

# Interface IONICS

Science on Interfacial Ion Dynamics for Solid State Ionics Devices

# Newsletter Vol.4

September 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

Vaccination rates are accelerating worldwide, and there is hope for a return to the daily life we enjoyed before COVID-19. In March 2021, we conducted a 4 hour international online symposium and enjoyed discussions. We hope that we can resume face-to-face international collaboration in 2022.

Within the Interface IONICS community, collaborative research related to experiments, advanced analyses, and computational science has actively progressed and the number of papers resulting from collaborative research has increased. In 2021, we will continue to deepen our understanding of the equilibrium state; in 2022, with the addition of new members, we will begin research to clarify our understanding of the steady state. Currently, we are developing a strategy for new activities, including new international collaborations.

Yasutoshi Iriyama, Principal Investigator  
Nagoya University

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# Member Introductions

## Postdoctoral Researchers



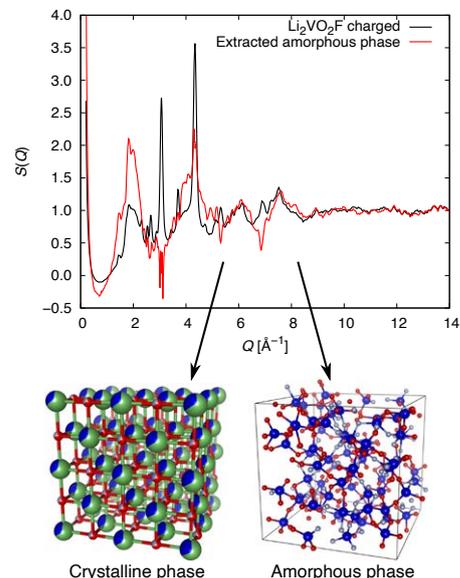
Gp-A02

**Satoshi Hiroi**

JASRI (Ohara Gr.)

/Local structural analysis, Amorphous structure

I received my PhD in 2014 from Niigata University, where I analyzed the structures of liquid chalcogen materials. I was later involved in the development of high-efficiency thermoelectric materials as a postdoctoral fellow at Toyota Technological Institute under Professor Tsunehiro Takeuchi. Since April 2020, I have been working in JASRI under researcher Koji Ohara through research at NIMS. I am currently conducting structural analyses for mixtures of crystalline and amorphous phases as practical materials. I recently developed a dedicated software for the mixtures using X-ray/neutron total scattering data, where I addressed several known problems related to the instrumental resolution function and momentum-transfer-dependent parameters. This software enabled the extraction of structural information for an amorphous phase in a mixture such as the Li-rich  $\text{Li}_2\text{VO}_2\text{F}$  cathode material shown in the figure. I hope this technique contributes to the development of mixed electrode materials by facilitating local structural analysis.



**Figure.**  $S(Q)$  of charged  $\text{Li}_2\text{VO}_2\text{F}$  and the three-dimensional atomic configuration of crystalline and amorphous phases.



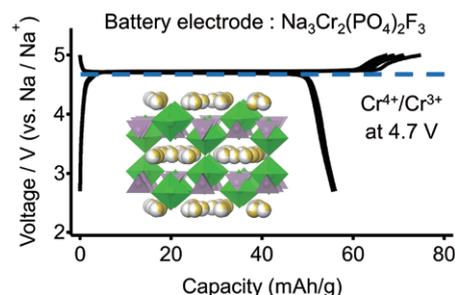
Gp-A04

**Kosuke Kawai**

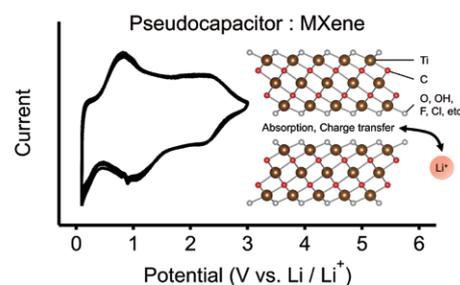
Waseda Univ. (Okubo Gr.)

/Energy storage materials

I graduated from the Undergraduate School of Industrial Chemistry, Kyoto University in 2016 and received my PhD from The University of Tokyo in 2021 under the supervision of Professor Atsuo Yamada. My research focuses on electrode materials for electrochemical energy storage. In my PhD course, I explored high-voltage cathode materials for rechargeable batteries. For example, using electrochemical measurements, X-ray diffraction, soft X-ray absorption spectroscopy, and first-principles calculations, I identified an extremely high operating potential of 4.7 V vs.  $\text{Na}/\text{Na}^+$  in  $\text{Na}_{3-x}\text{Cr}_2(\text{PO}_4)_2\text{F}_3$  ( $0 \leq x \leq 1$ ), which is attributable to the  $\text{Cr}^{4+}/\text{Cr}^{3+}$  redox couple (Fig. 1). In the Interface IONICS project, I explore electrode materials such as 2D metal carbides (MXenes, Figure 2) for solid-state energy storage devices and clarify the ion dynamics across electrode/electrolyte interfaces. I am grateful for this opportunity to participate in the Interface IONICS project and collaborate with excellent researchers in various fields.



