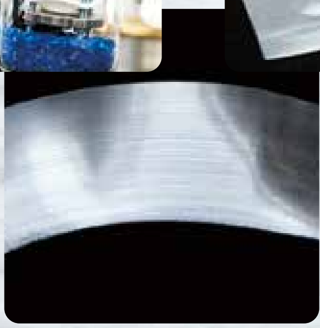
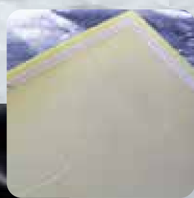
ALCA Advanced Low Carbon Technology Research and Development Program

SPRING

Specially Promoted Research for Innovative Next Generation Batteries





JST Japan Science and Technology Agency

ALCA Change the game with technologies!

Message from ALCA-SPRING PO

ALCA-SPRING Program Officer (PO)

Kohei Uosaki

(Fellow, National Institute for Materials Science)

Low-cost, high-performance next-generation secondary batteries are essential for reducing car emissions, which account for around 10% of 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.

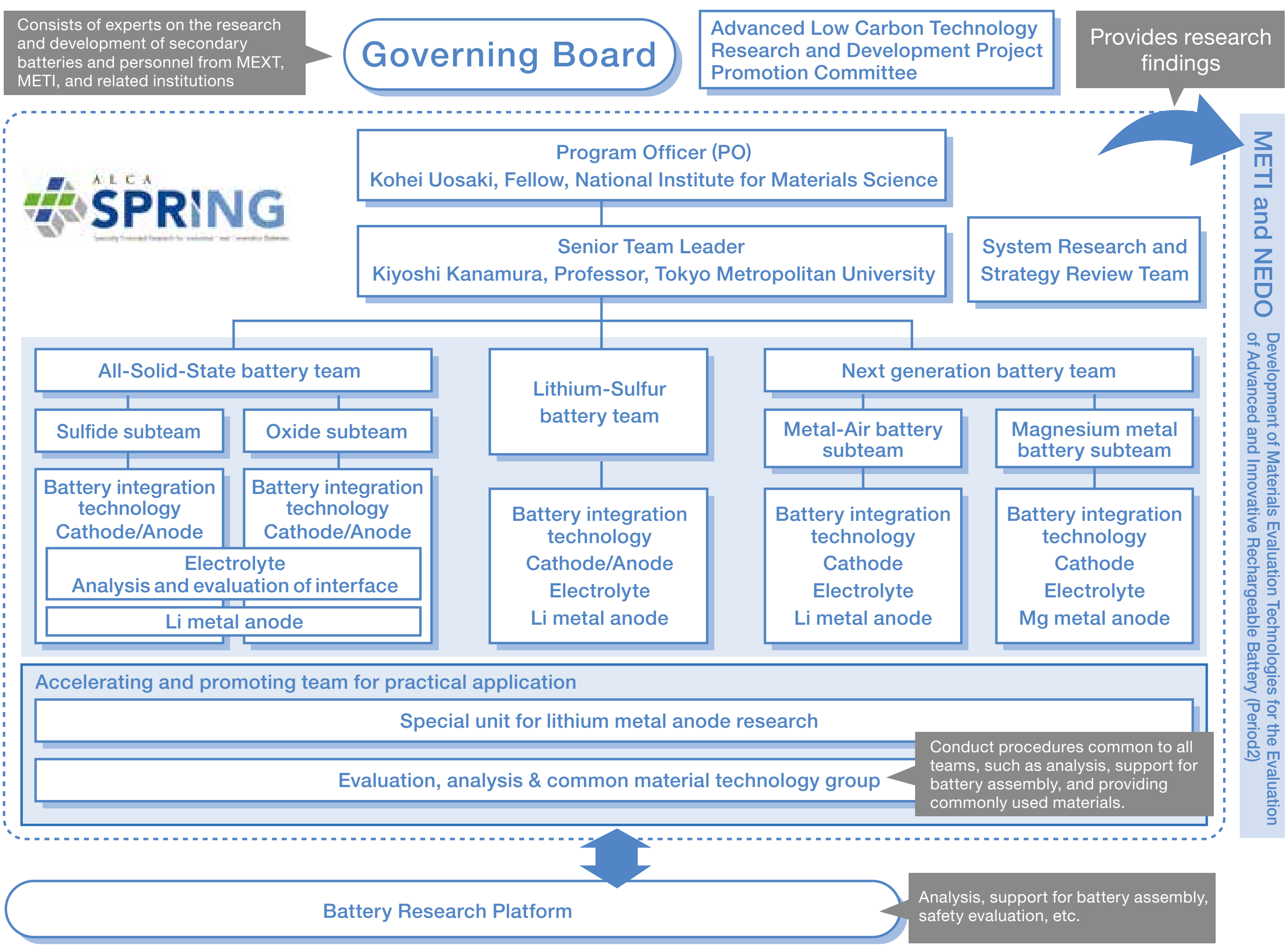
Following a joint panel conducted by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the Ministry of Economy, Trade and Industry (METI) in FY 2012, which focused on next-generation secondary batteries, this project was launched in July 2013. Four types of candidate next-generation secondary batteries—all-solid-state battery (sulfide type and oxide type), metal-air battery, medium to long term (lithium-sulfur battery), and long term (multivalent ion battery)—were selected to be studied by four teams. The teams were structured so that each 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 have made major organizational restructuring twice based on stage gates since its establishment. In April 2018, a part of Sulfide sub-team of All-Solid-State battery team, which has achieved significant progress, was transferred to the SOLiD-EV project supported by New Energy and Industrial Technology Development Organization. In addition, joint development with a private company was started for Li-Air battery based on the outcome of Metal-Air battery subteam of this project.

