

Interface IONICS

Science on Interfacial Ion Dynamics for Solid State Ionics Devices

Newsletter Vol.3

March 2021

Interface Ionics toward
Sustainable Society

2019 – 2023 Japan Society for the Promotion of Science
Grant-in-Aid for Scientific Research on Innovative Areas





Preface

The COVID-19 global pandemic has restricted various activities. Although the 1st international conference on “Interface Ionics” was postponed, the utilization of ICT as well as collaborative research and discussions have progressed more rapidly than originally planned. We are optimistic that the pandemic will end soon, but we will continue “Interface Ionics” by effective management utilizing virtual platforms, online meetings, on-demand video presentations, etc.

I hope that you and your family keep good health now and in the future.

Yasutoshi Iriyama, Principal Investigator
Nagoya University

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Member Introductions

Postdoctoral Researchers



Gp-A03

Hong-Kang Tian

NIMS (Tateyama Gr.)

/Multi-scale simulations for all-solid-state batteries

I grew up in Taiwan. I received my Ph.D. in Chemical Engineering from Michigan State University under the supervision of Professor Yue Qi. My research focuses on applying multi-scale simulation techniques, including continuum modeling (Finite Element Analysis) and first-principles calculations (Density Functional Theory), to investigate interfacial issues. Specifically, my studies explore contact area loss, stress induced at interfaces, and the mechanism of Li dendrite growth in the pores and grain boundaries. In the “Interface Ionics” project, I work to reveal how Li ions and electrons are transferred across the interface between the LATP solid electrolyte and the LiCoO₂ electrode. In collaboration with Prof. Muto and Prof. Iriyama, our proposed mechanisms well explain the experimental observations in different conditions, including before/after annealing and upon charging. I appreciate this opportunity to participate in this project and collaborate with talented researchers in experimental and computational research groups. I look forward to developing more exciting stories regarding the interfaces in all-solid-state batteries.

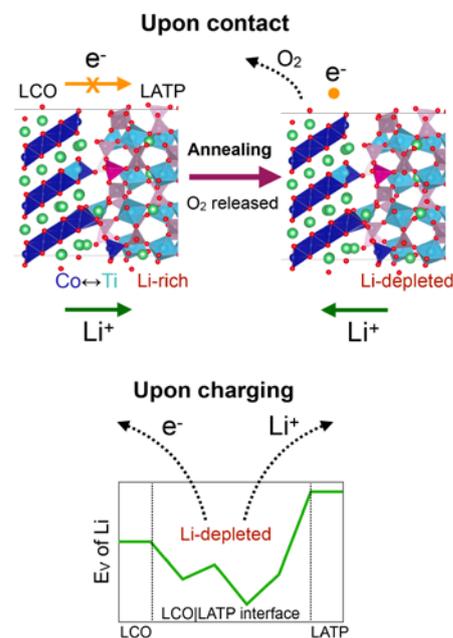


Figure. Li-ion and electron transfer at the LATP/LCO interface under different conditions.

Adapted with permission from “H.K. Tian, S. Muto, Y. Iriyama, Y. Tateyama *et al.*, ACS Appl. Mater. Interfaces 12, 54752–54762 (2020)”, the American Chemical Society.



Gp-A03

Magnus So

Kyushu Univ. (Inoue Gr.)

/Numerical simulations

My research is focused on simulating the effects of structural and mechanical properties on the durability and performance of all-solid-state batteries (ASSBs). I mainly focus on particle-based methods such as the Discrete Element Method (DEM) to investigate contact dynamics at interfaces and between particles. Recently, we simulated cold press fabrication and charge expansion in a sulfide ASSB electrode via DEM. We developed a new cohesive particle model that can simulate both particle consolidation during fabrication and material failure during charge expansion. A high pressure during fabrication induces plastic deformation and the build-up of cohesive contact between particles, which consist of a Si active material (AM) and sulfide solid electrolyte (SE). When AM expands during charging, it causes delamination and cracking, leading to substantial performance losses. In the future, I hope my research can be used to better understand the mechanical interactions between particles and interfaces toward the development of more durable ASSBs.