**Figure 1.** Research theme in my PhD course.



**Figure 2.** Research theme in my current project.

## Research Assistants (PhD Students)

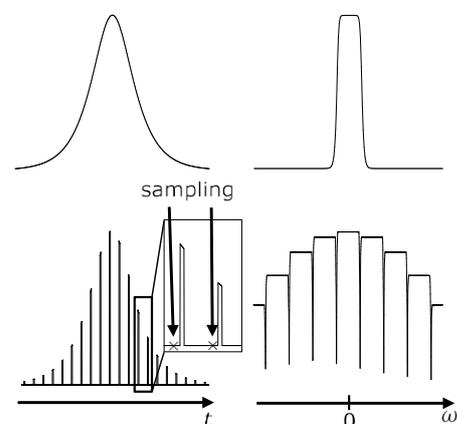


Gp-A02

**Yuta Hibe**

Kyoto Univ. D3 (Noda Gr.)  
/Magnetic resonance, Physical chemistry

Observing electric field distributions in solid electrolytes is difficult because the electric field is perturbed if a probe for observation contacts the electrolyte. Nuclear quadrupole resonance (NQR) provides clues about the electronic structure of materials through the electric-field gradient tensor at the site of a quadrupole nucleus, without requiring contact. However, finding unknown resonance frequencies, which are often scattered over a wide range, is a major challenge in NQR. Recently, we developed an efficient two-step NQR method by utilizing rapid scan and frequency comb techniques, which are based on the fact that NQR lines appear sparsely within the entire spectral range (right figure). This method, known as rapid-scan with gapped excitation with dual-mode operation (RASGADO) NQR, enables the rapid and easy acquisition of NQR spectra and can thus be used to observe the electric-field distribution in solid electrolytes.



**Figure.** Profile of the radio-frequency pulse (left) and excitation frequency (right) of a hyperbolic secant (HS) pulse (top) and a comb-modulated HS pulse (bottom). The inset describes the timing of sampling in RASGADO NQR. Y. Hibe *et al.*, *Phys. Chem. Chem. Phys.* **22**, 25584–25592. (2020).

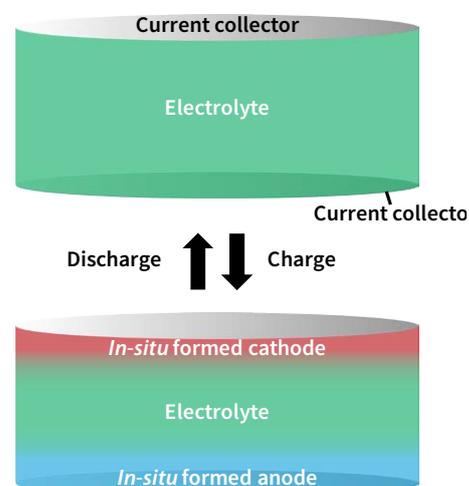


Gp-A04

**Akira Nishio**

Kyushu Univ. D3 (Inoishi Gr.)  
/ Polyanionic materials, Electrochemistry, X-ray analysis

Since joining the Okada–Kitajou–Inoishi group in 2017 for a master's course, I have been working on single-phase all-solid-state batteries constructed from a single material. The underlying objective of developing single-phase all-solid-state batteries is to reduce the interfacial resistance between the electrode/electrolyte in oxide-type batteries. Interfacial resistance is unavoidable in conventional oxide-type batteries because of side reactions during high-temperature sintering and impedance mismatching. Single-phase all-solid-state batteries enable the self-generation of electrodes from solid electrolytes as *in situ*-formed electrodes; thus, a dense interface is expected to form between the electrode and electrolyte. The materials of focus were mainly  $\text{Li}_{1.5}\text{Cr}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , which individually function as a cathode, anode, and electrolyte. We confirmed that the materials worked as single-phase all-solid-state batteries with a large current density, and we improved their electrochemical properties by adding borate salts. Having entered a doctoral course, I am now interested in cathode materials for high-voltage operation in all-solid-state  $\text{Na}^+$ -ion batteries. I highly appreciate this opportunity and look forward to contributing to this project.



**Figure.** Scheme of a single-phase all-solid-state battery during the charge/discharge process. The initial state is shown in the top schematic.

# Research Achievements

2021.1–2021.6

## Gp-A01 Model Interface

Gp-A01 has provided model electrode materials such as epitaxial thin-film electrodes and single-crystalline solid electrolytes to the members of Gp-A01, and collaborative research with Gp-A02 and Gp-A03 has also progressed. Relaxation analysis of charge accumulation in solid electrolytes and low-temperature

materials synthesis have provided new ideas. A novel approach for developing low-resistive electrode-solid-electrolyte interfaces using powdered materials and the results of our investigation regarding the effect of stress on the phase-transition mechanism of electrode materials are highlighted as follows.

