

Interface IONICS

Science on Interfacial Ion Dynamics for Solid State Ionics Devices

Newsletter Vol.6

September 2022

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 fourth year of Interface IONICS started in April 2022, and 22 researchers from 17 universities or institutes joined the project as “publicly offered research” members, conducting research for two years. The Interface IONICS program continues to promote the fusion of different academic research fields, promote the careers of young researchers, foster international friendship, and collaborate with national projects currently underway.

Finally, we hope that all of you maintain good health under these very difficult conditions.

Yasutoshi Iriyama, Principal Investigator
Nagoya University

Contents

New Members

Publicly Offered Researchers / 2022.4-2024.3

Model Interface (Gp-A01)	3
Advanced Analysis (Gp-A02)	4
Computational & Data Science (Gp-A03)	5
Design of Functional Interface (Gp-A04)	5

Research Achievements

Model Interface (Gp-A01)	7
Advanced Analysis (Gp-A02)	8
Computational & Data Science (Gp-A03)	9
Design of Functional Interface (Gp-A04)	10

Activity Reports

Interface IONICS Online Symposium 2022	11
The 3rd Interface IONICS Seminar	11

New Members

Publicly Offered Researchers 2022.4 – 2024.3

In April 2022, we welcomed 22 “publicly offered researchers,” who will contribute to our project with their proposal-based research.

Gp-A01 Model Interface



Yuki Maruyama

Assistant Professor / Univ. Yamanashi / Crystal growth

Bulk single crystals are useful for our understanding interfacial properties. The purpose of my study is to grow bulk single crystals of Li⁺-ion conductors by the floating-zone method and to clarify their basic physical properties such as their anisotropic ionic conductivity.



Yuta Maeyoshi

Researcher / AIST / Electrochemistry

I aim to develop organic solid electrolytes and design electrolyte/Li-metal interfaces that exhibit high ion transport and accumulation properties to facilitate dense Li deposition, high Li plating/stripping efficiency, and long cycle life of Li-metal anodes.



Yuta Kimura

Assistant Professor / Tohoku Univ. / Solid state ionics

Mechanical stress can strongly affect the interfacial properties of solid state ionics materials (SSIMs). In this study, I aim to quantitatively evaluate the influence of stress on material–interfacial properties of SSIMs and to provide deeper insights into the interfacial phenomena in SSIMs.



Takayuki Doi

Professor / Doshisha Univ. / Electrochemistry

We introduce a solid electrolyte interphase between a Si thick-film electrode and a solid electrolyte to facilitate interfacial Li⁺-ion transfer. The morphology, structure, and composition of the interphase are investigated to elucidate factors that enable the rapid interfacial transfer and high-density storage of Li⁺ ions.



Wataru Norimatsu

Associate Professor / Nagoya Univ. / Surface-structure physics and properties

I investigate the intercalation and desorption phenomena of Li⁺ ions in high-quality samples of large-area epitaxial graphene. Using atomic-force microscopy and Raman spectroscopy, I plan to reveal how and from where Li⁺ ions are intercalated.



Munekazu Motoyama

Associate Professor / Kyushu Univ. / Electrochemistry

My goal is to understand how stable Li plating/stripping cycles via Li/oxide–solid-electrolyte interfaces are possible under hydrostatic pressures on the order of 10^2 MPa, which are much greater than the yield strength of Li (approximately 1 MPa).

Gp-A02 Advanced Analysis



Takahiro Ito

Associate Professor / Nagoya Univ. / Photoemission spectroscopy

The purpose of my study is to elucidate the electronic structure of solid state ionic materials (bulk solid-electrolyte single crystals) using angle-resolved photoemission spectroscopy. Photo- or electric-field-induced modulations will also be investigated to gain insights into the mechanism of the ion-conduction process.



Ryotaro Aso

Associate Professor / Kyushu Univ. / Electron microscopy

The objective of my study is to reveal the relation between structural strain/distortion and ion diffusion at solid-state ionic interfaces using a combination of operando atomic-resolution scanning transmission electron microscopy, energy-dispersive X-ray spectroscopy, and electron energy-loss spectroscopy.



