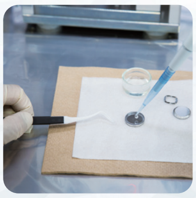
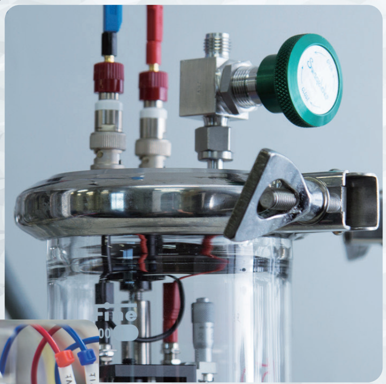
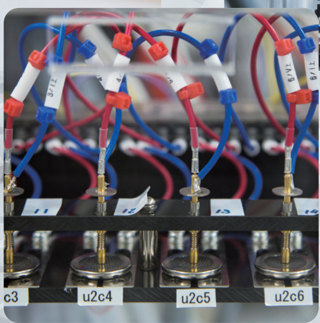
A L C A Advanced Low Carbon Technology Research and Development Program

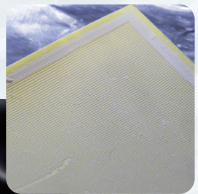
# SPRING

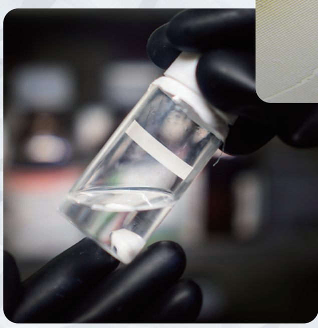
Specially Promoted Research for Innovative Next Generation Batteries









Japan Science and Technology Agency

ALCA
Change the game with technologies!