### Highlight 1 A01-A03 joint paper

## Low-resistive $\text{LiCoO}_2/\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_2(\text{PO}_4)_3$ interface formation by low-temperature annealing using aerosol deposition

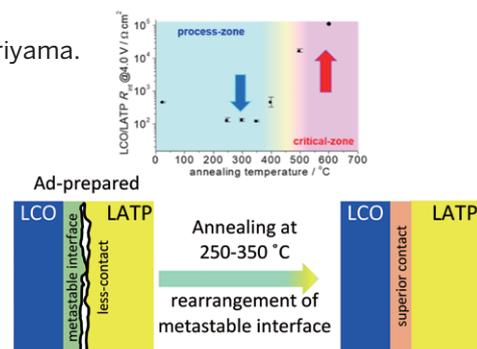
M. Sakakura, Y. Suzuki, T. Yamamoto, Y. Yamamoto, M. Motoyama, Y. Iriyama.

*Energy Technology*. vol. 9, 2001059 (2020)

<https://doi.org/10.1002/ente.202001059>

### Abstract

Crystalline electrode films of  $\text{LiCoO}_2$  (LCO) are formed on a high  $\text{Li}^+$  conductive crystalline-glass solid electrolyte sheet, LATP ( $\sigma_{25^\circ\text{C}} = 1 \times 10^{-4} \text{ S cm}^{-1}$ ), at room temperature by aerosol deposition (AD), and we investigate the effects of annealing temperature on the interfacial resistivities ( $R_{\text{int}}$ ) at the LCO/LATP. The  $R_{\text{int}}$  visibly increase by the annealing over  $500^\circ\text{C}$  with the growth of  $\text{Co}_3\text{O}_4$  as a reactant. On the other hand, the  $R_{\text{int}}$  is reduced to  $\sim 100 \Omega\text{cm}^2$  by low-temperature annealing at  $250\text{--}350^\circ\text{C}$  due to superior contact through



the structural rearrangement of an artificial metastable interface formed by the AD. We apply these results to bulk-type Ox-SSB, Li/LLZ/LCO-LATP, and our best Ox-SSB delivers discharge capacity at  $100 \text{ mA/cm}^2$  at  $100^\circ\text{C}$ . [Reproduced with permission of Wiley-VCH.]

### Highlight 2 A01-A02 joint paper

## Experimental evaluation of influence of stress on Li chemical potential and phase equilibrium in two-phase battery electrode materials

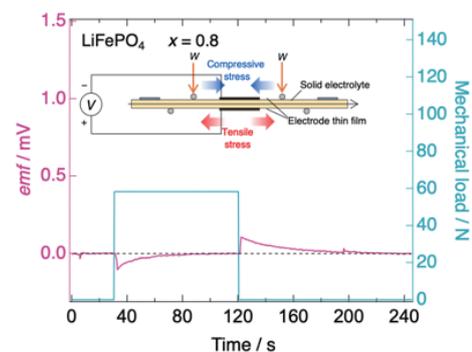
Y. Kimura, K. Funayama, M. Fakkao, T. Nakamura, N. Kuwata, T. Kawada, J. Kawamura, K. Amezawa.

*Electrochemistry*. vol. 89, issue 4, pp. 355-362 (2021)

<https://doi.org/10.5796/electrochemistry.21-00033>

### Abstract

We experimentally evaluated the influence of stress on Li chemical potential ( $\mu_{\text{Li}}$ ) and phase equilibrium in two-phase battery electrode materials through the *emf* measurements under a mechanical load, in collaboration with Advanced Analysis group (Gp-A02). Our results indicated that  $\mu_{\text{Li}}$  in the two-phase electrode materials ( $\text{LiFePO}_4$  or  $\text{LiCoO}_2$  in the two-phase region) immediately changed just after loading and gradually changed under a constant mechanical load. Besides, the loading/unloading led to the opposite  $\mu_{\text{Li}}$  variation. Such characteristic  $\mu_{\text{Li}}$  variations were explained by the change in the phase equilibrium between the two



phases, *i.e.* variations of the Li content and the volume fraction in the two phases. Our results can provide insights into the influence of stress on the performances of two-phase electrode materials. [Reproduced with permission of the Electrochemical Society of Japan.]

## Gp-A02 Advanced Analysis

In this group, we aim to understand unique ion transport/storage phenomena at solid-state interfaces through comprehensive analyses. We have been establishing and improving various novel and advanced analytical techniques and systematically applying them to model solid-state interfaces, such as a well-defined film electrode on a solid

electrolyte and glass-ceramic electrolytes, which were supplied by Gp-A01 and Gp-A04, respectively. Using the obtained results, together with the results of theoretical calculations and simulations carried out by Gp-A03, we will establish scientific principles that enable the design of high-performance solid-state interfaces.