Yasuto Noda

Assistant Professor / Kyoto Univ. / Magnetic resonance (NMR and NQR)

The purpose of my study is to develop a magnetic resonance method that enables noncontact and nondestructive probing of the electric field involving the conduction and accumulation of ions at the interface of an ionic conductor by using the nuclear spins as a spy.



Takuya Majima

Associate Professor / Kyoto Univ. / Ion-beam science

To reveal the ion transport and storage behavior near the interfaces of solid state ionic materials (SSIMs), we directly observe the spatial (depth) distribution of Li atoms and ions near the interface using time-of-flight elastic recoil detection analysis (TOF-ERDA) with MeV-energy heavy-ion beams.



Kentaro Yamamoto

Associate Professor / Nara Women's Univ. / Inorganic materials chemistry

The purpose of my study is to use operando time-resolved X-ray reflectivity to observe structural changes at solid–solid interfaces during ion transport reactions and to clarify the relationship between the structural changes and the ion transport at the interfaces.

Gp-A03 Computational & Data Science



Shusuke Kasamatsu

Associate Professor / Yamagata Univ. /Ab initio thermodynamics

My research aim is to provide a consistent picture of electrochemical solid–solid interfaces by considering the huge configurational degrees of freedom of carriers and dopants as well as the electrochemical potential of ions and electrons in electrodes.



Ryo Kobayashi

Assistant Professor / Nagoya Inst. of Tech. / Computational materials science

The goal of my project is to understand the mechanism of grain-boundary resistance to ion migration in solid-state electrolyte materials from an atomistic perspective. We have developed a high-throughput method of producing force fields and will use it to perform molecular dynamics simulations.



Koji Shimizu

Assistant Professor / Univ. of Tokyo / Density functional theory calculations

With the aid of DFT calculations and machine learning potentials, we will investigate the ion dynamics across electrode–solid-electrolyte interfaces. By analyzing structural factors and compositional variations, we will clarify the atomic-scale origin of the interface resistance.

Gp-A04 Design of Functional Interface



Atsunori Ikezawa

Assistant Professor / Tokyo Inst. of Tech. / Electrochemistry

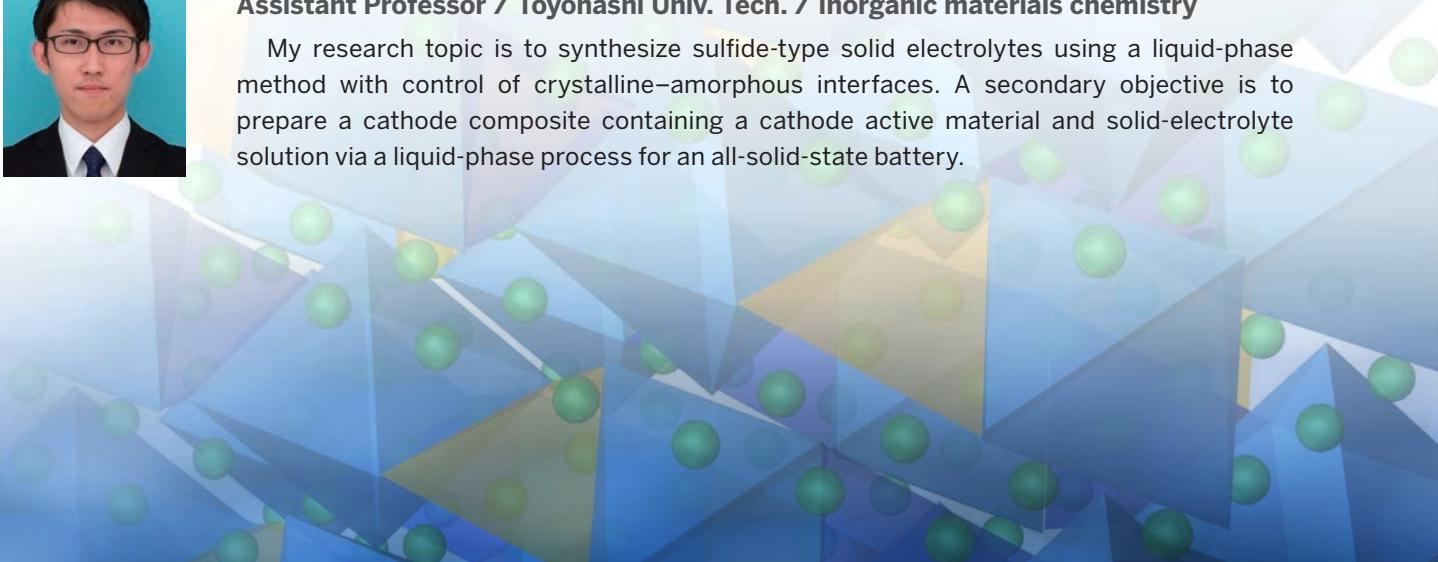
We develop reference electrodes applicable to solid electrolytes and construct all-solid-state four-electrode cells to investigate Li⁺-ion transfer at solid–solid interfaces using electrochemical measurements such as cyclic voltammetry and AC impedance spectroscopy.



