Scientific Achievement Award of The Electrochemical Society of Japan

Systematic Study on Materials for Lithium-, Sodium-, and Potassium-Ion Batteries

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ABSTRACT

Rechargeable batteries are capable of storing electric energy on the basis of pairing electrochemical redox reactions to realize sustainable energy society in our future. Since lithium-ion batteries with the highest specific energy among all the practical batteries were commercialized in 1991, many studies on lithium insertion materials and their electrochemical characterization have been reported to achieve even higher energy density, longer cycle life, and safer lithium-ion battery technologies. It is quite fortunate that the author had an opportunity to contribute to the research and development of lithium battery materials since 1997. In particular, studies on the influence of dissolved metallic ions like Mn^{2+} , Co^{2+} , Ni^{2+} , Na^+ , and K^+ ions in electrolyte solution on graphite negative electrodes in lithium-ion batteries motivated the author to extend the research scope to electrochemical sodium insertion chemistry. Furthermore, the author's research experiences as a postdoctoral fellow in Dr. Delmas' group in FY 2003 and a remarkable oral presentation on $\alpha\text{-NaFeO}_2$ electrode properties given by Professor Okada's group in 2004 provided motivations and opened up new avenue toward the successful demonstration of non-aqueous sodium-ion batteries later in the career. Since 2009, the author's research group has successfully demonstrated 3-volt class charge and discharge of a sodium-ion battery of a $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ // hard carbon cell and a brand-new potassium-ion battery of a $\text{K}_2\text{Mn}[\text{Fe}(\text{CN})_6]$ // graphite cell. The systematic studies of three different alkali-metal insertion systems synergistically induce deeper understanding and faster development of new materials for the next-generation rechargeable batteries.

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1. Introduction

When the author was an adolescent student in 1980s, the only rechargeable battery used for consumer electronics such as portable music player, i.e. cassette-tape player, was nickel-cadmium batteries. The author remembers that the portable music player looked so attractive and revolutionary, equipping the state-of-the-art technologies, and many people including the author enjoyed listening to music outside. However, primary cells such as an alkaline manganese cell was the most widely used power source because of the limited energy density of nickel-cadmium secondary battery. Although the battery run-time per single charge of the nickel-cadmium secondary batteries was not long enough, only approximately 1 hour, the author still used the secondary batteries for his own player because of economic and ecological reasons.

In the beginning of 1990s, both of lithium-ion and nickel metal-hydride batteries were first commercialized in Japan that show higher performance compared to any conventional batteries.^{1,2} Around the same time, other portable electronics such as cell phone, video camera, laptop computer, and digital camera were also commercialized with rapid growth of information technology and has been broadly spread all over the world until now.³ In particular, demand for lithium-ion cells is still increasing because lithium-ion batteries provide highest energy density and superior cycle life among the currently available secondary batteries. In 2000s, the batteries were further adopted to large-formatted stationary electricity storage and electromobility including electric vehicles.⁴ Therefore, research and development of battery materials are of significant importance in both engineering and scientific points of

view.^{3,5,6} Actually, electrochemical methods are essential to study kinetics and thermodynamics of battery materials and reactions and interfacial behavior at electrode/electrolyte interface. Moreover, research and development of new advanced materials for electrodes and electrolytes are essentially required to achieve higher performance because battery performance basically depends on selection of electrode and electrolyte materials.

Our research group in Tokyo University of Science (TUS) studies new materials and reactions for advanced Li-ion batteries, next-generation batteries, redox capacitors, ion sensors, biosensors, and biofuel cells. It is noted that our university and our campus, Shinjuku, Tokyo, are historically significant because Mr. Sakizo Yai who invented and commercialized the first manganese dry cells in 1880s studied in our campus when he was a student of TUS.⁷ We are proud that our laboratory working on the battery materials is located in the same campus. In March of 2019, the author was honored and humbled to be selected as a scientific achievement award winner by the Electrochemical Society of Japan on the basis of our systematic study of lithium-, sodium-, and potassium-ion batteries in the past two decades. Because the author was invited to submit a review article concerning the awarded research works by the chief of the editorial committee, our achievements of three different batteries are reviewed here along with the author's personal history and underlying motive of the day when we decided to study on new binders for LIBs, sodium-ion batteries, and potassium-ion batteries.