We appreciate your continuous support for our project.

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.



*cathode (anode): of the pair of electrodes, the electrode with the higher (lower) potential. plus (minus) electrode.

Message from ALCA PD

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.

ALCA Program Director (PD)
Kazuhito Hashimoto
(President, National Institute for Materials Science)

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**

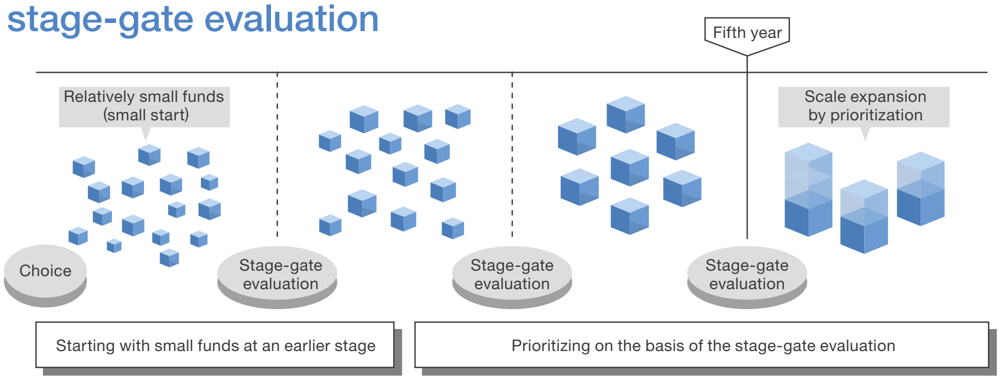
Type	Project title	Program Officer (PO)
Special Priority Technology Areas	Next Generation Batteries	Kohei Uosaki (Fellow, National Institute for Materials Science)
	White Biotechnology	Yoshiharu Doi (President, Japan Synchrotron Radiation Research Institute)
Game-Changing Technology Areas	Solar Cell and Solar Energy Systems	Atsuhiro Osuka (Professor, Kyoto University)
	Superconducting Systems	Hiroyuki Ohsaki (Professor, University of Tokyo)
	Electric Storage Devices	Tetsuya Osaka (Emeritus Professor, Senior Research 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 (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.

Research target

To realize all-solid-state batteries, high performance solid electrolyte, electrode, and battery integration technology are developed.

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)
- Developed a high plasticity electrolyte and active material / electrolyte interfacial bonding method to enhance the performance of oxide-based all-solid-state batteries.
- Developed a technology that enables direct observation of reaction distribution of electrodes for all-solid-state batteries using operando CT-XAFS.