Kazuhiro Hikima

Assistant Professor / Toyohashi Univ. Tech. / Inorganic materials chemistry

My research topic is to synthesize sulfide-type solid electrolytes using a liquid-phase method with control of crystalline–amorphous interfaces. A secondary objective is to prepare a cathode composite containing a cathode active material and solid-electrolyte solution via a liquid-phase process for an all-solid-state battery.





Daisuke Mori

Associate Professor / Mie Univ. / Solid-state chemistry

Both high electronic conductivity and high ionic conductivity of an electrode are desired to improve the input–output characteristics of all-solid-state batteries. In this study, a cathode material with high electronic conductivity is investigated to develop a cathode/electrolyte composite with high capacity and good input–output characteristics.



Saneyuki Ohno

Assistant Professor / Kyushu Univ. / Materials science

Although fast carrier transport within an electrode is paramount for energy storage devices, carrier mobility in solid state composite electrodes with a high interfacial area density is surprisingly slow. My research aims to better understand the origin of such sluggish transport, with the objective of opening a path for the use of insulating active materials.



Atsushi Inoishi

Assistant Professor / Kyushu Univ. / Inorganic materials

Conversion-type electrodes such as MgH₂ form the electrolyte LiH during lithiation. Understanding the mechanism of this *in situ* electrolyte formation enables the development of a solid-state battery with a high energy density. I study the details of the mechanism (e.g., the redox couple and the distribution of the formed electrolyte) in this type of electrode.



Teruo Kanki

Associate Professor / Osaka Univ. / Nanomaterials physics

My research objective is the development and analysis of an exotic transistor in which proton motion is controlled by an electric field at a VO₂ channel interface. This control leads to both switching and memory functions, accompanied by a structural transformation between insulating HVO₂ and metal-like VO₂.



Takashi Tsuchiya

Principal Researcher / National Inst. Materials Science / Solid state ionics

In my study, I will tackle the development of novel physical-property tuning devices based on the principles of solid state ionics by focusing on electric carrier accumulation mechanisms (e.g., redox and electric-double-layer effects) in the vicinity of solid (electrode)–solid-electrolyte interfaces.



Kan Hatakeyama-Sato

Assistant Professor / Waseda Univ. / Polymer chemistry

My research focuses on emerging glassy-type solid-polymer electrolytes composed of charge-transfer complexes. Although these electrolytes' ion-transport processes have not yet been revealed, optimal interface design should be a key to obtaining organic conductors with superionic properties.

Research Achievements

2022.1–2022.6

Gp-A01 Model Interface

Gp-A01 has been conducting fundamental research on model interfaces using thin-film and single-crystal materials. Some of their recent topics are highlighted as follows.