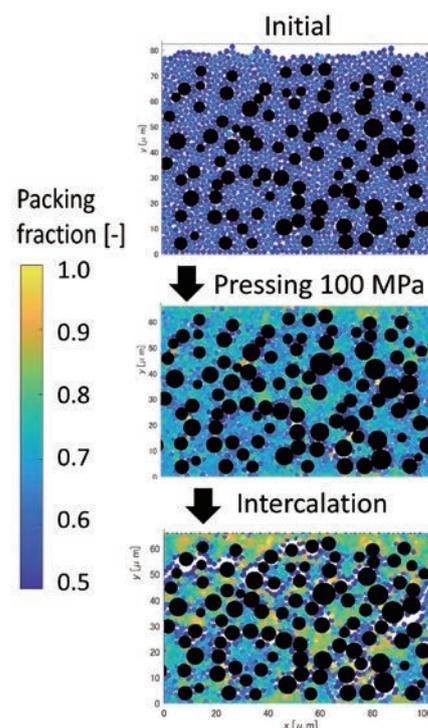
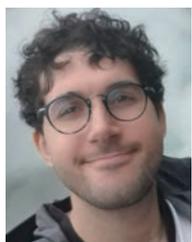


Figure. Simulation results of SE (colored) and AM (black) particles.



Gp-A04

Benoît Denis Louis Campéon

Yokohama National Univ. (Yabuuchi Gr.)
/Graphene, Electrochemistry

Since early 2016, I have been involved in research related to the electrochemical synthesis and functionalization of graphene materials for energy storage devices. During my doctoral thesis initiated in 2017, I developed an original non-destructive electrochemical synthesis method for graphene oxide, which eases, speeds up, and reduces the cost of its production. Following this work, I developed sophisticated methods, which allow tuning of the graphene oxide chemistry and morphology toward high performance lithium and sodium ion batteries. In October 2020, I started working in Prof. Yabuuchi's group at Yokohama National University. Currently, I am investigating the development of graphene-based all-solid-state batteries (ASSBs). My initial research aims to design and optimize the evaluation of a reference ASSB composed of LiFePO_4 with a polymer electrolyte. The preliminary cell evaluation conducted within a cold isostatic pressing (CIP) device (Fig. 1) allows the positive effect of pressure on ASSB interfacial resistances to be precisely studied (Fig. 2).

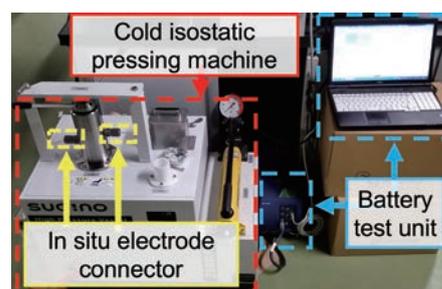


Figure 1. A digital image of the CIP device connected to a battery test unit.

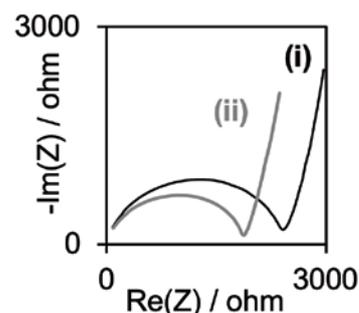


Figure 2. *In-situ* CIP Nyquist plots of ASSB at (i) ambient conditions and (ii) 10 MPa.



Gp-A04

Rajendra Hongahally Basappa

Yokohama National Univ. (Yabuuchi Gr.)
/All-solid-state batteries

Since 2014, I have been working on solid electrolytes for all-solid-state batteries (ASSBs). My doctoral research focused on a garnet-type solid electrolyte, which offers unprecedented safety and durability to enable the use of Li metal anodes in ASSBs. Prior to my doctoral research, I worked on developing tin anode materials for lithium-ion battery applications in India.