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	◎	—	◎	△

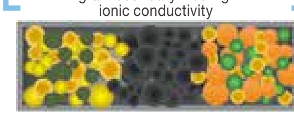
Argyrodite-type: Electrolyte suitable for a high-voltage cathode

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

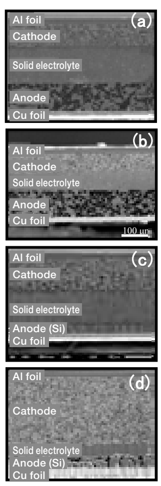


α-Li_3PS_4-type: electrolyte suited for anodes

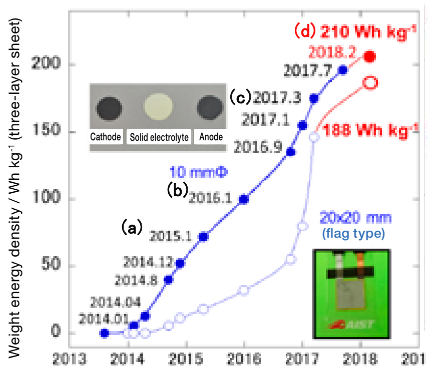
Electrolyte for anodes:
Resistance to reduction; anode-electrolyte interface
Ionic conductivity

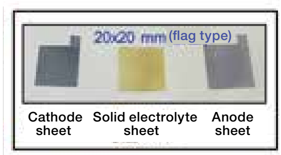
Li/In, Li/Al, Carbon, Li

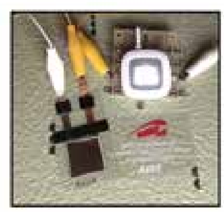
Contributes to practical implementation by applying appropriate solid electrolytes to each part of all-solid-state batteries



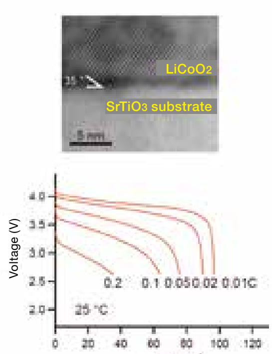
Energy density transition of seat type batteries by bringing together the techniques of the sulfide subteam



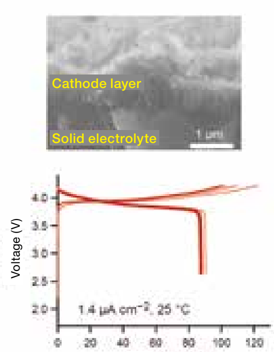




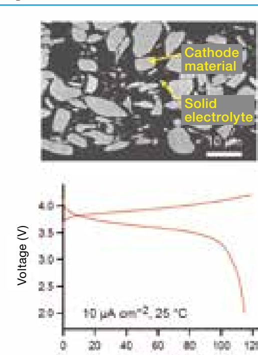
Interface formation for oxide-based solid electrolytes



① Interface formation by a sol-gel process



② Interface formation by a flux method



③ Interface formation using high plasticity electrolytes

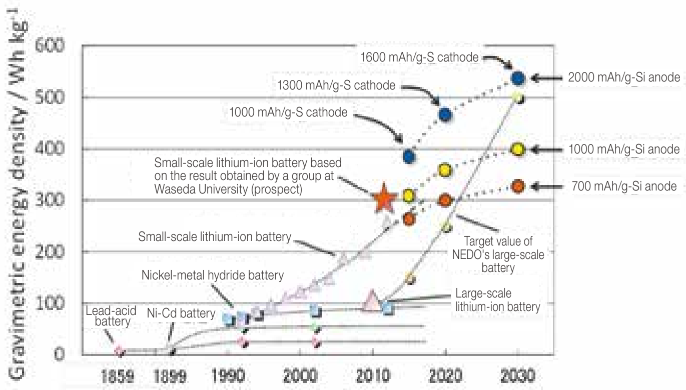
- The largest issue in the development of oxide-based all-solid-state batteries is the formation of a low-resistant interface.
- ALCA-SPRING succeeded in reducing the interface resistance by various methods (①-③) and succeeded in operating the oxide-based all-solid-state battery at around room temperature.

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.



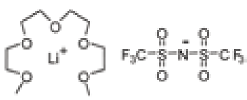
Changes in and target values of energy density of secondary batteries

Research target

- To develop low-cost lithium-sulfur batteries with a long cycle life and large capacity for stationary batteries.

