



Review—Practical Issues and Future Perspective for Na-Ion Batteries

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Research on electrochemical Na intercalation in battery system has been reported since the early 1980s but Na-ion batteries are not commercialized so far though studies on Li-ion batteries have been reported since the late 1970s and the practical batteries have been extensively utilized for portable device applications in the world since 1991. Now, targeted application of research and development for rechargeable batteries has changed toward realization of the sustainable energy society. With the change in social situation and development of the battery technology, studies on Na-ion batteries have been attracted significant interests since 2010. Although research interests of the electrode materials for Na-ion batteries are evoked in many researchers, advantages, disadvantages, and issues are not fully discussed for realizing the commercialization of Na-ion batteries. In this article, practical issues and perspective are reviewed on the basis of mainly our experimental experiences, know-how, and results, and the future direction is proposed to overcome the issues and to challenge the advanced performance.

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Manuscript submitted July 14, 2015; revised manuscript received August 18, 2015. Published October 9, 2015. *This paper is part of the JES Collection of Invited Battery Review Papers.*

Power storage technology has been dramatically developed since rechargeable lithium battery (LIB), which are often called a Li-ion battery as named by Sony Corp., was commercialized in 1991 and delivered great impact on economy with tapping into new markets. A high-energy powerful LIB for portable electronic devices such as lap top computers and mobile phones is one of the best examples, and indeed they become essential tools for our life. Thanks for the great research achievement, the price of the battery pack has been declining for more than 20 years, and LIBs are now able to be installed in power system for hybrid electric vehicles (HEV) and battery electric vehicles (BEV) with relatively affordable price. Continuous effort has been devoted on the development of LIBs toward higher-power/higher-energy performance, and they now become promising candidates for being a part of grid-scale energy storage incorporated with wind and solar power systems. When it comes to large-scale power system more than that for electric vehicles, the priority in research is shifted to production cost from performance and thus minor-metal free or low-cost materials that can be derived from more abundant resources have become increasingly desirable. Although LiMn_2O_4 , LiFePO_4 , and $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, which are utilized in HEV and BEV instead of costly LiCoO_2 , are recognized as low cost materials,^{1,2} lithium in the Earth's crust is unevenly distributed as minor-metal and consequently affecting to dependence on import of lithium resource and additionally to product costs. In contrast to lithium, sodium is unlimited in the Earth's crust and sea, and is one of the most abundant elements in the Earth's crust. Since the alternative to lithium is more desirable for realizing largescale power source and sodium is the second lightest alkali next to lithium, Na-ion batteries (NIBs) have attracted much attention as feasible technology for past 5 years.

Battery components and electric storage mechanisms of NIBs are basically the same as LIBs except ion carriers (Figure 1a). NIB consists of two electrodes of sodium insertion materials for positive and negative electrodes and they are ionically connected by sandwiching electrolyte which is generally a Na salt dissolved in organic solution. As sodium is the second-lightest and -smallest alkali metal next to lithium, the sacrifice in energy density is expected to be minimized when electrochemical Na insertion/deinsertion is same as that of Li-system. Furthermore, contrary to Li-Al alloy formation, a copper current collector for a negative electrode is able to be replaced with

much inexpensive aluminum because Na metal does not form alloy with Al, which is definitively advantageous of NIBs.

Although NIBs seem to bring numerous cost reduction, the atomic weight and standard potential of sodium are always placed on challenging issues to be considered. In general, potential and reversible capacity of electrode materials for use as practical batteries can play the first role in determining operating voltage and capacity of the cells, which affect the energy density. Table I compares the expected characteristics of Li, Na, Mg, and Al batteries studied currently. When transition metal oxides, ACoO_2 (A = Li, Na, Mg and Al), are used as positive electrodes, LIBs with LiCoO_2 show the highest operating voltage, leading to the highest gravimetric energy density if we assume the same intercalation reversibility and negative electrode of corresponding metals. NIBs are also able to achieve the second highest operating voltage more than 3 V, however, equilibrium potential of Na/Na^+ in PC solution is 0.3 V higher than that of Li/Li^+ , leading to lower operating voltage of NIBs compared to that of LIBs with the same cutoff anodic potential for positive electrode. As regarding capacity, although atomic weight of Na is 3.3 times heavier than that of Li, the formula weight of NaCoO_2 (114 g mol^{-1}) is only 16% heavier than that of LiCoO_2 (98 g mol^{-1}). In the $\text{C}_6/\text{LiCoO}_2$ and $\text{C}_6/\text{NaCoO}_2$ cell configuration, the total weight gain from the substitution of sodium for lithium is only +9%, resulting in insignificant difference in the gravimetric capacities of the full cell configuration. As additional discussion on capacity, Mg and Al battery are studied as "beyond lithium"^{3,4} in recent years because divalent Mg^{2+} and trivalent Al^{3+} ions realize multi-electron reaction, and theoretically, they are believed to bring larger gravimetric capacity. However, as seen in Table I, their theoretical limit of capacity is even lower than lithium case, and unfortunately the operating voltages of Mg- and Al-ion batteries^{5,6} are much lower than 3 V. Further, it is general that Mg and Al electrodeposition is complex and lower reversible, and their larger Stoke's ionic size by strong solvation, results in lower transport number in electrolyte solution. As a result, it is difficult for us to find remarkable merits as a new battery system which overwhelms LIBs in performance so far. On contrary, NIB can be recognized as a primary candidate for an alternative to LIB in terms of cost reduction with minimum sacrifice on performance and risk avoidance from export restrictions for lithium resources.