2. Lithium-ion Battery

Figure 1 shows the author's research chronology down to 1992.

Figure 1. Personal history of the author's research experience since 1992 in which the author joined the electrochemistry laboratory in Waseda University under supervision by Prof. T. Osaka. At the beginning of research career, the author learned fundamental of electrochemical (EC) analysis and then extended development of materials electrochemistry.

When the author was a graduate student in Waseda University, the author first studied electrochemical analyses^{8–10} and then moved to design of molecular functionality electrodes such as ionic sensors¹¹ and enzyme-immobilized electrodes.¹² This experience is quite advantageous to the author's career, because the author had sufficient time to learn the fundamental of electrochemistry in the beginning of research work while the author gained more experiences of electrochemical methods. The experience and knowledge gained in the graduate study bolstered the author's contribution to studies of new materials and reactions of rechargeable batteries as an assistant professor in Iwate University as seen in Fig. 1.

In general, lithium metal is the ideal choice of negative electrode material for higher energy density of battery because of the lightest atomic weight and lowest standard potential among any metal elements according to electrochemistry textbooks used in academic. In research field of secondary battery, the first contribution made by the author was on the improvement of lithium metal anode by PVDF-based gel electrolyte with carbon dioxide additive.¹³ In the late 1980s, the first-commercialized lithium *metal* secondary battery, a Li // MoS₂ cell, had been launched by Moli Energy, but then the Li metal cells were recalled from the market due to serious safety issue leading to explosions, triggered by unexpected heat generations via internal short-circuiting through uncontrolled Li dendrite growth upon cycling.⁶ The issue was solved by replacement of the lithium metal electrode with a lithium insertion carbon electrode, which became the basis of the commercial lithium-ion battery (LIB) because lithium insertion reaction into carbon electrode fortunately occurs at the lower potential close to the electrode potential of Li⁺/Li couple with high reversibility and gravimetric capacity.

Figure 2 shows a schematic illustration of lithium-ion battery operation mechanism. To attain higher energy density of LIB, typical lithium insertion materials used in LIB are lithium transition metal oxide and carbon as positive and negative electrodes, respectively.^{5,6} Basically, a voltage and capacity of LIB simply depends on the combination of positive and negative electrode materials. Moreover, lithium ion conducting electrolyte installed between the electrodes are equally critical for demonstrating the better battery performance of LIB, i.e. cycle life, safety, charge and discharge rate capability, low and high temperature operation, interface and so forth. Therefore, development of new materials of lithium insertion electrode and lithium ion conductor is indispensable to improve the battery performance.

When joining Iwate University as an assistant professor, the author started studying battery materials of LIB in earnest. As shown in Fig. 2, a collaborative effort of electrochemical analysis,

characterizations of electrode and electrolyte, surface analysis including solid electrolyte interphase (SEI)¹⁴ on negative electrode surface, and computational research is highly important for scientific understanding of complex battery chemistry. However, preparation of targeted materials is the first priority for those experimental work. We studied new synthesis and electrochemical performance of various manganese oxides^{15–19} including oxide anion redox reactions.^{20,21} In the late 1990s and the early 2000s, Professor Ohzuku reported the new insertion materials of spinel-type Li[Me_{1/2}Mn_{3/2}]O₄ (Me = Ti, Cr, Fe, Co, Ni, Cu, and Zn), LiNi_{1/2}Mn_{1/2}O₂, and LiCo_{1/3}Ni_{1/3}Mn_{1/3}O₂,^{22–25} and his students and co-workers delivered unforgettable and well-organized oral presentations on the new materials at domestic meetings of the Electrochemical Society of Japan and the Battery Symposia in Japan. The author learned about not only the science of new materials but also strategy, motivation, and history of R & D of new battery materials from Professor Ohzuku's talks. Just one example of what the author learned is lithium ion transport at the interface between solid electrode and carbonate-ester-based liquid electrolyte, as drawn in Fig. 3. According to the author's memory of his talk, Professor Ohzuku said that lithium ions are always coordinated with oxygen atoms of carbonate ester molecule and oxide solid, and coordination change, like ligand exchange, must occur at the interface during the lithium insertion into layered oxides as seen in Fig. 3a. Furthermore, he pointed out that as oxygen atoms always form the first coordination sphere of lithium surrounding whenever lithium is inserted into oxides, the lithium transfer at the interface becomes smoother and faster with lower energetic barrier compared to those at graphite electrode. On the contrary, because lithium atoms inserted into graphite are surrounded with twelve carbon atoms of opposite graphenes in stage-1 LiC₆, the solvated lithium ions must undergo the coordination change from four-oxygen to twelve-carbon surroundings as shown in Fig. 3b. Because of the notable change of lithium coordination, the lithium desolvation process is considered to be one of the predominant steps of lithium intercalation reaction of graphite.²⁶ According to a number of reports on surface components formed on lithium inserted carbon electrode such as Refs. 27, 28, we noticed that the SEI layer usually contains oxygen atoms in any cases of carbon electrode. The author believes that the oxygen atoms in SEI influence the intermediate desolvation process of lithium ions between electrolyte and electrode. It is worth noting that the lithium titanate, Li₄Ti₅O₁₂, is broadly known as SEI-free negative electrode,²⁹ due to the higher working potential than the cathodic decomposition of electrolyte solution as well as the similar oxygen surrounding of lithium ions in both of electrolyte and electrode unlike graphite.

