < 1), so it will not achieve the reduction in fossil fuel consumption and CO₂ emission. The research and development of vapor compression heat pump for generating steam about 120°C is still progressing. The multipurpose machine with a common COP range of 3–6 has a capability only for generating the temperature level less than 100°C. As a result, a further period is still needed for continuing the research to generate steam more than 150°C. Moreover, the vapor compression heat pump meets some problems during the development, such as refrigerant selection and the part of mechanical seal which should has durability

from heat and pressure. It is necessary to overcome the compatibility between mechanical seal and water if using water as the working fluid. Because the working fluid is not a condensable gas, so the system operates at high compression ratio⁵⁻⁸⁾.

Still depending on the vapor compressor cycle, the treatment for recovering the cycle-rejected steam in order to compress again is capable for a vapor recompression cycle (VRC) type⁹⁾. It is mostly used to heat up the low pressure an low temperature steam from 100°C to 110°C.

In addition, an absorption heat pump on heating mode for generating steam becomes also a consideration. However, the result actually offers only less than 120°C using lithium bromide as absorbent. The development of material with high corrosion resistance is necessary because increasing the temperature increases the corrosion growth¹⁰⁾.

3. Overview of Adsorption Heat Pump for Steam Generation

Many researches of adsorption heat pump are reported concerning on the technology of heat generation for heating and cooling system¹¹⁾. As so far as the authors know, an attempt for generating steam using heating mode is only reported by Miwa, but the contents of the investigation focused on the basic research only¹²⁾.

Without considering heat generation for heating and cooling system, one of the barriers in the practical use of adsorption heat pump is the problem for maintaining the heat exchange rate between the working fluid and adsorbent at a high level. In other words, the order of the effective thermal conductivity of particulate adsorbent filled in the reactor is very small, only equals to 10^{-1} W/(mK). This small value of the effective thermal conductivity causes an insufficiency of the heat exchange rate. The adsorbent, as also heat transfer medium, cannot transport the accumulated thermal energy through the installed heat exchanger inside an adsorbent vessel of the reactor. For overcoming the problem, the technology for enlarging the heat transfer area inside the heat exchanger that can spray and dry the adsorbent is developed¹³⁾. Based on the experiences, more device installations are still required, such as a vent tube for distributing gas¹¹⁾ and material with high thermal conductivity. However, the installations of heat exchanger and gas distributor inside the reactor are not preferable because of increasing the sensible heat.

With regard to steam generation using adsorption system, the installation of heat exchanger is not preferable because the heat transfer medium is also water (steam). In this paper, the possibility of adsorption system using zeolite-water as the working pair for generating steam is proposed. Silica gel is actually a powerful candidate as adsorbent. But, if applied for the proposed system, generally, there is a problem on the water resistance and heat resistance. Using silica gel becomes difficult in the proposed system for generating steam at 180°C because the reactor temperature reaches more than 200°C from the process of direct heat exchange between adsorbent and water.

Figs. 1 and 2 show the schematic of a zeolite-water pair adsorption cycle in equilibrium isobaric curve and the corresponding operations of the proposed adsorption heat pump, respectively. Zeolite is assumed at the initial state (State 1, Fig. 1). The waste hot water enters to the reactor and the part of the introduced water is adsorbed by zeolite. Because of adsorption heat, the temperature inside the reactor increases, then the part of hot water becomes steam. As a result, the temperature rise of steam occurs (A: Preheating process) and reaches temperature of T_2 at the pressure of p_2 (State 2, Fig. 1). Afterwards, the hot

water is continuously introduced to the reactor and the steam will generate until its temperature reaches the target point (B: Steam generation). At this time position, the maximum zeolite adsorption is reached (State 3). The above-mentioned operations, it does by controlling the pressure. After that, the valve of the reactor is opened at state 3 to decompressing until the condition reaches state 4 (Purge operation). From state 4, the desorption is conducted by spraying the heated dry air to the zeolite and the condition returns to state 1 (C-D: Regeneration process).

Because the adsorption heat pump is working based on an intermittent cycle, it needs the multiple bed reactor for generating steam continuously.

4. Performance Estimation

Considering the conservation equations of mass and energy, the estimation of performance is calculated for an actual steam generator with 1000 kg zeolite 13X contained inside the stainless cylinder. The adsorption equilibrium between zeolite and steam is assumed and the thermal capacity of the reactor is considered in the conservation equations. The temperature rise of steam regenerated by zeolite is used to heat up the waste hot

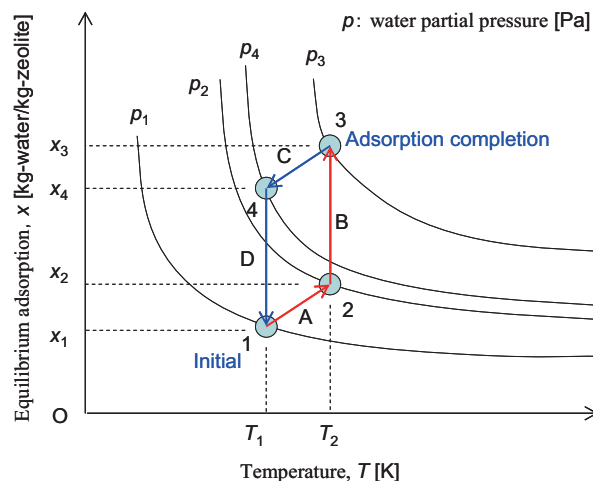


Fig. 1 Isobaric curve and adsorption heat pump cycle

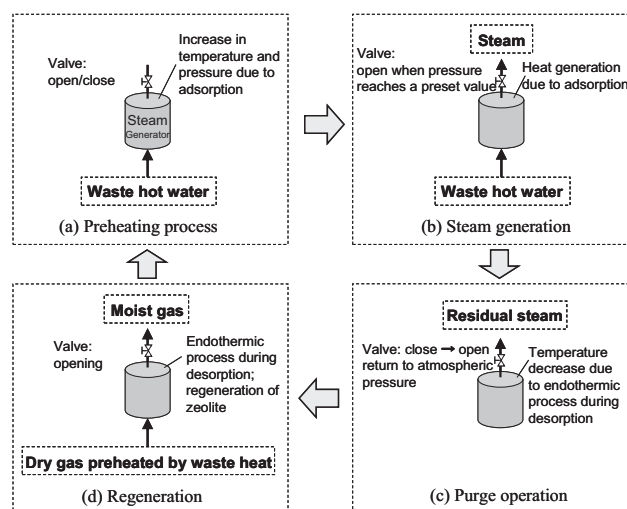
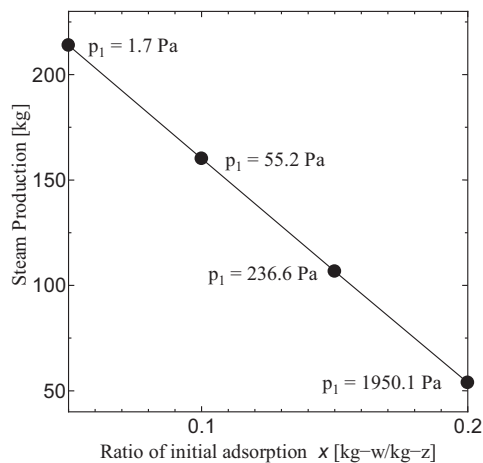
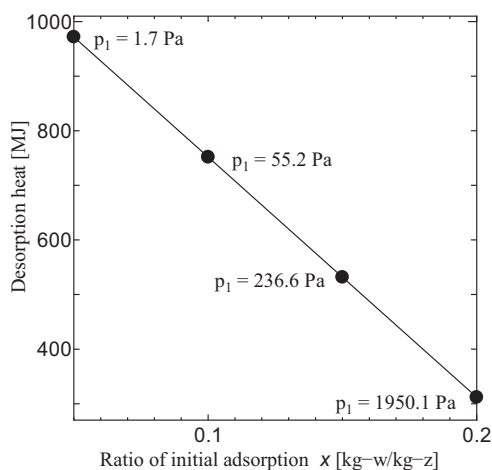


Fig. 2 Outline of the proposed adsorption heat pump



(a) Steam production



(b) Desorption heat

Fig. 3 Variations of steam production and desorption heat with the initial adsorption ratio

water. A detailed description of the model is found in our previous publication¹⁵⁾.

Fig. 3 shows the variations of steam production and desorption heat with the initial adsorption ratio x_1 in the case for generating steam at temperature of 180°C from the waste hot water at temperature of 80°C. Reducing as much as possible the initial adsorption ratio x_1 is necessary (Fig. 3a). For this purpose, the partial pressure of moisture in the dry gas during desorption process is important to reduce as much as possible. The partial pressure of moisture for the desorption air corresponding to the initial adsorption ratio is shown in the Fig. 3b. As shown in the Fig. 3, the partial pressure of moisture for the air equals to 55.2 Pa (at dew point temperature of -26°C) is obtained $x_1 = 0.1$ for the waste water condition at 80°C. But, using desiccant refrigerator will need air with the dew point temperature of -60°C to provide the same condition dry gas.

Figs. 4 and 5 show the variation of the mass ratio and enthalpy ratio, respectively, with the generated steam temperature at various inlet temperature of the waste water. Compared to the steam temperature, the inlet waste water temperature influences the steam generation heat and mass of the generated steam more significantly. The mass of the generated steam reaches about 5% of the waste water mass if

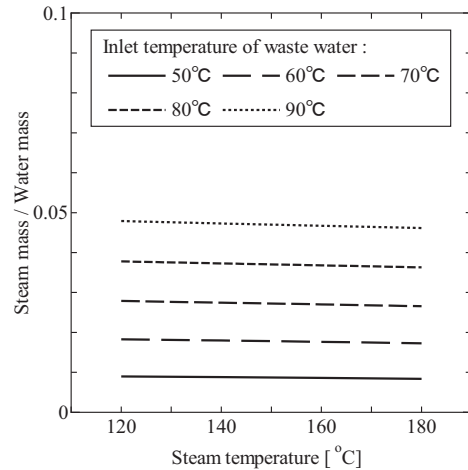


Fig. 4 Variation of the mass ratio with the steam temperature at various temperature of the waste water.

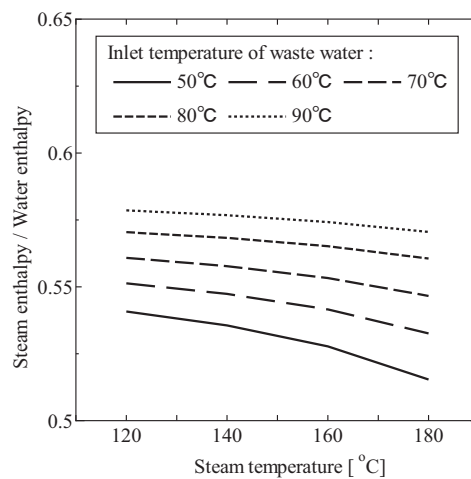


Fig. 5 Variation of the enthalpy ratio with the steam temperature at various temperature of the waste water.

the waste water at temperature of 90°C, but only about 1% steam is generated from 50°C. These values of the generated steam mass is not low if considering how many huge the waste heat from low temperature in the industry is. The mass ratio of about 0.038 and enthalpy ratio of about 0.57 are offered from the steam generation from the waste water at temperature of 80°C to steam at temperature of 140°C. But, only about 0.5–0.6 heat from the waste water at temperature of 50°C can be generated. The heat loss is mostly as sensible heat of zeolite. However, this value is resulted from the heat calculation controlled by the referenced temperature.

5. Estimation of Energy Conservation and Effect of CO₂ Reduction

5.1. Energy Source of CO₂ Separation for CSS

Based on the above-mentioned calculation, the following estimation is conducted for the case where the proposed system is applied in the iron and steel industry. In the iron and steel industry, the most important purpose of the implementation of CO₂ separation and utilization technology is how to save the necessary energy source. As one of the big expected results of COURSE50 Project promoted by NEDO from the main of the

iron and steelmaking industries in the domestic (consists of 10 iron and steel industries – 12 districts), the present research purpose is to cover the required energy for CO₂ separation if the proposed system is implemented for regenerating water-steam in the amine process. Focusing 10 iron and steelmaking industries in the domestic (12 districts), the system utilizing the waste hot water for generating steam at high temperature will offer the CO₂ reduction of about 1.5 million-t/year for each district. Totally, the CO₂ reduction becomes 18 million t-CO₂/year in domestic. For achieving the COURSE50 goals, the following steam is necessary considering the assumption that for heating amine liquid at temperature of 120°C consumes about 2.0 GJ/t-CO₂, steam at temperature of 140°C about 2.8 GJ/t-steam and the average efficiency of heat exchanger equals to 80% : $1.8 \text{ million t-CO}_2/\text{year} \times [(2.0 \text{ GJ/t-CO}_2 / 2.8 \text{ GJ/t-steam}) / 0.8] = 1.6 \text{ million t-steam}$. This steam is regenerated from the waste heat at low temperature.

In the case, here, the energy conservation and CO₂ reduction are achieved without the underground CO₂ sequestration. This reason is recently clarified by the research efforts that using the gas from blast furnace in the iron and steelmaking industries as a fuel of the power generation will remove CO₂ from blast furnace and increase the efficiency of the gas turbine combined power generation from 48–52%¹⁴⁾. In addition, from the total power generation of about more than 30 billion kWh/year produced by gas in the 10 iron and steel industries (12 districts), the great energy conservation and CO₂ reduction will be provided and the electric power of 25 billion kWh/year can be created if the waste hot water is utilized for CO₂ separation without the underground CO₂ sequestration. This created electric power has a possibility by using the present storing energy and CO₂ separation with COURSE50 based on the current enforced physical adsorption method.

If the steam regeneration technology is not applied, steam is generated using a fossil fuel combustion boiler. If assuming the thermal efficiency of the combustion boiler of 96%, the following energy is required for generating about 16 million t-steam/year using oil source: $16 \text{ million t-steam} \times 2.8 \text{ GJ/t-steam} / 0.96 / (38.2 \text{ GJ/kL} \times 0.95) = 12.9 \text{ million kL/year}$. If the oil fuelled combustion boiler is used, the CO₂ separation and recovery will meet the problem since the amount of about 3.4 million t-CO₂/year releases as a result of the increase in consuming the fossil fuel about 1.3 million kL/year.

5.2. Replacement of the Oil-fuelled Low-pressure Steam Generation

The amount of 0.2 t-steam/t-steel is demanded in the iron and steelmaking industries. It obtains mostly the waste heat recovery, therefore, only about 10% oil fuel is burned in the boiler. Thus, there is the amount of $0.2 \text{ t-steam/t-steel} \times 0.1 \times 80 \text{ million t-steel/year} = 1.6 \text{ million t-steam/year}$. Assuming that the thermal efficiency of the combustion boiler is 96%, the following heat is necessary for generating the demanded steam of 1.6 million t-steam/year if using the oil source: $1.6 \text{ million t-steam} \times 2.8 \text{ GJ/t-steam} / 0.96 / (38.2 \text{ GJ/kL} \times 0.95) = 0.13 \text{ million kL/year}$. It means considerably that the system for generating the high temperature steam from the waste heat at low temperature becomes an alternative for the replacement of the steam generation using the combustion boiler.

Assuming that the steam production cost is 2000 yen/t, the potential of economic merit reaches 3.2 billion yen/year. However, it is extremely undervalued considering the value for strategy of energy conservation and CO₂ emission reduction. From this reason, for the purpose of the energy conservation

technology innovation, the advantage value of this proposed technology is the possibility of the utilization of the waste heat at a low temperature as a core for the elements of energy conservation technology.

6. Concluding Remarks

In this paper, the performance of the proposed heat pump for steam generation and the advantages for energy conservation were calculated and explained clearly. The results shows that the proposed heat pump provides a great advantages. However, the performance estimation was assuming at the equilibrium condition of adsorption without considering the theory of rate. The experimental investigation was carried out to perform the adsorption and desorption processes. The non-equilibrium phenomena was confirmed during heat generation in the adsorption process. Moreover, how to shorten the needed time for desorption process and proceed the dry gas met some problems. The optimal operation and the development of continuous steam generation using multi bed are necessary and also becomes the remaining problems.

Three universities together with three companies supported by NEDO for the Project on Technology Development of Energy Conservation Innovation (2012–2013) will collaborate for overcoming and solving the problems from the fundamental research conducted in the laboratory through the attempts for practical use including the required equipments. The research and development progress in advance is expected.

References

- 1) METI, Japan's Energy White Paper 2010, 160, (2010) [Japanese].
- 2) T. Nakagawa, J. JSER, 32-4, 1-3 (2011) [Japanese].
- 3) MOE, Global Warming Dev. Report, 17 (2009) [Japanese].
- 4) NEDO, Fiscal Year 2009 Report, 09002771-0, 09002773-0 (2009) [Japanese].
- 5) H. Endou, Improvement of Compression Heat Pump Performance, Proc. 3rd IEA Heat Pump Conference, 797-806 (1990).
- 6) I. Tamura, H. Taniguchi, H. Sasaki, R. Yoshida, I. Sekiguchi and M. Yokogawa, *Energy Convers. Mgmt.*, **38**, 1007 (1997).
- 7) N. Endo, A. Yabe, I. Yamashita, *J. JSME B*, **64**, 2991 (1998) [Japanese].
- 8) K. Ozaki, N. Endo, A. Yabe, T. Kobayashi, *J. JSME B*, **57**, 202 (1991) [Japanese].
- 9) E. R. Canales and F. E. Márquez, *Ind. Eng. Chem. Res.*, **31**, 2547 (1992).
- 10) T. Kato, H. Yasunaga, T. Kashiwagi, SCEJ Energy Dev. - Big-boned Policy of Energy Road Map 2nd ed., 239-244 (2010) [Japanese].
- 11) Y. Kokura, M. Kanomori, J. Matsuda, T. Makoto, CaO / H₂O / Ca(OH)₂ - Chem. Eng. Thesis Collection, 19. 941 (1993) [Japanese].
- 12) K. Miwa, *Chem. Eng.*, **46**, 347(1982) [Japanese].
- 13) H. Tanaka, I. Ando, Y. Hirota, T. Sumiya, N. Kobayashi, M. Hasatani, Proceedings of Int'l. Symp. on Eco Topia Science 2007, 376(2007).
- 14) Y. Tsuji, S. Shiba, N. Nakagawa, JSME Annual Meeting, 3, 13 (2010) [Japanese].
- 15) K Nakaso, E. Octariani, A. Noda, Y. Itaya, T. Nakagawa. Fukai, *J. JSER*, **32**, 316 (2011) [Japanese].

Introduction of Research Projects

Creation of Eco-Materials from Geomimetics

A research project involved in the Program for Next-Generation World Leading Researchers (NEXT Program)

Keiko Sasaki

Department of Earth Resources Engineering, Kyushu University

1. Introduction

Following the previous volume, this article introduces a project involved in the NEXT Program. This program aims to support young researchers, female researchers and/or researchers in regional institutes who are expected to play leading roles in future research advancement (<http://www.jsps.go.jp/j-jisedai/gaiyou.html>). From 5618 proposals in all scientific fields, 141 projects for Green Innovation and 188 projects for Life Innovation were selected with 14 projects currently being developed at Kyushu University.

2. Background and Outline of Research Project

Because of a shortage of natural resources advancements in synthesis and regeneration techniques of effective materials for separation of rare elements and contaminated species are essential to maintain economic development in Japan. Factors influencing the sustainability of separating materials include safety, availability cost, and handling ability. Even ubiquitously available geomaterials and industrial wastes can be commercially developed, if they reach critical mass, are found in even quality and can be exploited at reasonable cost. “Geomimetics” include natural minerals, biogenetic minerals, industrial wastes and their analogues. Their structural properties will be

investigated by understanding the reaction mechanism at atomic levels, to optimize the modification, assembly and systemization, aiming for Green Innovation in recovery of rare elements and immobilization of contaminants in environments.

In the present project, the following three target groups are focused for the development of novel sorbents (Fig. 1).

1) Synthesis of sorbents for fluoride and borate by calcinations of Mg-bearing minerals

Hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2$) which for example occurs locally in China can be calcined to produce magnesia (MgO), which is known as an effective sorbent for fluoride (F^-) and borate ($\text{B}(\text{OH})_4^-$) by destructive sorption. Here “sorption” implies both “adsorption” and “absorption”. After sorption of these species, the sorbent is basically transformed into burcite ($\text{Mg}(\text{OH})_2$). With increase in calcinations temperatures, the specific surface areas decreased, but the sorption density of fluoride and borate increased. This phenomenon is considered to be caused by transition from two-dimensional sorption into three-dimensional deposition (e.g., co-precipitation and precipitation) depending on the concentrations of targets, pH and other water quality factors (Fig. 2). In the present work, regenerating conditions of solid residues to sorbents will

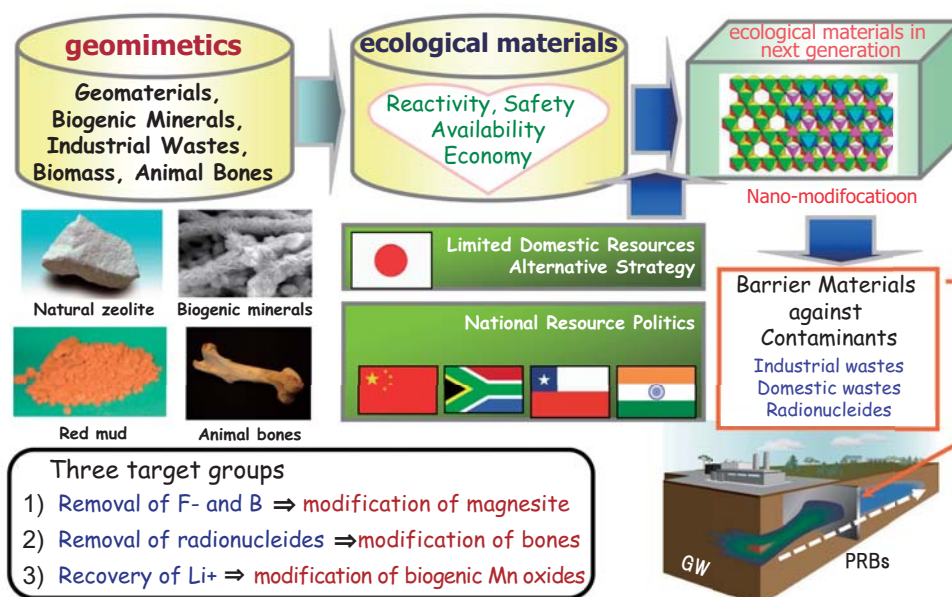


Fig. 1 Background and outlines in the project.

also be optimized. An analogical approach will be tried by replacement MgO with bimetallic oxides. Bimetallic oxides are basically transformed into layered double hydroxides (LDHs) after destructive sorption of fluoride and borate. Hydrotalcite, which is one of the most well known LDHs, possesses the property to intercalate anionic species between host layers. The efficiency is expected to depend on metals in host layers. It is known that boric acid behaves as a monomer at less than 25 mM, and as a polymer at more than 25 mM. This material can be flexibly designed according to the target sizes.

2) Synthesis of sorbents for radionuclides from animal bones

Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$, HAP) is known as an anionic and/or cationic exchanger with high bio-affinity. Its mechanism of ion-exchange provides benefits in maintaining its porosity over long periods if used as environmental sorbent in removing radionuclides in groundwaters by permeable reactive barriers (PRBs).

Natural HAP is a scarce resource in Japan. However, HAP is included with a purity of approx. 60 % in animal bones and its purity level can be easily improved by calcination. A bacterium of *Serratia sp.*, which is an acid-phosphatase producer, decomposes glycerol-2-phosphate into glycerol and phosphate to intake only glycerol, leading to the formation of nano-sized HAP with needle shapes by reaction of phosphate with Ca^{2+} ions in the medium. After calcination of nano-sized HAP, uniformed size and crystallized HAP particles can be obtained (Fig. 3). In the present work, the relationship between crystallinity of HAP from “Geomimetics” and its ion-exchangeability with radionuclide surrogates will be investigated.

3) Synthesis of Li^+ -ion sieve using biogenic Mn oxide as a precursor

Lithium (Li) is regarded as a rare metal and its current demand in Japan is exclusively satisfied by imports from China. Geothermal waters in Hachobaru, Oita prefecture include Li^+ ions with 50-100 times in the level

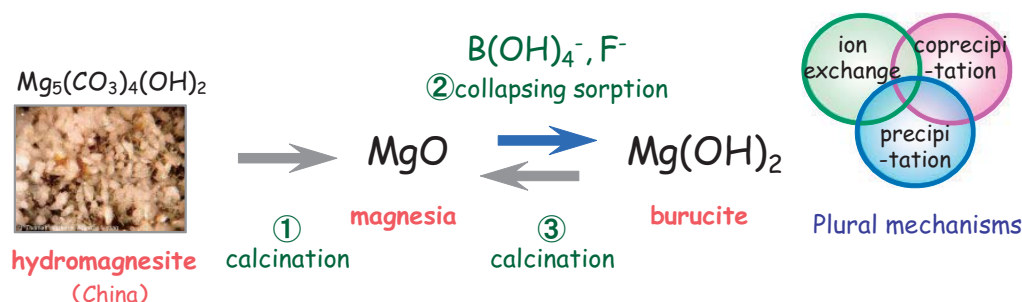


Fig. 2 Synthesis and regeneration of Mg-bearing sorbents for fluoride and borate.