### Highlight 3 A02-A03-A04 joint paper

## Visualization of structural heterogeneities in particles of lithium nickel manganese oxide cathode materials by ptychographic X-ray absorption fine structure

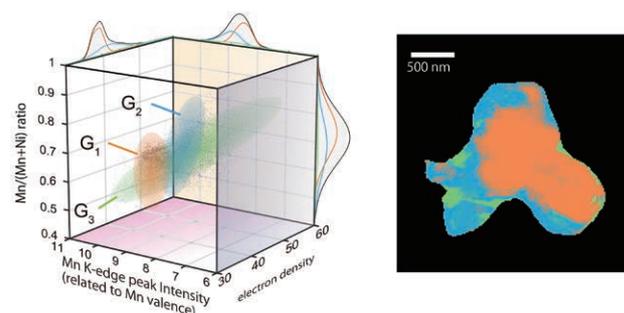
H. Uematsu, N. Ishiguro, H. C. Dam, M. Okubo, Y. Takahashi, *et al.*

*J. Phys. Chem. Lett.* vol. 12, pp. 5781–5788 (2021)

<https://doi.org/10.1021/acs.jpcllett.1c01445>

### Abstract

A heterogeneous phase/structure distribution in the bulk of active materials is the key to maximize the performance and stability of cathode/anode of lithium-ion batteries. In this paper, we report the use of two-dimensional ptychographic X-ray absorption fine structure to visualize the density and valence maps of manganese and nickel in as-prepared lithium nickel manganese oxide particles and unsupervised learning to classify the three-phase group in terms of different elemental compositions and chemical states. The described approaches may increase the supply of information for nanoscale characterization and promote



the design of suitable structural domains to maximize the performance and stability of batteries. [Reproduced with permission of the American Chemical Society.]

### Highlight 4 A02-A04 joint paper

## Microstructure and charge–discharge mechanism of a $\text{Li}_3\text{CuS}_2$ positive electrode material for all-solid-state lithium-ion batteries

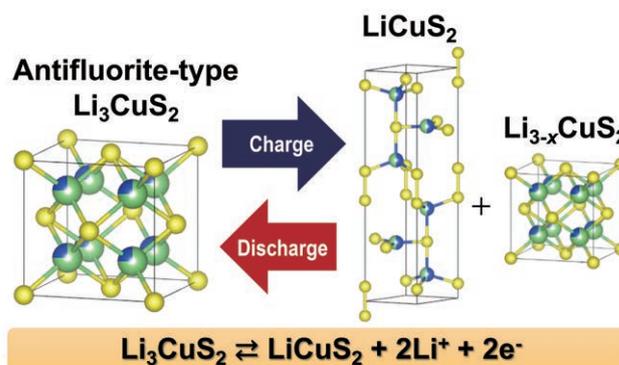
T. Ayama, H. Tsukasaki, A. Hayashi, S. Mori, *et al.*

*ACS Appl. Energy Mater.* vol. 6, pp. 6290–6295 (2021)

<https://doi.org/10.1021/acsaem.1c01074>

### Abstract

$\text{Li}_3\text{CuS}_2$  is a promising candidate for positive electrodes for sulfide-based all-solid-state batteries exhibiting excellent cycle characteristics. To clarify the charge–discharge mechanism of  $\text{Li}_3\text{CuS}_2$ , we examined the microstructural changes during charge–discharge cycles by transmission electron microscopy (TEM). The hollow-corn dark-field imaging technique was employed to evaluate the crystallite size distribution. The result shows that the crystallite size of  $\text{Li}_3\text{CuS}_2$  reversibly decreases/increases in the charging/discharging state, respectively. The electron diffraction pattern shows that  $\text{LiCuS}_2$  was formed during charging by  $\text{Li}^+$  extraction from  $\text{Li}_3\text{CuS}_2$ . In discharging, the crystallite size increased



and  $\text{Li}_3\text{CuS}_2$  was reproduced. The TEM results suggest that such reversible structural changes of  $\text{Li}_3\text{CuS}_2$  would contribute to high charge–discharge characteristics. [Reproduced with permission of the American Chemical Society.]

## Gp-A03 Computational & Data Science

To construct a theoretical framework for Interface IONICS, Gp-A03 has introduced two strategies: a computational approach and a data science approach. With the development of novel techniques and deep collaboration with the experimental groups (Gp-A01, -A02, and -A04), we have achieved new understanding

of interfacial phenomena. Recently, a new simulation approach was developed to understand mesoscale fabrication and degradation behaviors. Besides, a microscopic electrochemistry concept has been demonstrated via density functional theory simulations.