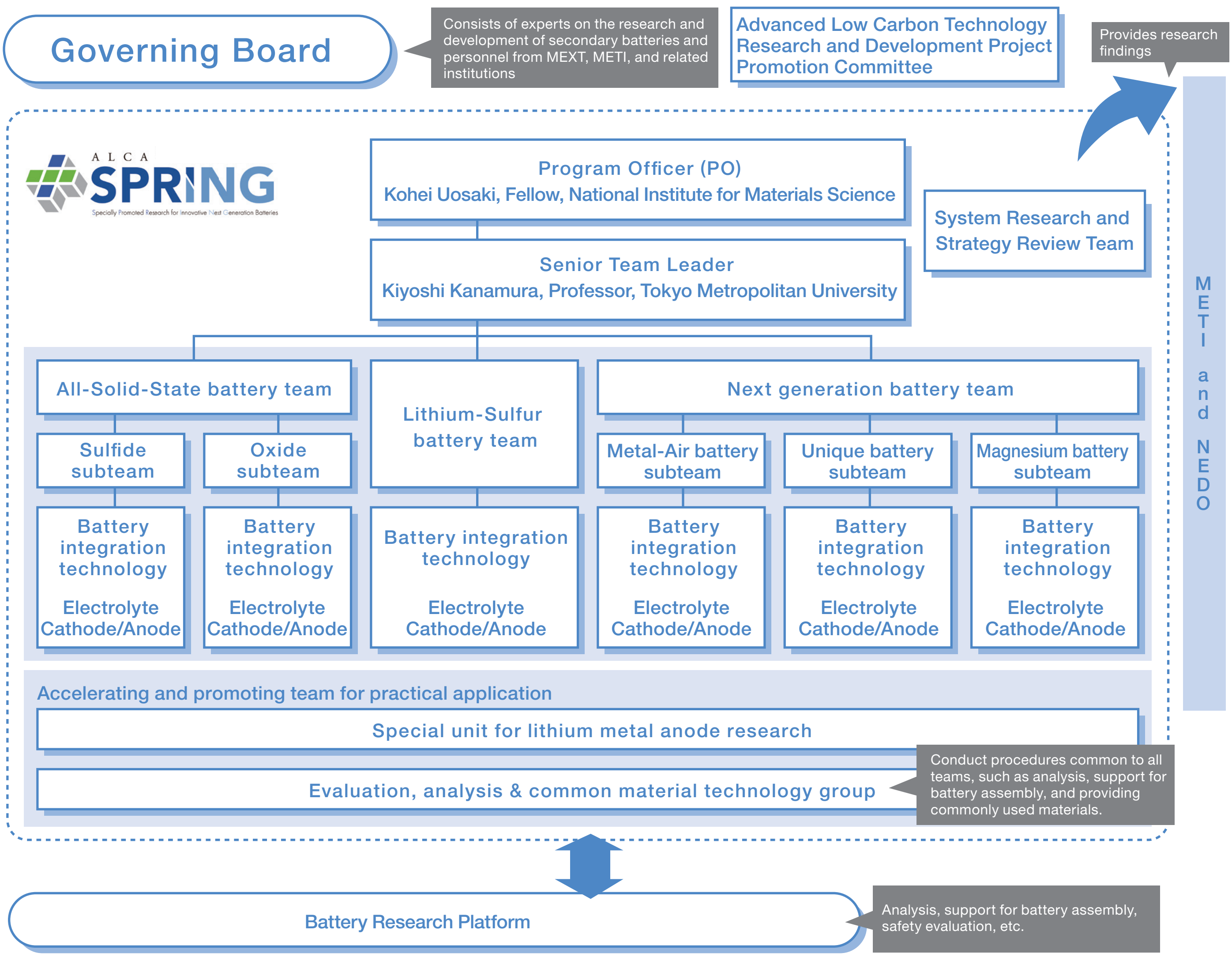
# Message from ALCA-SPRING PO

Low-cost and high-performance next-generation secondary batteries are essential for reducing car emissions, which account for around 10% of the total carbon dioxide emissions, and for stabilizing renewable energy supply, and yet, the energy and power densities of currently popular lithium ion batteries are limited, requiring the development of innovative next generation secondary batteries.
Following a joint panel conducted by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the Ministry of Economy, Trade and Industry (METI) in the FY 2012, which focused on next generation secondary batteries, this project was launched in July 2013.
Four types of the candidate next generation secondary batteries were selected to be studied by four teams. The teams were structured so that each of them could undertake a complete study of the respective battery cells. The project is massive in scale, consisting of over 40 institutions and over 80 research representatives in total. We appreciate your support for the efforts of many researchers, which we hope will lead, as a whole, to achievements on next generation secondary batteries.

ALCA-SPRING Program Officer (PO)
Kohei Uosaki
(Fellow, National Institute for Materials Science)

## Features of ALCA-SPRING

ALCA-SPRING promotes research adopting a top-down approach, with the clear goal of making batteries. It is often the case that even if a battery material shows excellent properties under specific conditions set by the researchers, it is insufficient for practical use. ALCA-SPRING is promoting research on materials with the aim of battery fabrication. To advance such work smoothly within a limited budget and to put it to practical use, a top-down approach will be effective. To actually use a battery developed as part of this project in real applications, various technical issues such as those concerning the cycle life and safety need to be resolved and the energy density needs to be improved. Through steady efforts to identify the functions of a battery, design them according to required specifications, and develop and test several prototypes, we aim to produce innovative batteries for application.



# Message from ALCA PD

ALCA Program Director (PD)

Kazuhito Hashimoto

(President, National Institute for Materials Science)

At ALCA, we have traditionally adopted a bottom-up research and development approach where we encourage individual researchers to submit project proposals. However, as we operate under this system, we have come to strongly recognize the need to promote the "top-down research and development approach with predetermined target products and systems that enhance the probability of achieving a low carbon society."
To accelerate the implementation of our findings in the society, we have already begun to submit our findings to the New Energy and Industrial Technology Development Organization (NEDO) under METI. With regard to our intellectual property, which is an important issue in transferring our findings, our System Research and Strategy Review Team discuss our patent managements based on both open and close strategies.
Through these efforts, we will continue to operate our projects that will hopefully contribute to our country and ultimately to the world. We appreciate your continued support.

## Outline of ALCA

Advanced Low Carbon Technology Research and Development Program (ALCA) is a project launched in 2010 with the aim of promoting competitive research and development of promising technologies for the reduction of greenhouse gas emissions. Aiming toward a low-carbon society, ALCA has been attempting to reduce $CO_2$ generation through energy generation, energy storage, and undertaking of carbon neutral processes and to lower $CO_2$ emissions through energy saving.

## ALCA operation system

According to the current operation system, the Program Director (PD) of ALCA oversees its entire operations and each Program Officer (PO) is responsible for the general management of the project running under Special Priority Research Areas, Innovative Technology Areas and ALCA Enabling Technology Projects. The Advanced Low Carbon Technology Research and Development Project Promotion Committee—the supreme decision-making body—is chaired by the PD and consists of POs and external experts and professionals. The Committee is responsible for discussing important matters regarding the operation of ALCA, including determining the technological areas, selecting candidate projects, and deciding on the continuation of projects based on stage-gate evaluations.