Highlight 1 A01 and A04 joint paper

Reaction mechanism of Li_2MnO_3 electrodes in an all-solid-state thin-film battery analyzed by operando hard X-ray photoelectron spectroscopy

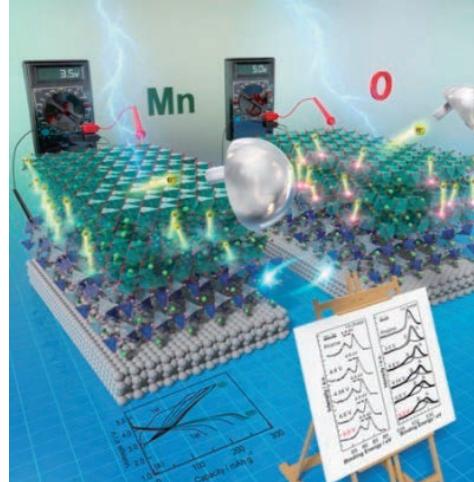
K. Hikima, K. Shimizu, H. Kiuchi, Y. Hinuma, K. Suzuki, M. Hirayama, E. Matsubara, R. Kanno.

J. Am. Chem. Soc. vol. 144, pp. 236–247 (2022)

<https://doi.org/10.1021/jacs.1c09087>

Abstract

Li_2MnO_3 is a promising cathode candidate for Li-ion batteries because of its high discharge capacity; however, its reaction mechanism during cycling has not been sufficiently explicated. Observations of Mn and O binding energy shifts in operando hard X-ray photoelectron spectroscopy measurements enabled us to determine the charge-compensation mechanism of Li_2MnO_3 . The O 1s peak splits at an early stage during the first charge, and the concentration of lower-valence O changes reversibly with cycling, indicating the formation of a low-valence O species that intrinsically participates in the redox reaction. [Reproduced with permission of the American Chemical Society.]



Highlight 2 A01 and ALCA-SPRING joint paper

In-situ X-ray diffraction of LiCoO_2 in thin-film batteries under high-voltage charging

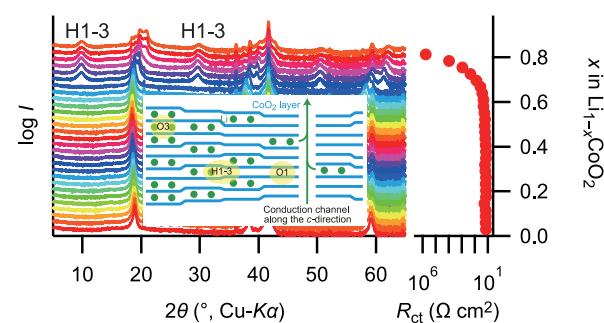
T. Ohnishi, K. Mitsuishi, K. Takada.

ACS Appl. Energy Mater. vol. 4, pp. 14372–14379 (2021)

<https://doi.org/10.1021/acsaem.1c03046>

Abstract

LiCoO_2 has been used as the cathode material employed in lithium-ion batteries since their birth, and efforts to improve its performance are still in progress. For example, complete use of lithium provides the theoretical capacity as high as 274 mAh g^{-1} ; however, charge-discharge cycling with such a high capacity leads to rapid degradation. The degradation mechanism has been intensively studied in order to increase the practical capacity. Although phase transitions taking place in high-voltage charging has been considered to affect the cycling performance, side reactions induced by the high-voltage charging always overlap to blur the effects of phase transitions on the electrode properties. This study has unveiled the relation between the phase



transition and electrode properties by employing a solid electrolyte that suppresses the side reactions efficiently. Electrochemical impedance spectroscopy combined with in-situ X-ray diffraction shows the clear correlation between phase transition from O3 to H1-3 and drastic increase in the electrode resistance. The increasing resistance is attributable to formation of narrow interlayers with gallery height of 4.2 Å that impede lithium-ion diffusion. [Reproduced with permission of the American Chemical Society.]