### Highlight 5

## Simulation of fabrication and degradation of all-solid-state batteries with ductile particles

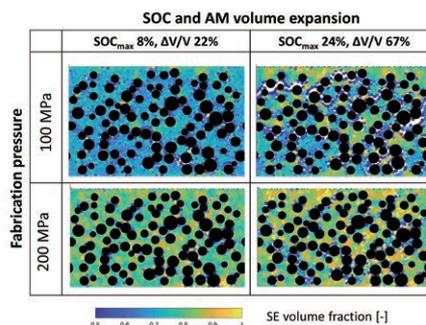
M. So, G. Inoue, R. Hirate, K. Nunoshita, S. Ishikawa, Y. Tsuge.

*J. Electrochem. Soc.* Vol. 168, pp. 030538 (2021)

<https://doi.org/10.1149/1945-7111/abed23>

### Abstract

We simulated cold press fabrication and intercalation damage in a sulfide All-Solid-State Battery (ASSB) electrode using the Discrete Element Method. We developed a new cohesive hybrid-particulate model that both can simulate particle consolidation during fabrication and material failure during intercalation expansion. In this way, the effect of the fabrication conditions on the mechanical degradation of the electrode can be simulated. The high pressure in the cold press fabrication cause plastic deformation and build-up of cohesive contacts between the particles, consisting of Si active material (AM) and sulfide solid electrolyte (SE), resulting in densification of the electrode. During charging, when AM expands during lithiation, the AM-SE contact area increases but the



effective SE conductivity decreases. When the expansion is small, the contact area and conductivity may recover to their original value. However, large expansion may cause plastic deformation and cracking that cause permanent reduction of both contact area and SE conductivity. This type of mechanical degradation was significantly less for electrodes fabricated at higher pressures. This model can become a valuable tool to improve the durability and performance of future ASSBs. [Reproduced with permission of IOP Science.]

### Highlight 6

## First-principles study of microscopic electrochemistry at the LiCoO<sub>2</sub> cathode/LiNbO<sub>3</sub> coating/ $\beta$ -Li<sub>3</sub>PS<sub>4</sub> solid electrolyte interfaces in an all-solid-state battery

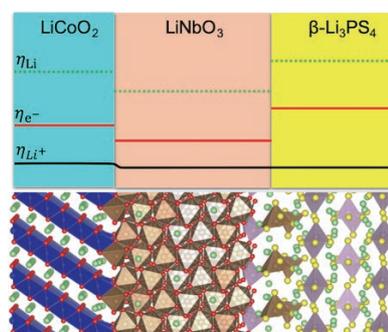
B. Gao, R. Jalem, Y. Tateyama.

*ACS Appl. Mater. Interfaces* vol. 13, pp. 11765 (2021)

<https://doi.org/10.1021/acsami.0c19091>

### Abstract

“Microscopic electrochemistry” for the electrochemical potential and the distribution of Li<sup>+</sup> around the interface has not been well established yet. Herein, we have introduced a potential energy profile for Li<sup>+</sup>,  $\eta_{\text{Li}^+}$ , and demonstrated that the interfacial  $\eta_{\text{Li}^+}$  can be evaluated from the calculated interfacial Li vacancy formation energy or the bulk vacancy formation energy and the interface band alignment. Through computational analysis of LiCoO<sub>2</sub> cathode/LiNbO<sub>3</sub> coating/ $\beta$ -Li<sub>3</sub>PS<sub>4</sub> solid electrolyte interfaces, we found that  $\eta_{\text{Li}^+}$  at the LiCoO<sub>2</sub>/ $\beta$ -Li<sub>3</sub>PS<sub>4</sub> interface is highly disordered under the influence of the interface reconstruction and is



rather electronic conductive. LiNbO<sub>3</sub> coating results in the appropriate changes in band alignments, leading to a decrease of difference in the interfacial  $\eta_{\text{Li}^+}$  and thus lower resistances at the interfaces. [Reproduced with permission of the American Chemical Society.]

## Gp-A04 Design of Functional Interface

Gp-A04 designs innovative solid-state ionic materials (SSIMs) through interface engineering. With an increase in the concentration of grain boundaries, charge carriers are efficiently accumulated in SSIMs, resulting in new structures and functionalities. Such

### Highlight 7

#### Nonpolarizing oxygen-redox capacity without O-O dimerization in $\text{Na}_2\text{Mn}_3\text{O}_7$

A. Tsuchimoto, X.-M. Shi, K. Kawai, B. M. Boisse, J. Kikkawa, D. Asakura, M. Okubo, A. Yamada.

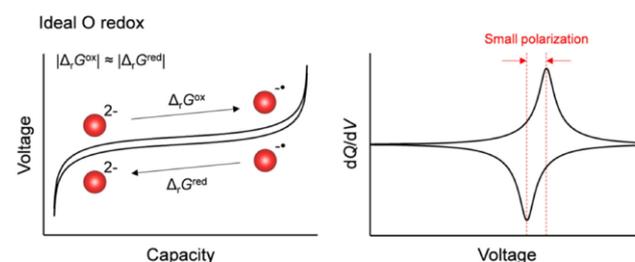
*Nature Communications* vol. 12, Article number: 631 (2021)