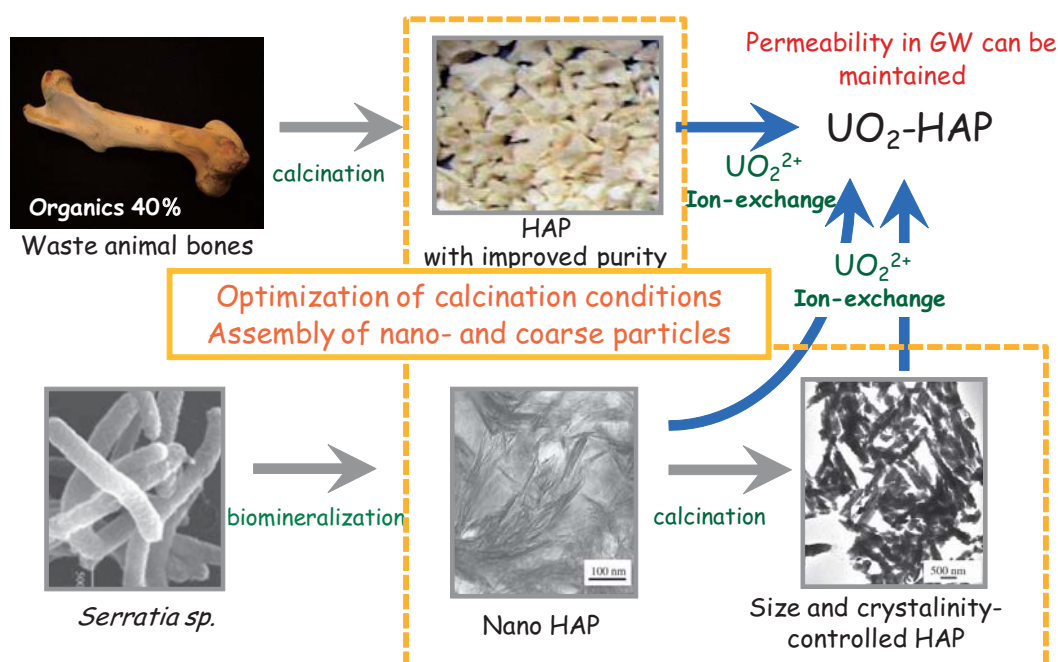


Fig. 3 Modification of biogenic hydroxyapatite by calcinations.

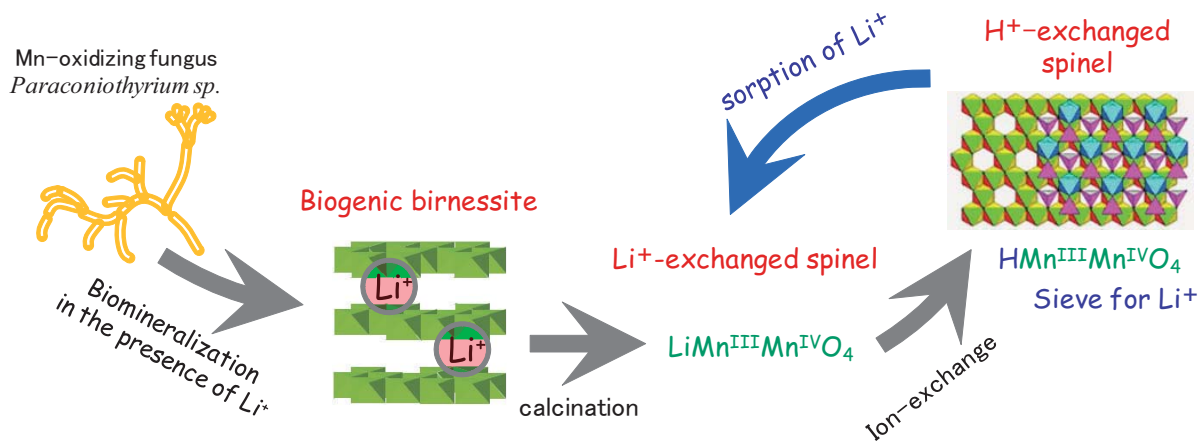


Fig. 4 Synthesis of Li-ion sieve using enzymatic reaction by a Mn-oxidizing fungus.

found in sea water and could be exploited commercially. Synthesis of porous manganese oxide crystals of lithium ion sieve has been investigated in various methods of mold formation followed by acid-treatment. Precursors for mold formation are usually formed by hydrothermal reaction under strongly acidic or alkaline conditions in wet system or by heating in a dry system.

It is known that Mn(II)-oxidizing fungi are widely distributed in phylogenetic trees. However, only a few microbes possess Mn(II) tolerance of over several hundred ppm. *Paraconiothyrium sp.* WL-2 produces Mn-peroxidase enabling it to oxidize more than 400 ppm Mn(II) into Mn(III, IV) at neutral pH and room temperatures, resulting in the formation of layer types of octahedral MnO_6 including Mn(III, IV) and vacancies. In the present work, the precursor for mold of Li^+ -ion sieve is produced during

the cultivation of the fungus, followed by calcinations. The calcination conditions will be optimized for efficiency of ion-exchange of H^+/Li^+ (Fig. 4).

3. Prospects

The process of “calcination” is not only used for the decomposition of organic matters and transformation of carbonates to oxides in “geomimetics” but also to force structural changes in the nano-domain. This is expected to affect interfacial reactions between solid surface and aqueous solutions, like sorption, surface complexation, co-precipitation, precipitation, ion-exchange, in various degrees. Furthermore we expect to contribute through this research to the development of a “low carbon society”

Research and Development of Post-Olivine Type Cathodes for High-Performance Li Batteries

(NEDO Li-EAD Project)

Shigeto Okada

Institute for Materials Chemistry and Engineering, Kyushu University

1. Li-EAD Project Overview

The development of a high-performance battery system for next-generation vehicles, known as the Li-EAD Project, is part of a new energy development program started by New Energy and Industrial Technology Development Organization (NEDO) in 2007. The goal is to contribute to the rapid practical use of next-generation clean energy vehicles, such as fuel cell vehicles, plug-in hybrid vehicles and electric vehicles. Including the additional accepted 17 themes in 2008, there are a total of 42 selected research themes underway with a total annual budget of 3 billion yen; of these, 17 are focused on elemental technologies for high-performance lithium-ion storage batteries and vehicle drive motors, 22 are for next-generation technologies to revolutionize storage batteries based on new concepts, and 2 are for developing battery evaluation technology such as life prediction and equalization, respectively.

The direction for this project's development of vehicle batteries was clarified by the NEDO statement on the

future of batteries for next-generation vehicles released in 2006 (Figure 1). As seen in Table 1, elemental technology development teams were to make advanced batteries with 2015 as the target for implementation, and next-generation technology development teams were to make revolutionary batteries with 2030 as their goal. The theoretical upper limit of the gravimetric energy density of lithium-ion batteries using carbonaceous anodes can be estimated at approximately 250 Wh/kg. So, advance batteries will likely be within lithium-ion battery limits. On the other hand, revolutionary batteries will be going beyond the limits of lithium-ion batteries.

The present theme was selected in 2007 as an elemental technology development theme. It was developed jointly by IMCE of Kyushu University, Mitsubishi Heavy Industries, Ltd. and Kyushu Electric Power Co., Inc. This year is the final year of the five-year plan. From Kyushu University, Professor Tatsumi Ishihara were also selected in 2008 with a theme of lithium air secondary batteries as one of the revolutionary battery.

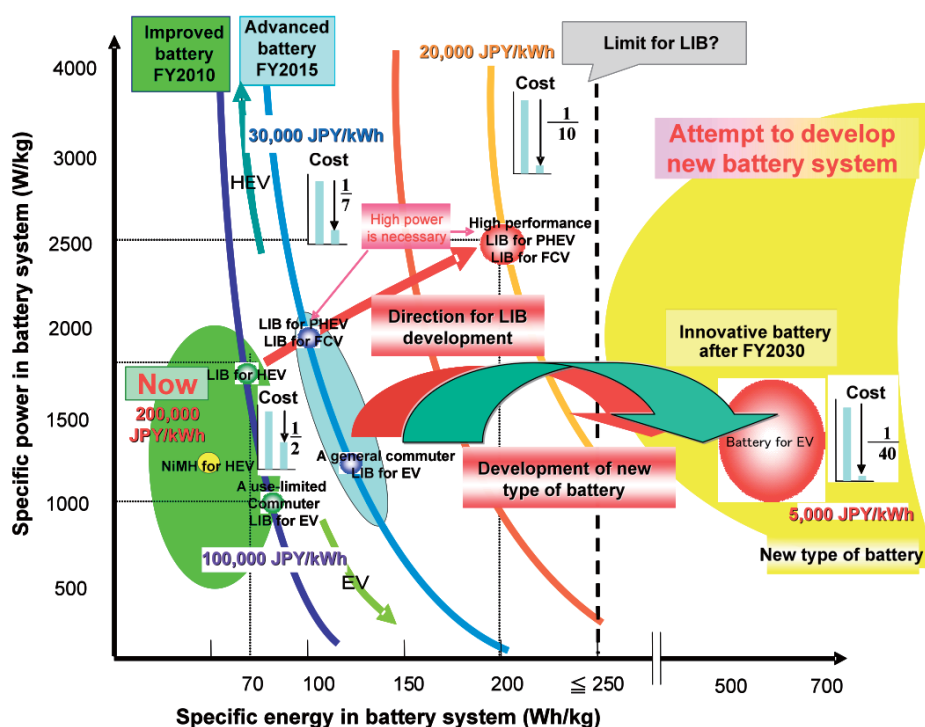


Fig. 1 Future vision for next-generation vehicle batteries¹⁾

Table 1 Targets of Li-EAD Project by NEDO

FY		2010	2015	2020	2030
EV	Gravimetric energy density [Wh/kg]	100	150	-	700
	Gravimetric power density [Wh/kg]	1000	1200	-	1000
HV	Gravimetric energy density [Wh/kg]	70	100	200	-
	Gravimetric power density [Wh/kg]	2000	2000	2500	-
Cost [yen/kWh]		100000	30000	20000	5000

2. Overview of Theme

Battery system technology is a core technology for all next-generation clean-energy vehicles such as fuel cell vehicles, electric vehicles (EV), and plug-in hybrid vehicles (PHEV). It is one of the basic next-generation vehicle energy technologies. To realize the next-generation clean-energy vehicles, especially PHEVs, it is necessary to develop secondary batteries that have a higher energy density and higher power density than existing batteries. At the present time, lithium-ion battery is a one of the candidates, because it has the highest energy density in the market. In lithium-ion batteries, it is possible to achieve high energy density by using $\text{LiCo}_{1-x-y}\text{Ni}_x\text{Mn}_y\text{O}_2$ type layered oxide cathode, but there are still issues about the cost and safety. On the other hand, as an economical and safe choice, olivine-type iron phosphate LiFePO_4 is promising as the unique minor-metal free cathode active material, but the relatively low energy density and poor rate capability should be improved. In order to obtain the target performances for advanced batteries, two possible approaches can be considered: reducing the cost of $\text{LiCo}_{1-x-y}\text{Ni}_x\text{Mn}_y\text{O}_2$ by eliminating cobalt, or finding a new iron-based cathode active material that has superior energy density to LiFePO_4 . We are the only team which focuses on the latter route among the elemental technology development themes.

Our research team includes Mitsubishi Heavy Industries, Ltd. and Kyushu Electric Power Co., Inc. who jointly created a lithium-ion battery for electric vehicles with LiMn_2O_4 cathode, and Kyushu University with experiences researching battery safety and inexpensive polyanionic cathode active materials such as olivine-type iron phosphate. Through collaboration using these complementary skills and experiences, the plan is to develop a new high-performance lithium battery based on iron-based compounds that is superior to olivine-type iron phosphate. The final target of the energy density is 200 Wh/kg based on the battery weight, corresponding to 1000 Wh/kg based on the cathode weight.

3. Candidates for Post-iron Olivine Cathodes

Four material groups were selected as the post-olivine candidates beyond LiFePO_4 's theoretical energy density capacity of 561 Wh/kg ($=170 \text{ mAh/g} \times 3.3 \text{ V}$).

1) LiMPO_4 (Figure 2-a): A cathode material group that has the same Pnma olivine structure as LiFePO_4 includes LiMnPO_4 , LiCoPO_4 and LiNiPO_4 . A parallel shift of their discharge potential is caused by the $\text{M}^{2+}/\text{M}^{3+}$ redox potential of each transition metal, so by transition-metal substitution of LiFePO_4 from $\text{Fe} \rightarrow \text{Mn} \rightarrow \text{Co} \rightarrow \text{Ni}$, the discharge potential can be changed from 3.3 V $\rightarrow$ 4 V $\rightarrow$ 4.8 V $\rightarrow$ 5.2 V, and the theoretical energy density can be increased from 555 Wh/kg $\rightarrow$ 670 Wh/kg $\rightarrow$ 800 Wh/kg $\rightarrow$ 870 Wh/kg. By a planetary ball milling with 25 wt % carbon and annealing in an argon atmosphere at 500 °C, the energy density of carbon-coated LiMnPO_4 was greater than that of LiFePO_4 ²⁾. LiCoPO_4 and LiNiPO_4 bring oxidative decomposition of a non-aqueous electrolyte, because their cathode potential is too high. Thus, a sebaconitrile electrolyte was found as an oxidation resistant electrolyte that allows charging of 5 V cathodes, demonstrating their validity³⁾.

2) $\text{Li}_2\text{MPO}_4\text{F}$ (Figure 2-b): The olivine composition of LiMPO_4 means that only 1Li insertion/extraction of the formula can be expected by $\text{M}^{2+}/\text{M}^{3+}$ redox reaction. On the other hand, $\text{M}^{2+}/\text{M}^{4+}$ redox reaction in $\text{Li}_2\text{MPO}_4\text{F}$ may allow 2Li insertion/extraction of the formula. By using a single-roll rapid cooling device, amorphous $\text{LiNaFePO}_4\text{F}$ was obtained. An annealing treatment was applied to create a $\text{LiNaFePO}_4\text{F}$ compound with Pnma that has never been reported before. The reversible capacity was 167 Ah/kg, corresponding to 1.25 electron reactions⁴⁾.

3) Li_2MSiO_4 (Figure 2-c): In order to improve the electronic conductivity of $\text{Li}_2\text{FeSiO}_4$, composite conditions with conductive carbon were optimized using a planetary mill. The top data of the reversible capacity was 225 Ah/kg, corresponding to 1.67 electron reactions⁵⁾.

4) MF_3 (Figure 2-d): It has been known that FeF_3 could accommodate a 1Li reversible insertion reaction, but by changing the discharge potential to lower potential levels it was possible to surpass the final goal value, 1000 Wh/kg. The theoretical value is 1090 Wh/kg for 2Li and 1422 Wh/kg for 3Li reaction⁶⁾, respectively (Figure 3). By monitoring the iron valence change of FeF_3 in the charge-discharge cycle deeper than 1 Li through XAFS measurement at the Kyushu Synchrotron Light Research Center, it was proven that this charge-discharge was caused by the reversible conversion reaction between Fe^{3+} and Fe^0 .

Unlike general oxide cathode materials, it was confirmed that generated heat amount from FeF_3 was

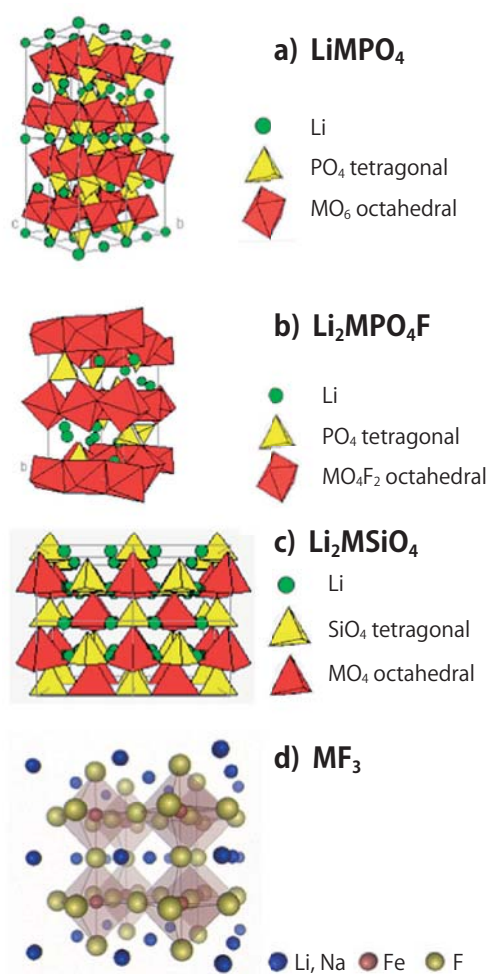


Fig. 2 Post- LiFePO_4 cathode candidates; a) LiMPO_4 , b) $\text{Li}_2\text{MPO}_4\text{F}$, c) Li_2MSiO_4 , d) MF_3

lower than that in an isolated electrolyte, because of the thermal stable discharge product, LiF . It means that FeF_3 is also an excellent cathode active material from a safety perspective⁷⁾. Investigations of the inexpensive starting materials and the production processes of FeF_3 performed mainly by Mitsubishi Heavy Industries were able to achieve the target cost of 2000 yen/kg or less for mass production.

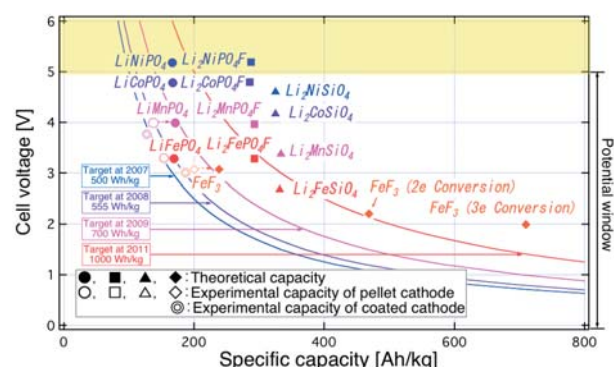


Fig. 3 Theoretical and practical capacity of post- LiFePO_4 cathode candidates compared to NEDO targets; a) LiMPO_4 , b) $\text{Li}_2\text{MPO}_4\text{F}$, c) Li_2MSiO_4 , d) MF_3

Acknowledgements

I express my thanks for the cooperation of Li-EAD project members, Ichiro Tanaka (Mitsubishi Motors), Eiji Kobayashi, Kuniko Chihara, Dr. Ayuko Kitajou, Dr. Liwei Zhao, Dr. Mingjiong Zhou, and master course students in Yamaki-Okada Lab., Tomoyuki Shiratsuchi (Sony Corporation), Manabu Nishijima (Toyota Motor Corporation), Akira Yoda (DENKA), Yuichi Kamimura (Sharp Corporation), Takashi Tanaka (Honda Motor Co., Ltd.) and Hideki Mizuta (Hitachi Maxell, Ltd.).

References

- 1) METI Report about Next-Generation Battery Technology for New-Generation Vehicles (www.meti.go.jp/report/downloadfiles/g60824b01j.pdf)(2006).
- 2) T. Shiratsuchi, S. Okada, T. Doi and J. Yamaki, *Electrochim. Acta*, **54**(11), 3145-3151(2009).
- 3) M. Nagahama, N. Hasegawa and S. Okada, *J. Electrochem. Soc.*, **157**, A748-A752 (2010).
- 4) H. Mizuta, A. Kitajou, S. Okada and J. Yamaki, Extended abstract of 218th ECS Fall Meeting (2010).
- 5) Y. Kamimura, E. Kobayashi, T. Doi, S. Okada and J. Yamaki, Abstract of 50th Battery Symposium, 2A03 (2009).
- 6) S. Okada, Y. Tanaka, I.D. Gocheva, I. Tanaka, T. Doi, J. Yamaki, M. Takeo and T. Nishida, Extended abstract of 216th ECS Fall Meeting, #619 (2009).
- 7) M. Zhou, L. Zhao, T. Doi, S. Okada and J. Yamaki, *J. Power Sources*, **195**, 4952-4956(2010).

Introduction of the Group Researches & Research Reports

Grand Design for Advanced Next Generation Cathode Active Materials

Shigeto Okada

Institute for Materials Chemistry and Engineering, Kyushu University

After the commercialization of the Li-ion battery with carbon anode, the researches for cathode-active materials have concentrated on lithium-containing first-row transition-metal oxides with 4V class high electromotive force, because it can serve as Li sources to a carbonaceous anode. However, all 4V-class rechargeable cathodes, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , have the essential problems about safety, cost and environmental impact. These problems become serious, especially for the large scale cell. To solve these intrinsic problems, basic design concepts for advanced next generation cathode active material are proposed.

1. Issues Common to the Current Transition-Metal Oxide Cathodes

In the latter half of the 1980s, Moli Energy commercialized a lithium secondary battery with lithium metal anode. The cathodes used in the battery were two-dimensional molybdenum sulfides, MoS_2 . Soon after commercial release, accidents from fires caused by dendritic shorts between the cathode and anode led to a halt in production. However, small-scale coin-type lithium secondary batteries with lithium metal anode and transition metal oxides cathodes such as MnO_2 and V_2O_5 continue to be commercially produced by several battery companies for memory back-up in digital cameras and smartphones.

If the two-dimensional transition-metal sulfide that never became widely released is considered the “first-generation” cathode, then the second-generation cathodes would be the group of 4V lithium-ion batteries including lithium transition metal oxides LiCoO_2 , LiNiO_2 and LiMn_2O_4 . By use of carbonaceous anodes, the second-generation oxide cathodes overcame the dendritic short issue and had improved charge-discharge efficiency. These continue to be widely used as commercial lithium-ion batteries. Among the second-generation transition-metal oxide cathodes, new cathode active material group with layered-rocksalt type solid-solution between Li_2MnO_3 and LiMO_2 (M: Co, Ni, Mn, etc.) were also discovered. The capacity exceeding 275 mAh/g which is the theoretical capacity of LiCoO_2 was found out in some layered-rocksalt type solid-solution oxide cathodes; thus ample attention has been paid to searches for optimal solid solution compositions, and the investigation of the charge/discharge mechanisms.

On the other hand, these second-generation cathode active materials have the following 3 common natures; a) minor metal compounds, b) oxides, and c) trivalent/tetravalent redox system, including anomalous valences. These similarities among these second-generation cathode active materials bring to the common weaknesses about the high cost and low thermal stability.

In order to solve these problems with second-generation

oxide cathodes and to create large lithium-ion batteries for electric vehicles and smart grids, research into third-generation cathode active materials is becoming more active not only in Japan but also in foreign countries. The olivine LiFePO_4 ¹⁾, which has seen practical use and is the most promising candidate for a third-generation polyanionic cathode, solves all 3 of these problems.

2. Grand Design for Advanced Next Generation Cathodes

1) Minor Metal-Based Compound→Minor Metal-Free Compounds

As can be seen from Figure 1, as batteries become larger there is no choice but to shift the redox couple in cathode from cobalt to iron, in order to decrease the environmental burden and cost. However, the battery venture companies in late-coming foreign countries precede Japanese major battery companies in this trend, development of eco-friendly battery with iron-based cathode.

Table 1 is a list of representative studies of iron-based cathode active materials. The highest experimental energy density in iron-based cathode active materials was reported in the ReO_3 -type metal fluoride FeF_3 ²⁻⁴⁾ (200 mAh/g×3.1 V = 620 Wh/kg). The top data obtained in FeF_3 is higher than the theoretical energy density of LiFePO_4 (170 mAh/g×3.3 V = 561 Wh/kg).

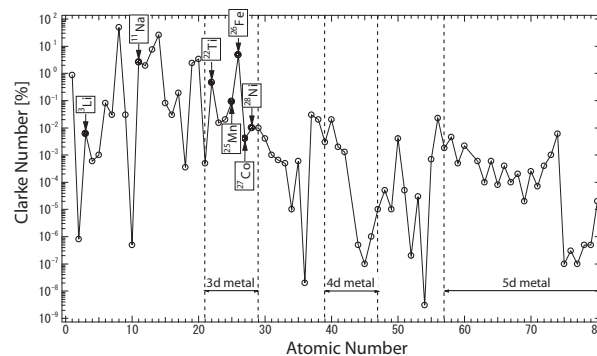


Figure 1 Clarke numbers of elements in the crust

Table 1 Theoretical energy densities of typical iron-based cathode active materials
[Values within () in the table are theoretical values based on conversion reactions, hatched items mean the active hosts against Na.]