Gp-A02 Advanced Analysis

This group aims to understand unique ion transport/storage phenomena at solid state interfaces through comprehensive analyses. We have been establishing/improving various novel and advanced analytical techniques and systematically applying them to typical 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. On the basis of the obtained results, together with assistance from theoretical calculations and simulations conducted by Gp-A03, we will establish scientific principles that enable the design of high-performance solid state interfaces.

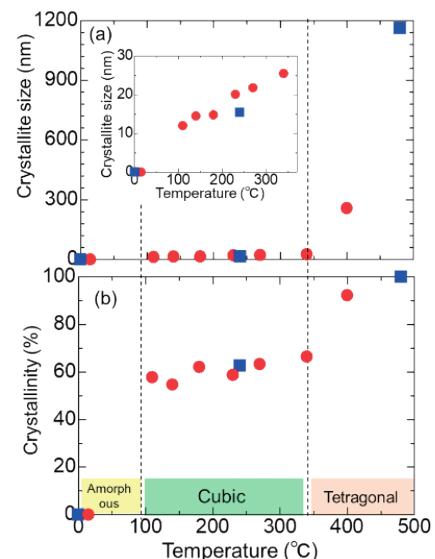
Highlight 3 A02 and A04 joint paper

Crystallization behaviors in superionic conductor Na_3PS_4

H. Nakajima, H. Tsukasaki, J. Ding, T. Kimura, T. Nakano, A. Nasu, A. Hirata, A. Sakuda, A. Hayashi, S. Mori
J. Power Sources. vol. 511, 230444 (2021)
<https://doi.org/10.1016/j.jpowsour.2021.230444>

Abstract

All-solid-state batteries based on sodium compounds are regarded as promising candidates for next-generation rechargeable batteries. A practical sodium battery requires an electrolyte with high conductivity. Cubic Na_3PS_4 exhibiting high conductivity of over $10^{-4} \text{ S cm}^{-1}$ is obtained by crystallizing amorphous. Amorphous Na_3PS_4 crystallizes in a cubic structure and subsequently is transformed into a tetragonal phase around 350°C upon heating. In-situ observation by transmission electron microscopy (TEM) demonstrates that the crystallite size rapidly increases during the cubic to tetragonal phase transition. Moreover, electron diffraction analyses reveal that amorphous domains and nano-sized crystallites coexist in the cubic phase, while the tetragonal phase contains micro-sized crystallites. The nano-sized crystallites and the composite formed by crystallites and amorphous domains are most likely attributed to the increase in ionic conductivity in the cubic phase. [Reproduced with permission of Elsevier.]



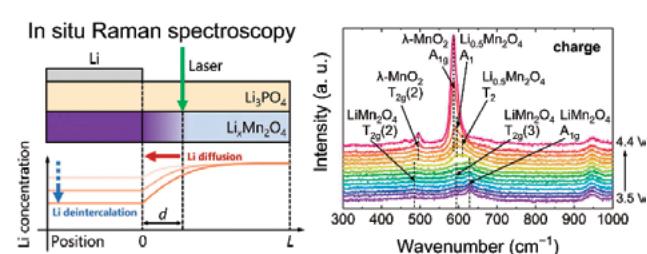
Highlight 4 A02 and ALCA-SPRING joint paper

Ion dynamics of the $\text{Li}_x\text{Mn}_2\text{O}_4$ cathode in thin-film solid-state batteries revealed by in situ Raman spectroscopy

N. Kuwata, Y. Matsuda, T. Okawa, G. Hasegawa, O. Kamishima, J. Kawamura.
Solid State Ion. vol. 380, 115925 (2022)
<https://doi.org/10.1016/j.ssi.2022.115925>

Abstract

In situ Raman spectroscopy of thin-film batteries is used to study the structural changes of $\text{Li}_x\text{Mn}_2\text{O}_4$ during battery operation. Thin-film batteries with $\text{Li}/\text{Li}_3\text{PO}_4/\text{LiMn}_2\text{O}_4$ structures are fabricated, and in situ Raman measurements are performed from both the front and back sides of the thin-film battery. The $\text{Li}_x\text{Mn}_2\text{O}_4$ in the thin-film batteries present characteristic Raman spectra originating from the α , β , and λ phases. Notably, the Raman intensity of $\text{Li}_x\text{Mn}_2\text{O}_4$ shows hysteresis during charging and discharging when observed from the front-surface configuration, whereas only small hysteresis is observed when



measured from the back surface. This behavior is explained by the lithium diffusion and phase transition behavior in $\text{Li}_x\text{Mn}_2\text{O}_4$. [Copyright 2022 The Authors, with permission from CC BY-NC-ND 4.0.]