<https://doi.org/10.1038/s41467-020-20643-w>

#### Abstract

Reversibility of an electrode reaction is important for energy-efficient rechargeable batteries with a long battery life. Additional oxygen-redox reactions have become an intensive area of research to achieve a larger specific capacity of the positive electrode materials. However, most oxygen-redox electrodes exhibit a large voltage hysteresis  $>0.5$  V upon charge/discharge, and hence possess unacceptably poor energy efficiency. The hysteresis is thought to originate from the formation of peroxide-like  $\text{O}_2^{2-}$  dimers during the oxygen-redox reaction. Therefore, avoiding O-O dimer formation is an essential challenge to overcome. Here, we focus on  $\text{Na}_{2-x}\text{Mn}_3\text{O}_7$ , which we recently identified to exhibit a large

functionalities have been applied to new solid-state ionic devices. Collaborative studies with members of Gp-A02 and Gp-A03 have further accelerated the development of new solid-state devices.



reversible oxygen-redox capacity with an extremely small polarization of 0.04 V. Using spectroscopic and magnetic measurements, the existence of stable  $\text{O}^{\cdot-}$  was identified in  $\text{Na}_{2-x}\text{Mn}_3\text{O}_7$ . Computations reveal that  $\text{O}^{\cdot-}$  is thermodynamically favorable over the peroxide-like  $\text{O}_2^{2-}$  dimer as a result of hole stabilization through a  $(\sigma + \pi)$  multiorbital Mn-O bond. [Reproduced with permission of Springer Nature.]

### Highlight 8

#### Why is O3 to O1 phase transition hindered in $\text{LiNiO}_2$ on full delithiation?

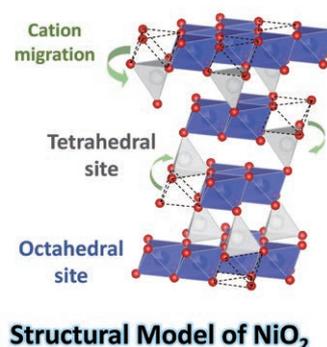
N. Ikeda, I. Konuma, R. H. Basappa, T. Aida, N. Yabuuchi.

*Journal of Materials Chemistry A* vol. 9, pp. 15963-15967 (2021)

<https://doi.org/10.1039/D1TA03066C>

#### Abstract

Ni-enriched layered materials are utilized as positive electrode materials of high-energy Li-ion batteries. Because electrode reversibility is gradually lost for stoichiometric  $\text{LiNiO}_2$  on continuous cycles, Ni ions are partly substituted by other metal ions (Co, Mn, Al etc.). However, the origin of deterioration in stoichiometric  $\text{LiNiO}_2$  is still not fully understood yet. Moreover, the loss of capacities is observed only for a high voltage region ( $> 4.1$  V), which is obviously different from a failure mode observed in other electrode materials. Here, we first report the origin of deterioration, which is revealed by *in-situ* X-ray diffraction study. For fully charged  $\text{NiO}_2$ , Ni ions migrate from original octahedral sites in  $\text{NiO}_2$  slabs to face-sharing tetrahedral sites in Li layers, by which the O3 to O1 phase transition is suppressed. Note that Ni migration is a reversible process, and the Ni ions migrate back to the original octahedral sites



on discharge. However, after continuous cycles, the reversibility of Ni migration is gradually lost, and Ni ions are partially left at the tetrahedral sites in Li layers. Electrode kinetics are also deteriorated because of the Ni occupation in Li layers, and the accumulation of Ni ions at tetrahedral sites results in the loss of reversible capacities at the high voltage region. This finding opens a new way to design high-capacity Ni-enriched electrode materials, leading to the development of high-energy Li-ion batteries. [Reproduced with permission of Royal Society of Chemistry.]

# Activity Reports

Conferences Partially Supported by the Interface IONICS Project

## Co-organized Symposium “Science on Interfacial Ion Dynamics for Solid State Devices” of the 101st CSJ Annual Meeting (Online)

Mar. 20, 2021

Prof. Kaoru Dokko, Yokohama National Univ.

The Symposium on Science on Interfacial Ion Dynamics for Solid-State Devices was held as a co-organized session during the 101st Chemical Society of Japan (CSJ) Annual Meeting. Seven members of the project delivered talks on recent progress in research on new solid-state ionics materials and their interfacial characteristics. Approximately 200 people participated in the online meeting. The Q&A session allowed the project members to discuss their work with symposium participants, including both those within and those outside the project, and led to insightful comments. The meeting was a fruitful opportunity to share recent results of the project.