Realizing discharge capacity of 1 Ah/cell using an electrode carrying sulfur of 17.5 mg/cm^2.

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 σ 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

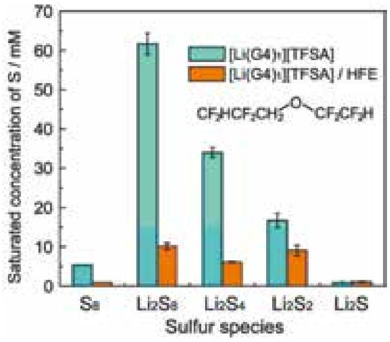


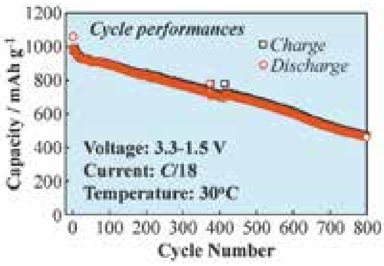
Figure. Comparison of S_8 and Li_2S_m solubility limits in [Li(G4)1][TFSA] and [Li(G4)1][TFSA]/HFE (molar ratio of Li[TFSA]/G4/HFE = 1:1:4) at 30℃. The structure of HFE is shown in the inset.

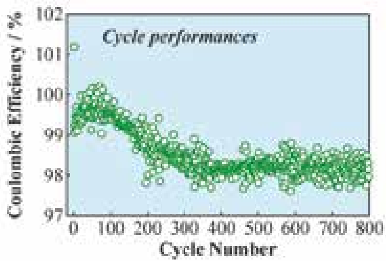
Development of such an elution-resistant electrolyte solution has been achieved for the first time

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.

Long-term test of lithium-sulfur batteries





☆ 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**

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.

Next generation battery team

- Team leader, Magnesium metal 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.

Research target

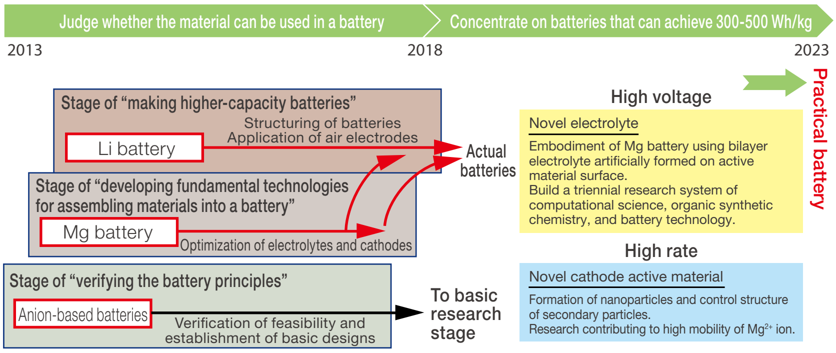
- To develop new high energy density secondary batteries that utilize multivalent ion transport.
- To develop low cost secondary batteries with ultimate energy density using air (oxygen) as an active material.

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-metal batteries. Mg is abundant and Mg-metal batteries have the potential of exceeding lithium-ion batteries in volume energy density.
- Significant results were achieved in the key technologies of the development of new electrolytes and electrode active materials by collaborative works between material scientists and computational scientists.
- We have found suitable structure for ion diffusion and electron transfer based on newly synthesized cathode materials of nanoparticles, nanosheets, and hierarchical porous structure.
- Experts are exchanging information and are promoting team research on Li-Air batteries that have an extremely high theoretical capacity density based on ideas deviating from common knowledge.