Program Director (PD)
**Kazuhito Hashimoto**

**Advanced Low Carbon Technology Research and Development Program Promotion Committee**

**ALCA Technology Areas**

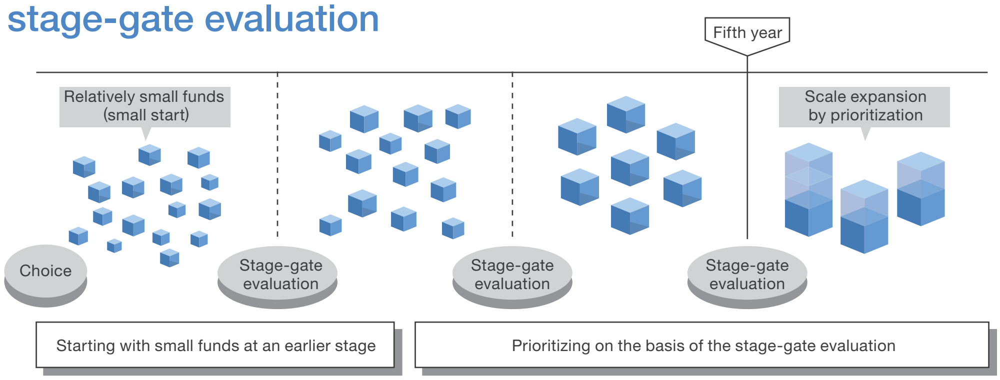
| Type | Project title | Program Officer (PO) |
|---|---|---|
| Special Priority Technology Areas | Next Generation Batteries | **Kohei Uosaki** (Fellow, National Institute for Materials Science) |
| | White Biotechnology | **Yoshiharu Doi** (President, Japan Synchrotron Radiation Research Institute) |
| Game-Changing Technology Areas | Solar Cell and Solar Energy Systems | **Atsuhiro Osuka** (Professor, Kyoto University) |
| | Superconducting Systems | **Hiroyuki Ohsaki** (Professor, University of Tokyo) |
| | Electric Storage Devices | **Tetsuya Osaka** (Advisor to the office of the President, Senior Research Professor, Emeritus Professor, Waseda University) |
| | Ultra-Heat-Resistant Materials and High Quality Recyclable Steel | **Kohmei Halada** (Invited Researcher, National Institute for Materials Science) |
| | Biotechnology | **Akihiko Kondo** (Professor, Kobe University) |
| | Innovative Energy-Saving and Energy-Producing Chemical Processes | **Takashi Tatsumi** (President, National Institute of Technology and Evaluation) |
| | Innovative Energy-Saving and Energy-Producing Systems and Devices | **Kenji Taniguchi** (Specially Appointed Professor, Osaka University) |

**ALCA Enabling Technology Projects**

After an initial five years spent on projects in the Innovative Technology Area, we will be integrating the elemental technologies in order to accelerate the projects toward implementation in 2030.

## Choice and focus by stage-gate evaluation

As one of the features of the project management at ALCA, we conducted a stage-gate evaluation during the research period to decide on whether to continue the research. The evaluation is made not only in light of the scientific merit, but also in the light of the potential to contribute toward a low-carbon society, the goal of ALCA.



# All-Solid-State battery team


- Team leader, sulfide subteam leader:
  Masahiro Tatsumisago (Professor, Graduate School of Engineering, Osaka Prefecture University)
- Oxide subteam leader:
  Kazunori Takada (Deputy Director-General, Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science)


## Why all-solid-state batteries?

All-solid-state batteries are leakage-free safe batteries without flammable electrolyte solutions and are expected to show potential for use over a wide temperature range, increased voltage owing to series connections, and increased energy density through the simplification of the safety mechanism. Recently, the sulfide subteam has discovered a solid electrolyte with an ionic conductivity exceeding that of conventional electrolyte solution systems and proposed the possibility that all-solid-state batteries are superior to conventional systems with respect to output and low-temperature performance, which have so far been considered disadvantages.
All-solid-state batteries are expected to be used as power sources such as for cars, in particular.

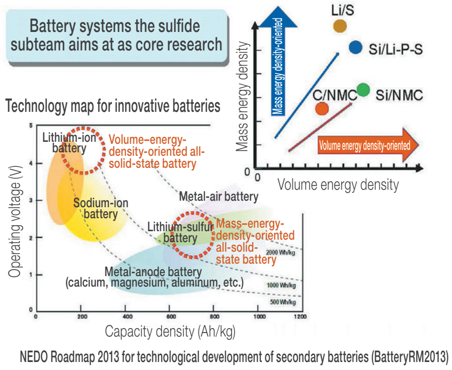
## World-leading research

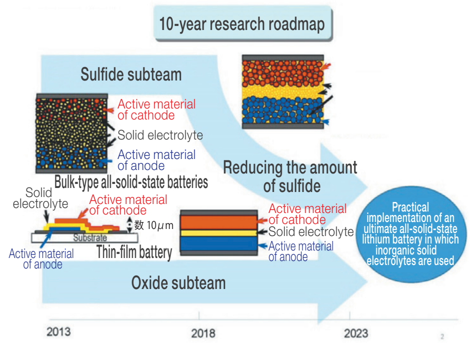
- Research conducted by the sulfide subteam is considered to be pioneering in the development of materials with high ionic conductivity and application of the materials.
- The oxide subteam has focused its efforts on ion conduction at the solid–solid interface and succeeded in stable operation of a battery.

## Results obtained

( Sulfide subteam )
- Developed a solid electrolyte with the highest conductivity ever achieved.
- Established a new electrode structure to make the maximum use of sulfur, which has an extremely high capacity density.
- Developed an original practicable process for making electrode composites.
- Started collaboration with the Consortium for Lithium Ion Battery Technology and Evaluation Center (LIBTEC).

( Oxide subteam )
- Made an oxide-based all-solid-state battery and succeeded in operation of the battery at temperatures under 50°C for the first time.