Historically, first reversible electrochemical sodium insertion at room temperature was demonstrated using TiS_2 in 1980.⁷ In the same year, the electrochemical properties of sodium-containing layered oxides, Na_xCoO_2 , were reported by Branconnier et al.⁸ As researches

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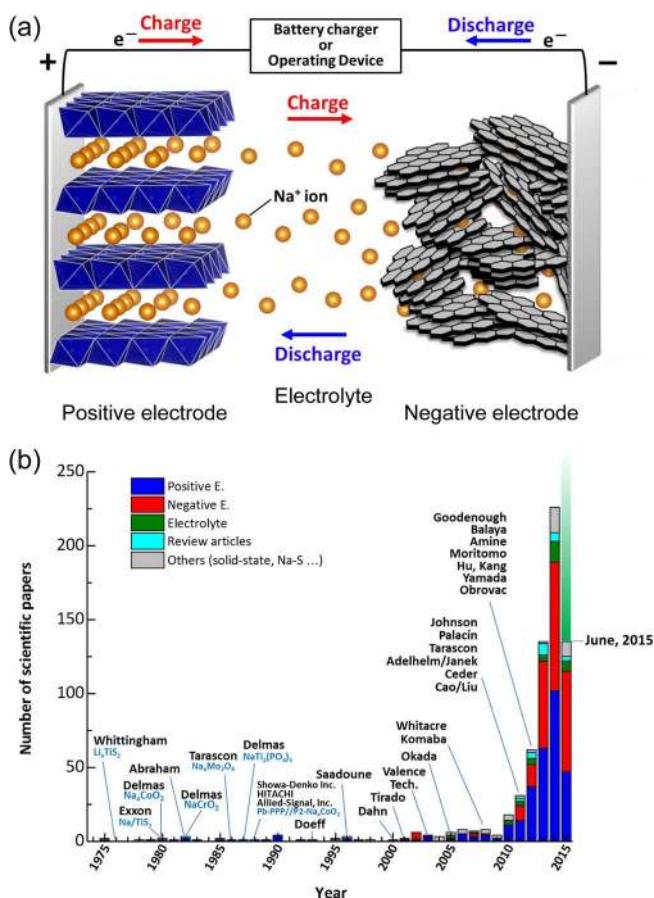


Figure 1. (a) Schematic illustration of Na-ion batteries, and (b) a number of publications, related to the sodium for energy storage devices, published in the past three decades (reproduced from the database of Web of Science, Thomson Reuters). The number in 2015 is limited to the articles published from January to June.

on lithium insertion materials had been just started during the same period and we actually experienced big rush for development of LIBs after the late 1980s, very limited studies on sodium insertion materials were conducted, and only small number of papers and patents were published since 1980's. In addition, research condition and apparatuses including electrolyte solution, binders, separators, and glove box were insufficient for handling sodium metal at that time, which resulted in difficulty in fairly observing potential of the electrode performance as batteries. A few US and Japanese companies developed NIBs in full cell configurations where sodium-lead alloy composite and P2-type Na_xCoO_2 were used respectively as a negative and a positive electrode in the 1980's.^{9,10} Surprisingly, these studies were published earlier than the commercialization of LIBs, and the sodium battery demonstrated excellent cyclability over 300 cycles. However, the average discharge voltage was lower than 3.0 V, which did not attract much attention against carbon//LiCoO₂ cells on the front-line of the day.

Table I. Physical properties for Li and Na as charge carriers for rechargeable batteries compared to Mg and Al.

A	Mass-to-electron ratio/g	Theoretical capacity of $\text{ACoO}_2/\text{mAh g}^{-1}$	Cell voltage	E° vs. $\text{Li}^+_{\text{aq.}}/\text{Li}$
₃ Li	6.941	274	4 V	0.000 V
₁₁ Na	22.99	235	3.5 V	0.331 V
₁₂ Mg	12.15 (= 24.31/2)	260 as $\text{Mg}_{1/2}\text{CoO}_2$	< 3 V	0.689 V
₁₃ Al	8.99 (= 26.98/3)	268 as $\text{Al}_{1/3}\text{CoO}_2$	< 2.5 V	1.369 V