Figure 2. Analyses for understanding materials, redox reaction, and interface inside rechargeable batteries.

Figure 3. Schematic illustration of electrochemical lithium insertion into (a) layered lithium transition-metal oxide and (b) graphite electrodes which is focusing on the variation in Li^+ coordination in electrodes and at the interface/interphase.

Since the desolvation of lithium ions is considered to be important interface-step, the author and co-working graduate students made an effort to induce the desolvation step by covering the carbon with a thin layer of polyion complex which has molecular sieve ability.^{30,31} We made an effort to achieve pre-formation of SEI on graphite electrodes and 100% coulombic efficiency from the first cycle, which will increase an energy density of LIBs simply by an efficient balance of positive and negative electrode active mass. Based upon the effort of pre-formed SEI when the author was in Iwate University,³² we found that the poly(acrylic acid), poly(vinyl alcohol), and poly(methacrylic acid) work as a functional binder for graphite composite electrodes.³³ By replacing conventional poly(vinylidene fluoride) (PVdF) binder with polyacrylate binders, as shown in Fig. 4a, the surface coating provided by polyacrylate binders are effective to reduce the initial irreversible capacity, and the well-known irreversible reaction in propylene carbonate electrolyte solution can be completely avoided.³⁴ Figure 4b shows the

Figure 4. Strategy of binder-coat acting as “pre-formed SEI” to realize 100% initial coulombic efficiency for Li-ion negative electrode. (a) Polymeric structure of conventional binder of PVdF and functional binder of PAA and (b) interphase structure at the graphite electrode for lithium ion intercalation.

effect of polyacrylate surface modifier on the lithium interaction into graphite. Because of molecular structure of polyacrylates, the lithium ions are most likely to interact with electron pairs of oxygen atoms of polyacrylate-based surface layer containing electrolyte-decomposition products,³² which is advantageous to minimizing the barrier of lithium transfer, leading to smooth desolvation of lithium ions during intercalation process.

Because the polyacrylate binder improves a mechanical strength of composite electrodes, we further applied the functional binders to high-capacity silicon electrodes. Although silicon provides much higher capacity than graphite because of formations of lithium silicides, such as $\text{Li}_{3.75}\text{Si}$, a silicon electrode suffers from a large volume change during successive cycles, leading to cracking and pulverization of silicon resulting in capacity fading.³⁵ Figure 5 compares the cross section of silicon composite electrodes with the conventional and functional binders.^{36–39} We successfully demonstrated that the enhanced mechanical strength of composite electrode

Figure 5. Schematic illustrations of the mechanism of improved reversibility for Si powder composite electrodes with (a) poly(vinylidene fluoride) (PVDF) and (b) polyacrylate binders.