### Creation of solid electrolytes showing the highest conductivity ever achieved

Proposing a solid electrolyte map as a guiding principle for practical use of all-solid lithium batteries

| Composition | Synthesis methods | Structure | Ionic conductivity (S/cm) | Stability against lithium | $LiCoO_2$ 3.9 V | $Li(Ni,Mn)O_4$ 4.7 V | Li-In 0.6 V | Li 0 V |
|---|---|---|---|---|---|---|---|---|
| $Li_{3+x}PS_4$ | Milling, sintering | α-$Li_3PS_4$ type | 9.50E-04 | Stable | ◎ | — | ◎ | ◎ |
| Li-(Sn,Si)-P-S, ss | Milling, sintering | Argyrodite type | 3.90E-05 | Unstable | — | — | — | — |
| $Li_{3.5}Ge_{1.5}P_{0.5}S_6$ | Sintering, annealing | Unknown | 3.20E-04 | Unstable | ◎ | — | ◎ | × |
| Li-(Sn,Si)-P-S, ss | Milling, sintering | $Li_{10}GeP_2S_{12}$ (LGPS) | 3.31E-03 | Stable | ◎ | — | ◎ | △ |
| $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ | Milling, sintering | $Li_{10}GeP_2S_{12}$ (LGPS) | 2.5E-02 | Unstable | ◎ | — | ◎ | △ |

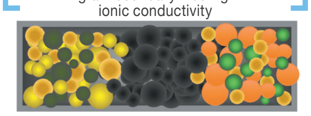
**Argyrodite-type: Electrolyte suitable for a high-voltage cathode**

Electrolyte for cathodes:
Resistance to oxidation; cathode–electrolyte interface
Ionic conductivity

$LiCoO_2$, $Li(Ni,Mn,Co)O_2$, $Li(Ni,Mn)O_4$

**$Li_{10}GeP_2S_{12}$ (LGPS)-type: Electrolytes with superionic conductivity for high-power application**

Electrolyte:
Formability (prevention of a short circuit), grain boundary-freeHigh ionic conductivity



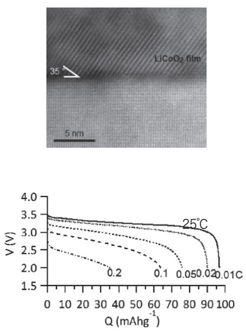
**α-$Li_3PS_4$-type: electrolyte suited for anodes**

Electrolyte for anodes:
Resistance to reduction; anode-electrolyte interface
Ionic conductivity

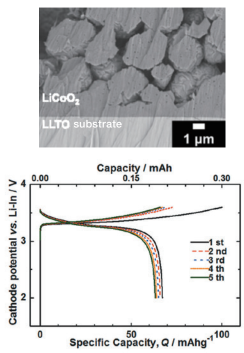
Li/In, Li/Al, Carbon, Li

Contributes to practical implementation by applying appropriate solid electrolytes to each part of all-solid-state batteries

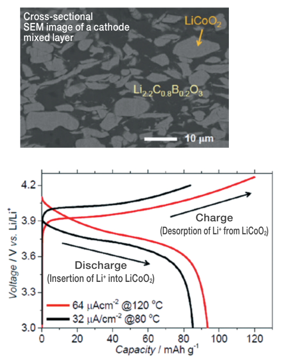
### Interface formation for oxide-based solid electrolytes




① Interface formation by a sol-gel process




② Interface formation by a flux method




③ Interface formation using plastic electrolytes

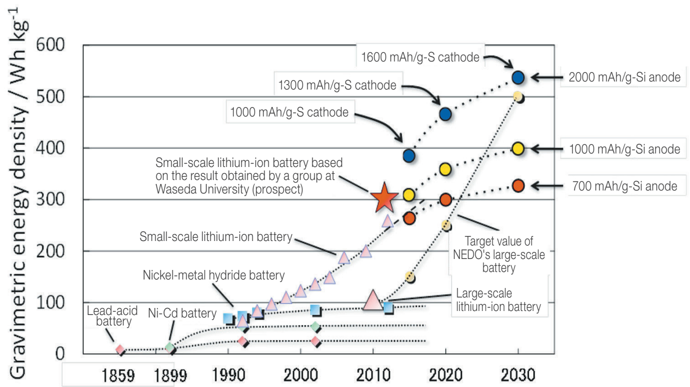
- The largest issue in the development of oxide-based all-solid-state batteries is the formation of a low-resistance interface.
- ALCA-SPRING succeeded in reducing the interface resistance by various methods ( ①-③ ) and also succeeded in operating oxide-based all-solid-state batteries in a temperature range from room temperature to about 120°C.

# Lithium-Sulfur battery team

Team leader:
Masayoshi Watanabe
(Professor, Faculty of Engineering, Yokohama National University)

## Why sulfur batteries?

We use sulfur, which has a capacity density about ten times higher than that of existing cathodes for lithium-ion batteries, as a cathode active material. Because high-purity sulfur produced from the desulfurization of oil is abundant in Japan, sulfur batteries are expected to be inexpensive batteries with high energy density.