My ongoing research activities are focused on a solvent-free hybrid solid electrolyte (HSE) system such as the integration of lithium-conducting ceramic electrolytes in a polymer matrix, which shows high ionic conductivity, and excellent mechanical and thermal properties for ASSB applications. Recently, to evaluate the full potential of our ASSB, electrochemical cells were prepared with a polymer membrane. This cell was assembled with a polymer membrane and electrode material. Cold isostatic pressing (CIP) effectively reduced the impedance of ASSB. Figure 1 shows a picture of the CIP device. Figure 2 shows the preliminary result, which demonstrates the advantage of CIP. After CIP treatment, the impedance of the all-solid-state battery is drastically reduced.



Figure 1. Picture of a cold isostatic pressing (CIP) device.

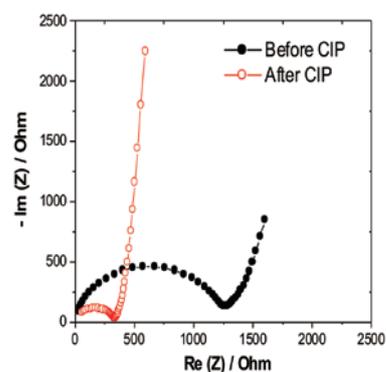


Figure 2. Nyquist plots of electrochemical cells before and after CIP.

Research Achievements

2020.7–2020.12

Gp-A01 Model Interface

Notable research progress includes the preparation of thin film materials and a model of solid electrolytes. These are useful for analyzing the electrode-solid electrolyte interface. From the viewpoint of suppressing side reactions during the interface formation process, several unique processes related to low-temperature interface formation and low-temperature material synthesis have been achieved. In addition, mechanisms for side reactions and regulating methods during

high-temperature sintering or thin-film formation on heated substrates have been proposed. Collaborative projects with Gp-A02 and Gp-A03 are underway, and include examples such as the provision of a model for all-solid-state batteries and single crystalline solid electrolytes, and elucidation of the reaction mechanism occurring at negative electrodes of (Li, Si, carbon)-solid electrolyte interfaces.

Highlight 1

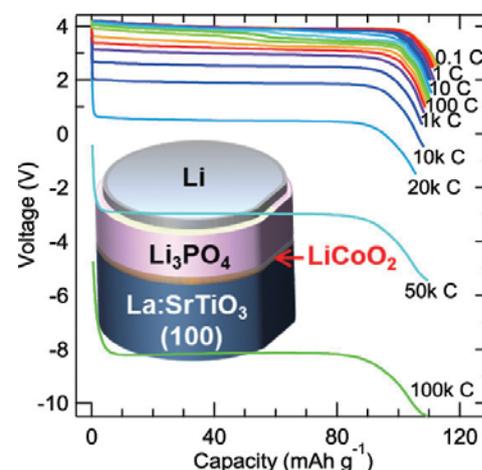
High-rate capability of LiCoO₂ cathodes

K. Kawashima, T. Ohnishi, K. Takada.

ACS Appl. Energy Mater. vol. 3, pp. 11803–11810 (2020)

Abstract

High-quality (104)-oriented LiCoO₂ epitaxial thin film cathodes exhibit an extremely large high-rate discharge exceeding 100,000 C and 100 mA cm⁻² without any capacity loss. A comparison with c-axis oriented epitaxial cathodes indicates a definite anisotropic rate capability in the layered rock-salt-type LiCoO₂. *ALCA-SPRING collaborating work* [Reproduced with permission of the American Chemical Society.]



Highlight 2

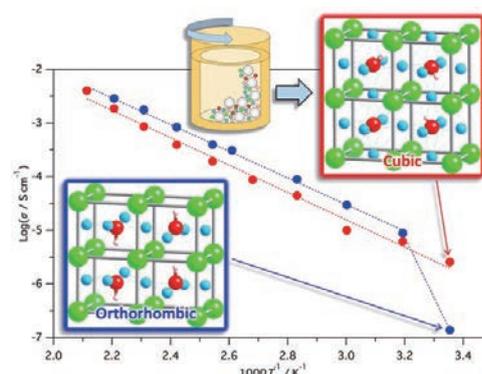
Synthesis of the metastable cubic phase of Li₂OHCl by a Mechanochemical method