Published Year	Cathode Active Materials	Anion	Discharge Voltage	Theoretical Energy Density	Crystal Structure
1977	FePS ₃	S ²⁻	1.7 V	249 Wh/kg	Layer
1978	FeOCl	O ²⁻ , Cl ⁻	2.3 V	574 Wh/kg	Layer
1980	FeS ₂	S ²⁻	1.7 V	(1521 Wh/kg)	Pyrite
1982	Fe ₂ O ₃	O ²⁻	1.4 V	470 Wh/kg	Defect spinel
1982	Fe ₃ O ₄	O ²⁻	1.5 V	521 Wh/kg	Spinel
1982	FePc	Phthalocyanine	1.6 V	—	Lamellar
1984	Fe ₂ (MoO ₄) ₃	(MoO ₄) ²⁻	3.0 V	271 Wh/kg	NASICON
1986	LiFe ₅ O ₈	O ²⁻	1.4 V	453 Wh/kg	Spinel
1987	Fe ₂ (WO ₄) ₃	(WO ₄) ²⁻	3.0 V	188 Wh/kg	NASICON
1989	Fe ₂ (SO ₄) ₃	(SO ₄) ²⁻	3.6 V	482 Wh/kg	NASICON
1990	FeMoO ₄ Cl	(MoO ₄) ²⁻ , Cl ⁻	3.4 V	363 Wh/kg	Layer
1994	Li ₃ Fe ₂ (PO ₄) ₃	(PO ₄) ³⁻	2.8 V	360 Wh/kg	NASICON
1995	FePO ₄	(PO ₄) ³⁻	3.0 V	533 Wh/kg	Quartz/Amorphous
1996	Li ₃ Fe ₂ (AsO ₄) ₃	(AsO ₄) ³⁻	2.7 V	263 Wh/kg	NASICON
1997	LiFePO ₄	(PO ₄) ³⁻	3.3 V	561 Wh/kg	Olivine
1997	FeF ₃	F ⁻	3.1 V(2V)	736 Wh/kg (1422 Wh/kg)	Perovskite
1999	β-FeOOH	O ²⁻ , OH ⁻	2 V	603 Wh/kg	2x2 Channel
2001	Li ₅ FeO ₄	O ²⁻	2.4 V	416 Wh/kg	Anti-fluorite
2002	FeBO ₃	(BO ₃) ³⁻	1.5 V	351 Wh/kg	Calcite
2004	NaFeO ₂	O ²⁻	3.3 V	798 Wh/kg	Layered rocksalt
2005	Li ₂ FeSiO ₄	(SiO ₄) ⁴⁻	2.8 V	463 Wh/kg	Wurtzite

2) Li Hosts→Na/Polyvalent Cation Hosts

As indicated in Figure 1, from a strategic elemental perspective, it is unavoidable that to make minor metal-free batteries, we must stop using cobalt for cathode and stop using lithium for anode, respectively. Figure 2 shows that the surplus electricity produced during night time in Japan is 700 GWh. It would be enough electric power for overnight charging of all 45 million vehicles registered in Japan if they were switched to pure EV such as i-MiEV with 16 kWh rechargeable battery. However, in order to store this amount of electricity in lithium metal with theoretical capacity ($3.8 \text{ Ah/g} \times 3.6 \text{ V} = 13.7 \text{ Wh/g}$), approximately 60,000 t of lithium would be necessary. It corresponds to nearly 3 times the amount of lithium produced annually worldwide. Thus, if the entire world began load-leveilling using lithium-ion batteries, it is clear lithium resources would quickly dry up. It becomes clear that in order to store the surplus electricity produced overnight, we have to replace lithium by sodium, for example sodium-sulfur battery. Because sodium resource is 1000 times larger than that of lithium.

Efforts to switch from Li⁺ to Ca²⁺, Mg²⁺ or even Al³⁺ polyvalent cation batteries are motivated from the perspective of increasing energy density as well as decreasing the environmental burden. There are no other

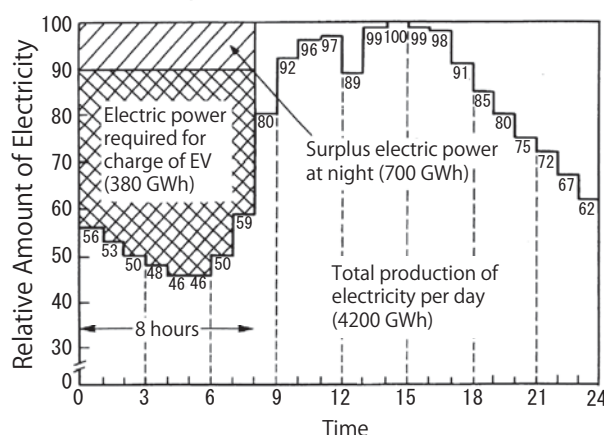


Figure 2 Surplus electricity at night-time in Japan

metal anodes that surpass lithium's 3.86 Ah/g gravimetric capacity density, but lithium's volumetric capacity density is only 2.05 Ah/cc. For example, in the case of divalent magnesium-ion batteries, the theoretical gravimetric and volumetric capacity densities provided by the oxidation reaction ($\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$) are 2.20 Ah/g and 3.83 Ah/cc, respectively. The theoretical volumetric capacity density is nearly twice the lithium. In the case of trivalent

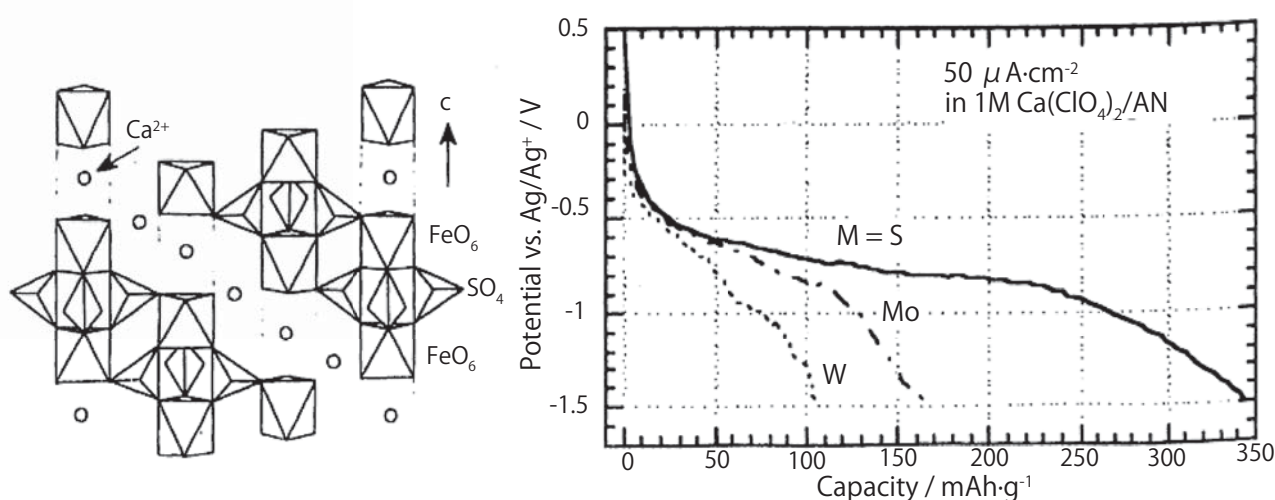


Figure 3 NASICON-type $\text{Fe}_2(\text{SO}_4)_3$ crystal structure and the discharge profiles of $\text{Fe}_2(\text{MO}_4)_3$ cathodes against $\text{Ca}^{5)}$

aluminum-ion batteries, the theoretical gravimetric and volumetric capacity densities provided by the oxidation reaction ($\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$) are 2.98 Ah/g and 8.05 Ah/cc, respectively. The theoretical volumetric capacity density is nearly four times larger than that of lithium. Figure 3 shows the discharge profile of NASICON-type $\text{Fe}_2(\text{XO}_4)_3$ /1M $\text{Ca}(\text{ClO}_4)_2$ /acetonitrile//Ca batteries ($\text{X} = \text{S}, \text{Mo}$ and W). The average discharge voltages for these batteries are almost -0.7 V against Ag, it means the cell voltages are 2.9 V against Ca anode.

3) Edge/Face-Sharing Matrix→Corner-Sharing Matrix

In Table 1, which shows crystal structures along with typical iron-based cathode active materials, the hatched items mean active hosts not only for lithium but also for sodium with its ionic volume around twice that of lithium. From this, it can be seen that all known Na intercalation hosts are corner-sharing structures with three-dimensional diffusion paths and large bottlenecks, or else layered structures with a two-dimensional van der Waals gap (Figure 4).

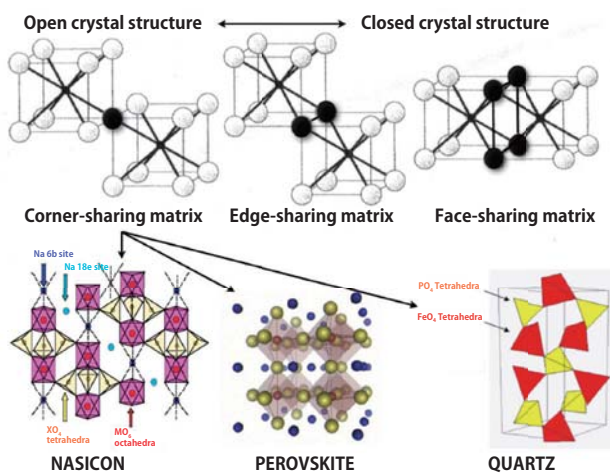


Figure 4 Typical Na hosts with corner-sharing matrix

The structure of glass structure is a typical example of corner-sharing matrix. There are four immediate benefits of this type of structure; a) composites that can't be formed as crystals can sometimes be combined (however, this requires that the desired compound be in a composition range where vitrification is possible); b) vitrification causes a corner-sharing structure, shifting to low density and encouraging 3 dimensional lithium diffusion; c) since it will be combined using melting, it must be possible to use an inexpensive oxide material with low reactivity; and d) since no calcination is necessary, it can be combined quickly. In fact, as the positive effect on the specific capacity through amorphization, there are reports of V_2O_5 capacity increasing from 147 mAh/g to 180 mAh/g⁶⁾, Cr_3O_8 capacity increasing from 123 mAh/g to 142 mAh/g⁷⁾, and MnO_2 capacity increasing from 265 mAh/g to 278 mAh/g⁸⁾.

Although Fe_2O_3 is inexpensive, it is usually difficult to use as an iron source for iron-based cathode, because of the low reactivity and high-thermal stability. However, phosphoric polyanions can react with the inactive Fe_2O_3 in a single-step process of brief fusion and phosphate itself can act as a network-former in the glass matrix. It is a big advantage of decreasing production cost⁹⁾, because there is no need of mixing and calcination process in the case of production of amorphous cathodes.

4) Oxides→Sulfide/Phosphide/Fluorides

The merits of oxides are that they can be combined in air and are chemically stable, but when fully charged, oxygen gas begins to release from the charged cathode around 150 °C, which can trigger the exothermic heat of the organic electrolyte, a significant issue for battery safety. The strong covalent bonding between hetero elements and oxygen in polyanionic cathodes can prevent oxygen release at elevated temperature and improve the thermal stability. However, if it were a cathode active material without oxygen, that could suppress the

exothermic reaction of electrolyte. Fluorides, which have been receiving particular attention in recent years among non-oxide cathode options, can easily become high-voltage cathodes due to the high electronegativity of fluorine (Figure 5). Also, since fluorine is a monovalent anion, there are many 3d transition metal candidates such as Fe and V with t factors that can provide B cations to fulfill the conditions (see the following formula) of the LiMF_3 perovskite structure.

$$t = \frac{A \text{ cation radius} + \text{anion radius}}{\sqrt{2} \times (B \text{ cation radius} + \text{anion radius})} \approx 1$$

This is the biggest difference of LiMF_3 from oxide perovskite LiMO_3 . Because no pentavalent transition-metal B cation exists to fulfill the tolerance factor in the case of ABO_3 -type oxides, when monovalent alkali metals such as lithium occupy at A cation sites.

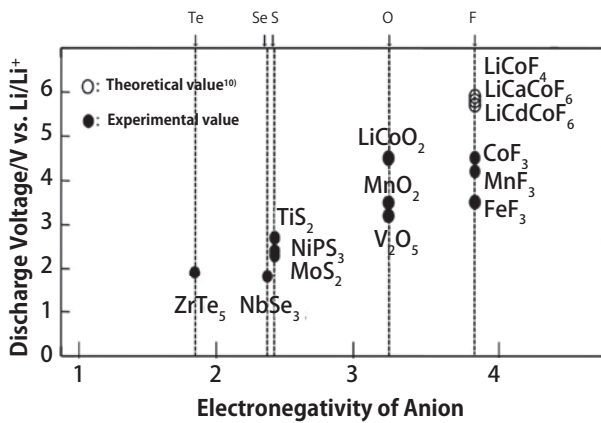


Figure 5 Correlation between cathode discharge voltage and anion electronegativity. Here, open circles mean theoretical voltage values¹⁰⁾ and closed circles means experimental voltage values vs. Li/Li^+ , respectively.

5) Intercalation Reaction→Conversion Reaction

Table 2 shows the average discharge voltage of MX_m -type iron, manganese and cobalt-based cathodes for the full discharge reaction ($n\text{Li} + \text{MX}_m \rightleftharpoons \text{M} + n\text{LiX}_{m/n}$) against lithium calculated by the Gibbs free energy, $\Delta G = n\Delta G_f^0(\text{LiX}_{m/n}) - \Delta G_f^0(\text{MX}_m) = -nEF$.

From Table 2 and Figure 6, fluorides can be recognized as the promising conversion-type cathode material group with high energy density. Conversion-type cathode active materials, unlike intercalation-type ones, do not need to contain a van der Waals gap for lithium diffusion and any vacancy sites within the host matrix for the intercalants. In addition, they do not need any transition metals for redox couple. It means that the conventional guidelines for seeking intercalation-type cathode active materials do not apply for conversion-type cathode active materials. Recently, systematic efforts have begun using combinatorial methods to seek for new fluoride cathode compositions by sputtering method with various mixing ratio between LiF or iron as starting materials. On the

Table 2 Discharge voltages of MX_n estimated by ΔG ¹¹⁾

FeX_n	ΔG_f	Discharge voltage	Theoretical capacity	Theoretical energy density
FeF_3	-972 kJ/mol	2.742 V	712 Ah/kg	1952 Wh/kg
FeS_2	-160 kJ/mol	1.861 V	893 Ah/kg	1662 Wh/kg
Fe_2O_3	-742 kJ/mol	1.631 V	1007 Ah/kg	1642 Wh/kg
Fe_4N	-3.7 kJ/mol	0.432 V	339 Ah/kg	146 Wh/kg

MnX_n	ΔG_f	Discharge voltage	Theoretical capacity	Theoretical energy density
MnF_3	-1000 kJ/mol	2.647 V	719 Ah/kg	1903 Wh/kg
MnS_2	-225 kJ/mol	1.692 V	900 Ah/kg	1523 Wh/kg
Mn_2O_3	-881 kJ/mol	1.431 V	1018 Ah/kg	1457 Wh/kg
Mn_4N	-105 kJ/mol	0.083 V	459 Ah/kg	38 Wh/kg

CoX_n	ΔG_f	Discharge voltage	Theoretical capacity	Theoretical energy density
CoF_3	-719 kJ/mol	3.617 V	694 Ah/kg	2510 Wh/kg
CoS_2	-146 kJ/mol	1.898 V	871 Ah/kg	1653 Wh/kg
CoO	-214 kJ/mol	1.802 V	715 Ah/kg	1288 Wh/kg
Co_3N	-34 kJ/mol	0.326 V	421 Ah/kg	137 Wh/kg

other hand, there are also concerns that since conversion reactions completely remake the host structure and cause a large volume change. So, the reversibility and the charge-discharge efficiency will be significantly decreased in comparison with intercalation reactions.

It is hoped that rigid binders such as imides and acrylics, which have been reported to dramatically improve the cycle properties of alloy-type anodes, will be able to improve cyclability for conversion-type cathodes as well.

Figure 7 shows the charge-discharge cycle after discharging FeF_3 to the conversion reaction range at a 3Li depth of discharge. Recently, conversion reactions using sodium instead of lithium have been also found for FeF_3 and FeS_2 (Figure 8). Iron sulfide FeS_2 has a reversible conversion reaction with 2Na ($2\text{Na} + \text{FeS}_2 \rightleftharpoons 2\text{Na}_2\text{S}_2 + \text{Fe}$), with an estimated theoretical energy density of 549 Wh/kg ($= 323 \text{ Ah/kg} \times 1.7 \text{ V}$) when the weight of both electrodes is considered. The energy density of conversion-type Na/FeS_2 battery is 1.5 times larger than that of the first-generation intercalation-type lithium-ion batteries ($0.5\text{C}_6 + \text{LiCoO}_2 \rightleftharpoons 0.5\text{C}_6\text{Li} + \text{Li}_{0.5}\text{CoO}_2$) with graphite anodes and LiCoO_2 cathodes, 360 Wh/kg ($= 100 \text{ Ah/kg} \times 3.6 \text{ V}$).

The first commercially available sodium sulfur battery in the world, commercialized by NGK Insulators in 2003, made possible the reversible charge-discharge reaction of $2\text{Na} + 5\text{S} \rightleftharpoons 2\text{Na}_2\text{S}_5$ at 300 °C high temperature operation, but its theoretical energy density is 520 Wh/kg ($= 260 \text{ Ah/kg} \times 2 \text{ V}$), meaning the room-temperature conversion reaction of iron sulfide for sodium has an even higher theoretical energy density. As storage batteries become larger, the ratio of material costs will increase. This is why sodium-ion battery, which simultaneously solve the

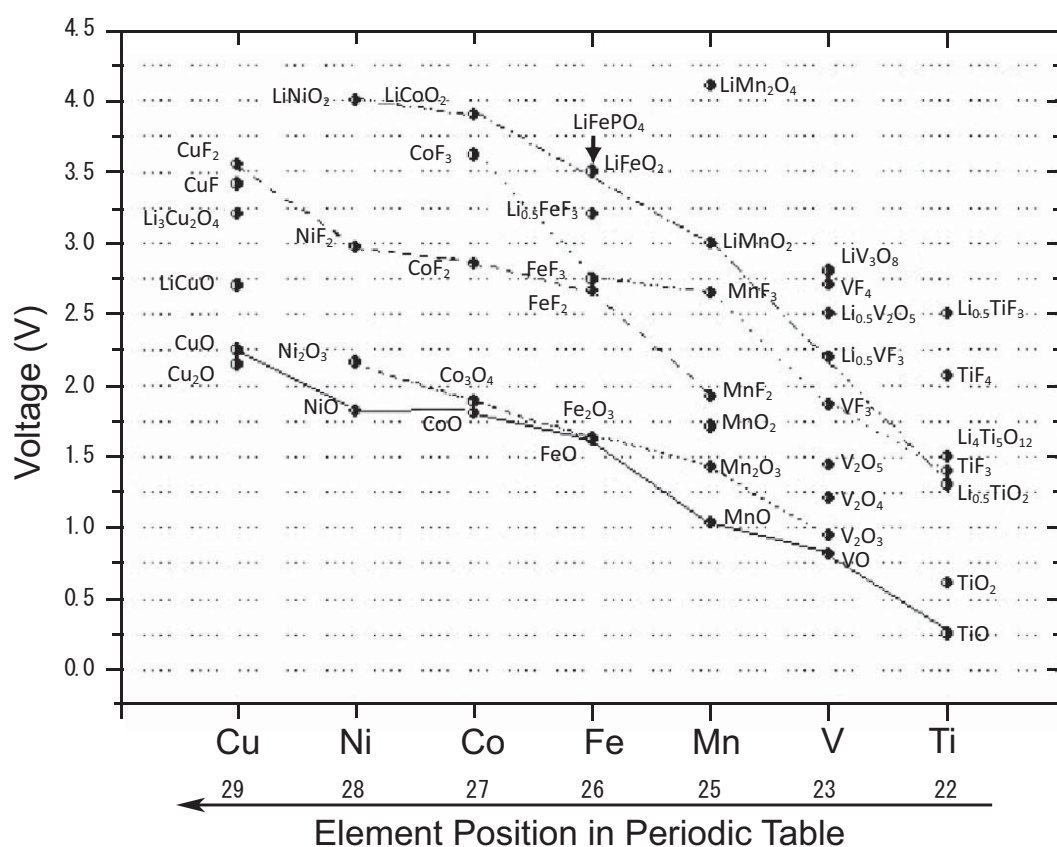


Figure 6 Average theoretical discharge voltage values for all discharge reactions estimated by $\Delta G^{11)}$

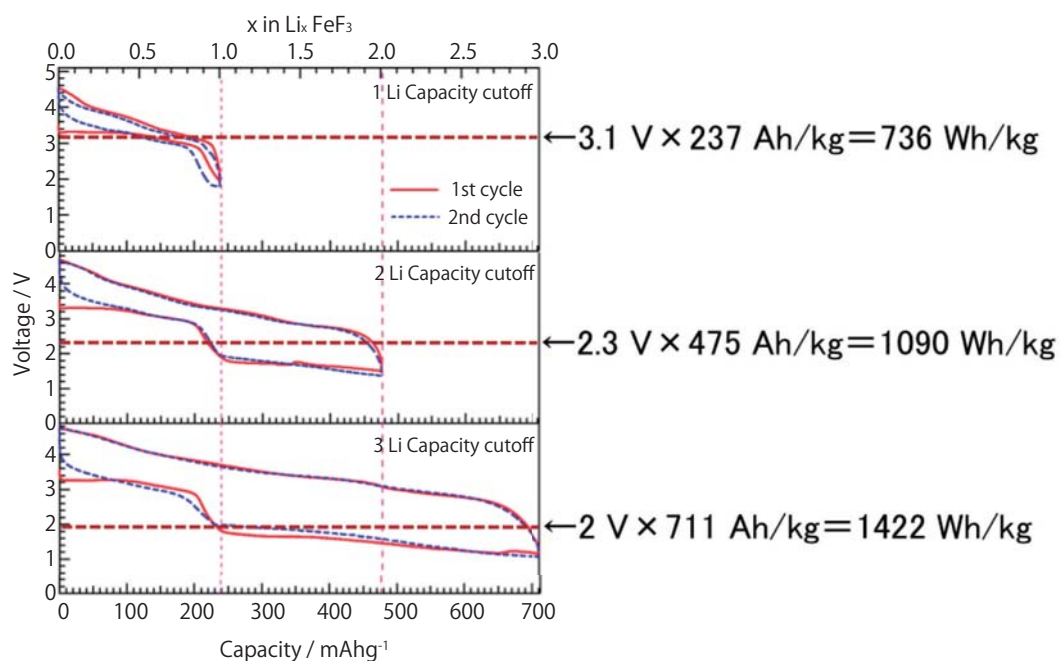


Figure 7 Charge/discharge profiles of FeF_3 at various cycle depth¹²⁾

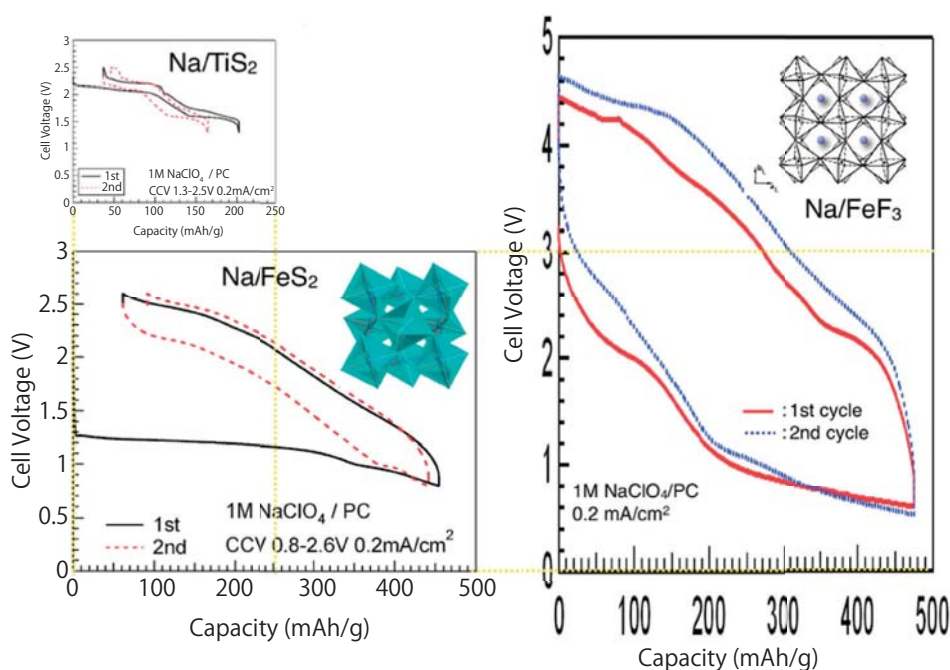


Figure 8 Charge-discharge properties for conversion Na/FeF₃ and conversion Na/FeS₂¹³⁾

Table 3 Several approaches to post-lithium-ion batteries

Current Issues of Li-ion Battery	Cathode	Anode	Electrolyte
Low Cost	• Minor-metal free	• Na	• Aqueous electrolyte
High Stability	• Polyanions • Non-oxides	• Non-carbonaceous compound	• Flame-resistance
High Capacity	• Conversion-type • Organic compounds	• Polyvalent cation	• Solid-state electrolyte
High Voltage	• Polyanions • Fluorides	• Alloy-type	• Oxidation resistance
High Output	• Conductive modification • Nanosized materials	• Conductive modification • Nanosized materials	• Low-solvation energy

issues of resource limitations of lithium-ion batteries and high temperature operation of sodium-sulfur battery, is one of the best candidates for post-lithium-ion batteries.

3. Summary

The best solution for post-lithium-ion batteries depends on the environmental, economic, and technological priorities for each applications. Table 3 presents an image of post-lithium-ion batteries based on these trends, as a summary for this paper.