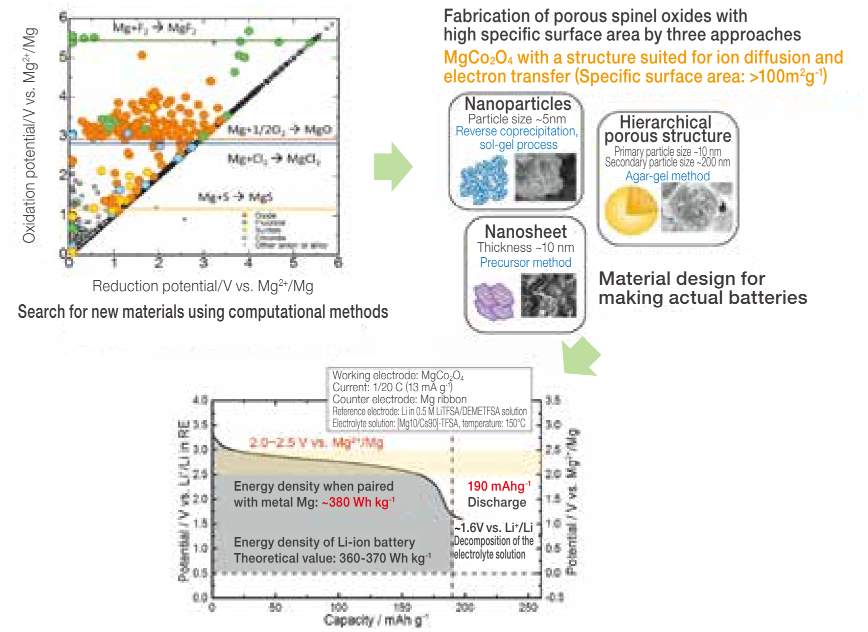
Results obtained

- Made it possible to stably perform reversible deposition-dissolution of magnesium using special electrolyte solutions and additives.
- By particle design, the cycle characteristics of the positive electrode for Mg metal battery have been improved.
- We have prototyped an air battery stack with the world's highest energy density (600 Wh/kg).
- We have developed a new electrolyte that greatly improves the energy efficiency and lifetime of Lithium-Air batteries.



We restarted from 2018 and focused on developing Mg metal secondary batteries.
We will make great progress in new development and practical application of positive electrode active material and electrolyte.

Development of magnesium metal batteries



Search for new materials using computational methods

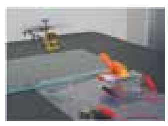
Electrode design for making actual batteries

Development of Lithium-Air batteries —Aiming toward the ultimate energy density

Purpose Development of a fundamental technology for Lithium-Air batteries, which is expected to have the highest energy density

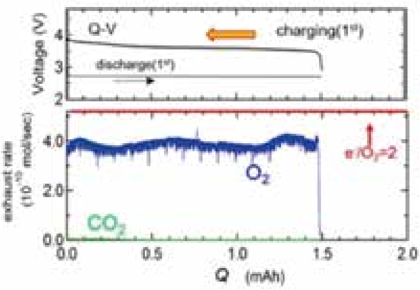
Result The world's first development of stack technology, indispensable for practical implementation of Lithium-Air batteries

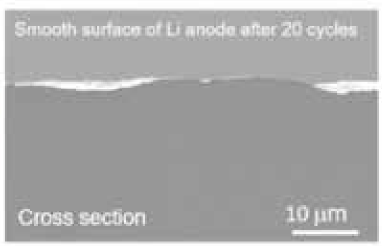
A coin cell made of a Lithium-Air battery and a stack of ten cells (internal structure)
The stack shows a capacity 100 times larger than that of the coin cell



Demonstration experiment using a stack of Lithium-Air batteries

Result Electrolyte capable of dramatically increasing the energy efficiency and life of Lithium-Air battery