Gp-A03 Computational & Data Science

To construct a new theoretical framework for Interface IONICS, Gp-A03 has introduced two strategies: a computational approach and a data science approach. With the development of several

new techniques and through deep collaboration with the experimental groups (Gp-A01, -A02, and -A04), we have achieved new understanding of interfacial phenomena.

Highlight 5

Simulation of the compaction of an all-solid-state battery cathode with coated particles using the discrete element method

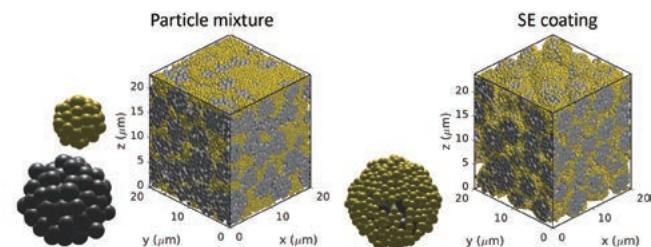
M. So, G. Inoue, K. Park, K. Nunoshita, S. Ishikawa, Y. Tsuge.

J. Power Sources. vol. 530, 231279 (2022)

<https://doi.org/10.1016/j.jpowsour.2022.231279>

Abstract

The simulation of a cold-pressed electrode, which consists of active material (AM) particles coated with a solid electrolyte (SE), of an all-solid-state battery, is presented. The aim of this study is to elucidate the effect of the SE coating structure. The new method we developed to simulate the SE-coated AM particles is based on a discrete element method. Simulation of the AM as clustered particles held together by fusion bonding allows the mechanical damage to the AM to be reproduced simultaneously. For a ductile SE material, new fusion bonding contacts with other particles could develop when pressure is applied. Our simulations suggest that the SE coating promotes more effective



ionic transport, in contrast to conventional particle mixture, owing to the superior percolating network. At low mold pressures, electron transport between the AM particles is disrupted because of the shielding effect of the SE coating. This effect vanishes at higher mold pressures. Both types of electrodes have similar damage profiles, with damage concentrated near the current collector. [Reproduced with permission of Elsevier.]

Highlight 6 A03 and A01 joint paper

STEM-EELS spectrum imaging of an aerosol-deposited NASICON-type LATP solid electrolyte and LCO cathode interface

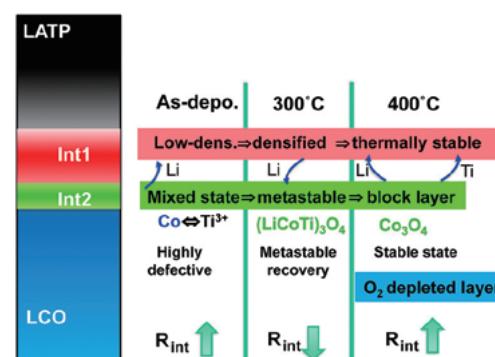
S. Muto, Y. Yamamoto, M. Sakakura, H.-K. Tian, Y. Tateyama, Y. Iriyama.