References

- 1) A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada and J. B. Goodenough, *J. Electrochem. Soc.*, **144**, 1609 (1997).
- 2) H. Arai, S. Okada, Y. Sakurai and J. Yamaki, *J. Power Sources*, **68**, 716 (1997).
- 3) F. Badway, N. Pereira, F. Cosandey and G.G. Amatucci, *J. Electrochem. Soc.*, **150**, A1209 (2003).
- 4) M. Nishijima, I. Gocheva, S. Okada, T. Doi, J. Yamaki and T. Nishida, *J. Power Sources*, **190**(2), 558 (2009).
- 5) K. Akuto, H. Ohtsuka, M. Hayashi and Y. Nemoto, *NTT R&D*, **50**, 592 (2001).
- 6) Y. Sakurai and J. Yamaki, *J. Electrochem. Soc.*, **132**, 512 (1985).
- 7) O. Yamamoto, Y. Takeda, R. Kanno and Y. Shinya, *J. Power Sources*, **20**, 151 (1987).
- 8) J. J. Xu, A. J. Kinser, B. B. Owens and W. H. Smyrl, *Electrochem. Solid-State Lett.*, **1**, 1 (1998).
- 9) S. Okada, T. Yamamoto, Y. Okazaki, J. Yamaki, M. Tokunaga and T. Nishida, *J. Power Sources*, **146**, No.1-2, 570 (2005).
- 10) Y. Koyama, I. Tanaka and H. Adachi, *J. Electrochem. Soc.*, **147**, 3633 (2000).
- 11) H. Li, P. Balaya and J. Maier, *J. Electrochem. Soc.*, **151**, A1878 (2004).
- 12) S. Okada, Y. Tanaka, I.D. Gocheva, I. Tanaka, T. Doi, J. Yamaki, M. Takeo and T. Nishida, Extend Abstract of 216th ECS Meeting, #619, Vienna (2009).
- 13) S. Okada, *Visual Guide: All About Advanced Storage Battery Technology*, Kogyo Chosakai Publishing Co., Ltd., Chapter 2, Section 10, p.70-75, (2010).

Research Report

Charge-discharge Reaction Mechanisms of Pyrite-type FeS₂ for Sodium-ion Batteries

Ayuko Kitajou¹, Junpei Yamaguchi²

¹Research and Education Center of Carbon Resources, Kyushu University

²Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

The structural change of FeS₂ during the discharge-charge process was investigated by XRD, Fe and S K-edge EXAFS. The Na/FeS₂ battery had a large first capacity above 450 mAh/g, although the cyclability of the Na/FeS₂ battery was poor. In the Fe K-edge XANES profiles of discharged FeS₂ pellets, there was no apparent trace of iron valence change. On the other hand, the S K-edge energy shifted to a lower energy with increasing sodium content in Na_xFeS₂ on discharge. This suggests that the charge neutrality of the cathode on 2Na discharge is maintained by an S valence change from (S-S)²⁻ to S²⁻ in FeS₂.

Lithium-ion batteries can be used in a wide variety of situations, as small power sources in mobile phones and laptops or as large power sources in hybrid or electric vehicle. Attempts to revolutionize the energy system have focused attention on renewable energy, such as solar and wind power. The creation of an energy storage system for load equalization is also desirable when generating power from natural energy sources. Most large storage batteries in use are based on NaS due to their lower cost and environmental impact than lithium-ion batteries, but the requirement for at least 300 °C operation has researchers looking for practical sodium-ion batteries that can operate at room temperature. However, the standard electrode potential of sodium (-2.71 V vs. SHE) is lower than that of lithium (-3.05 V vs. SHE); furthermore, the sodium metal is air-sensitive and the ionic volume is almost 2 times larger than that of lithium ion. Because of this, reports of cathode materials for insertion reactions with sodium-ion batteries are limited to structures that can support the insertion and extraction of Na with its large ionic radius, such as NaVO₂ and NaFeO₂, with their layered structures, or Na₃V₂(PO₄)₃ and Na₃Fe(PO₄)₃, which have NASICON structures¹⁻⁴). However, the actual energy density of Na₃V₂(PO₄)₃ is 420 Wh/kg (per cathode active material weight), significantly lower than that (600 Wh/kg) of LiCoO₂ used in lithium-ion batteries. One possible method to increase the energy density in sodium-ion batteries is using conversion reaction cathode materials such as FeF₃ and FeS₂, which have a discharge capacity of 400 mAh/g or more^{5, 6}). However, the poor cyclability of these conversion-type cathode materials remains an issue, therefore understand-

ing charge-discharge reaction mechanisms is vital in order to improve poor cyclability for conversion cathode material. We focused on pyrite iron sulfide (FeS₂), which has a lower overpotential compared to other conversion cathode materials, and used *ex situ* XRD and EXFAS to examine changes to crystal structure and local structure in FeS₂ charge-discharge reactions. Based on these results, we then sought to determine discharge products and the cause of cycle degradation.

The cathode pellets were fabricated by mixing the pyrite-type FeS₂ powder (69 wt%), acetylene black (24 wt%) and Polytetrafluoroethylene (7 wt%) in Ar atmosphere and punching in the form of disks (ca. 30 mg in weight and 10 mm in diameter). The electrochemical performances of FeS₂ were evaluated by a 2032 coin-type cell using a non-aqueous electrolyte (1 M NaClO₄ in polypropylene carbonate) against Na metal. The used cathode pellets were carefully taken out from the cells in the Ar-filled glove box, immersed with PC for 12 h to remove the electrolyte, and dried prior to being set in sealed aluminum laminate for XANES and in Ar-filled sample folder for XRD, respectively. XANES measurements of the iron and sulfur K-edge using synchrotron radiation were carried out at room temperature at beam line BL11 of Saga Light Source using a double Si(1 1 1) monochromator.

Figure 1 shows the discharge (Na insertion) and charge (Na extraction) curves for the first and second cycle of Na/FeS₂ battery at 25 °C. In the discharge process, the cell voltage gradually decreased to 0.8 V through an inflection point at around 1.2 V at the current of 0.2 mA/cm², and the first discharge capacity was 465 mAh/g, which cor-

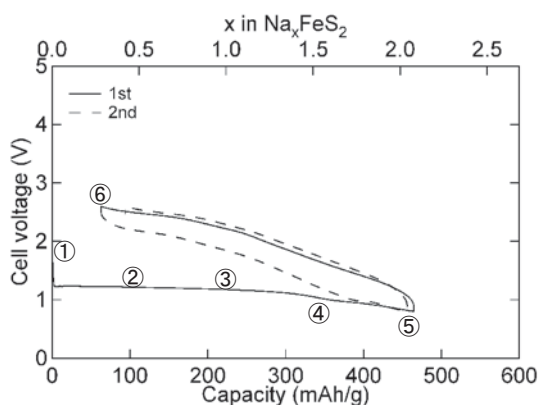


Figure 1 Discharge-charge curves for Na/FeS₂ at 0.2 mA/cm² between 0.8 and 2.6 V.

responds to 104 % of the theoretical capacity based on the 2.0Na reaction per FeS₂ (446 mAh/g). In the charge process, the slope sharp profile was increased up to 2.6 V. However, for the second cycle, the profile changed to a monotonically decreasing reaction. The conversion reaction for this reversible capacity can be hypothesized⁶), but there are no reports of any experimental evidence of this. To examine reaction mechanism between sodium and FeS₂ at discharge process, the XRD measurements for discharged FeS₂ pellets were taken under an Ar atmosphere. In addition, XANES measurements were performed to examine the oxidation states of iron and sulfur after charge or discharge. Figure 2 shows the XRD profiles of electrode pellets at ① the initial state, ② 0.5Na, ③ 1.0Na, ④ 1.5Na, ⑤ 2.0 Na discharge state and ⑥ 2.6 V charge state after 2.0 Na discharge. The results showed that as the amount of sodium inserted increases, the XRD peak strength from the FeS₂ decreases and when 2.0Na discharge was inserted the original peak was completely lost, becoming a halo peak. The FeS₂ peak position did not shift based on the amount of sodium inserted, so discharge products were likely either amorphous or particulates. On the other hand, the XRD peaks for 2.6 V charge after 2.0 Na discharge can be indexed FeS and FeS₂, and high background with a halo peak was observed as well as in the case of 2.0Na discharge. This indicates the possibility that discharge-charge reactions are

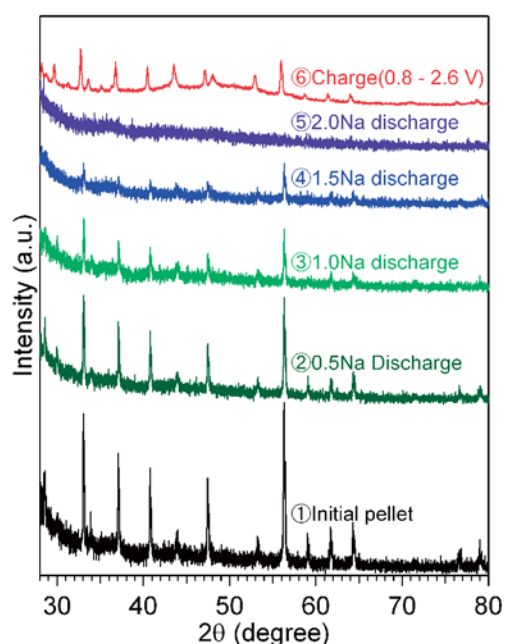


Figure 2 XRD profiles of FeS₂ electrode pellet during discharge-charge process.

in process. Since there is not only a peak from FeS, but also a high overall background, it is clear there is some that the discharge-charge reaction of FeS₂ is not completely reversible. Based on these results, it was not possible to determine whether the discharge results up to the 2.0Na insertion were an insertion reaction or a conversion reaction. Figure 3 shows the near edge X-ray absorption spectra for ① the initial state, and ③ 1.0Na and ⑤ 2.0Na discharge state. Also, in order to find the valence of the iron in the FeS₂ in its initial state, published Mössbauer measurements⁷) and divalent iron low spin were used to determine that its electron state was Fe²⁺(S₂)²⁻. The Fe K-edge position did not shift with increasing sodium content until reaction of 2.0Na discharge. Moreover, the small pre-edge feature near 7112 eV has changed, depending on sodium content per FeS₂. This pre-edge feature corresponds to 1s → 3d transitions which are dipole forbidden in octahedral symmetry and its strength therefore indicates that the symmetry decrease. These results suggested that there is no valence change in the iron for discharge reactions up to 2.0Na insertion, while the local structure around the iron is changing. In order to investigate local structural changes around the iron, Fourier transforms were calculated from the EXAFS spectra, and radial distribution functions calculated. Figure 4 shows the radial distribution functions for FeS₂ electrode pellets at ① the initial state, after ③

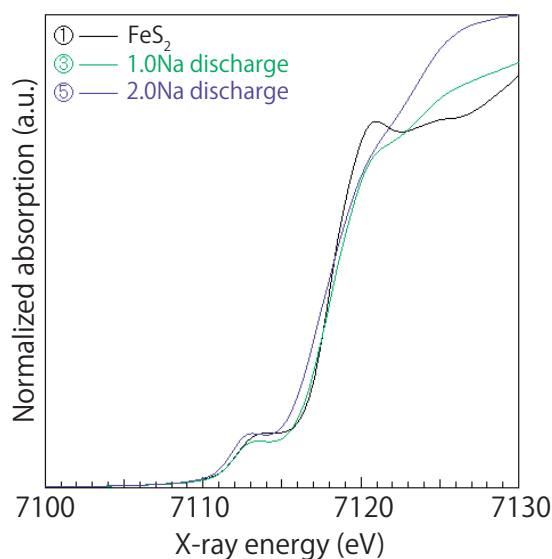


Figure 3 Fe K-edge XANES spectra of FeS_2 electrode pellet during discharge-charge process.

1.0Na and ⑤ 2.0Na discharge state. The position of Fe-S distance peak was extended as the amount of sodium inserted increased, while the intensity of Fe-Fe distance peak was decreased. From these results, sodium with a low atomic scattering factor is inserted between Fe-Fe as discharge reaction advances, and the Fe-S distance was also extended due to the insertion of sodium. These shows that discharge reactions up to 2.0Na are insertion reaction which sodium inserts into the FeS_2 structure. However, although the results of Fe XANES and EXAFS measurements show that insertion reactions with no iron valence change proceed up to 2.0Na insertion, it is not clear what redox reactions are contributing to these discharge reactions. Therefore, S K-edge XANES spectra measurements were performed. Figure 5 shows S K-edge XANES spectra of FeS_2 electrode pellets at the initial state, and after 1.0Na and 2.0Na discharge state. The edge position was shifted to lower energy with increasing sodium content until 2.0Na discharge reaction. It suggests that the charge neutrality of the cathode on 2.0Na discharge is kept by S valence change from $(\text{S-S})^{2-}$ to S^{2-} in FeS_2 . This result suggested that the average oxidation is lowered due to the decrease in binding energy of S 1s electrons, and the reaction until 2.0Na discharge has advanced by redox reaction of sulfur. The discharge reaction for FeS_2 with sodium proposed by Kim *et al.* was $2\text{Na} + \text{FeS}_2 \leftrightarrow \text{Na}_2\text{S}_2 + \text{Fe}^{2+}$, but

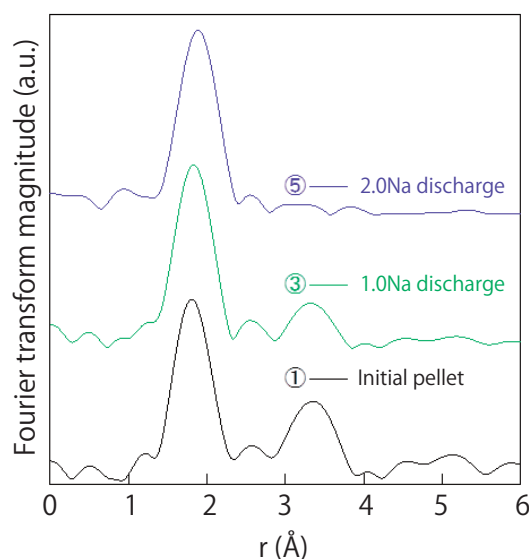
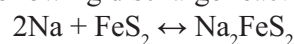
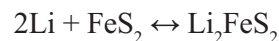


Figure 4 Fourier transform amplitudes of FeS_2 electrode pellet during discharge-charge process.

based on the results of this study, we have found it to be the following discharge reaction formula.



This result is the same as the discharge reaction for Li/FeS_2 ⁸⁾, as indicated below.



Additionally, it has been shown for Li/FeS_2 that the following discharge reaction using an iron conversion reaction also occurs, with the energy density by cathode active material weight increasing to 1270 Wh/kg.



Based on this, we plan to continue investigating Na/FeS_2 discharge reactions that use a similar iron conversion reaction. There is also a need to investigate what effect the discharge reaction products found in this study have on cycle life; nonetheless, this study demonstrated the possibility of increased discharge capacity, and FeS_2 was shown to be a new candidate for cathodes in sodium-ion batteries.

Acknowledgements

This work was financially supported by the Elements Science & Technology Projects of MEXT. Eiji Kobayashi (Research Associate) and Kuniko Chihara (NEDO Technical Support Staff) assisted with observations of electrochemical properties. EXAFS measurements were conducted with help from Dr. Toshihiro Okajima (Group Leader) and

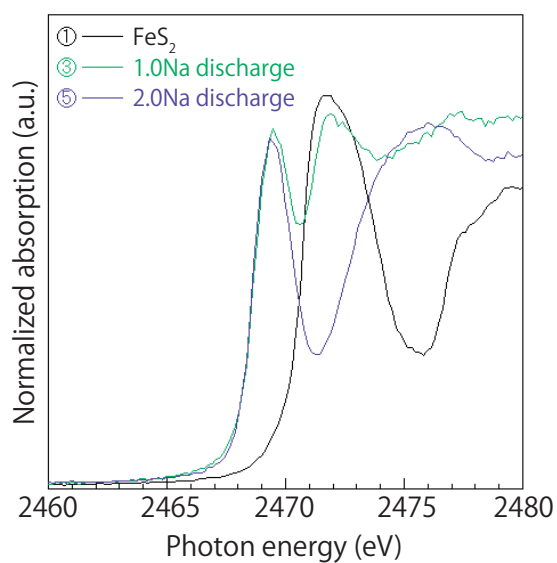


Figure 5 S K-edge XANES spectra of FeS_2 electrode pellet during discharge-charge process.

Dr. Ryota Otani at the Kyushu Synchrotron Light Research Center.

Works Cited

- 1) D. Hamani, M. Ati, J. M. Tarascon, P. Rozier, *Electrochem. Commun.*, **13** (2011) 938.
- 2) T. B. Kim, J. W. Choi, H. S. Ryu, G. B. Cho, K. W. Kim, J. H. Ahn, K. K. Cho, H. J. Ahn, *J. Power Sources*, **174** (2007) 1275.
- 3) L. S. Plashnitsa, E. Kobayashi, Y. Noguchi, S. Okada, J. Yamaki, *J. Electrochem. Soc.*, **157** (2010) A536.
- 4) C. Delmas, F. Cherkaoui, A. Nadiri, P. Hagemmuller, *Mat-er. Res. Bull.*, **22** (1987) 631.
- 5) I. Tanaka, Y. Tanaka, I. D. Gocheva, S. Okada, J. Yamaki, *The 50th Battery Symposium in Japan* (2009).
- 6) T. B. Kim, W. H. Jung, H. S. Ryu, K. W. Kim, J. H. Ahn, K. K. Cho, G. B. Cho, T. H. Nam, I. S. Ahn, H. J. Ahn, *J. Alloys Compd.*, **499** (2008) 304.
- 7) S. Miyahara, T. Teranishi, *J. Appl. Phys.*, **39** (1968) 896.
- 8) J. W. Choi, G. Cheruvally, H. J. Ahn, K. W. Kim, J. H. Ahn, *J. Power Sources*, **163** (2006) 158.

Micro Review

Tailored design and synthesis of catalysts for environmental processes

Yasutake Teraoka and Hisahiro Einaga

Department of Molecular and Material Sciences, Kyushu University

This paper reports recent achievements in our group focusing on the inorganic functional materials based on perovskite-type mixed metal oxides and metal nano-particles for environmental catalytic processes. Catalytic properties of these materials can be controlled by changing the crystal structure, constituent atoms and their nano/meso-order structures. Perovskite oxides have the oxidation ability for various types of hazardous materials and they are also useful as supporting materials for metal nano-particle catalysts by utilizing the interaction between perovskite oxides and metal nano-particles.

1. Introduction

Catalytic engineering is one of important key technologies and play important roles in carbon resource utilization and environmental protection. Generally, platinum-group metals (PGMs) such as Pt, Pd, and Pd are used as the active species in catalytic materials. PGMs are generally supported on high surface-area materials with and without the addition of co-catalyst to improve their catalytic properties, namely activity, selectivity and durability. PGMs are expensive and their commercial prices are greatly influenced by socio-economical situation. One of the important topics of catalytic science and technology is how to reduce the amount of PGMs used for catalytic materials.

One should pay attention to the diversity of air pollutants and their emission sources when catalytic technology is applied to air quality control. For instance, air pollutants are emitted from various kinds of mobile sources (*e.g.* automobiles) and stationary sources (*e.g.* factories). The kinds and concentrations of the pollutants in the flue gases and their temperatures are different depending on the sources.

A wide variety of air pollutants including NO_x, diesel particulate matter (DPM), volatile organic compounds (VOCs), and bio-aerosols are target materials to be treated. They are inorganic gases, organic compounds, and polymers, and the state of these materials are gases, liquids, and solids. These hazardous materials cannot be treated by a single technique, and the catalyst

composition and structures should be optimized for the control of the target pollutants. Moreover, the pollution control techniques should cope with the recent tightening of regulations of air pollution. One of main objectives of our research group is the catalyst design of metal oxides, metal nano-particles to maximize their catalytic properties and their application to environmental catalytic processes. Our recent achievements in environmental catalytic processes are reported herein.

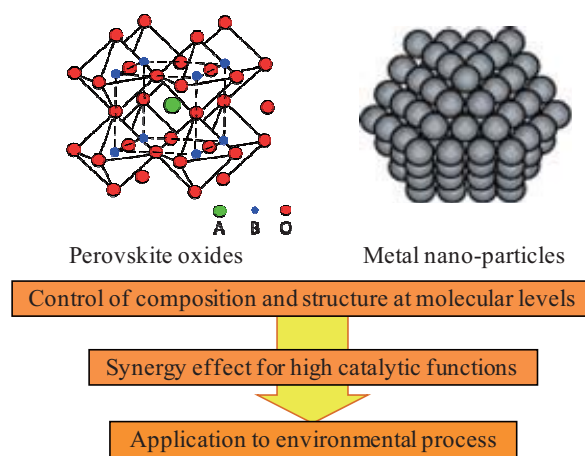


Figure 1 Strategy for catalyst design

2. Interaction between perovskite oxides and metal nano-particles in environmental catalysts

Perovskite-type mixed metal oxides (Figure 1) are represented by general formula ABO_3 , which have B metal ions coordinated with six oxide ions. The BO_6 units are connected by corner(vertex)-sharing manner, making

networks in which A-site metal ions are located in the dodecahedral site of framework. Perovskite oxides with transition metals at B sites have high oxidation ability and their catalytic properties can be controlled by changing the A and B ions. Therefore, perovskite oxides have been so far used for various types of catalytic reactions, such as catalytic combustion, NO_x reduction. We have been investigating the catalytic properties of perovskite oxides and have revealed that they are also effective for supporting materials enhancing the catalytic properties of metal nano-particles.

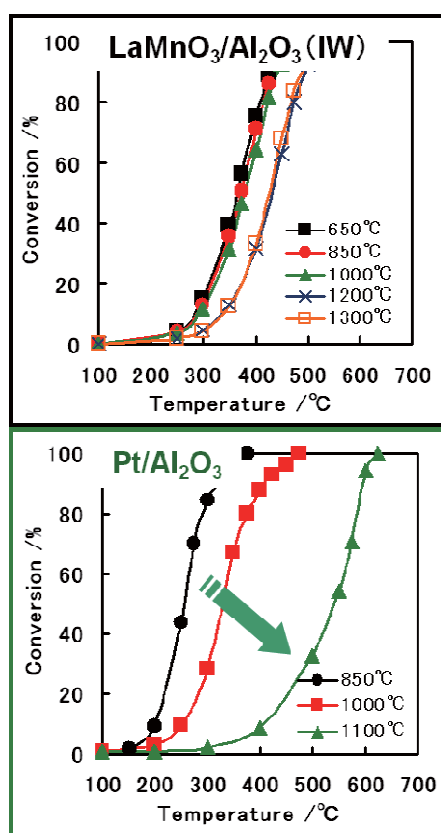


Figure 2 Catalytic activities of LaMnO₃ supported in inside pore of alumina for propane oxidation compared with Pt/Al₂O₃. (Catalyst treatment temperatures are indicated.)

The activity of LaMnO₃/Al₂O₃ retained after high-temperature pretreatment, in marked contrast with Pt/Al₂O₃.

2.1. Automobile emission catalysts

LaMnO₃ and LaFeO₃ perovskite oxides are prepared from metal nitrates and acetates *via* hydrolysis reaction or evaporation-to-dryness processes, followed by calcination at high temperatures¹. We modified these preparation procedures to obtain alumina-supported perovskite oxides

(LaMnO₃/Al₂O₃), in which perovskite oxides were selectively deposited inside or outside pore of alumina.

LaMnO₃ perovskite oxides deposited in alumina pores showed higher activities and higher thermal stability for propane oxidation than Pt/Al₂O₃ catalysts² (Figure 2). Our studies have also revealed that Pd and LaMnO₃ can be also selectively deposited in the pore of alumina and the Pd/LaMnO₃/Al₂O₃ catalysts thus prepared showed high activity for NO-CO reaction compared with Pd/Al₂O₃ catalysts. The detail of this work is reported in Research Report of this issue.

Pt, Rh and Pd metals can be dissolved into perovskite oxides phases when the metals and perovskite oxides are appropriately selected. Our target is to dissolve these metals in an ionic form on the surface shell of perovskite particles to create highly dispersed catalytic active sites by the following two methods. One method is ion-exchange process for K₂NiF₄-type perovskite oxides to substitute Pd ions for A site metal ions^{3,4}. Another method uses mechano-chemical reaction with planetary ball milling to form noble metal-containing thin layers on the perovskite surfaces.

2.2 PM combustion catalysts and PM sensors for diesel exhaust emissions.

One of the emergent technologies for diesel engine emissions is the removal of DPM (Diesel Particulate Matter) from diesel exhausts. In the commercially available system, DPM is removed by diesel particulate filter (DPF), which needs the regeneration process to remove trapped DPM. We have carried out basic research on the development of catalyst-coated diesel particulate filter (Cat.-DPF) for DPM removal. It has been shown that perovskite oxides which contained K ions in their A site (La_{1-x}K_xMnO₃) prepared by evaporation-to-dryness technique with malic acid showed high performance for DPM combustion (Figure 3)⁵.

Catalytic PM combustion proceeds by (1) “ignition of solid-state soot contacted with the catalyst” and (2) “Soot combustion”. The former is catalytic process and the latter includes catalytic and non-catalytic processes. These processes are much different from general catalytic processes of adsorption of gases substrates on the catalyst

surface, surface reaction, and desorption of products from the surface. We investigated the reaction mechanism for soot combustion reaction with $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ catalysts based on activation energy analysis and revealed that K ions improved the catalytic performance for soot combustion⁶.