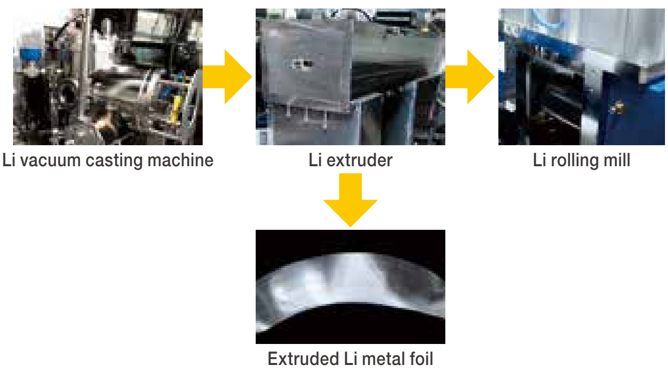




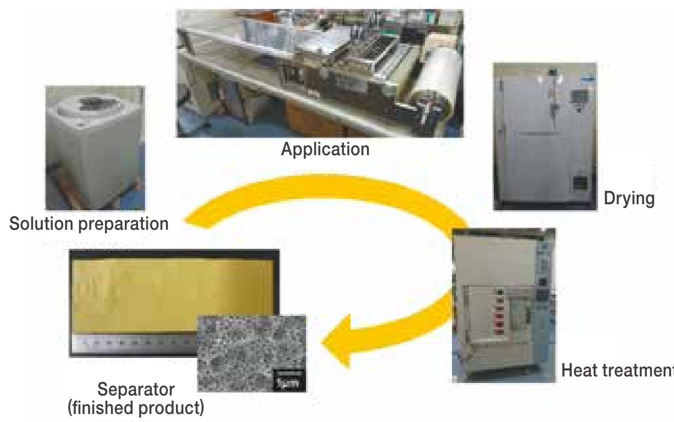
Accelerating and promoting team for practical application

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. In FY 2017 we installed lithium processing equipment for lithium metal negative electrode, aiming to correlate metallurgical characteristics with electrode characteristics.



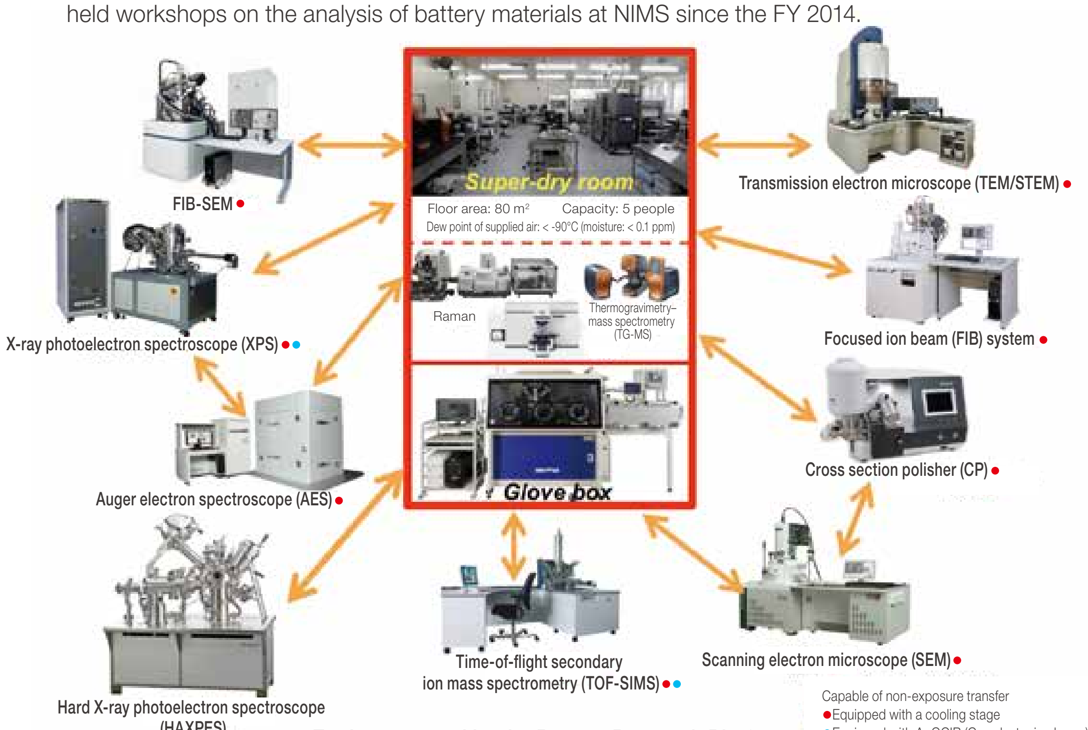
Considering even the conditions of casting, extrusion, and rolling under an inert gas atmosphere, there are no cases in the world where research on Li metal foil suitable for actual batteries is carried out.