T. Yamamoto, H. Shiba, N. Mitsukuchi, M. K. Sugumar, M. Motoyama, Y. Iriyama.

Inorg. Chem. vol. 59, pp. 11901–11904 (2020)

Abstract

A ductile oxide-based solid electrolyte, Li₂OHCl, is prepared at room temperature by a mechanochemical method. Li₂OHCl generally forms a low-conductive orthorhombic phase at 25 °C, but the as-prepared Li₂OHCl forms a cubic *Pm* $\bar{3}$ *m* structure and shows an ionic conductivity of 2.6×10^{-6} S cm⁻¹ at 25 °C. Upon heating the cubic phase to 200 °C, the orthorhombic *Pmc*2₁ structure appears at 25 °C and the ionic conductivity decreases to 1.4×10^{-7} S cm⁻¹. The formation of the metastable cubic phase can be explained in terms of the low crystallinity of Li₂OHCl derived from mechanochemical synthesis. [Reproduced with permission of the American Chemical Society.]



Gp-A02 Advanced Analysis

Our group strives to understand unique ion transport/storage phenomena at solid-state interfaces using comprehensive analyses. We establish and improve various novel and advanced analytical techniques as well as systematically apply them to typical model solid-state interfaces such as a well-defined film electrode on solid

electrolytes and glass-ceramics electrolytes supplied by Gp-A01 and Gp-A04. Based on the results obtained in collaboration with the theoretical calculations and simulations conducted by Gp-A03, we establish scientific principles that enable the design of high-performance solid-state interfaces.

Highlight 3

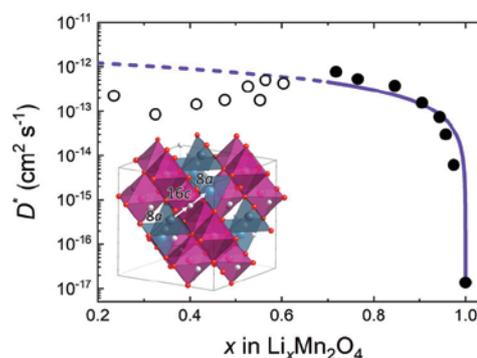
Tracer diffusion coefficients of Li ions in $\text{Li}_x\text{Mn}_2\text{O}_4$ thin films observed by isotope exchange secondary ion mass spectrometry

N. Kuwata, G. Hasegawa, D. Maeda, N. Ishigaki, T. Miyazaki, J. Kawamura.

J. Phys. Chem. C. vol. 124, pp. 22981–22992 (2020)

Abstract

Tracer diffusion coefficients D^* of lithium ions in $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0.2 < x < 1$) thin films were measured as a function of the composition x using secondary ion mass spectrometry (SIMS). For this purpose, a new “step-isotope-exchange method” was developed to observe the time dependence of the ^6Li isotope concentration ratio in the $\text{Li}_x\text{Mn}_2\text{O}_4$ film, which contacts a ^6Li -enriched electrolyte to exchange Li^+ ions. A steep decrease in D^* depending on the Li composition was observed for $\text{Li}_x\text{Mn}_2\text{O}_4$, with $D^* = 8 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ for $x = 0.2$ but decreases to $1.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ for $x = 1.0$ (bulk diffusion coefficient, D_b^*). Chemical diffusion coefficients \bar{D} were also measured in a range of $0.2 < x < 1.0$ by an electrochemical method and compared with the D^* to evaluate the effect



of thermodynamic factors. The thermodynamic factors and interactions between Li^+ ions strongly influenced the chemical diffusion coefficient. [Reproduced with permission of the American Chemical Society.]