Changes in and target values of energy density of secondary batteries

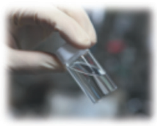
## World-leading research

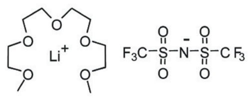
Using a unique solvated ionic liquid as the electrolyte solution solved the primary problem of sulfur batteries: the dissolution of cathode reactants in the electrolyte solution.

## Results obtained

- Developed an ionic liquid that can reduce dissolution of sulfur-based cathode active materials.
- A prototype battery with about 2 Ah capacity was produced and a cycle evaluation was conducted for about 800 cycles in the laboratory. Actual battery implementation is within sight.
- Problems of insulation and volume change observed upon charge-discharge cycles were resolved by optimizing the nanostructure of cathodes and anodes.

### Solvated ionic liquid-based electrolyte solution —Non-flammable! Elution-preventing!






[Li(G4)$_1$][TFSA]

- Liquid at room temperature
- Low vapor pressure and non-flammable
- Transport number of Li ion is > 0.5.
- Li ion concentration is > 3 mol/L.
- Ionic conductivity $\sigma$ is about $10^{-3}$ S cm$^{-1}$.

Combustion test

Fig. 1 mol dm$^{-3}$ Li[TFSA]/EC-DMC (left), and [Li(G4)$_1$][TFSA] (right).

Electrolyte solution that prevents polysulfide (PS) from eluting

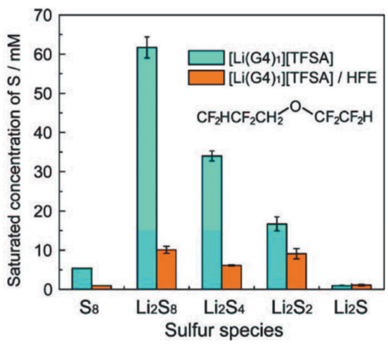
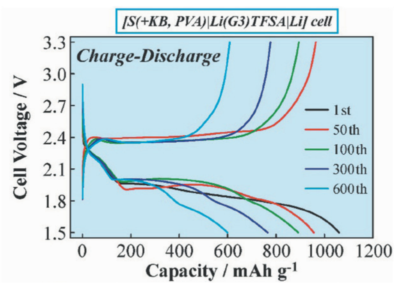
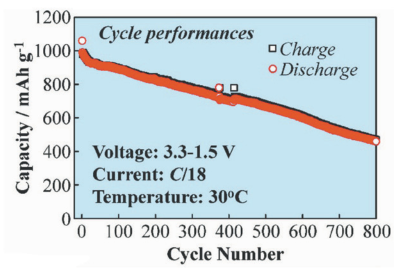


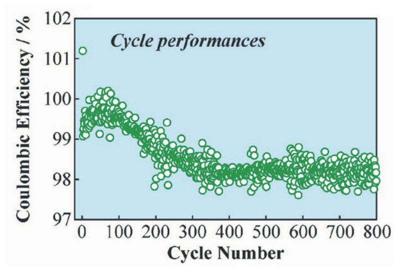

Figure. Comparison of $S_8$ and $Li_2S_m$ solubility limits in [Li(G4)$_1$][TFSA] and [Li(G4)$_1$][TFSA]/HFE (molar ratio of Li[TFSA]/G4/HFE = 1:1:4) at 30℃. The structure of HFE is shown in the inset.

**Development of such an elution-resistant electrolyte solution has been achieved for the first time**

### Long-term test of lithium-sulfur batteries




- [S/G3-LiTFSA 1:1 complex/Li] cell
- Measurement temperature: 30°C (around room temperature)
- Cutoff voltage: 3.3-1.5 V
- Current density: C/18

☆ Maintained a capacitance larger than 600 mAhg$^{-1}$ for more than 600 cycles
⇒ An issue of how to prevent capacity from declining remains.
☆ Showed extremely high coulombic efficiency (>98%) for 800 cycles
⇒ **The best in the world**

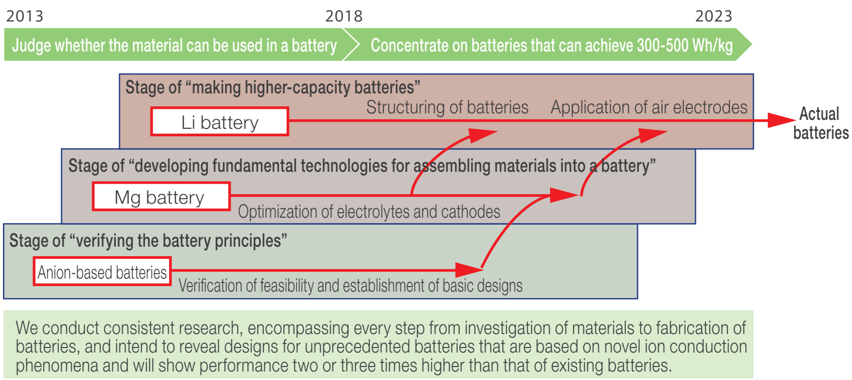
**Properties that could lead to 300 Wh/kg of energy density were obtained.**