## Symposiums and Seminars

### Interface IONICS Online Symposium 2021 Spring

Mar. 9, 2021

Assoc. Prof. Masaki Matsui, Kobe Univ.

The Interface IONICS Online Symposium 2021 Spring was held on March 9, 2021. The symposium provided an opportunity for scientists, engineers, and students to engage in deep discussions on specific topics. The Interface IONICS members and global scientists in academia discussed the following two topics: “The lithium metal/garnet-type solid-state electrolyte interface” and “the compositional nonstoichiometry issue at the solid–solid interface.” More than 60 participants, including 23 from overseas, joined the meeting.

The Keynote Lecture by Prof. Weppner of Kiel University provided an overview of the garnet/Li metal interface from a thermodynamics perspective. Prof. Zeier of the University of Münster presented a talk concerning the relationship between electrolyte degradation and ionic transport properties. Dr. Tateyama and Prof. Motoyama from Interface IONICS discussed the garnet/Li metal interface from theoretical and experimental perspectives. Prof. Amezawa delivered a talk about the thermodynamics of the solid–solid interface. Prof. Iriyama discussed

the influence of the change in Li concentration at the interface.

The symposium finished past the scheduled time because of the very active discussions related to each topic. We thank all of the participants and look forward to our next opportunity to host a topical symposium.



## Domestic Training Program Reports

### Visiting the Iriyama group in Nagoya University

Nov. 27, 2020

Assoc. Prof. Masaki Matsui, Kobe Univ.

We (Matsui and his student, Shuang Li) visited Prof. Iriyama's group at Nagoya University to learn the electrode fabrication process for Li-metal anodes using thermal vapor deposition. Because Li metal is highly reactive toward O<sub>2</sub> and moisture, even in an Ar-filled glove box, the deposition process must be carefully controlled to avoid unexpected passivation of the deposited Li. Mr. Kitagawa and Mr. Sugiura of Prof. Iriyama's group generously described the details of the experimental conditions and shared their expertise on Li deposition. They also demonstrated the Li-vapor deposition process on sintered pellets of our garnet-type solid electrolyte Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub> (LLZTO). Because of their informative lecture and demonstration, we can now prepare Li-deposited LLZTO samples for

electrochemical measurements in our lab. We also discussed the synthesis process of layered lithium cobalt oxide (LCO) at low temperatures with Prof. Iriyama. The low-temperature process enables us to avoid any side reaction between LCO and a solid-state electrolyte such as LAMP or LLZTO. We expect to use the new electrode fabrication process to prepare a model solid–solid interface. We are grateful to the Interface IONICS project for providing excellent collaboration opportunities.



## Domestic Training Program Reports

### Visiting the Kawada, Amezawa, and Kumatani groups in Tohoku University

Dec. 2 – 3, 2020

Lect. Munekazu Motoyama, Nagoya Univ.

From December 2 to 3, 2020, two graduate students and I visited three laboratories at Tohoku University. On the first day, we wanted to learn more about “chemical capacitance” and visited Prof. Tatsuya Kawada and Associate Prof. Keiji Yashiro, who have published numerous papers on the chemical capacitance of solid oxide fuel cells, on the Aobayama Campus. We discussed with Prof. Kawada and Prof. Yashiro whether chemical capacitance is negligible in all-solid-state Li batteries. After a few hours of discussion, we toured their laboratory. The opportunity for us to ask Prof. Kawada and Prof. Yashiro about their expertise in electrochemical measurements of solid-state cells was meaningful. We later visited Prof. Koji Amezawa's laboratory on the Katahira Campus, where we discussed the results of numerical simulations for the voltage profile of thin-film all-solid-state Li batteries during

charging and discharging. I also delivered a talk on our research on Li plating/stripping reactions on oxide solid electrolytes.

On the second day, we visited Associate Prof. Akichika Kumatani (Y. P. Chen–Kumatani–Tanigaki group) on the Katahira Campus and were granted a tour of his laboratory. We were fascinated by the numerous instruments and microscopes fabricated in the lab. We discussed new experiments and proposed new joint research themes. During this visit, we rediscovered the significance of face-to-face interactions.



## Domestic Training Program Reports

### Visiting the Aso group in Kyushu University

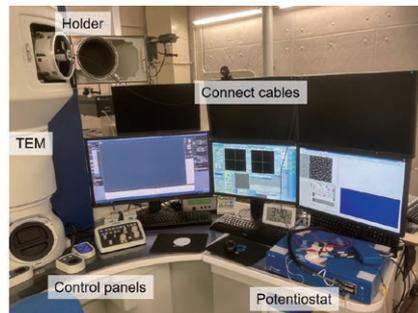
Apr. 1 – 2, 2021

Assoc. Prof. Ryotaro Aso, Kyushu Univ.