Highlight 4

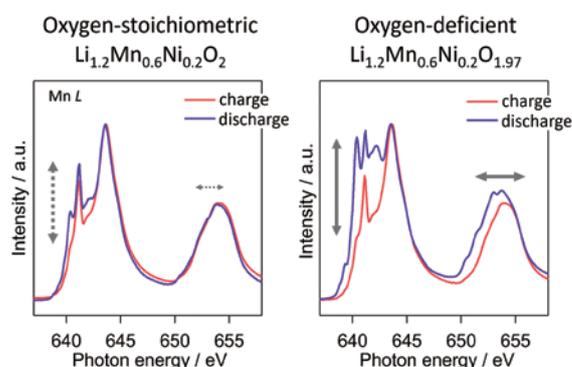
Impact of oxygen defects on electrochemical processes and charge compensation of Li-rich cathode material $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$

T. Nakamura, K. Ohta, Y. Kimura, K. Tsuruta, Y. Tamenori, R. Aso, H. Yoshida, K. Amezawa.

ACS Appl. Energy Mater. vol. 3, pp. 9703–9713 (2020)

Abstract

This work reports the impacts of oxygen vacancies on the electrochemical properties of a Li-rich cathode $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$. In the initial charge, the oxygen-deficient $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{1.97}$ showed a larger oxidation current due to oxygen release than the oxygen-stoichiometric $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$, suggesting that a preliminary introduced oxygen vacancy promoted further oxygen release during the initial charge. Vigorous Mn redox was observed in the heavily oxygen-deficient $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_{2-d}$ phase during the charge/discharge. In contrast, Mn was almost inactive in the oxygen stoichiometric phase. The modulation of oxygen defects can be an effective



strategy to control redox species in battery active materials. [Reproduced with permission of the American Chemical Society.]

Gp-A03 Computational & Data Science

To construct a new theoretical framework for “Interface Ionics,” Gp-A03 introduces two strategies: computational and data science approaches. For this challenging target, deep collaborations with the other groups (A01, A02, & A04) are crucial. Recently, we suggested insights into the ion transport in solid electrolytes and across electrolyte interfaces via DFT

Highlight 5

First-principles calculation study of Na⁺ superionic conduction mechanism in W- and Mo-doped Na₃SbS₄ solid electrolytes

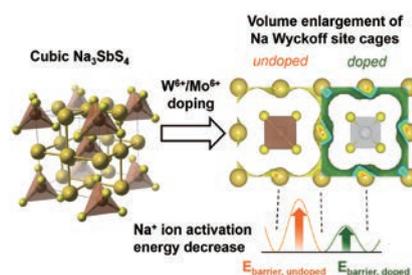
R. Jalem, A. Hayashi, Y. Tateyama, *et al.*

Chem. Mater. vol. 32, pp. 8373–8371 (2020) [A03-A04 joint paper]

Abstract

The guiding principle for the design of inorganic compounds with a high ionic conductivity has been extensively sought to realize next-generation all-solid-state batteries (ASSBs). Recently, a sulfide-type Na⁺ ion conductor, cubic Na₃SbS₄ with W doping (Na_{2.88}Sb_{0.88}W_{0.12}S₄), was reported. Its unprecedentedly high ionic conductivity of 3.2×10^{-2} S cm⁻¹ makes it a champion solid electrolyte for Na-ASSB (A. Hayashi *et al.*, *Nat. Commun.* 2019, 10, 5266). Herein density functional theory molecular dynamics (DFT-MD) calculations were performed for pristine, W-doped, and Mo-doped Na₃SbS₄ to examine the ionic conduction mechanism (Boltzmann factor vs. prefactor) and the aliovalent cation dopant effects in Na₃SbS₄. Na vacancies induced by cation doping play crucial roles in superionic conductivity, while the diffusion process is characterized by the concerted motion of Na⁺ ions.

calculations, together with the “Interface Ionics” experimentalists. We also constructed the work flow with machine learning techniques for efficient material synthesis as well as an accurate force field set based on the DFT calculations to investigate phenomena in larger-scale disordered systems.



A comparison between the two dopants, Mo⁶⁺ and W⁶⁺, revealed that the conductivity enhancement can be primarily explained by a decrease in the Na⁺ ion activation energy, which is strongly correlated to the enlargement of the Na Wyckoff site cages due to the smaller WS₄/MoS₄ tetrahedral volume relative to the host SbS₄ volume. In addition to explaining the superior performance of W-doped Na₃SbS₄, this descriptor of the pathway free volume suggests a general guiding principle for superionic conduction that can be applied to other cations. [Reproduced with permission of the American Chemical Society.]