# Next generation battery team


- Team leader, Unique battery subteam leader, Magnesium battery subteam leader:
  Kiyoshi Kanamura (Professor, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University)
- Metal-Air battery subteam leader:
  Yoshimi Kubo (Team Leader, Lithium Air Battery Specially Promoted Research Team, C4GR-GREEN, National Institute for Materials Science)


## Why next-generation batteries?

Next generation batteries will be based on game-changing technologies so their performance can exceed that of lithium-ion batteries. To achieve a further breakthrough, we need to work on the development of novel batteries by deviating from conventional ideas. We also seek new applications for not only batteries having high energy densities but also batteries with other distinguishing features, such as attractive cost and safety features.

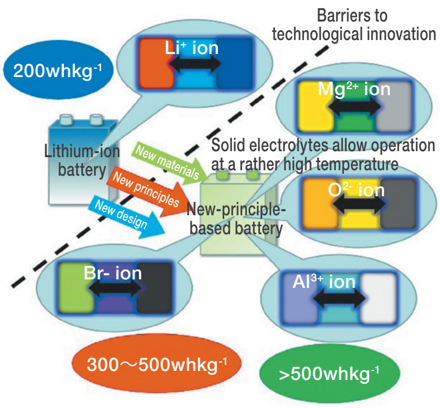



## World-leading research

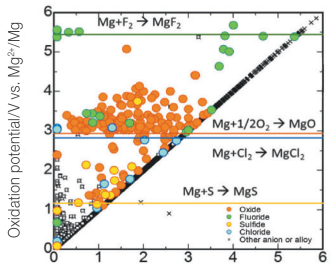
- The team focuses attention on multiple-charged ion batteries, in which multiple electrons move as one metal ion reacts, and is conducting a study on Mg-ion batteries. Mg is abundant and Mg-ion batteries have the potential of exceeding lithium-ion batteries in volume energy density. We have resolved the issues of dissolution and deposition of Mg and developed a new electrolyte solution system.
- In our team, experts are exchanging information and are promoting team research on, for example, Li-air batteries that have an extremely high theoretical capacity density, anion batteries with anionic carriers, and lithium-metal batteries with structured electrolytes, by implementing ideas deviating from common knowledge.

## Results obtained

- Made it possible to stably perform reversible deposition-dissolution of magnesium using special electrolyte solutions and additives.
- Made prototypes of zinc- and aluminum-metal secondary batteries using ionic liquids and found them to function successfully before anyone else in the world.
- Made a prototype of lithium air batteries with the highest energy density in the world.



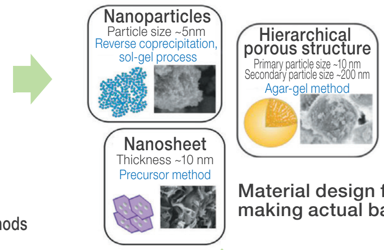

## Development of magnesium secondary batteries



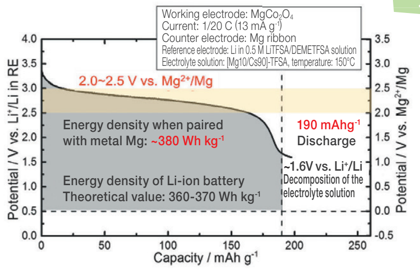
Search for new materials using computational methods

Fabrication of porous spinel oxides with high specific surface area by three approaches

$MgCo_2O_4$ with a structure suited for ion diffusion and electron transfer (Specific surface area: >100m$^2$g$^{-1}$)



Material design for making actual batteries

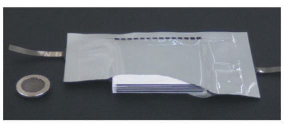


Electrode design for making actual batteries

## Development of lithium-air secondary batteries —Aiming toward the ultimate energy density

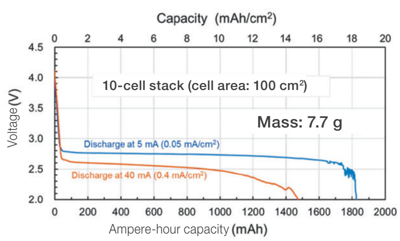
**Purpose** Development of a fundamental technology for lithium-air secondary batteries, which is expected to have the highest energy density

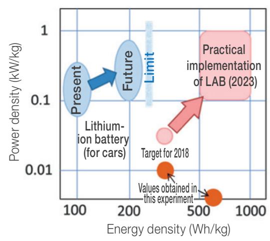
**Result** The world's first development of stack technology, indispensable for practical implementation of lithium-air batteries


A coin cell made of a lithium-air secondary battery and a stack of ten cells (internal structure) The stack shows a capacity 100 times larger than that of the coin cell