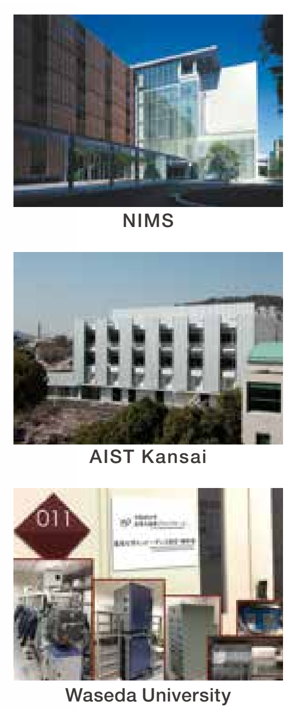
Reinforcement of facilities to provide project members with 3DOM polyimide (PI) separators (Tokyo Metropolitan University)

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

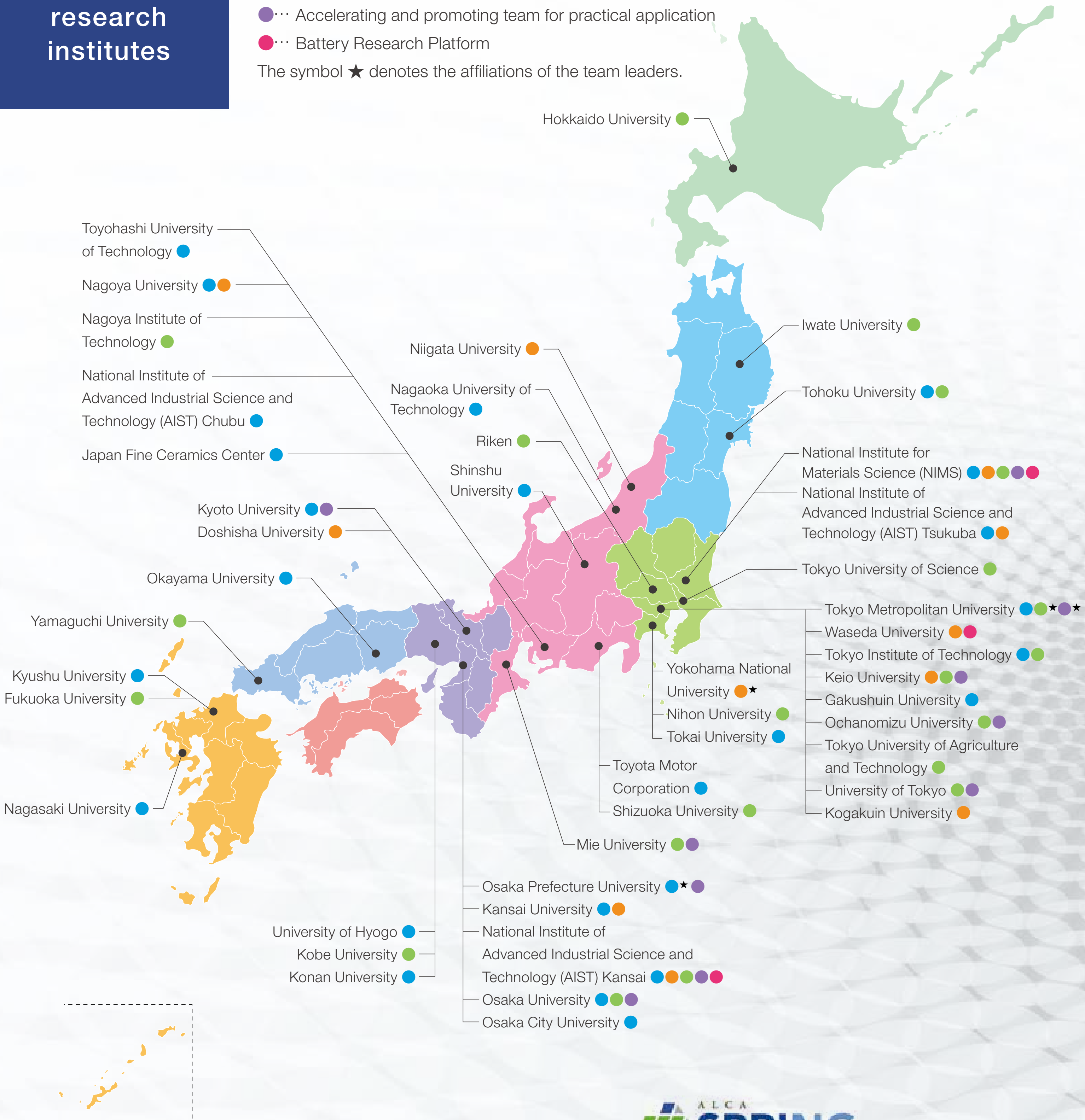


ALCA-SPRING

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

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