ACS Appl. Energy Mater. vol. 5, pp. 98–107 (2022)

<https://doi.org/10.1021/acsaem.1c02512>

Abstract

All-solid-state batteries (ASSBs) are promising candidates for application as next-generation high-power supply in electric vehicles. ASSBs offer; however, the high interfacial resistance between the positive electrode and solid electrolyte due to solid–solid contact reactions at elevated temperatures limits their applications. To address these issues, the effect of thermal annealing on the interfacial structure between a NASICON-type LATP solid electrolyte and a LCO cathode in an ASSB fabricated by aerosol deposition was investigated, using STEM-EELS spectral imaging. Metastable degraded low-density transition layers were formed between LATP and LCO in the as-deposited sample. A significant reduction in interfacial resistance was achieved after thermal annealing at 250–300 °C, which was mainly attributed



to structural recovery in this temperature range. However, thermal annealing at 400 °C resulted in increased interfacial resistance due to the formation of a Co_3O_4 -like spinel blocking layer at the LATP/LCO interface. These findings were consistent with theoretical predictions of Li and O transfer between the layers due to thermal annealing. [Reproduced based on Creative Commons license (CC BY 4.0).]

Gp-A04 Design of Functional Interface

Gp-A04 designs innovative solid state ionics 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

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

Highlight 7 A04 and A02 joint paper

Nanosized and metastable molybdenum oxides as negative electrode materials for durable high-energy aqueous Li-ion batteries

J. Yuna, R. Sagehashi, Y. Sato, T. Masuda, S. Hoshino, H. B. Rajendra,

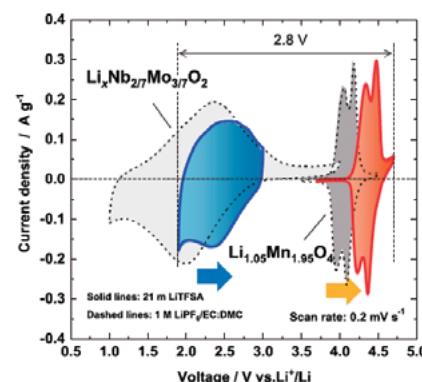
K. Okuno, A. Hosoe, A. S. Bandarenka, N. Yabuuchi.

Proc. Natl. Acad. Sci. U.S.A. vol. 118, e2024969118 (2021)

<https://doi.org/10.1073/pnas.2024969118>

Abstract

The development of inherently safe energy devices is a key challenge, and aqueous Li-ion batteries draw large attention for this purpose. Herein, a type of a negative electrode material (i.e., $\text{Li}_x\text{Nb}_{2/7}\text{Mo}_{3/7}\text{O}_2$) is proposed for high-energy aqueous Li-ion batteries. $\text{Li}_x\text{Nb}_{2/7}\text{Mo}_{3/7}\text{O}_2$ delivers a large capacity of $\sim 170 \text{ mA h g}^{-1}$ with a low operating potential range of 1.9 to 2.8 versus Li/Li^+ in 21 m lithium bis(trifluoromethanesulfonyl)amide (LiTFSAs) aqueous electrolyte. A full cell consisting of $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4/\text{Li}_{9/7}\text{Nb}_{2/7}\text{Mo}_{3/7}\text{O}_2$ presents high energy density of 107 W h kg^{-1} as the maximum value in 21 m LiTFSAs aqueous electrolyte, and 73% in capacity retention



is achieved after 2,000 cycles. Furthermore, hard X-ray photoelectron spectroscopy study reveals that a protective surface layer is formed at the surface of the negative electrode, by which the high-energy and durable aqueous batteries are realized with $\text{Li}_x\text{Nb}_{2/7}\text{Mo}_{3/7}\text{O}_2$. [Reproduced with permission of National Academy of Science.]

Highlight 8

Electrochemical control and protonation of the strontium iron oxide SrFeO_y by using proton-conducting electrolyte

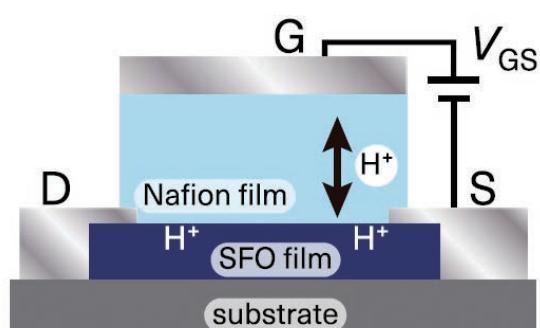
Y. Isoda, D. Kan, Y. Ogura, T. Majima, T. Tsuchiya, Y. Shimakawa.