Demonstration experiment using a stack of lithium-air batteries

**Result** Demonstrated 600 Wh/kg of energy density (the highest in the world: that of current LIBs is 100–150 Wh/kg.)



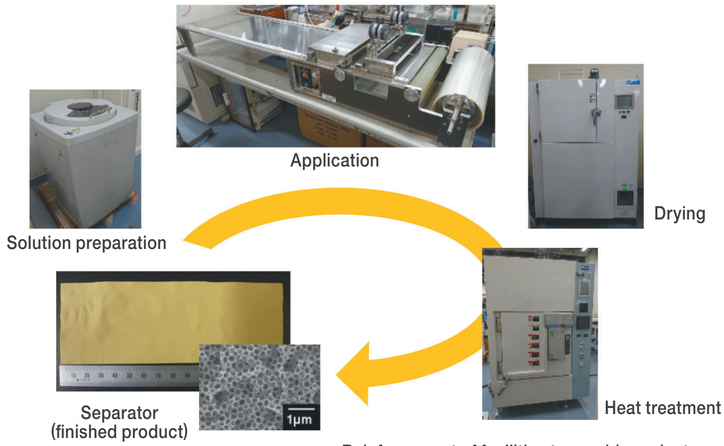



# Accelerating and promoting team for practical application

● Team leader:
Kiyoshi Kanamura
(Professor, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University)

- Experts from each team work in collaboration on issues shared by all types of batteries studied at ALCA-SPRING.
- Special unit for lithium metal anode research, works on solving issues such as the safety and self-discharge characteristic of lithium metal, which has a high theoretical specific capacity.
- The evaluation, analysis & common material and technology group employs the facilities at the Battery Research Platforms in order to assist with procedures shared by all teams such as advanced and sophisticated analysis, battery assembling, and provision of commonly used materials.

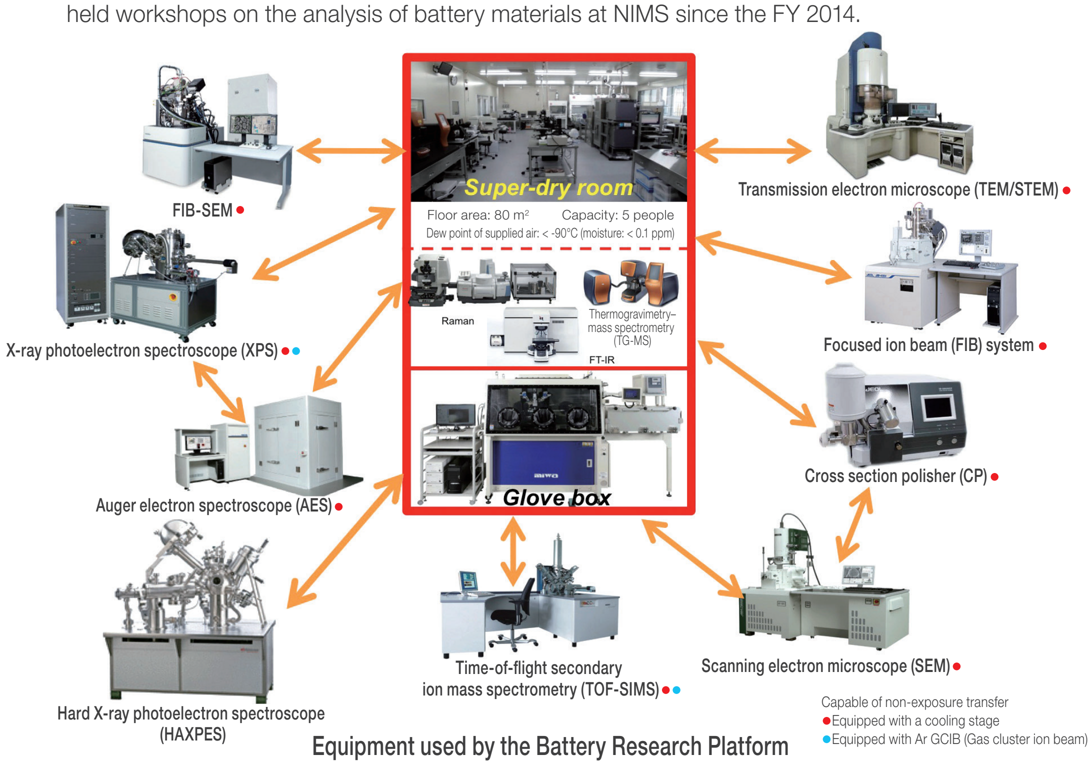
SEM (Scanning Electron Microscope)
(National Institute for Materials Science)
This SEM can detect elements over 50 eV
and can detect Li, which is generally undetectable.




Reinforcement of facilities to provide project members with 3DOM polyimide (PI) separators
(Tokyo Metropolitan University)

# Battery Research Platform

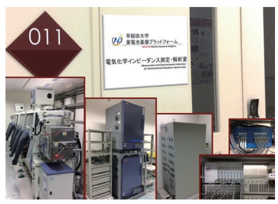
- The Battery Research Platform was established in the National Institute for Materials Science (NIMS), National Institute of Advanced Industrial Science and Technology (AIST), Kansai, and Waseda University in 2012.
  The Platform provides preferential support to ALCA-SPRING for research and development on next-generation batteries.
- To promote research and development on next-generation batteries across the nation, the Platform also supports universities, incorporated administrative agencies, private sector entities, and other institutes. As a part of its activities, the Platform has annually held workshops on the analysis of battery materials at NIMS since the FY 2014.