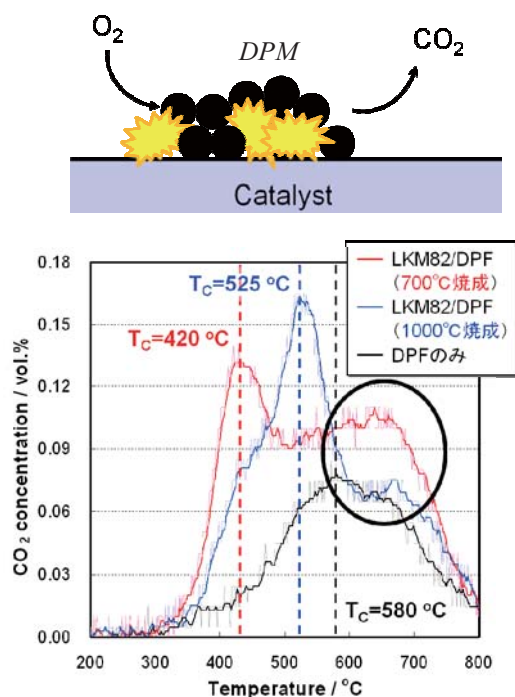


Figure 3 Temperature programmed oxidation of PM trapped on ceramic foam filters with and without coating of catalyst ($\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$: LKM82). ※Catalyst coating on DPF promoted soot combustion.

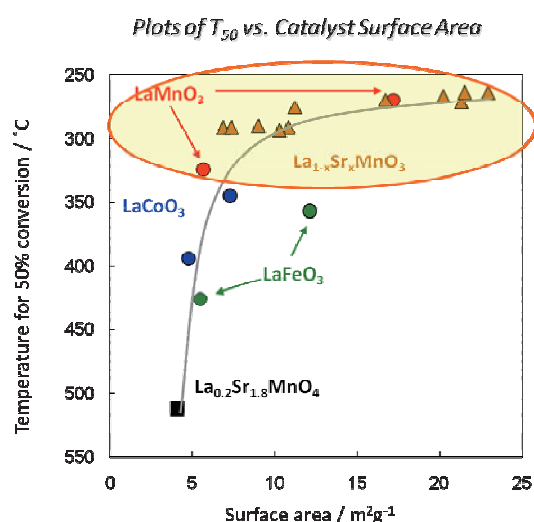


Figure 4 Catalytic oxidation of benzene over perovskite oxides. ※The reaction temperature needed for 50% conversion (T_{50}) decreased with the increase in catalyst surface area.

Ag nano-particles are effective in promoting the ignition of soot contacted with the catalysts. The soot ignition activity and soot combustion performance are controlled by changing the catalyst active species, catalyst supports and their structures. For instance, Ag catalysts supported on perovskite oxides show high performance for DPM combustion under quasi-real conditions. Soot combustion behavior especially depends on the contact condition between the catalyst and DPM. Thus catalyst surface area, the concentration of active species on the catalyst surface, and the morphology of the catalyst materials are the important factors controlling the DPM combustion performance.

Real DPM consists of soot and soluble organic fraction (SOF). Our studies revealed that the combustion behaviors of these two components are very much dependent on the active species. This finding indicates that soot and SOF can be selectively combusted by optimizing the active species (Ag, Pt, and Pd) and supporting materials (CeO_2 , TiO_2). We are now developing novel combustion-type PM sensor for the selective quantification of soot and SOF⁷⁻⁹.

2.3. Oxidation catalysts for CO and VOC abatement

1) Perovskite oxide catalysts

Catalytic oxidation of VOCs is still one of the important technologies in the research area of catalytic science and Technology. Catalytic oxidation properties of ABO_3 perovskite oxides can be controlled by optimizing the A and B elements, preparation techniques, and their deposition on high-surface area supports. VOC oxidation properties strongly depend on the B site metals: Mn-containing perovskites show high catalytic activities for VOC oxidation. Catalytic properties of Mn-containing perovskites can also be improved by the A site substitution and by the increase of the surface area of catalysts (Figure 4)¹⁰. Although our catalysts showed lower activity for benzene oxidation than supported Pt catalysts, the activity of perovskite oxides can be further improved by their deposition on metal oxide supports with high surface area and oxidation ability.

Perovskite oxide catalysts are also effective for the oxidation reaction under microwave (MW) irradiation.

These materials have advantages over other kinds of metal oxides in the following points: (1) steady-state reaction temperatures are attained, and (2) the behavior of catalyst temperature and catalytic properties are controlled by changing the constituent metals. Our research has revealed that the oxidation reaction proceeds at lower temperature under MW heating than conventional outer heating. We are now developing high-performance catalysts comparable to noble metals under MW heating.

2) Supported noble metal catalysts

CO oxidation catalysts generally consists of noble metals (Pt and Pd) supported on high-surface area oxide supports (Al_2O_3 and CeO_2). Supported noble metal catalysts are generally prepared by impregnation techniques, which involve deposition of metal precursors on the supports, followed by drying, oxidation and reduction. Our preparation techniques, on the other hand, involve the preparation of metal nano-particles and their deposition on the supports in liquid phase. Pt/ TiO_2 catalysts thus prepared showed higher activity for CO oxidation than the catalyst prepared by the conventional impregnation technique¹¹⁻¹² (the details of this work is described in Research Report of this issue). This preparation method is promising for minimizing the amount of noble metals in supported metal catalysts.

3. Control of catalytic properties at molecular levels

3.1 Control of cation arrangement in double perovskite and their catalytic properties

Perovskite oxides with equal molar of two kinds of metals (M and M') at B sites have a tendency to take ordered structures when the difference in oxidation states of two metal ions is large. Such kinds of perovskites are called double perovskites, and they have the M-O-M' linkages in their bulk and surface sites. Therefore, unique catalytic properties are expected with them, which cannot be observed for perovskite oxides consisting of single B-metal ions.

Our research revealed that the arrangement of metal cations in the double perovskite, $\text{Sr}_2\text{AlNbO}_6$, can be controlled by changing the preparation conditions (Figure

5) and that the cation ordering is one of the important factors controlling their photocatalytic properties^{13,14}. This is practically the first report to reveal the photocatalytic activity of $\text{Sr}_2\text{AlNbO}_6$ as well as the effect of cation ordering in oxides on the photocatalytic activity. These results reflect the intrinsic properties of perovskite oxides that the catalytic properties can be controlled by changing the constituent atoms.

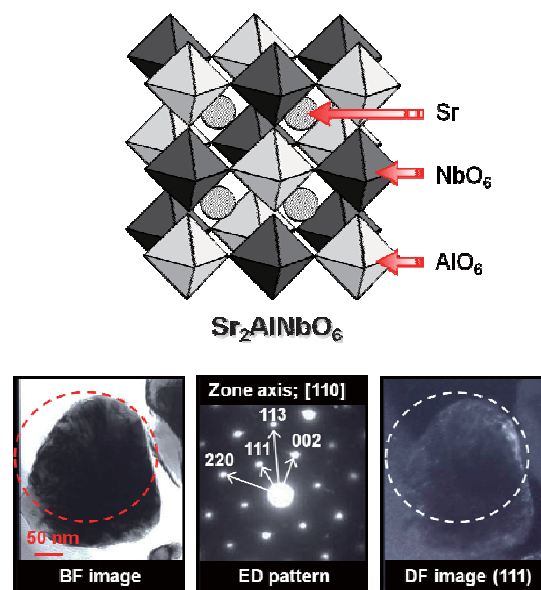


Figure 5 Structure of $\text{Sr}_2\text{AlNbO}_6$.

3.2 Preparation of bimetallic nano-particles with controlled metal distribution

Our attention has been also paid to the bimetallic nano-particles with “random” structure, in which two kinds of metals are randomly coordinated (the left in Figure 6) and “core-shell” structure, in which one kind of metals are surrounded by other kind of metal (the right in Figure 6). One can expect that the control of these two structures can control the structure of catalytic active sites, leading to the improvement in catalytic functions. The formation of these bimetallic nano-particles strongly depends on the dispersion of metal precursors in the mother solution and the rate of metal reduction during the preparation processes. We therefore consider that bimetallic structures with controlled metal distribution can be fabricated by optimizing the reaction conditions and metal reduction methods.

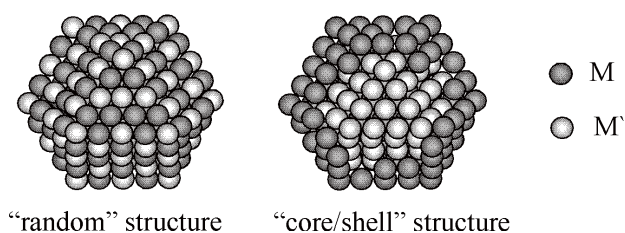


Figure 6 Structure of bimetallic nano-particles

References

- 1) T. Asada, T. Kayama, H. Kusaba, H. Einaga, Y. Teraoka, “Preparation of Alumina-supported LaFeO₃ Catalysts and their Catalytic Activity for Propane Combustion”, *Catal. Today*, **139**, 37-42 (2008).
- 2) T. Asada, H. Kusaba, H. Einaga, and Y. Teraoka, “Preparation of supported LaMnO₃ catalysts by selective deposition in intra-pore and/or on extra-pore of alumina and their catalytic properties”, *Catalysts and Catalysis*, **50**, 487-489 (2008). (in Japanese)
- 3) R. Karita, H. Kusaba, K. Sasaki, and Y. Teraoka, “Superiority of nitrate decomposition method for synthesis of K₂NiF₄-type La_xSr_{2-x}MnO₄ catalysts”, *Catal. Today*, **126**, 471-75 (2007).
- 4) R. Karita, H. Kusaba, K. Sasaki, and Y. Teraoka, “Synthesis, characterization and catalytic activity for NO-CO reaction of Pd-(La, Sr)₂MnO₄ system”, *Catal. Today*, **119**, 83-87 (2007).
- 5) H. Shimokawa, H. Kusaba, H. Einaga, Y. Teraoka, “Effect of Surface Area of La-K-Mn-O Perovskites Catalysts on Diesel Particulate Oxidation”, *Catal. Today*, **139**, 8-14 (2008).
- 6) H. Shimokawa, Y. Kurihara, H. Kusaba, H. Einaga, Y. Teraoka, “Comparison of catalytic performance of Ag- and K-based catalysts for diesel soot combustion”, *Catal. Today*, doi: 10.1016/j.cattod.2011.10.030.
- 7) C.-B. Lim; H. Kusaba; H. Einaga; and Y. Teraoka, “Catalytic performance of supported precious metal catalysts for the combustion of diesel particulate matter”, *Catal.Today*, **175**, 106-111 (2011).
- 8) C.-B. Lim, H. Einaga, Y. Sadaoka, and Y. Teraoka, “Preliminary study on catalytic combustion-type sensor for the detection of diesel particulate matter”, *Sens. Act. B: Chem.* **160**, 463-470 (2011).
- 9) C.-B. Lim; H. Kusaba; H. Einaga; and Y. Teraoka, “Response of Catalytic Combustion-type Sensor to Different Amounts of Diesel Particulate Matter”, *J.Nov. Carbon Res.Sci.*, **4**, 1-7 (2011).
- 10) H. Einaga, S. Hyodo, and Y. Teraoka, “Complete Oxidation of Benzene over Perovskite-type Oxide Catalysts”, *Topics in Catal.*, **53**, 629-634, (2010).
- 11) K. Kimura, H. Einaga, Y. Teraoka, “Catalytic Properties of Platinum Supported on Titanium Dioxide by Liquid-phase Adsorption of Colloidal Nanoparticles”, *Catal. Lett.*, **139**, 72-76 (2010).
- 12) K. Kimura, H. Einaga, Y. Teraoka, “Preparation of highly dispersed platinum catalysts on various oxides by using polymer-protected nanoparticles”, *Catal.Today*, **164**, 88-91 (2011).
- 13) H. Iwakura, H. Einaga, and Y. Teraoka, “Photocatalytic Properties of Ordered Double Perovskite Oxides”, *J.Nov. Carbon Res.Sci.*, **3**, 1-5 (2011).
- 14) H. Iwakura, H. Einaga, and Y. Teraoka, “Relationship between Cation Arrangement and Photocatalytic Activity for Sr-Al-Nb-O Double Perovskite”, *Inorg. Chem.*, **49**, 11362-11369 (2010).

Preparation of Highly Dispersed Noble Metal Catalysts Using Liquid-Phase Adsorption of Colloidal Nanoparticles

Kyushu University Kana Kimura, Hisahiro Einaga, Yasutake Teraoka

We have investigated a colloidal deposition method which consists of the synthesis of colloidal Pt particles by photoreduction in the presence of poly (N-vinyl-2-pyrrolidone) (PVP) and their deposition on various oxide supports in liquid phase. The Pt/TiO₂ catalyst prepared by the colloidal deposition method showed higher platinum dispersion and CO oxidation activity than that prepared by a conventional impregnation technique. This method could be also applicable to the preparation of supported bimetallic catalysts from colloidal bimetallic nanoparticles. We succeeded in the synthesis of Pt-Rh bimetallic nanoparticles with random and core-shell structures by controlling the reduction process of two kinds of metal ions as well as the deposition of the bimetallic nanoparticles on TiO₂ supports.

Supported noble metal catalysts are widely used in industrial catalytic processes. They are generally prepared by a conventional impregnation technique in which precursor metal salts are adsorbed onto supporting materials and then they are oxidized and reduced to form metal particles. Although the inexpensive and simple conventional technique has been mostly applied, there are drawbacks in difficulties to control the size and shape of metal particles on supporting materials.

We have been studying alternative techniques for the preparation of supported metal catalysts. One method is the colloidal deposition method consisting of the synthesis of colloidal metal particles by chemical reduction in the presence of protective agent and following their deposition on supporting materials¹⁾. Colloidal metal particles are synthesized by the photochemical or chemical reduction by alcohol, NaBH₄ and H₂ in the presence of protecting polymers and organic ligands. The advantage of this method as compared with the conventional impregnation technique is the easy control of size, shape and dispersion of the metal particles.

We have applied the colloidal deposition method for the preparation of

highly dispersed Pt particles on oxide supports: colloidal Pt particles protected by poly (N-vinyl-2-pyrrolidone) (PVP) were synthesized by photoreduction, they were deposited on various supports in liquid phase^{2,3)}. The amount of Pt adsorbed on supports depended on the kinds of supporting materials during liquid phase adsorption process. Pt particles were completely deposited on TiO₂, Al₂O₃ and MgO, whereas they were partially deposited on CeO₂ and SiO₂. In particular, Pt particles were mostly deposited even when TiO₂ with lower surface area (7~9 m²/g) was used as the supports. Pt particles were completely adsorbed on to TiO₂ (P25) up to the higher Pt loading level (10 wt% of Pt). These findings indicated that adsorption capacity for Pt deposition, defined as the amount of Pt adsorbed per the surface area of supporting

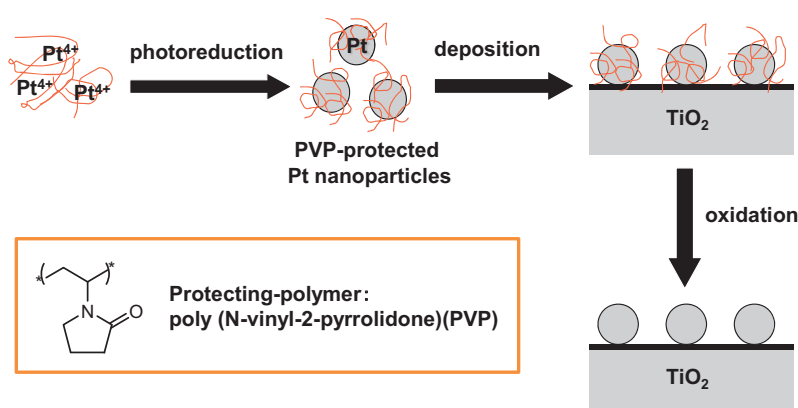


Figure 1 Preparation of supported Pt catalyst by colloidal deposition method

materials, depended on the kinds of supporting materials. Pt dispersion also depended on the kinds of supporting materials. The Pt/TiO₂ (P25) catalyst showed the highest dispersion among the supported Pt catalysts. On the other hand, Pt dispersion on TiO₂ decreased with the decrease in the surface area of TiO₂, indicating that the surface area of supporting materials was also one of important factors for obtaining the supported Pt catalyst with high dispersion.

Figure 2 shows the results for CO oxidation activities of Pt/TiO₂ catalysts. Pt/TiO₂ prepared by the colloid deposition method showed higher activities than Pt/TiO₂ prepared by impregnation (IMP) and photodeposition (PD) methods. This finding indicates that the catalytic properties of supported Pt catalysts depended on preparation method. The order of the CO oxidation activity corresponded to that of Pt dispersion. Pt/TiO₂ (O₂-H₂) prepared by the colloid deposition showed the higher dispersion than Pt/TiO₂ prepared by the impregnation method, although turn over frequency (TOF) for CO oxidation at 343 K was almost the same for the Pt/TiO₂ (O₂-H₂) ($2.1 \times 10^{-3} \text{ s}^{-1}$) and Pt/TiO₂ (IMP) ($2.3 \times 10^{-3} \text{ s}^{-1}$). The CO oxidation activity also depends on pretreatment condition. Pt/TiO₂ with the treatment of H₂ reduction showed higher activity than that without H₂ reduction, as shown in Figure 2.

We have also focused on the applicability of the colloidal deposition method to prepare supported

bimetallic nanoparticles. Pt-Rh bimetallic nanoparticles were prepared by co-reduction or successive reduction of two kinds of metal ions to control the structure of bimetallic nanoparticles. Pt-Rh bimetallic nanoparticles with a “random” structure (Figure 3) could be synthesized by rapid chemical co-reduction of Pt and Rh ions using sodium borohydride as strong reducing agent in the presence of PVP. The structure of the bimetallic nanoparticles was determined by extended X-ray absorption fine structure (EXAFS) and transmission electron micrograph (TEM)^{4,5}. PVP-protected Pt-Rh bimetallic particles with a “core-shell” structure were prepared by the successive reduction in which Pt particles (core of bimetallic particles) was photochemically synthesized in the presence of PVP and the reduction of Rh³⁺ by refluxing in alcohol-water solution was performed in the presence of PVP-protected Pt nanoparticles. STEM observation and EDX analysis showed that the particle size of Pt-Rh particles increased with increase the molar ratio of Rh to Pt (1/4–4/1). EXAFS studies also confirmed that Pt particles were covered with Rh atoms.

The Pt-Rh bimetallic nanoparticles with random and core-shell structures were adsorbed on TiO₂ surface by mixing the colloidal solution with TiO₂ powder. Therefore, TiO₂-supported Pt-core/Rh-shell bimetallic nanoparticles can be prepared by the colloidal deposition method.

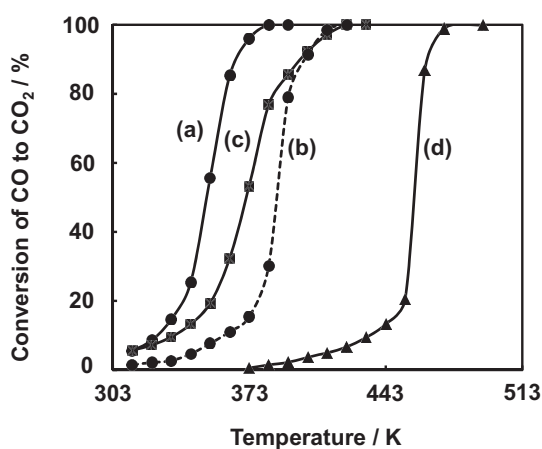


Figure 2 Oxidation of CO over 1 wt% -Pt/TiO₂ prepared by (a) colloidal deposition (O₂-H₂), (b) colloidal deposition (O₂), (c) impregnation, and (d) photodeposition methods.



Figure 3 Cross sections of Pt-Rh bimetallic nanoparticle

Reference

- 1) H. Einaga, M. Harada, *Langmuir*, **21**, 2578 (2005).
- 2) K. Kimura, H. Einaga, Y. Teraoka, *Catal. Lett.*, **139**, 72 (2010).
- 3) K. Kimura, H. Einaga, Y. Teraoka, *Catal. Today*, **164**, 88 (2011)
- 4) N. Toshima, T. Yonezawa, *New J. Chem*, **22**, 1179 (1998)
- 5) H. Einaga, M. Harada, *J. Colloid. Inter. Sci.*, **308**, 568 (2007)

Research Report

Development of active catalysts for automobile exhaust treatment based on the interaction between Pd and LaMnO₃

Kyushu University Akihiro Tou, Hisahiro Einaga, Yasutake Teraoka

The catalytic activity of Pd on Al₂O₃ for NO-CO reaction was improved by the co-deposition of Pd and LaMnO₃ (LM) inside of alumina pores (Pd/LM/Al₂O₃, LM/Pd/Al₂O₃). The role of LM on the improved catalytic activity of Pd for NO-CO reaction was investigated. Temperature programmed reduction results indicated that Pd was in close proximity to LM in the Pd/LM/Al₂O₃ and LM/Pd/Al₂O₃ catalysts. FTIR spectra showed that isocyanate and NO-related species were formed on the catalysts under the NO-CO flow. Comparative studies between Pd/Al₂O₃ and Pd/LM/Al₂O₃ showed that isocyanate formation was inhibited and its consumption was promoted by coexistence of Pd and LM in the pore of alumina.

1. Introduction

Automotive three-way catalysts contain platinum group metals (PGMs) as active species. However, the amount of PGMs should be reduced because of limited supply and high cost of PGMs. Perovskite-type oxides have been studied as alternative materials for PGMs because the catalytic activity per surface area of perovskites are comparable to that of PGMs. Recently, PGM-containing perovskite oxides have been used for commercial automotive catalysts [1]. Since the specific surface areas of perovskites are usually small, development of preparation methods which give nano-sized particles in either supported or unsupported form is of primary importance for the practical application of perovskites. Our previous studies have revealed that LaFeO₃ is selectively deposited inside and outside of the pore of an alumina support by different sophisticated preparation methods and that the intra-pore deposited catalyst shows higher activity for complete oxidation of propane than the extra-pore deposited one [2]. We have also reported that, when LaMnO₃ and Pd are co-deposited inside of alumina pores, the catalytic activity of Pd for NO-CO reaction is improved. The aim of this study is to investigate the role of LaMnO₃ on the improved catalytic activity of Pd for NO-CO reaction.

2. Preparation of catalysts

Fig.1 shows preparation methods of supported catalysts. γ -Al₂O₃ (JRC-ALO-8, supplied by Catalysis Society of Japan) was used as a support and pretreated at

850 °C for 5h in air. Alumina-supported Pd with intra-pore deposition (Pd/AL) was prepared by incipient wetness (IW) method using *aq.* Pd(NH₃)₄(NO₃)₂. LaMnO₃ (LM) was deposited inside pore of the Pd/AL catalyst by the IW method with *aq.* metal nitrates to obtain the serial intra-pore deposited catalyst (LM/Pd/AL). By changing the deposition order of Pd and LM, another serial intra-pore deposited catalyst (Pd/LM/AL) was prepared. To deposit LM on the outside of pores (LMout/Pd/AL), Pd/AL and hydroxide precursor of LM were dispersed into water, followed by ultrasonication and evaporating-to-dryness under vigorous stirring. The nominal contents of LM and Pd were 10 wt% and 1 wt%, respectively. These catalysts were finally calcined at 650 °C for 5h in air.

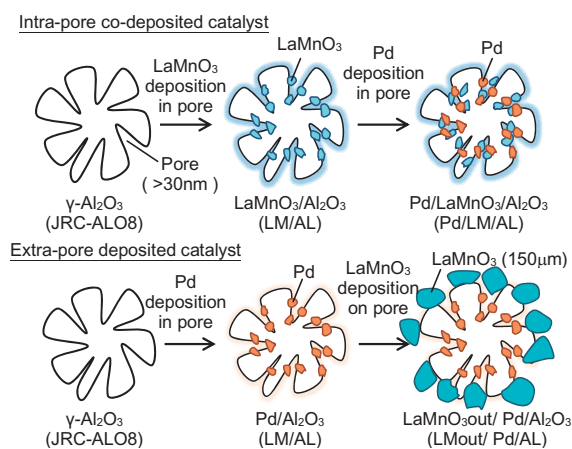


Fig.1 Preparation methods of Al₂O₃ supported Pd and LaMnO₃ catalysts.

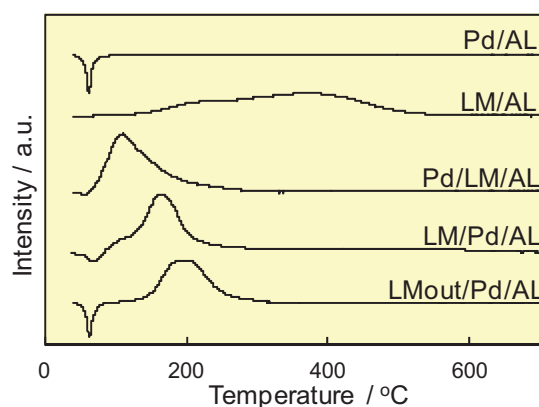


Fig. 2 Temperature programmed reduction of Al_2O_3 supported Pd and LaMnO_3 catalysts by hydrogen.