suppressed the cracking and pulverization of the silicon composite electrodes. More importantly, the polyacrylate coating around the particles acts as pre-formed SEI to reduce irreversible reaction of electrolyte decomposition, resulting in less expansion of the entire composite electrode layer³⁷ as drawn in Fig. 5b. In our laboratory, a doctoral student, Dr. Z. Han currently working in BASF, Japan, mainly contributed to the study on the binders by investigating the effects of a ratio of $-\text{COOH}$ and $-\text{COONa}$ groups in sodium polyacrylate modulated by changing neutralization degree of poly(acrylic acid) with NaOH solution for powdery silicon electrode.³⁷ Moreover, she first clarified the effects of different neutralization agent⁴⁰ and found an original slurry additive cross-linking poly(acrylic acid) binder.⁴¹ We extended further development of new functional binders of cross-linked polyacrylate newly synthesized through co-polymerization,⁴² and biopolymers of polysaccharide,⁴³ and polypeptide.⁴⁴

Meanwhile, our group studies positive electrode materials and electrolyte additives because our goal is to improve performance of lithium-ion full cell. When the author was in Iwate University, a motivated Ph.D. student, who is now Prof. S.-T. Myung, Sejong University, Korea, joined our research group in 1999. We concentrated our focus on new synthesis and new materials for active materials of positive electrodes in LIBs. For example, we studied spinel-type manganese oxides,^{15,45} layered manganese-based oxide,^{16,46,47} and LiFePO_4 and carbon composite⁴⁸ prepared via unique emulsion drying method. We hydrothermally synthesized and characterized corrugated layered LiMnO_2 and its derivatives.^{17,49} Additionally, manganese (di)oxides having different crystal structures^{50,51} and dopants¹⁸ were researched with the contributions of a doctoral student, Dr. A. Ogata presently working in Panasonic. He also significantly assisted the author to establish new laboratory and start research on new topics, sodium-ion battery and redox capacitor, in Tokyo University of Science from 2005 (see Fig. 1).

The author also wants to remark that Dr. N. Yabuuchi who was a Ph.D. student supervised by Professor Ohzuku and then a post-doctoral researcher at MIT joined our group as a research staff in 2009. His work immensely accelerated the development and understanding of solid-state redox reactions not only of transition metals but also lattice oxide anion as the redox center for lithium and sodium batteries.^{19–21,52} He was promoted as a professor at Yokohama National University in 2018 and is still continuously studying high capacity materials for Li and Na batteries.⁵³ In a scientific point of view, the author and colleagues have uniquely studied electrochemistry and solid-state chemistry of layered alkali

cobalt oxides of O2-, O3-, and new O4-type Li_xCoO_2 ,^{54–57} Na_xCoO_2 ,⁵⁸ and K_xCoO_2 .⁵⁹ We also developed a series of iron-based high-capacity materials such as nano-sized particles of Fe_2O_3 ⁶⁰ and Fe_3O_4 ,^{61,62} FeF_3 ,⁶³ and so on.

Along with the development of transition metal based materials, dissolution of transition metal species from the electrodes into electrolyte solutions in Li cells was recognized as one of the biggest reasons for LIB degradation process. Dissolution of vanadium and manganese ionic species from V_2O_5 and MnO_2 , respectively, in non-aqueous Li cells had been reported by Japanese groups.^{64,65} The ionic species are cathodically deposited on the opposite Li electrode, triggering the complicated deterioration process of the entire Li cells. In the late 1990s, the author's industrial partner detected a manganese dissolution phenomenon from a LiMn_2O_4 and following deposition on opposite carbon electrode in LIB schematically drawn in Fig. 6a. Because of the valuable information given by the partner, the author decided to investigate the dissolution behavior and an influence of dissolved Mn(II) , Co(II) , and Ni(II) ions in an electrolyte solution on performance of graphite anodes.^{66,67} Because of higher standard potentials, E^0 , of Mn(II)/Mn , Co(II)/Co , and Ni(II)/Ni , than that of Li^+/Li , any metal plating of dissolved metal

Figure 6. (a) Schematic illustration of dissolution and release of Mn^{2+} ions from a manganese spinel cathode and migration to reach at the surface of a negative electrode and (b) a potential axis to compare working potential of lithium insertion materials and standard potentials of manganese, cobalt, and nickel.