Equipment used by the Battery Research Platform

NIMS

AIST Kansai



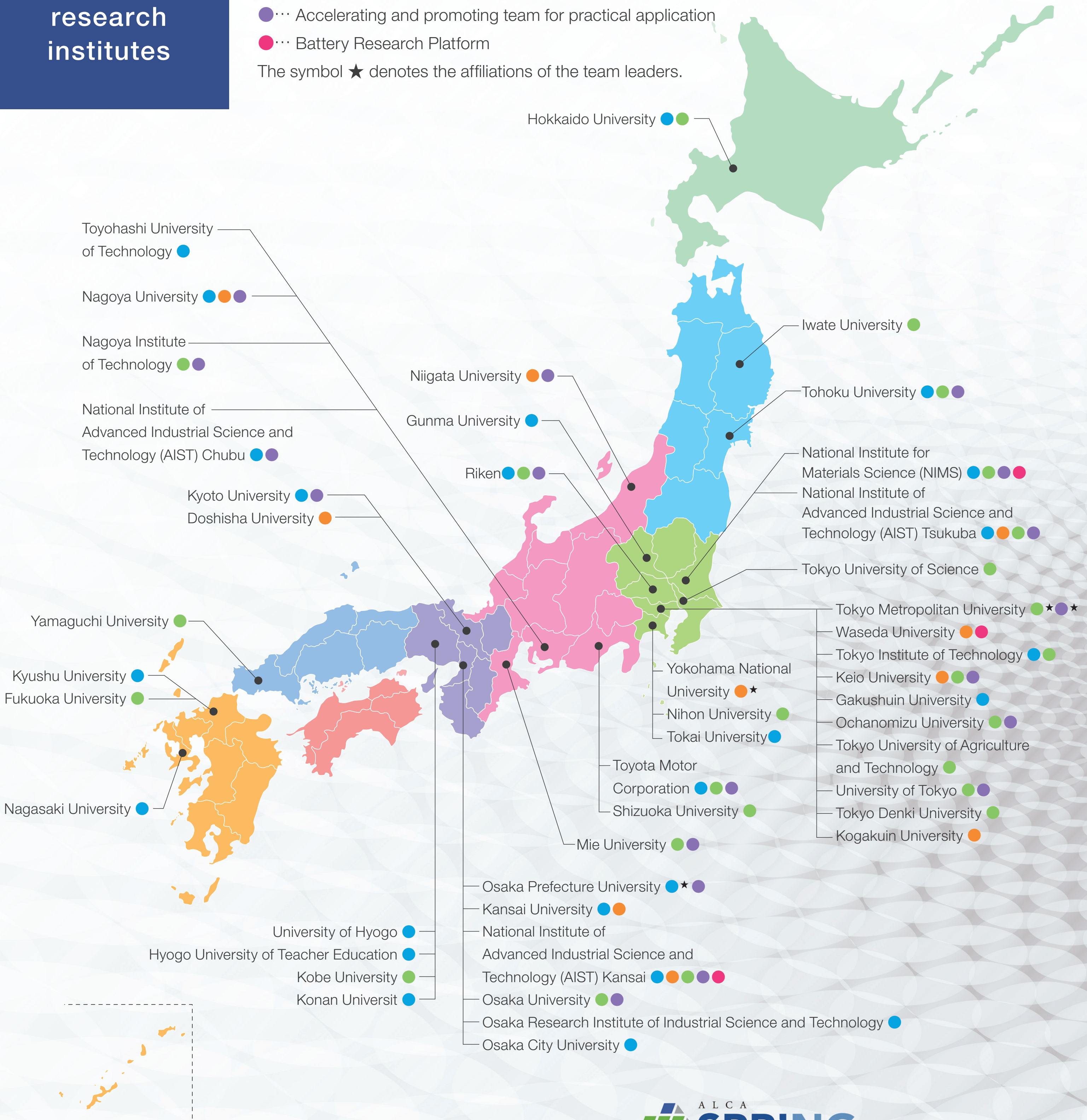

Waseda University

ALCA-SPRING

# Participating research institutes

- ··· All-Solid-State battery team
- ··· Lithium-Sulfur battery team
- ··· NEXT generation battery team
- ··· Accelerating and promoting team for practical application
- ··· Battery Research Platform

The symbol ★ denotes the affiliations of the team leaders.




ALCA SPRING
Specially Promoted Research for Innovative Next Generation Batteries


**Japan Science and Technology Agency (JST)**
**ALCA group, Department of Green Innovation**

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URL: http://www.jst.go.jp/alca/alca-spring/en/index.html


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JST Japan Science and Technology Agency

ALCA Change the game with technologies!

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