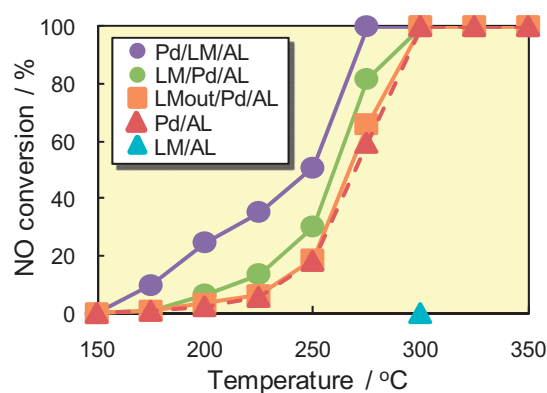


Fig. 3 NO-CO reaction over Al_2O_3 supported Pd and LaMnO_3 catalysts.

3. Reduction behavior of the catalysts

The deposition sites of Pd and LM are clarified by the reduction behaviors of the catalysts (Fig. 2) measured by H_2 -TPR (temperature programmed reduction). Negative peak due to H_2 -desorption from Pd below 60°C was observed for Pd/AL, while broad positive peaks ranging from 150°C to 550°C due to the consumption of H_2 by the reduction of LM were observed for LM/AL. In Pd and LM co-deposited catalysts, the deposition of Pd led to the decrease in reduction temperature of LM, because activated H_2 on Pd promoted the reduction of LM. The reduction temperature of the intra-pore co-deposited catalysts (Pd/LM/AL, LM/Pd/AL) was lower than that of LMout/Pd/AL. Therefore, the amounts of H_2 -desorption from the intra-pore co-deposited catalysts were smaller than that of the extra-pore deposited catalyst. These results indicated that the proximity of Pd to LM depended on the deposition methods.

Table 1 Pd dispersion and $\text{TOF}^{\text{a)}}$

Sample name	Pd dispersion (%)	$\text{TOF}_{\text{NO}} \times 10^4 (\text{s}^{-1})$
Pd/AL	33.3	0.2
LM/Pd/AL	3.6	2.4
Pd/LM/AL	32.8	1.9
LMout/Pd/AL	23.6	0.3

a) Turnover frequency of NO conversion at 200°C

3. Catalytic activity for NO-CO reaction

Fig. 3 shows the activities of the supported catalysts for NO-CO reaction. LM/AL was inactive to this reaction below 300°C . Pd was the active site for NO-CO reaction. The conversions of NO and CO with Pd/AL at 250°C was close to those of LMout/Pd/AL, indicating that LM on the outside of alumina pores had no effect on catalytic activity of Pd for NO-CO reaction. The intra-pore co-deposited catalysts showed higher activity than the others, revealing that intra-pore deposition of Pd and LM catalysts improve Pd-catalyzed NO-CO reaction.

Table 1 lists Pd dispersions and turnover frequency of NO conversion per a surface Pd site (TOF_{SNO}) at 200°C . The Pd dispersion, which was evaluated from the amount of CO adsorbed on the catalysts, was almost the same among Pd/AL, Pd/LM/AL and LMout/Pd/AL, indicating that pre-deposited LM in pores (Pd/LM/AL) and post-deposited LM out of pores (LMout/Pd/AL) have little influence on the dispersion of Pd post- and pre-deposited in pores, respectively. The amount of adsorbed CO and the calculated Pd dispersion of LM/Pd/AL were much lower than the other three catalysts because pre-deposited Pd was mostly covered with post-deposited LM. The catalytic activity for NO-CO reaction (Fig. 3) and thus TOF_{NO} were almost the same between Pd/AL and LMout/Pd/AL, indicating that there is no physical and chemical interaction between intra-pore deposited Pd and extra-pore deposited LM. For the catalysts in which Pd and LM coexist in pores of alumina (Pd/LM/AL, LM/Pd/AL), on the other hand, TOF_{SNO} were comparable each other and much higher than the other two catalysts. Because of high TOF_{NO} and Pd dispersion, Pd/LM/AL showed the highest weight-normalized activity for NO-CO reaction (Fig. 3).

These results indicated that the simultaneous deposition of Pd and LM inside the pore of alumina was effective in improving the activity per a Pd site. Moreover the intra-pore co-deposited catalysts (Pd/LM/AL, LM/Pd/AL) sustained the higher catalytic activity up to 800 °C.

4. Preliminary study on the origin of synergic effect of co-deposited Pd and LM

FTIR spectra showed that isocyanate and NO-related species were formed on the catalysts in the flow of NO-CO under the reaction conditions. Comparative studies between Pd/AL and Pd/LM/AL showed that isocyanate formation was inhibited and its decomposition was promoted by the coexistence of Pd and LM.

Fig. 4 shows the mechanism for catalytic NO-CO reaction under the present condition. NO-CO reaction proceeds via (1) adsorption of NO(g) and CO(g) on the active sites of the catalysts, (2) dissociation of adsorbed NO, NO(a), to form atomic radicals N(a) and O(a), (3) reaction of NO(a) with N(a) for N₂O formation, (4) combination of two N(a) radicals for N₂ formation, (5) reaction of CO(a) with O(a) to form CO₂. The reaction rate of NO dissociation (Step 2) was compared with that of the surface CO oxidation reaction (Step 5) by comparing the activity for NO-CO and CO-O₂ reactions at 175°C (Table 2). CO conversions in CO-O₂ reaction were higher than those in NO-CO reaction for all the catalysts. If one assume that the step 5 which is common to both reactions is rate-determining step, the observed conversion (activity) must be comparable. Therefore, the rate of step 2 is slower than that of step 5 in NO-CO

reaction. The observed difference in catalytic activity must originate in the different ability for the dissociative adsorption of O₂ and NO. In case that NO dissociation (Step 2) is rate-determining as discussed above, the higher activity of Pd/LM/AL than Pd/AL for NO-CO reaction strongly suggests that the NO dissociation on Pd is promoted by LM deposited in close proximity to Pd in the pores of alumina. FTIR studies also revealed that the wavenumber of liner CO species formed at 40 °C on Pd/LM/AL was higher than that of Pd/AL. These results indicate the electron density of Pd decreased by the intra-pore co-deposition of LM, which might contribute to the modification of the catalytic property. In the future, we will design active catalysts by utilizing the interaction between precious metals and metal oxides.

Table 2 CO conversion for NO-CO and CO-O₂ reaction

Sample name	CO conversion for NO-CO (%)	CO conversion for CO-O ₂ (%)
Pd/AL	0.0	24.5
LMout/Pd/AL	1.5	17.4
Pd/LM/AL	7.3	38.6
LM/Pd/AL	0.4	15.4

NO(0.51%)-CO(0.49%)-He, CO(0.5%)-O₂(0.25%)-He, 100 mL min⁻¹, 175 °C, W/F= 0.06 g s cm⁻³

Reference

- 1) Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto and N. Hamada, *Nature*, 418 (2002) 164-167.
- 2) T. Asada, T. Kayama, H. Kusaba, H. Einaga and Y. Teraoka, *Catalysis Today*, **15** (2008) 37-42.

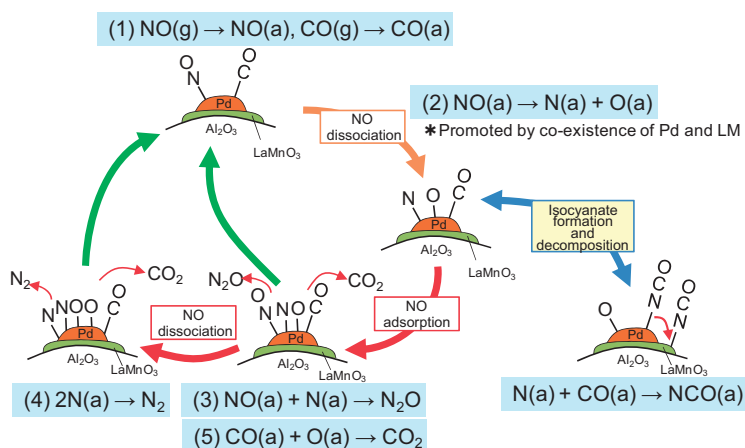


Fig. 4 Proposed mechanism of NO-CO reaction over Al₂O₃ supported Pd and LaMnO₃ catalyst.

Micro Review

Game Theoretic Analyses of International Environmental Agreements

Toshiyuki Fujita

Faculty of Economics, Kyushu University

International environmental agreements are said to be self-enforcing if no country has an incentive to change decisions on the accedence. It is necessary to find the scheme to realize the large self-enforcing agreement. We incorporate matching schemes into a model of international environmental agreements and investigate their effectiveness using three-stage game model. The analysis of a matching agreement game with symmetric countries as players suggests the existence of a self-enforcing agreement leading to an efficient and equitable outcome, and thus shows that matching schemes are effective.

1. Introduction

Various transboundary environmental problems become obvious nowadays. For domestic environmental issues, there exist defined regulatory authorities, such as the government, which can implement policies, including direct regulation, pollution emission tax, and emissions trading. For solutions to global environmental problems influencing many countries, however, voluntary negotiation among nations is essential. To protect the environment, it is necessary to abate the emission of pollutants causing damages at some costs. International environment agreements refer to an agreement among nations on abatement, which is decided upon negotiation, and, if necessary, supplemental rules. Examples include the Montreal Protocol on Substances that Deplete the Ozone Layer and the Kyoto Protocol for the handling of global warming.

If the international environmental agreement in which all related countries participate is reached and each country complies with it, an efficient level of abatement will be attained. A certain amount of financial burden, however, is incurred by abatement, and abatements by one country benefit all countries. This causes an incentive for some countries to enjoy “free riding” (benefited by other country’s abatements) without implementing their own abatement efforts. As a result, it is often the case that some countries do not sign environment agreements. In this situation, it is difficult to penalize “outsiders.” In 2001, the U.S. announced its withdrawal from the Kyoto Protocol, which was brought into effect in 2005 by other COP countries, including EU nations, Japan and Canada, without U.S.’s participation. Although the U.S. might not intend free riding, it

eventually seems to succeed in free riding.

Agreements that generate no incentives for any countries to enjoy free riding are said to be self-enforcing. In other words, in a self-enforcing international environment agreement, participation and national interest do not contradict for all countries, and each country voluntarily signs it without coercion from other nations. The design of the agreement should prevent any free riding and thus realize the large self-enforcing agreement. In this review, the outline and research results of economic analyses on international environment agreements, one of the author’s major research themes, are introduced.

2. Game Theory

International environment agreements are typically analyzed with game theory. Game theory is a study field for analyzing decision-making processes in the so-called game situations, where many rational agents’ decision-makings interact with each other. Game theory has played a crucial role for today’s economics.

A decision-making agent is called “a player,” whereas decision-making is called “strategies.” The outcome of a game is decided upon the strategies of all the players, whereby players’ evaluation value for outcome is called “payoff.”

If every player maximizes his/her payoff against the combinations of strategies by other players, thus adopting an optimal response strategy, this combination of strategies of all the players is said to be constitute a Nash equilibrium. Under Nash equilibrium, on the assumption that the strategies of other players would not change, there are no incentives for every player to

change his/her strategies. In this sense, Nash equilibrium is a stable situation. Nash equilibrium is an important solution concept of a game.

3. Game of international environmental agreement

Let us consider international environment agreements as two-stage games played by nations as players. In the first stage, each country decides independently whether it will accede to an agreement or not. It is assumed that only one agreement would be formed, and cases whereby two or more agreements exist simultaneously are not considered. In the second stage, signatories, through negotiation, determine abatements that maximize the total gain of the signatories. Non-signatories, meanwhile, determine their own abatements independently. Payoff of a country is defined as the benefits from abatements (avoided damage) by all countries minus its abatement costs. In the first stage, each country makes a decision whether it will accede to an agreement by taking into account its final payoff. This decision is made rationally without any external coercion. Agreements formed under Nash equilibrium are considered to be self-enforcing.

Unfortunately, it is known that the size of self-enforcing agreements is extremely small if agreements set out only abatements without any supplemental rules^{1), 2)}. For example, in case of a game played by symmetric countries under the identical conditions, if each country's abatement cost is a convex function of the amount of abatement, and if damage from pollution is proportional to the emission of pollutants, it is proved that only agreements by up to three countries can be self-enforcing³⁾. In an agreement signed by four countries or more, individual countries, on the assumption that other countries remain in the agreement, decide not to join the agreement because they can get higher payoffs by doing so.

Let us look at a numerical example. Let there be 10 identical countries. Assume that when the abatement of country i ($=1, \dots, 10$) is x_i , the final payoff of country i is:

$$\pi_i = \sum_{j \in S} x_j - \frac{x_i^2}{2},$$

where S is a set of signatories. Abatements selected in the second stage by signatories and non-signatories are s ($\equiv |S|$) and 1 , respectively. The payoff of a country depends on the number of signatories and on whether it

accedes to the agreement or not. If the number of signatories is s , and if the payoffs of signatory and non-signatory are denoted by $\pi^S(s)$ and $\pi^N(s)$ respectively, the agreement of size s is self-enforcing as long as the following two inequalities are established.

$$\pi^S(s) \geq \pi^N(s-1), \pi^N(s) > \pi^S(s+1).$$

The former inequality means that any signatory cannot gain from withdrawal, which is called internal stability. The latter one means that, if non-signatory accedes to the agreement, it will suffer loss, which is called external stability. Agreements with these two characteristics are self-enforcing.

In Table 1, the final payoffs of signatory and non-signatory after the second stage are given as a function of the number of signatories. Also given are internal stability and external stability, which are judged based on these payoffs. For example, if the number of signatories is 6, the payoff of signatory is 22.0. If one signatory withdraws from the agreement and acts as a non-signatory, international stability is not satisfied, because payoff increases to 29.5 (the payoff of non-signatory when the number of signatories is 5). On the contrary, if one non-signatory joins the agreement, payoff will decrease from 39.5 to 27.5, so external stability is satisfied. As can be seen from Table 1, both internal stability and external stability are satisfied only if the number of signatories is 3. If the number of signatories is 4 or more, internal stability is not satisfied.

The results of asymmetric cases, where each country has different conditions, are almost same as those of symmetric cases⁴⁾. What is obtained is a pessimistic conclusion that self-enforcing international environment agreements are possible only if they are signed by a small number of countries.

Table 1 Numerical result of international agreement game

Number of signatories	Payoff of signatories	Payoff of non-signatories	Internal stability	External stability
0	–	9.5	N.A.	Not stable
1	9.5	9.5	Stable	Not stable
2	10.0	11.5	Stable	Not stable
3	11.5	15.5	Stable	Stable
4	14.0	21.5	Not stable	Stable
5	17.5	29.5	Not stable	Stable
6	22.0	39.5	Not stable	Stable
7	27.5	51.5	Not stable	Stable
8	34.0	65.5	Not stable	Stable
9	41.5	81.5	Not stable	Stable
10	50.0	–	Not stable	N.A.

It is then necessary to set up supplementary rules on the content of agreements. It can be considered that the most straightforward rule is to impose serious penalties on countries that do not comply with the agreement. However, there remain concerns over which agents with what authorities can impose a fine on sovereign countries.

The rule that has attracted the attention of many researchers is the lump-sum income transfer rule, whereby a certain amount of money will be transferred as a reward for non-withdrawal to countries with an incentive for departure from the agreement. In case of emissions trading, income transfer can be done through the arrangement of the initial allocation of emission permits. It may seem that this is effective for asymmetric cases, but in reality, it does not work well. The reason is that even if money is transferred, it becomes a problem where that money shall come from. It is then concerned that a country that is supposed to pay money may withdraw from the agreement¹⁾.

So far, the most promising is the system that combines the income transfer scheme with a rule that bans partial agreement among part of member nations^{5, 6)}. In other words, the agreement will be nullified immediately after the withdrawal of one country from the agreement. Although this is a little unrealistic, it is true that there are no merits at all for countries to withdraw from agreements with the presence of such kind of rule.

4. Application of matching schemes

Recently, the author explores in several papers the effectiveness of “matching agreements,” one type of international environment agreements^{3), 4), 7)}. Matching in this context means that a person coordinates his/her own behavior with the actions of others. Under matching agreements, countries negotiate what is called the matching rates, instead of abatements. Afterwards, all the countries independently set up the level of their flat abatement. Eventually, each country is imposed not only its flat abatement but also an additional abatement which depends on the total of all the other countries' flat abatements and its matching rate. The concept of matching is first proposed by Guttman⁸⁾. The first application of matching scheme in the context of international environmental agreements is done by Rübhelke⁹⁾.

Matching agreement games comprise three stages. In the first stage, after the announcement of rules on matching, each country decides whether it will accede to the agreement or not. In the second stage, through negotiation among signatories, the common matching rate that maximizes the total payoff of the signatories is determined. In the third stage, both signatories and non-signatories decide their flat abatements based on the matching rate determined in the second stage. The values of matching rates and flat abatements are assumed to be non-negative.

The signatories of matching agreements shall commit themselves to their own flat abatement, as well as additional abatement, the amount equal to the multiplication by the matching rates determined in the second stage of the total of flat abatement of all the countries including non-signatories. It is assumed that a matching agreement once concluded has a certain binding authority, whereby signatories shall comply with additional abatements determined by the rule of agreements after the third stage. Non-signatories, meanwhile, do not have to follow the matching rule, and actual abatement corresponds to their own flat abatement determined in the third stage. The final payoff of each country will be decided after the completion of actual abatements.

Solving for equilibria of matching agreement games reveals that a socially efficient agreement comprising all countries (hereafter referred to as “full agreement”) is self-enforcing, regardless of the number of nations, both for symmetric and asymmetric cases^{4, 7)}. A country that withdraws from the full agreement is exempted from additional abatement decided upon the matching rule. In this case, however, remaining signatories will set their flat abatements as zero. The deviator, after all, is forced to increase flat abatement, and departure from the full agreement does not lead to an increase in gains. That is, matching rates and the arrangement of flat abatement function as penalties for countries withdrawing from the full agreement.

Also, in the full agreements of symmetric case, the matching rate determined in the second stage is unity, and the final payoffs have the same value for all the countries. Therefore, it is shown that the equilibria of matching agreements lead to the outcomes desirable also from the perspective of equity.

Table 2 Numerical result of matching agreement game

Number of signatories	Matching rate	Payoff of signatories	Payoff of non-signatories	Internal stability	External stability
0	–	–	9.5	N.A.	Not stable
1	0.17	10.7	11.6	Stable	Not stable
2	0.25	13.5	16.9	Stable	Not stable
3	0.30	17.3	23.7	Stable	Stable
4	0.35	21.9	31.7	Not stable	Stable
5	0.40	27.0	40.5	Not stable	Stable
6	0.46	32.6	49.5	Not stable	Stable
7	0.54	38.6	57.6	Not stable	Stable
8	0.68	44.6	61.7	Not stable	Stable
9	0.97	50.1	47.6	Not stable	Not stable
10	1.00	50.0	–	Stable	N.A.

Again let us look at the same numerical example used in Section 3 to examine the self-enforcement of agreements in the matching agreement game. Table 2 shows matching rates, in case of the presence of matching agreements, and the final payoffs of signatories and non-signatories as a function of the number of signatories. Internal stability and external stability are judged in the exactly same way described in Section 3. The full agreement, where the number of signatories is 10, allows every country to gain the payoff of 50. If one country withdraws from the full agreement, its payoff decreases to 47.6, whereas those of signatories slightly increase to 50.1. Therefore, it is confirmed that the full agreement is self-enforcing. At the same time, however, note that agreements comprising three countries are also self-enforcing. This means that once an agreement of this small scale is formed, it is difficult to expand the scale of the agreement.

5. Conclusion

In this review, the outline of the game theoretic analyses of international environment agreements has

been introduced, together with the results of author's research. As many papers in this field obtain pessimistic conclusions, the fact that the matching rule enables self-enforcing full agreements seems to deserve certain attention. Future challenges include the exploration of the problem of multiple equilibria, which is briefly mentioned at the end of the preceding section, analyses with more general payoff functions, analyses in the cases whereby multiple agreements are allowed to coexist, and analyses in the dynamic framework.

Reference

- 1) C. Carraro and D. Siniscalco, *Journal of Public Economics*, **52**, 309-328 (1993).
- 2) S. Barrett, *Oxford Economic Papers*, **46**, 878-894 (1994).
- 3) T. Fujita, *Kankyo Keizai Seisaku Kenkyu (Review of Environmental Economics and Policy Studies)*, **2**, 28-38, in Japanese (2009).
- 4) T. Fujita, *International Journal of Environmental, Cultural, Economic and Social Sustainability*, **7**, in press (2011).
- 5) T. Fujita, *Environmental Economics and Policy Studies*, **6**, 103-118 (2004).
- 6) P. Chander, H. Tulkens, *International Journal of Game Theory*, **26**, 379-401 (1997).
- 7) T. Fujita, *Proceedings of the 18th Annual Conference of the European Association of Environmental and Resource Economists*, (2011).
- 8) J. M. Guttman, *American Economic Review*, **68**, 251-255 (1978).
- 9) D. T. G. Rübelke, *Environmental Economics and Policy Studies*, **8**, 1-31 (2006).

Research Report

Diffusion of next-generation vehicles and environmental-energy problem in China

Kana Moroga

Research and Education Center of Carbon Resources, Kyushu University

China, with its remarkable economic growth, is regarded as the world's largest car market. Further development of its automotive industry is then expected. Although the demand for next generation vehicles such as electric vehicles (EVs) is increasing because of the struggle against global warming and energy policy goals, it is questionable whether their diffusion in China can be expected to engender a large-scale reduction of CO₂ emissions. This paper reviews not only the present conditions of China's automotive industry but also in addition the environmental and energy problems that China is confronting. Based on that review, issues related to EVs diffusion in China are analyzed.

1. Present status of China's car market

Recently, several of the main car manufacturers are promoting full-scale development of electric vehicles (EVs). Sales for individuals began in 2010. With the rapid worldwide progress of motorization, automobile-related air pollution, global warming, and energy supply became urgent issues. Furthermore, rising ecological consciousness of consumers and increased control for fuel-efficient automobile engines and CO₂ emissions in developed countries have promoted sales of hybrid vehicles (HVs) and fuel-efficient vehicles, and have encouraged the wider use of EVs, pressing car manufacturers to develop next-generation vehicles. In addition, the development of better batteries installed in EVs, which account for most of the cost of EVs manufacturing, has made EVs diffusion increasingly likely. Although the worldwide automobile market is experiencing a downturn except in rapidly developing nations such as China and India, EVs introduction is raising expectations related to energy policy and global-warming countermeasures.

The Chinese auto-industry is achieving remarkable

growth concomitantly with its economic growth, and the car demand there maintains high. As demonstrated in Tables 1 and 2, in 2009, the annual production of Chinese cars attained approximately 13.79 million units, with annual sales in China of approximately 13.64 million units, making that nation the world's largest consumer of automobiles, surpassing even Japan and the United States. In addition, both annual car production and sales in 2010 exceeded 18 million units, and auto fleets in 2009 reached approximately 62.81 million units (Figure 1). Production and sales of China are expected to increase further in the future. However, because of the wide economic disparities between urban and rural areas and that between coastal area and inland, diffusion of automobiles differs greatly from one area to another. However, the introduction of "One Thousand Vehicles in Ten Cities", a project promoting new energy vehicles such as EVs, and a subsidy system for eco-cars have triggered the diffusion of cars by routing subsidies to farm villages in inland areas¹⁾.

Amid these areas of progress, the expectation of increased oil consumption caused by the increasingly large auto fleet is creating concern about shortages in energy

Table 1 Top ten countries in automobile production

(unit)

Ranking*	Country	2008	2009	2010
1	China	9,299,180	13,790,994	18,264,667
2	Japan	11,575,644	7,934,057	9,628,920
3	United States	8,672,141	5,709,431	7,737,502
4	Germany	6,045,730	5,209,857	5,905,985
5	Korea	3,806,596	3,492,942	4,250,303
6	Brazil	3,220,475	3,185,243	3,644,034
7	India	2,328,557	2,631,731	3,517,675
8	Spain	2,541,644	2,170,078	2,387,900
9	Mexico	2,180,294	1,564,169	2,347,524
10	France	2,568,978	2,047,658	2,229,381

*The ranking is related to 2010.
Source: FOURIN (2011)³⁾

Table 2 Top ten countries in automobile sales

(unit)

Ranking*	Country	2008	2009	2010
1	China	9,336,326	13,644,794	18,061,936
2	United States	13,493,165	10,601,368	11,772,278
3	Japan	5,082,235	4,609,256	4,956,138
4	Brazil	2,867,565	3,207,731	3,572,307
5	Germany	3,425,039	4,049,359	3,198,417
6	India	1,973,524	2,256,328	3,027,868
7	France	2,573,715	2,718,581	2,708,884
8	United Kingdom	2,483,179	2,220,454	2,291,445
9	Italy	2,422,673	2,357,479	2,168,919
10	Russia	3,218,214	1,599,488	2,108,474

*The ranking is related to 2010.
Source: FOURIN (2011)³⁾

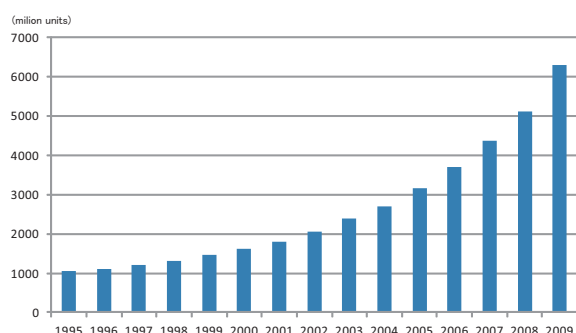


Figure 1 Evolution of vehicle fleet in China (1995-2009)
Source: National Bureau of Statistics of China (2010)

supplies¹⁾. Increasing anxiety about oil supply shortages particularly might affect the economy negatively because of escalating crude oil prices. Therefore, the Chinese government is seeking for the diffusion of next-generation vehicles such as EVs from the viewpoint of suppressing increasing oil consumption by the ever increasing fleet of automobiles. The background of diffusing next-generation vehicles includes a movement of extrication from oil dependence. It is expected to enhance the emergence of technological development and diffusion of next-generation vehicles.