ions should thermodynamically occur on the surface of lithium inserted carbon as shown in Fig. 6b. Comparison studies of the influence of Mn(II), Co(II), and Ni(II) ions led us to the unique understanding on the difference of electrocatalytic effects by the deposited Mn, Co, and Ni metal species on irreversible electrolyte decomposition. Since degradation resulted from irreversible side reactions at the graphite electrode surfaces was most pronounced in the case of manganese deposition,⁶⁷ we further expanded our strategy to develop new electrolyte additives to suppress such manganese-induced degradation.^{68–71} Furthermore, since we recognized the importance of passivation and protection layers on electrode materials, we demonstrated efficient coatings of the active materials of cathode^{72,73} and anode^{74,75} with inorganic materials to enhance battery performance.

When we consider the working potentials of carbon anode in LIBs and standard potentials of metal elements, any metal ions except Li^+ ion should not be dissolved in electrolyte solution, because of thermodynamically inevitable electroplating (electro-reduction) of metals, which hinders access of Li^+ ions to an electrode.⁶⁷ If carbon anode is entirely covered with an SEI layer possessing ideal single ion conduction of Li^+ and blocking access of any other ions, we reasonably expect that any electroplating of metals can be avoided completely, resulting in no influence on carbon anode. These assumptions inspired us to examine the influence of various metal ions such as Na^+ , K^+ , Al^{3+} , Cu^{2+} , Sn^{2+} , Al^{3+} , Ag^+ , etc. dissolved in electrolyte solutions and the author reported these results at Joint International Meeting of the 200th Meeting of ECS, and the 52nd Meeting of ISE in 2001. We found that addition of these metal ions greatly influenced on electrochemical charge and discharge properties of graphite electrodes. Before the experimental work, the author was expecting that Na^+ ions can be co-intercalated with Li^+ ions into graphite, possibly leading to a ternary Li and Na graphite intercalation compound (GIC). To our surprise, we observed the same GIC in a Li and Na salts co-dissolving solution with Li-GIC and did not have any evidences of sodium plating even after applying 0.0 V vs. Li (corresponding to approximately -0.3 V vs. Na). However, when we carefully checked the electrochemical data, we discovered that a sodium salt as an additive into Li-ion electrolyte impacted on the improvement of the initial coulombic efficiency and reduction of interfacial resistance of graphite negative electrode.^{76,77} These observations are in agreement with the fact that sodium carboxymethyl cellulose is broadly utilized as a binder component for graphite composite electrode in commercial LIBs.⁷⁸

Based on the studies on electrode materials, binders, electrolytes, electrolyte additives, and interfaces including passivation layers, we have focused our strategy to design the entire battery system because all of the battery components chemically interact each other, and that as a whole impacts the battery performance. Furthermore, the author was highly motivated to replace lithium ions with sodium ions to demonstrate new sodium-ion batteries when the author moved to the current university as a new faculty member shown in Fig. 1.

3. Sodium-ion Battery

As already mentioned, the author studied the influence of sodium ions added in electrolyte and binder on LIB performance. In order to further acquire knowledge of crystallography of battery electrode materials, the author also stayed one year in Bordeaux to work as a post-doc in Dr. Claude Delmas' group, ICMCB-CNRS, France, in FY2003 (see Fig. 1). It was really fortunate that the author experienced synthesis of metastable $\text{Li}_{2/3}[\text{Co}_{2/3}\text{Mn}_{1/3}]\text{O}_2$ through Na/Li ion exchange of a $\text{Na}_{2/3}[\text{Co}_{2/3}\text{Mn}_{1/3}]\text{O}_2$ precursor in lithium nitrate chloride eutectic melt.⁷⁹ After coming back to Japan, the author also had an opportunity to listen to a very impressive and pioneering work on layered NaFeO_2 given by Professor Okada's and

Figure 7. Open question; can we replace Li^+ ions with Na^+ or K^+ ions to demonstrate sodium- and potassium-ion batteries? Drawbacks of the new batteries for the demonstration which are widely known before our demonstration of them.

his colleagues in 2004 and later years.⁸⁰ At the 45th Battery Symposium in Japan on Nov. 29, 2004, they presented that a layered NaFeO_2 electrode exhibited electrochemically activity of Fe(III)/Fe(IV) couple at 3.3 V in a non-aqueous Na cell while Fe(III)/Fe(IV) was inactive in layered LiFeO_2 having the same crystal structure as that of NaFeO_2 . The author was astonished to see the difference in redox activities between NaFeO_2 and LiFeO_2 . This research work by Professor Okada strongly influenced the future direction of the author's research. In April 2005, when the author started working as a faculty member of TUS and establishing own laboratory, the author decided to take a challenge and began researching about sodium insertion materials.