Highlight 6

High-throughput production of force-fields or solid-state electrolyte materials

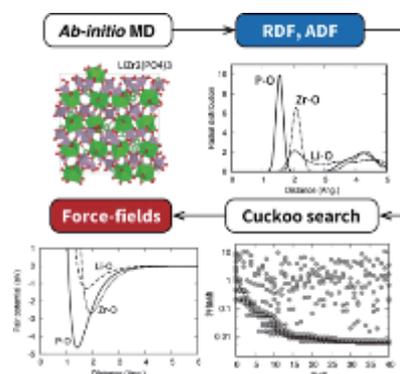
R. Kobayashi, M. Nakayama, *et al.*

APL Mater. vol. 8, pp. 081111-1–10 (2020).

[Selected as Featured Article & AIP Scilight]

Abstract

An automatic and high-throughput method to produce interatomic force-fields for solid-state electrolyte materials is proposed. The proposed method employs the cuckoo search algorithm with an automatic update of the search space to optimize the parameters in empirical potentials and reproduce the radial and angular distribution functions and equilibrium volume obtained from *ab initio* molecular dynamics simulations. The force-fields for LiZr₂(PO₄)₃ and LaF₃ systems parameterized using the present method well reproduce key physical properties required to study ion conductivity of solid-state electrolyte materials. The



current approach, including the *ab initio* calculation to create reference data, takes only one or two days to produce a force-field. This will greatly enhance the speed of exploration and screening of candidate materials. [Reproduced with permission of the AIP Publishing.]

Gp-A04 Design of Functional Interface

Gp-A04 designs innovative solid-state ionic materials (SSIMs) through interface engineering. By increasing the concentration of grain boundaries, charge carriers are efficiently accumulated in SSIMs. By further adjusting and optimizing the interfacial

structures, new functionalities appear. Such functionalities are applied to new solid-state ionic devices. Collaborative studies with members of Gp-A02 and Gp-A03 further accelerate the development of new solid-state devices.

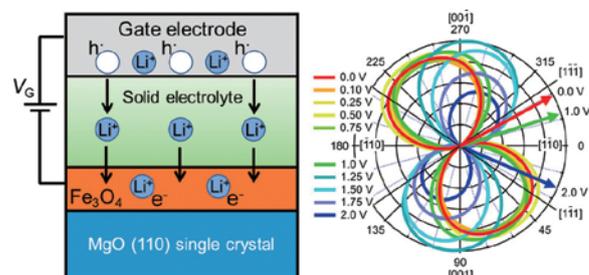
Highlight 7

Room-temperature manipulation of magnetization angle, achieved with an all-solid-state redox device

W. Namiki, T. Tsuchiya, M. Takayanagi, T. Higuchi, K. Terabe. *ACS Nano*. vol. 14, pp. 16065–16072 (2020)

Abstract

An all-solid-state redox device, which was composed of a magnetite (Fe_3O_4) thin film and Li^+ conducting electrolyte thin film, was fabricated to manipulate the magnetization angle at room temperature (RT). Although this is a key technology for creating efficient spintronics devices, it has yet to be achieved at RT by other carrier doping methods. Variations in the magnetization angle and magnetic stability were precisely tracked via planar Hall measurements at RT. The magnetization angle was reversibly manipulated at 10° by maintaining the magnetic stability. Meanwhile,



the manipulatable angle reached 56° , although the manipulation became irreversible when magnetic stability was reduced. This large manipulation of the magnetic angle was achieved by tuning the 3d electron number and modulation of the internal strain in Fe_3O_4 due to the insertion of high-density Li^+ (approximately 10^{21} cm^{-3}). This RT manipulation is applicable to highly integrated spintronics devices due to its simple structure and low electric power consumption. [Reproduced with permission of the American Chemical Society.]