2. Problems with the spread of EVs in China

Worldwide introduction of HVs and EVs, next-generation vehicles, into markets is promoted to reduce the environmental load of automobiles in general. Augmentation of this trend through the popularization of fuel cell-powered vehicles might contribute greatly to the realization of a low-carbon society in the future.

As shown by the sectoral ratio of worldwide CO₂ emissions (Fig. 2), the power and heat supply sector head the list with 41%; the transportation sector follows with 23%. The CO₂ emission from automobiles account for a large fraction of that by the transportation sector.

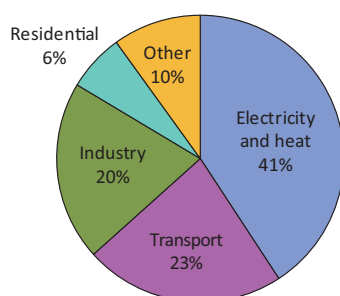


Figure 2 Sectoral ratio of worldwide CO₂ emissions (2009)
Source: IEA (2011)⁵⁾

Therefore, its reduction is an urgent issue.

Practical use and popularization of energy-saving technologies and next-generation vehicles are encouraged worldwide and introduction of HVs and EVs into market is promoted simultaneously, but will the prevalence of EVs in China truly lead to the reduction of CO₂ emissions?

In 2007, China became the top CO₂ emitting country, surpassing the United States. The remarkable increase of the Chinese vehicle fleet occurred simultaneously. Therefore, CO₂ emissions by the transportation sector must increase greatly. However, the ratio of CO₂ emissions by the power and heat supply sector in China is characteristically high (Fig. 3); among those emissions, those from coal-fired power stations are exceptionally high (Fig. 4). Chinese thermal generation facilities typically use cheaper and less-efficient coal. Consequently, an effective utilization of such coal persists as an important issue, and the promotion of clean and effective coal firing is highly demanded. Therefore, in China, the reduction of CO₂ emissions by introduction of EVs might be limited unless energy sources for power generation and efficiency are improved drastically.

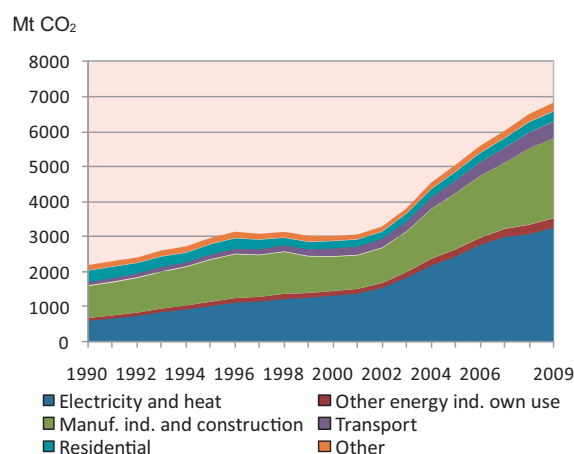


Figure 3 CO₂ emissions by sector in China
Source: IEA (2011)⁵⁾

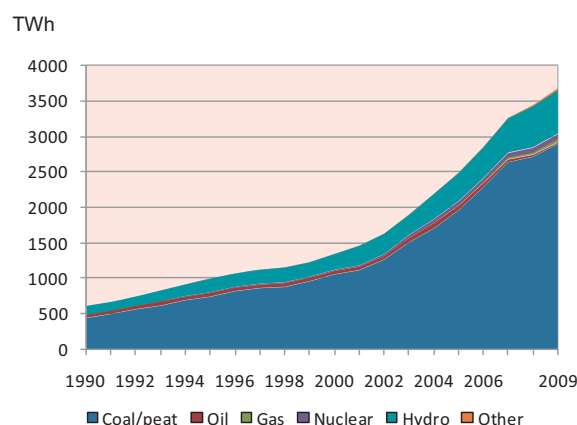


Figure 4 Trend of electricity generation by power sources, China
Source: IEA (2011)⁵⁾

3. Problems in the diffusion of next-generation automobiles

Realization of energy savings for effective utilization of limited fossil fuels and reduction of CO₂ emissions will become particularly important in the future to cope with issues of global warming and energy supplies.

The scenario that includes popularization of next-generation vehicles is strongly dependent on factors such as regulations supporting fuel-efficient car engines, economic policies related to subsidy and taxation, and the extent of infrastructure preparation. That applies to power generation sector as well. In China, for example, the energy sources for power generation differ from one area to another, producing different effects on the reduction of CO₂ emissions by introducing next-generation vehicles from one place to another⁴⁾.

The Chinese government has recently strengthened its environmental regulations to tackle environmental issues such as air pollution. However, merely introducing EVs might not reduce CO₂ emissions in China, where most power is generated by thermal power stations burning less-efficient coal and because specific CO₂ emissions depend on such energy sources for power generation. A cost-benefit analysis for the popularization of next-generation vehicles from the viewpoint of economic efficiency, taking into account the reduction of CO₂ emissions in power generation and automobile sectors, in addition to reduced consumption of gasoline, indicated a higher benefit-cost (B/C) ratio for HVs comparatively to

EVs⁶⁾. It is estimated that HVs pose a higher probability of reducing CO₂ emissions than EVs as it stands now. Furthermore, our results suggest preferential development of power generation technology to enhance the efficiency of thermal power stations earlier than improving car technology in the transportation sector. It might be important to estimate the future diffusion of eco-cars, perform quantitative analysis of energy consumption of automobiles, and assess the reduction of CO₂ emissions while considering power generation and automobile sectors, CO₂ emissions related to energy sources used for power generation, environmental regulations, and subsidies.

References

- 1) China Automotive Technology and Research Center (CATARC), China Association of Automobile Manufactures (CAAM), *China Automotive Industry Yearbook*, Tianjin, China Automotive Industry Yearbook House (2010) (in Chinese).
- 2) National Bureau of Statistics of China, *China Statistical Yearbook*, Beijing, China Statistics Press (2010).
- 3) FOURIN, *Monthly Report on the Global Automotive Industry*, **310** (2011).
- 4) H. Huo, Q. Zhang, M. Q. Wang, D. G. Streets, and K. He, *Environmental Science and Technology*, **44**, 4856 (2010).
- 5) International Energy Agency (IEA), *CO₂ Emissions from Fuel Combustion Highlights* (2011).
- 6) K. Moroga, Y. Ito, S. Managi and T. Fujita, *The Proceedings of the 10th International Conference of the Japan Economic Policy Association* (2011).

SYMPOSIUM & WORKSHOP

SYMPOSIUM >>>

The 21th Banyu Fukuoka Symposium - Evolving functionalized molecule - **Joint Hosting**
Date May 21, 2011 **Venue** Centennial Hall Kyushu University School of Medicine

The 7th International Symposium on Novel Carbon Resource Sciences **Hosting**
- Green Materials for Sustainable Society -
Date June 23-24, 2011 **Venue** Yonsei University, Seoul, Korea

The 3rd Asian Symposium on Advanced Materials **Joint Hosting**
Date September 19-22, 2011 **Venue** Chikushi campus, Kyushu University

Global COE "Novel Carbon Resource Sciences" Open Lecture (and Forum I/II/III) **Hosting**
- Challenges and Visions for the Next Energy Best Mix -
Date November 5, 2011 **Venue** Chikushi campus, Kyushu University

The 7th International Conference on Clean Coal Technology and Fuel Cells (CCT&FCs-2011) **Joint Hosting**
Date November 8-9, 2011 **Venue** Chikushi campus, Kyushu University

Cross Straits Symposium on Materials, Energy and Environmental Sciences 13 **Joint Hosting**
Date November 23-24, 2011 **Venue** Chikushi campus, Kyushu University

International Symposium on Earth Science and Technology 2011 **Joint Hosting**
Date December 6-7, 2011 **Venue** INAMORI Foundation Memorial Hall, Ito campus, Kyushu University

2011 Sino-Australian Symposium on Advanced Coal and Biomass Utilisation Technologies **Joint Hosting**
Date December 9-11, 2011 **Venue** Wuhan, China

The 8th International Symposium on Novel Carbon Resource Sciences **Hosting**
- Eco-friendly Materials and Processes for Low-Carbon & Sustainable Society -
Date December 15-16, 2011 **Venue** National Environmental Engineering Research Institute (NEERI), Nagpur, India

WORKSHOP >>>

The 4th G-COE International Workshop on Energy and Environment in Chemical Engineering **Joint Hosting**
Date September 28, 2011 **Venue** Research Center for Steel, Ito Campus, Kyushu University

The 4th KU-KU (Kyushu Univ. - Korea Univ.) Joint Workshop on Functional Materials **Joint Hosting**
Date September 29-30, 2011 **Venue** Seiryu-sou, Yamaga, Kumamoto

Co-sponsored Seminar >>>

Japan-Korea Joint Symposium 2011 on Hot Trends of Polymeric Materials in INT and IBT
Date October 20-22, 2011 **Venue** Institute for Materials Chemistry and Engineering (IMCE), Chikushi Campus, Kyushu University

SYMPOSIUM & WORKSHOP REPORT



SYMPOSIUM

Hosting

01

The 7th International Symposium on Novel Carbon Resource Sciences

- Green Materials for Sustainable Society -

Date June 23-24, 2011

Venue Yonsei University, Seoul, Korea

Faculty of Engineering Sciences, Kyushu University Yasutake Teraoka

Our COE has held international symposiums twice a year, one in Japan (Fukuoka) and one abroad (co-organized with partner institution) since the inaugural year 2008. As we plan to hold the 9th symposium in Fukuoka in autumn 2012, we decided to co-organize the 7th and 8th symposium in FY 2011 at the overseas partner institutions in Korea and India, respectively.

The 7th symposium was held under the theme of "Green Materials for Sustainable Society" at Yonsei University (Seoul, Korea) on June 23-24, 2011. There were 64 participants from Korea, 37 from Japan, and 1 each from China, Australia, Indonesia and India. In addition to keynote and invited lectures and oral and poster presentations, the student debate session and poster pre-talk Session, which was first introduced and performed successfully at the previous 6th symposium, were organized and conducted.

In the symposium, two keynote lectures were given by Prof. Seong-Ho Yoon (Kyushu University; "Carbon Nanofiber as a Green Material for Energy and Environmental Devices [KN1]) and Dr. Jong-Huy Kim (Korea Institute of Energy Research; "CNT/RuO_x/MnO_x Nano-Composite Electrode Prepared by an In-Situ Hydrothermal Method" [KN2]). KN1 was on synthesis of carbon nanofiber and its application to electrochemical devices and environmental catalysts, and KN2 was on preparation and performance of nano-composite electrode for super capacitor comprised of carbon nanotube, ruthenium oxide and manganese oxide. Both presentations were much beneficial and interesting ones in terms of "Green Materials", which was the subject of the symposium.

General oral presentations were divided into two parallel sessions of "Green Materials" (12 presentations) and "Energy & Environment" (13

ones). There were 12 presenters from Korea (Korea Institute of Energy Research, Yonsei University and others), 10 from Kyushu University, and 1 from the respective partner institutions (Shanghai Jiao Tong University, Curtin University, Institute of Technology Bandung, and National Environmental Engineering Research Institute, India).

In the poster session, 51 presentations (25 from Kyushu University, 25 from Korea, and 1 from India) were given. The pre-talk session, in which poster presenters introduced briefly the contents of his/her own presentation in three minutes, was conducted this time too following the precedent of previous symposium. Participants could grasp the general outline of each presentation beforehand and this resulted in more active and deep discussion in the poster session.

Following the precedent of previous symposium



again, the student debate session, of which students were fully responsible for planning and organizing, was conducted under the theme of "About Energy and Safety". Students from both universities engaged in active and content-rich discussion on this theme, which was adopted in response to the situation after the accident of Fukushima-Daiichi nuclear power plant. The content of the discussion is reported by the students on the next page.

I would like to take this opportunity to thank Prof. Yong-Gun Shul, staff and students of Yonsei University and G-COE Office for their dedicated contributions for preparation and management of the successful symposium.

List of Lectures

Keynote Lectures

Seong-Ho Yoon, Kyushu University

"Carbon Nanofiber as a Green Material for Energy and Environmental Devices"

Jong-Huy Kim, KIER, Korea

"CNT/RuOx/MnOx Nano-Composite Electrode Prepared by an In-Situ Hydrothermal Method"

Invited Lectures

Dehua Dong, Curtin University, Australia

"Template Synthesis of Porous Cathodes for Solid Oxide Fuel Cells"

Sudarto Notosiswoyo, ITB, Indonesia

"Contribution of Coal Mine and Coal Fired Power Plant to CO₂ Emission in Indonesia"

Nitin Labhsetwar, NEERI-CSIR, India

"New and Improved Materials for Cleaner Energy and Environment"

Yangqing Wu, Shanghai Jiao Tong University, China

"Three Dimensional Numerical Modeling of Seawater Intrusion into Coastal Aquifers, Shanghai, China"



Report on the Student Debate in the 7th International Symposium on Novel Carbon Resource Sciences

- Green Materials for Sustainable Society -

Date June 24, 2011

Venue Yonsei University, Seoul, Korea

Representative member of student participants

Takamitsu Masunaga

As part of the 7th international Symposium on Novel Carbon Resource Sciences held at Yonsei University, Seoul, Korea, on June 23-24, 2011, the Student Debate Session was planned and organized at the initiative between Yonsei university and Kyushu university students.

In the occasion of the 6th international Symposium on NCRS held on November 12-13, 2010, our G-COE had held student debate session about technical assistance such as building and popularization of nuclear power plants supported by advanced countries in developing countries. As the result of debate with the object of economy, environmental and safety, it has been reported that we could recognize the issue of global warming caused by CO₂ emission as a common challenge for both advanced and developing countries, and the topic of the debate shifted from initially proposed theme of whether technical assistance and construction of nuclear power plants in developing countries necessary, to the problem of whether nuclear power plants are necessary. In addition, nuclear power plants is the one of the important electric power distribution methods to support human life and technology in the world because this it has the advantages of excellent energy efficiency and low green house gas (carbon dioxide) emissions which is an important issue for NCRS. Furthermore, the problem of Fukushima nuclear power plants damaged by massive earthquake in Japan on March 11, 2011 was featured on not only Japan but also all the countries of the world. Especially, a lot of countries which have the nuclear power plants have the important issues to promote its safety. In response to this accident, these countries are promoted in-depth discussion about the nuclear power plants, and there is some debate as to whether nuclear power plants are necessary. From the above premise, we

focused on nuclear electric power generation as one of the effective technologies for sustainable electricity supply, and discuss a contentious subject of nuclear power plants. The important purpose of this session is to enhance knowledge of efficacy and safety of nuclear electric power generation, and also develop internationally viable debate skills.

The student debate session was carried out as the final program of the 7th international Symposium about one hour with the participation of Yonsei and Kyushu university students including foreign ones. At first, 4 representatives of both university students explained about principle, creation process of nuclear electric power generation, Fukushima nuclear accidents hit by the great east Japan earthquake and others by using prepared materials, and divided the students into two groups depending on whether they agree or disagree on the theme stated above. And then, we moved on to the discussion about energy and safety of nuclear electric power generation. In this discussion, the most common opinion among the various arguments is as follows: "We should reduce the number of nuclear power plants which exists throughout the world and limit its usage rate to the fullest extent possible because it is difficult to develop the electric power-generating technology equivalent to nuclear electric power generation.", "If some of reactors of nuclear power plants is stopped, it will be caused serious adverse effects on industrial, economic development, people's lives and others. Thus, the nuclear power stations had to be kept going. At the same time, we should develop the usage of alternative and renewable energy sources, while continuing nuclear power generation.", "Nuclear power generation is poorly safety, but it can provide a stable electric power supply. Thus, we can continue to use the

nuclear electric power generation in the future if we thoroughly investigate the cause of Fukushima nuclear power accident, and then gave increased safety of that." However, there were various contrasting views about this issue as follows: "We should shut down the nuclear power plants which have an increased risk for natural disasters.", "The serious nuclear accidents occurred at a nuclear power plant in Japan which is relatively safe country. As a result, we could not control it. Thus, we have a hard time continuing to rely on nuclear power energy.", "The radioactivity wrecks incalculable damage on the human health." As stated above, the safety of nuclear electric power generation became a major topic of discussion.

Following is a summary of the arguments, Fukushima nuclear power accidents are triggered by our technical overconfidence. If we can achieve safety enhancement for nuclear power plants, the nuclear power stations had to be kept going. On the other hand, opponents made the statement that we should give first priority to the human life, and had better abolish the use of nuclear because it is difficult for us to predict the consequences of natural disasters. Among them, the various opinions concerning renewable energy such as solar and wind power, biomass fuel and coal were expressed, we also could learn whole concept of electricity supply technology at this active discussion.

Both university students have been having a lot of idea and perspective about nuclear power plants, and expressed their own opinions in the spirited discussion because this debate was right after the Fukushima nuclear accident occurred on March, 2011. After all, this debate gave a good opportunity for researchers who have a role in making global community to enhance debate techniques as well as to get various objective opinions about nuclear electric

power generation. However, the most of opinions from Kyusyu university students were expressed by overseas students. Thus, we have to participate actively in the debate session in English, and enhance more debate techniques to express own opinion from a global point of view in respect of others.



The 21st Banyu-Fukuoka Symposium

- Functional Molecules on Progress -

Date May 21, 2011

Venue 100th Anniversary Hall, Faculty of Medicine, Kyushu University

Institute for Materials Chemistry and Engineering, Kyushu University

Katsuhiko Tomooka

Banyu-Fukuoka Symposium is aimed at mutual exchange and activation of researchers of organic chemistry in Kyushu and Chugoku area and the 21st symposium of this time was held with 570 participants. As Prof. Akira Suzuki, Prof. Eiichi Negishi and Prof. Richard Hack received the Nobel Prize in Chemistry last year, "Nobel Prize Commemorative Special Session" was introduced in the symposium of this year. At the beginning of this session, the video message from Prof. Akira Suzuki concerning the awarded theme of "Cross-coupling reaction using palladium catalysts" was presented, and then an explanation of related field by Prof. Hideo Nagashima and research introduction by Prof. Jiro Tsuji, who is a pioneer in the field of reaction of palladium catalysts, were given. After that, Lectures by Dr. Shigeaki Suzuki, Dr. Tetsuro Tsuji, Dr. Yasuyuki Goto and Dr. Shinichi Soga,

who are researchers at corporate enterprises, were given concerning how cross-coupling reactions are being practically applied. After the poster session (17 presentations including those by winners of Best Poster Awards at Sapporo Symposium), invited lecture session was given. In this session, lectures by Prof. Shigeaki Matsunaga (Precise synthetic chemistry using dinuclear metal catalysts), Prof. Dionicio Siegel (Net synthesis research of alkaloids with complex structure), Prof. Shigeru Yamako (development of new materials-oriented radical polymerization method and chemistry of cycloparaphenylene), Prof. Atsuhiko Osuga (Chemistry of ring-expanded porphyrin which shows mobius aromaticity), and Prof. Yoshinori Yamamoto (New synthesis method using nanoporous metal catalysts) were presented.

List of Lectures

[Nobel Prize Commemorative G-COE Special Session]

Prof. Akira Suzuki (Hokkaido University)
"Video Message"

Prof. Jiro Tsuji (Tokyo Institute of Technology) and
Prof. Hideo Nagashima (Kyushu University)
"Fascination of palladium synthesis and cross-coupling reactions"

Dr. Shigeaki Suzuki (Kuraray Co. Ltd.)
"Industrial process of palladium catalyzed butadiene telomerization and commercialization of new high-temperature polyamide"

Dr. Tetsuro Tsuji (Ube Industries Ltd.)
"Pd-catalyzed Oxidative Coupling Reaction. -Industrialization of Biphenyl Derivatives Production"

Dr. Yasuyuki Goto (JNC Corporation)
"Development of LC Compounds using Cross-Coupling Reaction"

Dr. Shinichi Soga (Tosoh Corporation)
"Pd-Catalyzed Arylamination in the Industrial Application"

[Invited Lectures]

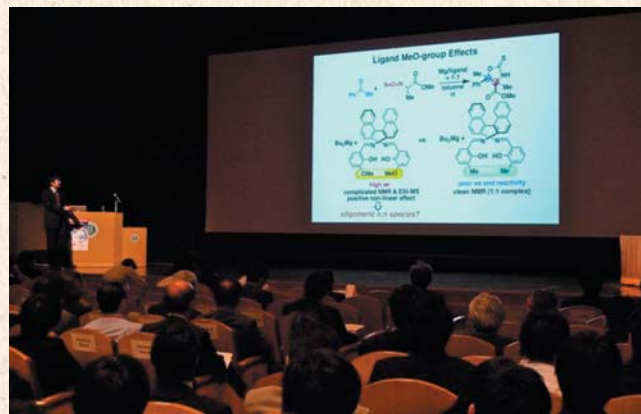
Prof. Shigeaki Matsunaga (University of Tokyo)
"Precise synthetic chemistry using concert function of dinuclear metal catalysts"

Prof. Dionicio Siegel (The University of Texas at Austin)
"Synthesis and study of regenerative natural products"

Prof. Shigeru Yamako (Kyoto University)
"Development of new materials led by organic synthesis"

Prof. Atsuhiko Osuga (Kyoto University)
"Chemistry of ring-expanded porphyrin which shows mobius aromaticity"

Prof. Yoshinori Yamamoto (Tohoku University)
"From molecular catalysts to nanostructured materials catalysts"



The 3rd Asian Symposium on Advanced Materials (ASAM-3)

Date September 19-22, 2011

Venue Chikushi Campus, Kyushu University

Institute for Materials Chemistry and Engineering, Kyushu University **Atsushi Takahara**

This symposium is aimed at research discussion, internationalization and cultivation of human resources of advanced materials, especially in its interdisciplinary fusional fields. In the 3rd symposium of this time, we introduced encouraging prize for young researchers selected from oral and poster presentations. Winners were choosed by about 60 requested referees of top researchers including invited lecturers, members of international advisory committees and the organizing committee.

In this symposium, 6 keynote lectures, 26 invited lectures, 52 oral presentations, and 113 poster presentations were given. About half of them were presented by young researchers under 35 year old. The topics of the symposium were as follows.

- Chemistry and physics of soft materials
- New biomimetic engineering
- Mesoporous materials and nanosystems such as nanocomposite
- New carbon-based materials
- Application of radiation light sciences to advanced materials
- Energy-related materials

Keynote lectures were set at the beginning and the end of each day's program at Chikushi Hall, which has 300 seats. The series of keynote lectures were given by Prof. Chihaya Adachi

(Kyushu University; on new organic EL devices; "Nearly Zero-gap Formation Between Singlet and Triplet Excited States and Their Application for Organic Electroluminescence") and Prof. H.-J. Sue (Texas A&M University, USA; on organic/inorganic nano-composing based on control of interactions among nanoparticles; "Dispersion and Assembly of Nano-materials in Organic Media and Their Nano-scaled Phenomena") on Sep. 20, by Prof. S.C. Kim (KAIST, Korea; on development of fuel cell membrane based on non-fluorine methanol; "Multi-component Polymer Membranes for Direct Methanol Fuel Cell") and Prof. D. Y. Zhao (Fudan University, China; on synthesis of highly-ordered mesoporous carbon materials; "Hydrothermal Synthesis of Ordered Mesoporous Carbon Materials for Applications") on Sep. 21, and by Prof. Dr. B. Ameduri (CNRS, Montpellier, France; on current situation and prospects of fuel cell membrane based on fluorine; "Fluoromembranes for Fuel Cell: Myth or Reality?") and Prof. Masatsugu Shimomura (WPI, Tohoku University; on new biomimetic engineering; "Engineering Biomimetics: Biomimetic Surface Materials Prepared by Self-organization"). All of these lectures were related to new material sciences, and more than 150 participants attended and actively engaged in discussion. After the plenary lectures,

3 subsessions were conducted and invited lectures and oral presentations were given in them. All subsessions had many attendee and productive discussions.

The banquet was held on the evening of Sep. 21, in which many participants attended and winners of encouraging award for young researchers (including 6 oral presenters and 6 poster presenters from Japan, Korea, Taiwan and Russia) were announced and honored. On the last day, participants visited Kyushu Synchrotron Light Research Center and Nakatomi Medicine Museum.