Some of sodium insertion materials and an idea of non-aqueous rechargeable batteries were proposed in 1980s, and different types of sodium metal battery and sodium-ion battery were reported as we described in our review articles.^{7,58,81} However, no successful carbon anode for Na-ion battery was demonstrated at that time to the best of our knowledge. As summarized in Fig. 7, the idea of replacing Li^+ with Na^+ and K^+ ions looks so simple, however, its effects on the chemistry and materials are not that simple. If we were to replace the Li^+ with Na^+ in a LiCoO_2 // graphite cell, the positive and negative electrodes suffer from unsatisfactory voltage and low capacity. In the case of substituting K^+ for Li^+ , stability of K_xCoO_2 is much lower than that of LiCoO_2 because of its hydrolytic decomposition. In addition, Na-ion and K-ion electrolyte solutions were not commercially available before 2010. Some battery researchers tried to convince the author that passivation layers on negative electrodes fail to form in the case of sodium-ion batteries.

In the earlier reports by Stevens and Dahn,^{82,83} a hard-carbon electrode delivers high reversible capacity of ca. 300 mAh/g at low potential approaching to $E^0(\text{Na}^+/\text{Na})$ for a few cycles, however, the issue of cycle life and irreversibility of the hard-carbon // Na cell had remained to be unsolved. Therefore, we carefully examined the dependence of electrolyte solvents and sodium salts on sodium insertion property in beaker-type Na cells, and finally we found the suitable electrolyte compositions and the importance of much higher purity and an additive for satisfactory performance of Na // hard carbon cells.^{58,84,85} Higher capacity hard-carbon materials were recently introduced in literatures.^{7,86,87}

For positive electrode materials, we first examined birnessite type manganese dioxides because we thought that the wider interlayer space between MnO_2 slabs in the birnessite⁸⁸ might be beneficial to sodium insertion of which an ionic size is larger than that of lithium.

Inconveniently, the crystal water in birnessite phase results in water contamination of non-aqueous electrolyte solution in Na cells, and counter sodium electrode was severely damaged in beaker-type sodium cell.

We first succeeded in demonstration of sodium insertion of nano-sized Fe_3O_4 in a NaClO_4 EC:DMC solution by using lithium reference electrode separated with glass filter.⁶¹ After our continuous efforts to optimize the Na cell assembly process, electrolyte solution purity and glove box condition for three years, we first reported two sodium layered oxides for the positive electrode application, O3-type $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ and NaCrO_2 ,⁸⁹ of which ideas were inspired by the previous reports by Kang et al.⁹⁰ and our group,¹⁶ respectively. In 2011, we first published the long life hard-carbon electrode as well as Na-ion full cell as shown in Fig. 8.⁸⁴ Frankly speaking, we initially submitted a manuscript on the long life hard-carbon electrode as a communication article to a journal of Wiley in 2009, however, it was rejected as the referees recommended to drastically revise the manuscript and resubmit it as full paper. After struggling against the disappointing comments provided by the referees especially on possibility of the water contamination of commercial NaClO_4 powder in electrolyte, the manuscript was accepted for the publication at last.