Appl. Phys. Lett. 120, 091601 (2022)

<https://doi.org/10.1063/5.0083209>

Abstract

To electrochemically control structural and transport properties of oxygen-deficient perovskite SrFeO_y ($2.5 \leq y \leq 3$) (SFO) epitaxial films, we employed electric-field-effect transistor structures in which the proton-conducting solid electrolyte Nafion is used as a gate insulator. When a positive gate voltage (V_{GS}) is applied and protons are injected toward the film channel layer, the SFO films are electrochemically reduced, leading to increases in the channel resistance. On the other hand, when a negative V_{GS} is applied and protons are removed, the SFO films are oxidized, and as a result, the channel resistances decrease. In addition, we found that the electrochemically reduced SFO films accommodate



protons, forming the proton-containing oxide $\text{H}_x\text{SrFeO}_{2.5}$ whose proton concentration is determined by elastic recoil detection analysis to be $x \sim 0.11$. Our results indicate the usefulness of the proton-conducting solid electrolyte for electrochemically controlling transition metal oxides and for exploring proton-containing oxides. [Reproduced with permission of the American Institute of Physics.]

Activity Reports

Symposiums and Seminars

Interface IONICS Online Symposium 2022

Mar. 29, 2022

Dr. Yoshitaka Tateyama, NIMS

The Interface IONICS International Online Symposium 2022 was held on March 29, 2022. The focus was “solid electrolyte ionics” and “cathodes for higher energy density,” and two California professors who are theorists were invited. Prof. Shyue Ping Ong (UC San Diego) talked about the cutting-edge computational analysis of room-temperature ion conductivity, including works based on machine-learning potentials. Prof. Hayashi and Prof. Kobayashi presented their recent studies on ion diffusion in sulfide electrolytes and ion diffusion around grain boundaries, respectively. Prof. Anton Van der Ven (UC Santa Barbara) introduced the latest works on positive electrode mechanisms, including oxygen redox phenomena. Prof. Okubo and Prof. Yabuuchi then provided their observations and



theories on the oxygen redox mechanisms in Li-rich positive electrode materials. Intensive debates ensued about the interpretation of the calculation results and the underlying mechanisms in both topics. We thank all of the speakers and participants for the active and substantial discussion and look forward to our next opportunity to host a topical international symposium.

Symposiums and Seminars

The 3rd Interface IONICS Seminar

Jan. 6–7, 2022

The 3rd Interface IONICS seminar was held as a hybrid meeting on January 6 and 7, 2022. We had 51 in-person and 24 virtual attendees in total. The plenary lectures were delivered by Dr. Hikari Sakaebi (AIST) and Prof. Naoaki Yabuuchi (Yokohama National University). Moreover, Dr. Hiroki Yamada (JASRI) reported on his

Assoc. Prof. Gen Inoue, Kyushu Univ.

interesting experience in the “International Training Program” in Budapest, Hungary. From the oral presentations by students/postdocs, two outstanding young researchers were awarded Interface IONICS awards.



Interface IONICS Award Winners



Keisuke Yoshikawa
Iriyama Lab, Nagoya Univ.

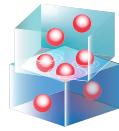
Interfacial reactions at anti-perovskite-structured Li₂OHBr/electrode interfaces



Makoto Takayanagi
Higuchi Lab, NIMS and Tokyo Univ. of Sci.

In-situ observations of oxygen transfer behaviors at various Li⁺-conducting solid-state electrolyte/electrode interfaces

Newsletter vol.6



Interface
IONICS

Publisher/Contact

Office for Scientific Research on Innovative Areas:
Science on Interfacial Ion Dynamics for Solid State Ionics Devices
TEL: +81-52-789-3235
E-mail: office@int-ionics.material.nagoya-u.ac.jp
<https://interface-ionics.jp/en/index.html>

Date of issue: September 2022