Highlight 8

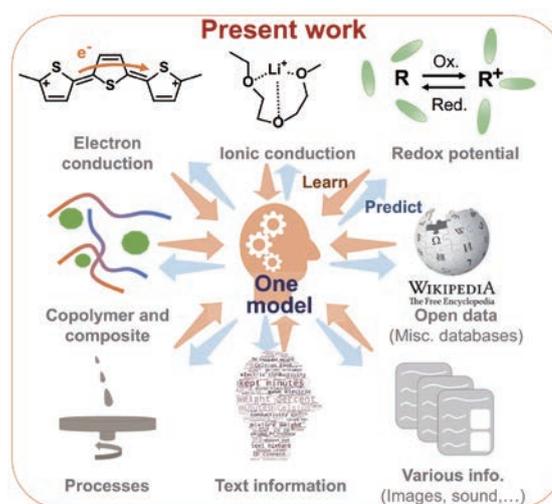
Integrating multiple materials science projects in a single neural network

K. Hatakeyama-Sato and K. Oyaizu.

Comms. Mater. vol. 1, Article number: 49 (2020)

Abstract

In data-intensive science, machine learning plays a critical role in processing big data. However, the potential of machine learning is limited in the field of materials science due to difficulties treating complex real-world information as a digital language. Here, we propose using graph-shaped databases with a common format to describe almost any materials science experimental data digitally, including chemical structures, processes, properties, and natural languages. The graphs can express real-world data with little information loss. Unlike traditional approaches, which require individual models to process each database and property, in our approach, a single neural network treats versatile materials science data collected from over ten projects. Multitask learning of miscellaneous factors



increases the prediction accuracy of the parameters synergistically by acquiring broad knowledge in the field. The integration is beneficial for developing general prediction models and for solving inverse problems in materials science. [Reproduced with permission of Springer Nature.]

Activity Reports

Conferences Partially Supported by the “Interface Ionics” Project

Specific session “18: Materials and ‘Interface Ionics’ for Solid-state Ionics Devices” of the 33rd Fall Meeting of the Ceramic Society of Japan (Online)

Sep. 3–4, 2020

Prof. Akitoshi Hayashi, Osaka Prefecture Univ.

The first domestic research meeting centered on “Interface Ionics” was held as a special session during the 33rd fall meeting of the Ceramic Society of Japan. The session consisted of 24 lectures, including 1 keynote speech, 4 invited talks, 15 oral presentations, and 4 text presentations by researchers inside and outside the project. Dr. Hideki Iba (Toyota Motor) gave the keynote speech on current issues and future prospects of all-solid-state batteries. Prof. Iriyama,

Prof. Amezawa, Prof. Nakayama, and Prof. Yabuuchi gave invited talks about their research progress in the “Interface Ionics” project. The other research presentations focused on solid electrolytes with good formability, high-capacity electrodes with an anion-redox mechanism, synthesis of battery materials, characterization of bulk and interface by structural analyses, and first principles calculations. About 100 participants attended the online meeting.

Conferences Partially Supported by the “Interface Ionics” Project

“All Solid-state Battery Special Session” in The 61st Battery Symposium in Japan (Online)

Nov. 18–20, 2020

Prof. Yasutoshi Iriyama, Nagoya Univ.
Lect. Munekazu Motoyama, Nagoya Univ.
Asst. Prof. Takayuki Yamamoto, Nagoya Univ.

The 61st Battery Symposium in Japan (Y. Iriyama, Chair of Organizing Committee) was held online. With 1742 participants, 299 video presentations were screened in an on-demand style. Many researchers from “Interface Ionics” participated and presented. On the second day, the “All-solid-state battery special session” was held. Recent progress of “Interface Ionics” was reported in the special session, and the number of video views was 795.



Symposiums and Seminars

The 2nd Public Symposium on “Interface Ionics” in Tokyo International Forum (& Online)

Sep. 28, 2020

Prof. Naoaki Yabuuchi, Yokohama National Univ.