Figure 9 reveals that during the period from 2009 and 2011 the number of publication on sodium battery materials began to increase, and then the number has skyrocketed. Although sodium is located right next to lithium in the periodic table and their chemical nature is similar, it is not the same. For example, sodium monovalent ions show strong ionic character having different ionic size, providing moderate Lewis acidity of Na^+ ions and rich solid-state chemistry including polymorphism and stoichiometry of Na_xMeO_2 , where $x \leq 1.0$ and Me = (transition) metal(s), compared to those of lithium and potassium counterparts as summarized in Fig. 10.^{91–93} Because the advantages of sodium batteries offer, many review articles on negative electrode,⁹⁴ positive electrode,⁹² binder,⁹⁵ and sodium-ion batteries,^{7,58} and practical perspective^{81,96} were published in recent years, and the state-of-the-art progress of Na-ion materials is reviewed and related literatures are cited herein. We believe that the further advancement in materials chemistry and battery performance will contribute toward the development of sodium insertion materials and electrolytes to achieve competitive

Figure 8. Na-ion battery performance demonstrated by our group: (a) schematic illustration of the Na-ion battery of $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ // hard carbon cell and (b) charge and discharge curves and rate capability data.

Figure 9. Yearly number of original papers on sodium batteries. Data are based upon a search result in Web of Knowledge on March 26, 2019.

	²¹ Sc	²² Ti	²³ V	²⁴ Cr	²⁵ Mn	²⁶ Fe	²⁷ Co	²⁸ Ni	²⁹ Cu
Li _x MeO ₂	--	--	O3	O3	--	--	O3	O3	--
Na _x MeO ₂	O3	O3	O3 P3 P2	O3	O3 P2	O3	O3 P3 P2	O3	--
K _x MeO ₂	--	--	--	O3 P3	P3 P2	--	P3 P2	--	--

Figure 10. Directly crystallizable layered oxides and their crystal structure types of A_xMeO₂, where A = Li, Na, or K, Me = 3d-block metals, and x = 1 or less. In order to classify layered structures of A_xMeO₂ in which the MeO₂ slabs consisting of edge-sharing MeO₆ octahedra are stacked with different orientations, the structures can be categorized as O3, P2, and P3 by using the classification proposed in a literature, C. Delmas, C. Fouassier, and P. Hagenmuller, *Physica B*, **99**, 81 (1980). Also see our paper, K. Kubota, S. Komaba et al., *Adv. Energy Mater.*, **8**, 1703415 (2018).

battery technologies with only abundant elements^{97,98} such as manganese, iron, aluminum, sodium, carbon, oxygen, and so on.

4. Potassium-ion Battery

When we began the research work of sodium-ion materials in 2005, we did not expect to expand our work towards potassium-ion battery in the future. In general, the third alkali metal, potassium, has much heavier atomic weight than those of lithium and sodium, and potassium shows higher standard potential and reactivity compared to lithium cases. These facts were not attracting the researchers targeting for new battery having high energy, high power, and high safety.

However, when the author attended a domestic meeting in Japan, a speaker from Professor Hagiwara's research group talked about lithium plating in a ternary LiFSA-KFSA-CsFSA (FSA = bis(fluorosulfonyl)amide) eutectic melt on glassy carbon electrode and the result was published in papers.^{99,100} This result implies that electrochemical deposition of potassium and cesium occurs at lower potential than that of lithium in the molten electrolyte, and similar observation was also reported in the case of room-temperature ionic liquids.¹⁰¹ What the author had learned in lectures and textbooks of electrochemistry during the student years is that lithium possesses the lowest standard potential among any metal elements. At that time, the author noticed that the lowest potential is calculated by assuming aqueous medium as well as hydration of metal ions. An effect of solvents such as water, PC, alcohols, etc. on the standard potentials was quantitatively clarified by calculating them from the standard molar Gibbs energy of hydrated and propylene carbonate-solvated alkaline ions¹⁰² indicating that deposition potential of potassium is lower than lithium. Taking into account these facts, our group experimentally confirmed for the first time potassium plating/stripping on a Ni electrode in a 0.5 mol dm⁻³ KPF₆ ethylene carbonate and diethyl carbonate (1:1 in volume) solution occurring at lower potential of ca. -0.1 V vs. Li⁺/Li,¹⁰³ as schematically compared in Fig. 11. Simultaneously, we demonstrated highly reversible cathodic potassium intercalation into graphite in the non-aqueous K⁺ solution, resulting in the reversible formation of stage-1 K-GIC.¹⁰³ Around almost the same time, Ji's research group also reported carbons as potassium insertion host material. The group concluded that disordered carbon is suitable for long life battery application compared with graphite.^{104,105} We are now studying on the factors affecting electrochemical performance of graphite materials in K cell and will report the results elsewhere because excellent capacity retention is achieved after optimizations of graphite structures.