Mr. Yuki Nojima (Prof. Iriyama's lab, Nagoya University) and Dr. Kazuo Yamamoto (Japan Fine Ceramics Center) visited the Ultramicroscopy Research Center (URC) in Kyushu University on April 1–2, 2021. The URC offers shared-use facilities for electron microscopy. During this visit, we used the atomic-resolution analytical

transmission electron microscope (JEOL JEM-ARM200CF) and an *in situ* electric-biasing TEM sample holder. We had previously discussed the shape of the TEM sample and how to set it on the TEM holder and connect it to a potentiostat. Thus, we could conduct *in situ* observations as a voltage was applied to the sample

in the transmission electron microscope (see figure). We observed the atomic structures in the vicinity of the interfaces in a Cu/LiLaNbO/Cu cell using scanning transmission electron microscopy (STEM). In addition, by applying the voltage *in situ*, we could observe the nanostructures at the atomic scale during the charge-discharge process. This visit was productive, and we hope that the technique established during this visit will be useful for observing various solid-state interfaces.



## Domestic Training Program Reports

### Visiting the Mori group in Osaka Prefecture University

Mar. 1 – Apr. 23, 2021

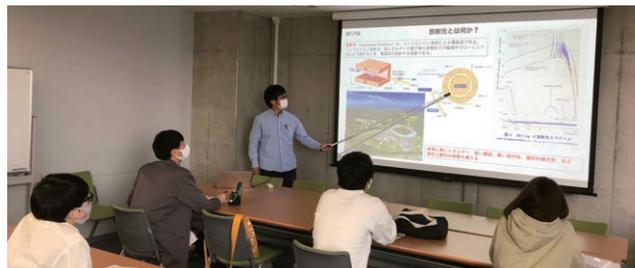
Dr. Satoshi Hiroi, JASRI

I visited Mori laboratory at Osaka Prefecture University in Osaka from March 1st to April 23rd. The purpose of this visit was to share the X-ray experimental data obtained by the Ohara group and the electron-beam experimental data obtained by the Mori group. Assembling the structural information obtained by Gp-A02 is expected to contribute to the material development by Gp-A04. My discussions with the members of the group and observations of the electron-beam measurements were exciting experiences.

During this visit, we shared information related to the structural analysis of  $\text{Li}_3\text{PS}_4$  glass-ceramic electrolytes and  $\text{Na}_3\text{PS}_4$  electrolytes. The Ohara group has already performed total X-ray scattering measurements on these electrolytes and have obtained the atomic pair distribution functions (PDFs). By contrast, the Mori group has been carrying out structural analyses of the  $\text{Li}_3\text{PS}_4$  and  $\text{Na}_3\text{PS}_4$  electrolytes using electron-beam measurements. The results of each measurement technique have unique features depending on the probe. We expect that understanding of the atomic arrangement of solid electrolytes will be improved by the complementary use of these data. Through this visit, we have achieved an understanding of the structural analysis data of both groups.

To deepen the group members' understanding of structural analysis techniques, seminars on X-ray diffraction/total scattering measurements were conducted

by the Mori group and the Hayashi group (Gp-A04) during this visit. In this seminar, I discussed the principles of the X-ray total scattering measurements, the calculation procedures and interpretation of the atomic PDFs, structural analysis methods for amorphous materials using reverse Monte Carlo modeling, and the application of the PDF method to the analysis of crystalline materials. The local structure information obtained by the atomic pair correlation function is promising for investigating the changes caused by the charging and discharging processes of energy storage devices. Therefore, X-ray total scattering is expected to play a critical role as an analysis method in the future development of materials. By sharing these analysis techniques with other researchers, I hope to contribute to the development of new processes for synthesizing and improving the performance of energy storage devices from the viewpoint of the local structure.



A basic seminar held at Osaka Prefecture University for undergraduate students in the Mori group.

## Award Winners

 **The Chemical Society of Japan Award for Creative Work for 2020**

**Akitoshi Hayashi (Gp-A04) Professor / Osaka Prefecture Univ.**

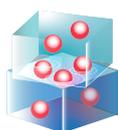
“Solid electrolytes based on inorganic chemical process and their application to all-solid-state batteries”

 **The 75th CerSJ Awards for Academic Achievements in Ceramic Science and Technology**

**Masanobu Nakayama (Gp-A03) Professor / Nagoya Institute of Technology**

“Materials informatics for discovery of ion-conductive ceramics for batteries”

# Newsletter vol.4



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**Publisher/Contact**

Office for Scientific Research on Innovative Areas:  
Science on Interfacial Ion Dynamics for Solid State Ionics Devices

TEL: +81-52-789-3576

E-mail: [office@int-ionics.material.nagoya-u.ac.jp](mailto:office@int-ionics.material.nagoya-u.ac.jp)

<https://interface-ionics.jp/en/index.html>

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