The 2nd Public Symposium on “Interface Ionics” was held at the Tokyo International Forum on Sep. 28, 2020, and the symposium was streamed online. For the more than 400 registered participants, this symposium provided an opportunity for scientists, engineers, and students to discuss diverse aspects of interfacial phenomena related to solid-state chemistry, science, and technology. This conference featured three invited talks from academia and industrial communities. Additionally, four representatives, one from each group in “Interface Ionics,” presented recent research progress in this project. These presentations triggered exciting in-depth discussions throughout the symposium.

Our first invited speaker was Prof. Akira Yoshino, who was awarded the 2019 Nobel Prize in Chemistry. He delivered an engaging talk related to the development and history of commercial lithium-ion batteries and

their prospects in our daily life. Our second speaker, Prof. Ryoji Kanno, is a pioneering researcher in lithium-ion conducting solid-state electrolyte. He presented the history of the research on solid-state electrolyte with an emphasis on sulfide-based materials and the materials design methodology for a new generation of solid electrolytes. Finally, our third invited speaker, Dr. Wataru Ogihara, a senior researcher from Nissan Motor Corporation, shared the history and development of electric vehicles in Nissan and the future perspective of electrification of automobile applications.

This public conference was designed as an on-site/online “hybrid” symposium. It successfully closed with enthusiastic discussions. Our next public symposium is scheduled for 2021. We anticipate sharing our advances in “Interface Ionics” with all participants in the near future.



Invited talks were delivered from three speakers at the Tokyo International Forum. From the left, Nobel Laureate Yoshino, Prof. Kanno, and Dr. Ogihara.



Members attending (on-site) the 2nd Public Symposium on “Interface Ionics.” In addition, over 300 members joined the online symposium.

Symposiums and Seminars

The 2nd “Interface Ionics” Seminar (Online)

Sep. 30, 2020

Assoc. Prof. Takashi Nakamura, Tohoku Univ.

The 2nd “Interface Ionics” seminar was held online on September 30, 2020. This seminar shared fundamental and state-of-the-art knowledge on electrochemical phenomena at solid electrolyte interfaces, discussed the latest findings in interfacial ion/electron dynamics, and enhanced collaborations in this research project. Highlights included 114 participants, 2 plenary lectures, 13 invited talks, and 7 short oral presentations from young researchers.

The plenary lecture by Prof. Tatsuya Kawada (Tohoku University) provided an overview of interfacial phenomena in high-temperature solid electrolyte devices such as solid oxide fuel cells. The second plenary lecture given by Prof. Yasutoshi Iriyama (Nagoya University) discussed recent studies on the interface of all-solid-state batteries. There was a lively discussion on the differences and similarities between high-temperature and room temperature solid electrolyte systems. Afterwards, 13 professors gave invited talks about their specialities. To promote collaborations in the research program “Interface Ionics,” a wide variety of synthesis/analysis/calculation techniques were introduced. From the oral presentations by students/post-docs, two outstanding young researchers were awarded “Interface Ionics.” The 2nd “Interface Ionics” seminar provided a great opportunity to share the latest research in the project and to enhance future research cooperation. We are grateful to all of the speakers and attendees.



“Interface Ionics” Award Winners



Satoshi Hiroi
Postdoctoral researcher / JASRI (Ohara Gr.)

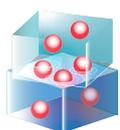
I am honored to receive the “Interface Ionics” Award. Previous researchers in solid-state physics have applied X-ray total scattering measurements for structural analysis of disordered materials. Recently, this technique has been recognized as a powerful tool for the structural analysis of advanced materials due to its applicability to crystalline materials and advances in the differential pair-distribution function (PDF) method. I plan to contribute to the progress of functional materials by expanding the capability of the structural analyzing technique using total scattering measurements.



Koki Nakano
Doctoral student / Nagoya Inst. of Tech. (Nakayama Lab.)

I am honored to receive the “Interface Ionics” award. First, I would like to express my sincerest gratitude to the professors who kindly teach me and group members who support my research. Although the topic I discussed is evolving, I would like to reveal the mechanism of ionic transportation through solid electrolyte interfaces and contribute to the research project “Interface Ionics.”

Newsletter vol.3



**Interface
IONICS**

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