Although the typhoon No. 15, which was approaching on the first day of symposium, worried us, we could complete the program of the symposium without any trouble. I would like to take this opportunity to thank the Society of Polymer Science, Japan, Tokuyama Science Foundation, Global COE Program "Novel Carbon Resource Sciences", and "Science for Future Molecular Systems" and World Premier International Research Center (WPI) Program "International Institute for Carbon-Neutral Energy Research", Kyushu University and all the other co-hosting organizations.



▲ Plenary talk by Dr. B. Ameduri



▲ Invited talk by Prof. Al Crosby



▲ Poster Session



▲ Group Photo



▲ Nakatomi museum of medicine



▲ SAGA Light Source

4th G-COE International Workshop on Energy and Environment in Chemical Engineering

Date September 28, 2011

Venue Research Center for Steel, Ito Campus, Kyushu University

Faculty of Engineering, Kyushu University **Yoshio Iwai**

The 4th G-COE International Workshop on Energy and Environment in Chemical Engineering was held at Research Center for Steel, Ito Campus, Kyushu University on 28 September, 2011. The workshop was co-organized by School of Engineering, Kyushu University as part of its 100th anniversary celebrations. Four speakers were invited from Canada, Italy, Taiwan, and Korea. The number of attendants were 64. The discussions were active during the workshop.

First, Prof. Nagashima who is the project reader of G-COE introduced the project of G-COE at opening address. Then, Dr. Dingan Zhang (Schlumberger, Canada) presented "Reservoir fluid characterization using equation of state". Next, Dr. Jui-Yuan Lee (National Taiwan University, Taiwan) presented "Process integration for water and energy conservation using mathematical approach". After coffee break, Dr. Young Jun Sohn (Korea Institute of

Energy Research, Korea) presented "Fabrication of microstructure controlled cathode catalyst layers and their effect on water management in polymer electrolyte fuel cells". Finally, Dr. Cristiana Figus (Sassari University, Italy) presented "Hybrid organic-inorganic films: from self-organisation to microfabrication".

List of Lectures

Dingan Zhang, DBR Technology Center, Schlumberger, Canada
"Reservoir fluid characterization using equation of state"

Jui-Yuan Lee, National Taiwan University, Taiwan
"Process integration for water and energy conservation using mathematical approach"

Young Jun Sohn, Fuel Cell Research Center, Korea Institute of Energy Research, Korea

"Fabrication of microstructure controlled cathode catalyst layers and their effect on water management in polymer electrolyte fuel cells"

Cristiana Figus, Sassari University, Italy

"Hybrid organic-inorganic films: from self-organisation to microfabrication"



▲ Lecture by Dr. Dingan Zhang



▲ Qs and As with Dr. Young Jun Sohn



▲ Lecture by Dr. Cristiana Figus



▲ Lecturers and G-COE Members

The 4th KU-KU (Kyushu Univ.-Korea Univ.) Joint Workshop on Functional Materials

Date September 28-29, 2011

Venue Seiryu-so, Kumamoto

Faculty of Engineering Sciences, Kyushu University **Tetsuya Kida, Kengo Shimano**

The KU-KU Workshop was launched as an international exchange workshop between Kyushu University and Korea University, managed mainly by students of each university. The 1st workshop was hosted by Korea University in Seoul, Korea in November 2008, the 2nd was hosted by Kyushu University in Oita, Japan in May 2009, and the 3rd hosted by Korea University in Korea University in Seoul in September 2010. The 4th workshop of this time was held in Kumamoto, Japan, hosted by

Kyushu University again.

In this workshop, students from both universities discuss several topics concerning functional devices using oxides in English through oral and poster presentations and Q&A sessions. As exchange events, such as reception party and excursion, are also conducted before and after the seminar, students can learn culture of the host country.

For this workshop, students need to make a lot of kind of arrangements by themselves, such as meeting

with persons in charge, preparation of required equipments, confirmation of operation manner, and management of expenses. All of the hosting students are required to comprehend the whole picture of and act flexibly in the process of the event. It is one of the aims of this workshop to give the students opportunities to get such valuable experiences.

Oral Presentation: 10
Poster Presentation: 9

Research Performance 2011

Awards & Articles

●Award
Distinguished Presentation Award,
The 48th Joint Kyushu Meeting of
Branches Related to Chemistries
(2011/07)

Junpei YAMAGUCHI, Ayuko KITAJOU, Kuniko CHIHARA,
Eiji KOBAYASHI, Shigeto OKADA, Jun-ichi YAMAKI

"Reaction mechanism of Iron sulfide cathode for sodium
secondary battery"

●Award
Chemical Engineering Poster Award,
the 48th Joint Kyushu Meeting of Branches
Related to Chemistries (2011/07)

Koji NAGANO, Shigeru FUJINO, Toshihisa KAJIWARA

"The research of non-contact viscosity measurement
method of melts"

●Award
Asian Young Aerosol Scientist Award
(2011/08)

Toshihiko TAKEMURA

Outstanding contributions to the field and pioneering
works on aerosol-cloud-climate interactions and
the atmospheric aerosol modeling.

●Award
Poster Award, 8th Doctor Students
Seminar in Kyushu University (2011/08)

Kotaro KUNIKAWA, Shigeru FUJINO, Toshihisa KAJIWARA

"Structural changes of silica glass at high temperature
by in situ Raman scattering"

●Award
Award from Steel Foundation of
Environmental Protection Technology
(2011/09)

Koyo Norinaga

"Study on mechanism for catalytic partial oxidation and
steam reforming of coke oven gas"

●Award
Excellent Poster Presentation Award,
Kyushu Branch of the Electrochemical
Society of Japan Talk Shower in kyushu
2011 (2011/09)

Kousuke NAKAMOTO, Sun-Il PARK, Eiji KOBAYASHI,
Shigeto OKADA, Jun-ichi YAMAKI

"Improvement in Anode Performance of NASICON-type
 $\text{Li}_{1-x}\text{Ti}_x\text{PO}_4$ anode for aqueous Li-ion battery"

●Award
Excellent Poster Presentation Award,
Kyushu Branch of the Electrochemical
Society of Japan Talk Shower in
kyushu 2011 (2011/09)

Tetsuro OHKUBO, Norio MIURA

"Improvement in Oxygen Sorption Property of
Sr-Fe-based Perovskite-type Oxides by Substituting
Fe with Ga"

●Award
Best Poster Award, Asian Joint
Conference on Advanced Polymer
Processing (2011/09)

Yue DANDAN, Hironori MIYAKE, Rika YAMADA,
Shigeru FUJINO, Toshihisa KAJIWARA

"Fabrication of nanopatterns on silica glass using
 SiO_2/PVA nanocomposite"

●Award
National Mine Safety Award 2011
(2011/10)

Kikuo Matsui

Contribution to the improvement of mine safety in Japan

●Award
Tanaka Keiichi Prize of the Japan Section
of the Regional Science Association
International (2011/10)

Tadahisa OHNO

"Economic Analysis of Fiscal Externalities and Soft Budget
Constraint"

●Award
Excellent Poster Presentation Award,
Korea-Japan Forum International
Conference on Organic Materials for
Electronics and Photonics (KJF-ICOMEF)
2011 (2011/09)

Takahiro UENO

"Durability improvement of the cycle number in the organic
resistive memory composed of gold nanoparticles and
hyper-branched polymer"

●Award
Japanese Liquid Crystal Society Rainbow
Award (2011/09)

Kota KAKISAKA

"Characteristics of Chiral Liquid Crystal Phases Induced
by Fluorinated Chiral Dopant with Binaphthyl Skeleton"

●Award
Young Scientist Poster Award,
The Fullerenes, Nanotubes and Graphene
Research Society (2011/10)

Yui OGAWA

"Domain structure of CVD graphene grown on
hetero-epitaxial Cu films"

●Award
Best Contribution Award for Young
Scientists, the 12th International
Conference on Organic Nonlinear Optics
(2011/10)

Yuichi MORI

"Synthesis of EO Hyperbranched Polymer having High
Glass Transition Temperature and Temporal Stability"

●Award
Best Paper Award, International
Conference on Pipelines and Trenchless
Technology (2011/10)

Yanlong Chen, Hideki Shimada, Takashi Sasaoka,
Kikuo Matsui, Koichi Araki, Dai Watanabe

"Application and Numerical Analysis of Chemical Grouting
Restoration Method for Pipeline Position"

●Report
Research paper written by Dr. Hironori
Tsutsumi was selected as a "Hot Article"
for Chemical Communications and currently
featured on its website and blog.
(2011/06)

Hironori TSUTSUMI, Yusuke SUNADA, Hideo NAGASHIMA
"New catalyst systems for iron-catalyzed hydrosilane
reduction of carboxamides", Chem. Commun., 47, pp.
6581-6583 (2011).

●Report
The Nikkei (2011/09/06)
Tsuyoshi HIRAJIMA

福岡県は6日、三井金
属子会社の日本イットリ
ウム(福岡県大牟田市)
など使用済み蛍光管から
レアアース(希土類)
を回収する事業を2011
1年度内に始めると発表
した。蛍光管からイット
リウムやランタンなど5
種類のレアアースを抽出

蛍光管から レアアース

して、磁石やセラミック 備の規模や回収したレア
アースの原料として再資源化 アースの販売価格の決め
する。同県によると事業 方を固めたうえで事業を
化は全国初という。 始める。ジェイ・リライ
福岡県など、今年度に事業化
同県と日本イットリウ ムが九州地区などの事業
ム、蛍光管リサイクルの 所や家庭から蛍光管を集
ジェイ・リライツ(北九 めて蛍光管を取り出し、
州市)などが共同で、設 日本イットリウムがレア

「国内資源」に期待

アースを抽出する。 年間約57で、約25億円
に相当する。
蛍光管からのレアア ー レアアースは中国が主
な産地で、日本は安定調 達が必要になっている。
算を確保することが難し かつたが、効率よく不純
物を取り除く方法にメド は「うまく取り出せば、
国内に資源があること」に なる。海外依存を減らせ
る5種類のレアアースは 「と期待感を示した。

●Report
Nikkan Kogyo Shimbun (2011/08/17)
Shigeru FUJINO, Toshihisa KAJIWARA

●Report
Asahi Newspaper (2011/09/06)
Tsuyoshi HIRAJIMA

福岡県は6日、ハイテク製品に欠
かさないレアアース(希土類)を全
国初めて使用済み蛍光管から回収
し、来年3月に事業化すると発表
した。レアアースは主要輸出国の
中国が生産量を激増、価格が急騰
中。記者会見で川津知事は「資源
の乏しい日本にとっては資源の安全
確保の上で重要」と語った。
県によると、事業化に向け、蛍光
管回収処理業者ジェイ・リライツ
(北九州市や山崎大学の平瀬南
教授が代表取締役)と三井金属など
と共同プロジェクトを立ち上げる。
蛍光管に使われる蛍光粉にはイッ

福岡県が事業化 全国初

トリウム(ランタン、セリウム、テル
ビウム、ユロビウム)の5つのレア
アースが含まれる。蛍光粉はシリ
コンの微粒子、LED蛍光管は
オキシドにも使われる九州では使用
済み蛍光管が年間350万本、本
県へ手回数は約57万(約6割)と
多い。レアアースを取り出す
5つのレアアースはほとんどが中
国産。輸入価格は高騰を続け、1年前
に比べセリウムは約1.5倍、イットリ
ウムは約1.8倍、最も高いユロビウム
は1日現在、1.5倍に達している。来
年度は計9ヶ所、販売価格4億
円の回収を目指す。

レアアース 福岡県が回収

福岡県は6日、三井金属
業(東京)や九州大など共
同で、使用済み蛍光管からレ
アアース(希土類)を回収、
再資源化する事業を来年3月
から始めること発表した。蛍光
管からのレアアースリサイク
ルを事業化するのは全国で初
め。県は来年度「環境・エネ
(約1億円相当)の販売を規
定しており、輸入価格が高騰
しているレアアースの安定需
求を目指す。
レアアースはイットリウム、テルビ
ウム、ユロビウムなど約10種類の元素
の総称でパソコンや携帯電話の部品
やデジタルカメラのレンズなどに使わ
れる。蛍光管では一本当たり1.4
3.5グラム使用されている。発表によ
ると、他に参加するのは東リサイクル
合資会社(福岡市)と三井物産有
限責任会社(福岡市)と九州大と
福岡県環境・エネルギー部。日本
イットリウム(福岡県大牟田市)ジェ
イ・リライツが九州、四国、中国地方
の自治体や企業から、使用済み蛍光
管を回収し、使用済み蛍光管
を分解して蛍光粉を取り出す。
日本イットリウムがセリウムなど希
土類のレアアースを抽出し、精製する。
レアアースについては、日本は輸入
量の8割を中国に依存。中国産が輸
出を縮小し、価格が高騰している。

●Report
Yomiuri Newspaper (2011/09/06)
Tsuyoshi HIRAJIMA

使用済み蛍光灯から

石英ガラス 焼成前に微細加工 九大が成形法 高いメツキ密着性



【福岡】九州大学大
学工学研究科の藤野茂准
教授らは、穴あけやメッ
キなどの加工を焼成前
に行うことで、微細加工や
密着性が高いメッキが可
能な石英ガ
ラスの成形
法を開発し
た。
実験では
直径23・7
クロは10
0万分の
1)の穴を
成形、穴表
面のひらに
乗せた石英
ガラスを焼
結前と焼
結後(左)

面に通電性を持つメッキ
加工も可能。微細加工や
機械システム(MEM
S)なへの応用が期待
できるという。
材料は石英とポリニ
ルアルコール(PVA)
など。材料の水溶液を
攪拌し、乾燥させた後に
焼成して製作する。水溶
液中に材料を均一に分散
させる素材を使うこと
や、水素イオン濃度
(pH)調整剤でpHを調整
することが技術のポイント
だという。
焼成にお収縮する前
に加工するため、微細加
工しやすい。また、焼成
前は直径数ミリの(ナノ

は10億分の1)ほどの穴
があいた多孔質のため、
メッキ液が浸透しやす
い。
材料や焼成環境を操作
することで色を付けるこ
とも可能。カーボンナノ
チューブ(CNT)を分
散させれば導電性を持つ
透明な石英ガラスも作れ
る。凹凸を作るには液体
の段階で泡に流し込む。
従来、石英ガラスの加工
には酸を使うこともあっ
た。開発した製法は環境
負荷の低減にもつながる
という。
石英ガラスは絶縁性や
透明性、薬品に強いなど

が特徴。今回の成果は半
導体製造装置部品やエレ
クトロニクス分野の光デ
バイス、バイオテクノロ
ジー分野の研究で使われ
る反応装置部品などに使
われる可能性がある。
藤野准教授は「さまざ
まなユーザーに提案して
技術的要望を聞き、製法
に反映させながら事業化
につなげたい」と話して

蛍光灯からレアアース 県など全国初の回収事業

福岡県は6日、使用済み蛍光灯からレアアース（希土類）を回収し再資源

化する事業に産学官共同で乗り出すと発表した。全国初の試みで本年度中に事業化する見通し。県などによると、現在使用済み蛍光灯はリサイクル企業で分解処理され、ガラスや金属、水銀は回収・再利用されるが、蛍光灯内の蛍光粉に含まれるレアアースは抽出技術が確立されてない上、採算に合わずほとんど再利用されていないという。

福岡県リサイクル総合研究センターは、北九州市のリサイクル蛍光灯製造・販売会社「ジェイ・リライツ」と九州大学理工学研究院が共同で取り組んできた回収蛍光粉のレアアース濃度を高める技術と、三井金属と大牟田市のレアアースメーカー「日本イットリウム」の蛍光粉からレアアースを抽出・精製する技術に着手。

レアアースの市場価格が1年前から7〜17倍に伸び、採算ベースに乗るようになったため、事業化に乗り出すことになった。

蛍光粉に含まれるレアアースはイットリウム、ランタン、セリウム、テルビウム、ユーロビウムなどの種類で、ほとんどが中国で産出される。九州で排出される1年間の使用済み蛍光灯が全て回収されればレアアースの回収量は約57ト、約25億円分と推定されるという。

県循環型社会推進課は「輸入に依存しているレアアースの安定確保に貢献できる」としている。

蛍光灯からレアアース

今年度から 福岡県が産官共同で

福岡県の小川洋知事は6日、古くなった蛍光灯からレアアース（希土類）を取り出し、精製・販売する事業を今年度から産官共同で始めると発表した。蛍光灯には「イットリウム」などレアアース5種が使われているが、国内では再資源化する仕組みがなく、全国初の試みという。

県環境部によると、事業は、抽出・精製技術をもつ三井金属鉱業（東京）、回収処理業（北九州市）など3社との共同プロジェクトで実施する。九州、中国地方でジェイ社が蛍光灯を回収してきた実績などから、事実上の

初年度にあたる12年度は9ト、約4億円の販売を目指している。廃蛍光灯の排出量は全国で年間約4億本に上り、ガラスや水銀は再利用されているが、含まれるレアアース類約500トはほとんどが廃棄されている。一方、レアアースの産出国は中国などに限られる、「ユーロビウム」などは時価1ト約38万円と高騰している。

これまでは、各業者が個別に回収や抽出をしていたが、県がそれらの業者を結びつけ、資源の有効利用を図ることにした。小川知事は「事業化が軌道に乗れば、資源外交面での安全保障の強化にもつながる」と話した。

【林田雅浩】

使用済み蛍光管の レアアース回収へ

福岡県の小川洋知事は6日、使用済み蛍光管から、ハイテク機器の部品に使われるレアアース（希土類）を抽出、精製して販売する事業に、来春から産官学共同で取り組みと発表した。蛍光管には5種類のレアアースが使われているが、これまで再利用する仕組みがなく、事業化は全国初となる。

県リサイクル総合研究センター、三井金属鉱業と関連会社の日本イットリウム（福岡県大牟田市）、蛍光管回収処理業のジェイ・リライツ（北九州市）、九州大との共同プロジェクト。初年度はレアアース約9トン（市場価格約4億円）の精製、販売を目指す。

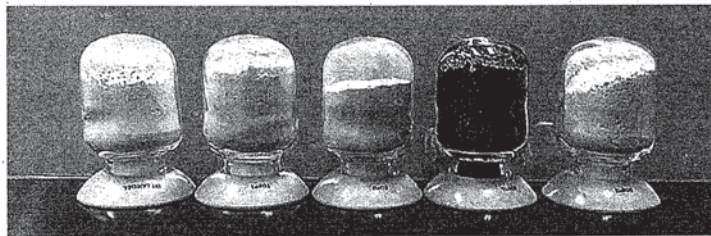
県によると、蛍光管の内側にまぶされている「蛍光粉」には5種類のレアアースが1本あたり計1・4～3・5g含まれている。

蛍光管は年間約4億本が廃棄され、ガラスや金属、水銀は再利用されている。レアアースは技術面や採算面からほとんど再利用されなかったが、共同プロジェクトによる新技術開発の結果、レアアース全5種類の抽出が可能になった。

県によると、ジェイ・リライツが蛍光管から蛍光粉を回収。三井金属鉱業と日本イットリウムが抽出・精製し、ハイテク製品メーカーなどに販売する。

レアアースの輸入価格は高騰が著しく、蛍光管に含まれるイットリウムはこの1年間で約16倍の1・1約1万2300円に、ユーロビウムは約

5種類抽出→精製→販売 福岡県など来春にも事業化



蛍光管に使用されている5種のレアアース。左からイットリウム、ランタン、セリウム、テルビウム、ユーロビウム（福岡県提供）

9倍の1・1約38万円に跳ね上がっている。一方、国内で使用済み蛍光管に付着したまま破棄されるレアアースは年約500トンにのぼるとみられている。

小川知事は「これだけの量を再利用できれば海外依存度を大きく下げられ、資源外交面での安全保障の強化にもつながる」と話している。

●Report
Sankei Newspaper
(2011/09/07)
Tsuyoshi HIRAJIMA

ナトリウムイオン二次電池 電解質に水溶液 試作成功



水溶液のナトリウムイオン二次電池（九大・岡田准教授提供）

九大

九州大学の岡田重人准教授らの研究グループは、安価な次世代二次電池として期待されるナトリウムイオン二次電池で、電解質に水溶液を使った電池の試作に成功した。実用化すれば、既存のリチウムイオン二次電池に比べ4分の1程度にコストを下げられるという。

コスト4分の1に
充放電できる負極発見

試作した電池は「リチウムイオン二次電池」で、容量は既存のリチウムイオン二次電池と比べ5分の1程度。今後、大容量を進めるとともに、より実用に近いコインセルタイプでも動作できるように改良を進める。容量はリチウムイオン二次電池の75%程度まで高められる可能性があると、岡田准教授は語る。

新入道 道人 新入道

●Report
Nikkan Kogyo Shimbun
(2011/11/10)
Jun-ichi YAMAKI, Shigeto OKADA

できるが、電圧が高くないセルタイプで、容量は既存のリチウムイオン二次電池と比べ5分の1程度。今後、大容量を進めるとともに、より実用に近いコインセルタイプでも動作できるように改良を進める。容量はリチウムイオン二次電池の75%程度まで高められる可能性があると、岡田准教授は語る。

既存のリチウムイオン二次電池の電解質に使われている有機溶媒は、材料コストやプロセスコストがかさむ上、燃えやすく取り扱いが難しい。電解質を水溶液に置き換えることが欠点解消

したタイプは、経済性や安全性のメリットを生かせるとして、電力平準化など大型電池を主な用途に想定している。

一方、リチウムイオン二次電池のリチウムイオンをナトリウムイオンに置き換え、ナトリウムイオン二次電池が、安価な材料が負極として使えることが、電圧が低くないセルタイプで、容量は既存のリチウムイオン二次電池と比べ5分の1程度。今後、大容量を進めるとともに、より実用に近いコインセルタイプでも動作できるように改良を進める。容量はリチウムイオン二次電池の75%程度まで高められる可能性があると、岡田准教授は語る。

Fuels and Energy Research in Curtin University

Dehua Dong

Fuels and Energy Technology Institute, Curtin University



Curtin University is a largest university in Western Australia where resources and energy sector has grown phenomenally in the past few decades and is now the powerhouse of the national economy and an international leader. For example, it is home to over 80% of Australia's natural gas reserves. [1] There are plenty of mallee trees, which are promising for WA's energy of future. [2] The strategic area of resources and energy is one of the five Curtin University's research foci and major areas of research strength.

The Fuels and Energy Technology Institute (FETI) is the research hub of Curtin University for research into energy science and engineering and developing low-emission energy technologies. Since its establishment (previously as Curtin Centre for Advanced Energy Science and Engineering), FETI has been growing into a primary research centre of excellence in this strategic area, recognised locally and internationally. At present, FETI has a total of close 40 research staff and postgraduate students. FETI is a world-leading research institute in developing innovative clean energy technologies, with various patents in this important area. FETI has over 8 research laboratories dedicated to research into clean fuels and energy technologies. It also houses ~\$8 million worth of research infrastructure including a series of advanced reactor systems and state-of-the-art analytical instruments.

The research conducted in the FETI covers six areas:

1. Coal Science and Technology

- Gasification;
- Oxy-fuel combustion;
- Production of liquid fuels and chemicals from the lignite via pyrolysis and refinery;
- Transformation of inorganic species in coal during conversion;
- Utilisation of solid wastes from coal gasification and combustion;
- Coal structure and properties.

2. Bioenergy Science and Technology (e.g. mallee trees)

- Biomass gasification for distributed power generation;
- Production of liquid fuels/chemicals from biomass via pyrolysis and bio-refinery;
- Production of liquid fuels/chemicals from biomass via hydrolysis and subsequent fermentation;
- Bio-char for soil conditioning and carbon sequestration.

3. Natural Gas Conversion Engineering

- Catalytic and/or electrochemical partial oxidation (reforming);
 - > Synthesis gas generation.
 - > Hydrogen production.
 - > Liquid fuels/chemicals.
- Fundamental research on radicals desorption from catalyst surface
 - > Initiation of gas-phase reactions with catalyst;
 - > Reduction of coke formation and catalyst deactivation;
 - > Formation of carbon materials;
 - > Ultra-short contact time catalysis.

4. Fuel Cells

- Solid oxide fuel cells (oxygen ion conductor and proton conductor), low temperature proton exchange membrane fuel cells and solid oxide electrolysis cells;
- Development and synthesis of nanostructure electrodes and novel catalysts;
- Hydrocarbon-fuelled fuel cells such as methanol and natural gas.

5. Energy Storage

- Hydrogen storage materials;
- Material characterisation such as X-ray diffraction.

6. Environmental Impacts of Energy Processes:

- Life cycle analysis: Analysis of energy balance and CO₂ emission in terms of full life cycle;
- Reduction of air pollutants such as NO_x, SO_x and particulates.

FETI has a substantial international collaboration network, especially with researchers in China, Japan, Korea, Denmark and USA. The Institute continues to seek productive international collaboration, particularly with top research organisations in the Asia-Pacific region. As a principal member of partner institutions of NCRS G-COE, FETI had successfully hosted the 5th International Symposium in April 2010.

References

1. <http://www.chemlink.com.au/gas.htm>
2. <http://www.sciencewa.net.au/3256-is-mallee-was-energy-of-the-future.html>



Kyushu UniversityG-COE program
“Novel Carbon Resource Sciences” secretariat

6-1 Kasuga-Koen, Kasuga, Fukuoka, 816-8580 Japan
TEL: 092-583-7616 FAX: 092-583-7619
Email: ncrs@cm.kyushu-u.ac.jp
URL: <http://ncrs.cm.kyushu-u.ac.jp>