Figure 11. Comparison of standard electrode potential, E^0 , of alkali metals in aqueous and carbonate ester solutions. Detailed discussion appears in S. Komaba et al., *Electrochem. Commun.*, **60**, 172 (2015).

If a working potential of positive electrodes is the same in Li-ion and K-ion batteries, voltage window of potassium battery will be expanded compared to that of lithium battery because of the lower potential of K plating. Additionally, since solvated or hydrated shell of K⁺ ion is generally known to be smaller than Li⁺ and Na⁺ ions because of lower Lewis acidity of K⁺ ion, superior mobility as well as larger transportation number of K⁺ ions in electrolyte solutions must be realized, and the fact is highly advantageous to lowering resistance and viscosity of K-ion electrolyte solution.⁷ In fact, a KOH (not NaOH nor LiOH) aqueous solution efficiently contributes to lower internal resistance of practical alkaline batteries of manganese dry cell and nickel-metal hydride battery. These thoughts stimulated our team to develop good potassium insertion materials which are redox active in the potential range up to 4.5 V vs. K⁺/K equal to 4.4 V vs. Li⁺/Li corresponding to practically available potential range, which can avoid unfavorable electrolyte decomposition at positive electrode in practical Li-ion batteries. Of course, atomic weight of potassium is much heavier than those of lithium and sodium, which should be detrimental to high capacity design of insertion materials according to Faraday's law.

It is crucial to note that we have to handle potassium metals safely with special care during experimental work because potassium metal is extremely reactive.¹⁰³ We recently found that metallic potassium electrode shows unstable and unreliable potential, so that electrochemical pretreatment of K metal electrode is efficient to obtain stable and reliable potential for electrochemical measurement.¹⁰⁶ We first examined K₂Mn[Fe(CN)₆] and K₂Fe[Fe(CN)₆] electrodes as a potential candidate for a realistic high-energy K-ion battery. Based upon our knowledge and experience of Na-ion and Li-ion batteries, we predicted its high-capacity redox showing around four volts versus K. The result aligned with my expectations and we first achieved the demonstration of a new K-ion battery of graphite // K₂Mn[Fe(CN)₆] cells in Fig. 12.¹⁰⁷ Recently, a review article of polyanion compounds for K-ion batteries appeared in which experimental data of FePO₄, KFePO₄, KMnPO₄, K₂FeP₂O₇, K₂MnP₂O₇, KVPO₄F, KVOPO₄, and KFeSO₄ materials were discussed and compared in scientific and practical points of view.¹⁰⁸ Our study on potassium insertion materials is still ongoing. Figure 13 compares battery performance by plotting reversible capacity vs. average discharge voltage in K cell. According to our knowledge, higher energy K-ion battery will be realized by employing Prussian blue analogues. As the new research field of potassium insertion materials just started from 2015, we are striving to further advance the development of new materials to achieve higher energy K-ion battery.

Figure 12. 4-volt class potassium-ion battery: (left) schematic sketch of electrode active materials and charge/discharge reactions and (right) charge and discharge curves of a graphite // $\text{K}_2\text{Mn}[\text{Fe}(\text{CN})_6]$ cell.

Figure 13. Perspective: potential positive electrode materials for high energy density K-ion batteries as “beyond lithium-ion batteries.”

5. Summary and Future Perspectives

Our research and development of Li-, Na-, and K-ion battery materials are reviewed in this article along with the personal history. Since the first commercialization of Li-ion battery in 1991, the lithium insertion chemistry has been regarded as one of the most sophisticated and successful rechargeable battery technologies with the highest specific energy densities. Many studies on lithium insertion materials and their electrochemical characterization has focused to achieve even higher energy density, longer cycle life, and safer lithium-ion batteries. It is quite fortunate that the personal history and inspirations guided the author to a successful demonstration of non-aqueous sodium-ion and potassium-ion batteries by adopting and modifying research experience and knowledge of lithium-ion chemistry. The systematic studies of three different alkali-metal insertion systems described here will synergistically facilitate an efficient development and present unique science of new materials for the next generation batteries.

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