With growing global energy issues in the 21st-century, research interest in sodium insertion materials has now been completely renewed. The number of publications on NIBs has drastically increased in recent years since 2010 (Fig. 1b). Moreover, NIB session in international conferences has been established since 2012 at Pacific Rim Meeting on Electrochemical and Solid State Science (PRiME) and 1st International Conference on Sodium Batteries was held in 2013. Researchers have made best use of their abundant knowledge developed in LIBs to explore new materials and discussion for NIBs, leading excellent results of battery performance published in the literatures. Various positive electrode materials have been reported for NIBs such as layered and tunnel-type transition metal oxides,^{11–16} transition metal sulfides and fluorides,^{17–21} oxoanionic compounds,^{22–31} Prussian blue analogues^{32–34} and organic carboxylates and polymers.^{35,36} Sodium insertion materials show relatively higher rate performance than lithium materials due to the low Lewis acidity of Na^+ ion and the estimated energy density of some positive electrode materials are comparable to those of positive electrode materials for LIBs. Electrochemical properties of negative electrode materials have been also investigated in Na cells and reported by many researchers. Although graphite often utilized in LIBs is electrochemically inactive in Na cells, hard carbon delivers more than 300 mAh g^{-1} of rechargeable capacity at low operation voltage as discussed in the later section. As investigated in LIBs, the electrode performances of sodium alloys,^{37–48} phosphides^{49–51} and organic carboxylates^{52–54} were studied. Although silicon regarded as a next generation material in LIBs is electrochemically inactive in Na cells, phosphorus delivers more than 1,500 mAh g^{-1} of rechargeable capacity.

As next step, we are now reaching an inflection point to consider issues for practical usage of NIBs. However, discussion on NIBs is more complicated than that on LIBs especially in measurement with half coin-type cells to test fundamental electrode performance, because Na metal used as a counter electrode is highly reactive compared to Li metal. In addition, formation of stable passivation film on Na metal and negative electrode materials in Na cells is more difficult,⁵⁵ and experimental conditions including glove box, purity of Ar gas, and electrolyte quality rather influence the performance of Na battery cells. Hence reported results and data cannot be simply compared to reach unanimous conclusions.

In this paper, practical issues and material designs with future perspectives for NIBs with recent research progress are reviewed. Recently, battery performances with larger scale full cells than coin- and Swagelok-type cells have been reported by Sumitomo Chemical Co., Ltd., Sumitomo Electric Industries, Ltd., and Faradion Ltd. In the large scale cells, layered transition metal oxide and hard carbon are utilized as a positive and a negative electrode material, respectively. Now, these cells would most successfully simulate practical NIBs so far to the best of our knowledge. Therefore, the electrochemical properties are discussed mainly using layered transition metal oxides and hard carbon in this manuscript. To direct the research on NIBs and further understand the chemistry in NIBs, experimental and practical issues on electrode materials, binders, electrolyte salts, solvents, additives, and operating voltage are reviewed and future perspectives will be also added from our viewpoint.

Carbon Negative Electrode Materials

Graphite is widely used as a negative electrode material in commercialized LIBs and its reversible capacity has reached to more than 360 mAh g^{-1} approaching to theoretical capacity of 372 mAh g^{-1} .⁵⁶ In contrast to Li cells, graphite is hardly electrochemically active in Na cells with conventional electrolyte solvent of carbonate ester.⁵⁷ Only the way to insert Na into graphite was believed to be heating it with Na metal under helium or vacuum atmosphere, resulting in formation of NaC_{64} .⁵⁸ Recently, reversible Na insertion into graphite was reported using diglyme (diethylene glycol dimethyl ether) solution. By using diglyme as electrolyte solvent, Na^+ -solvent co-intercalation occurs and the Na/graphite cell exhibits reversible capacity of more than 100 mAh g^{-1} over 1,000 cycles as shown in Fig. 2a.⁵⁹ Even

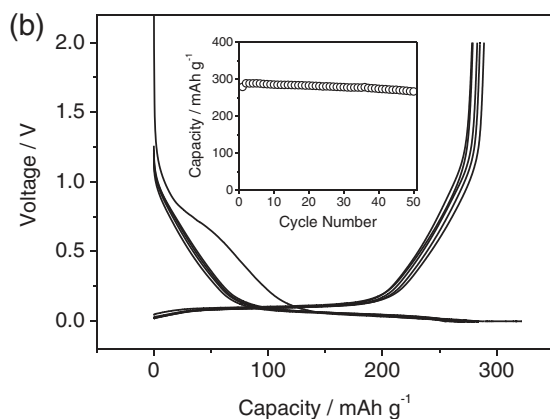
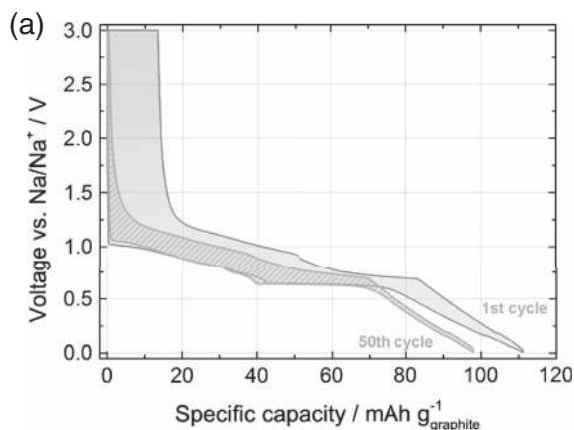


Figure 2. (a) Charge/discharge curves of Na/1 mol dm⁻³ CF₃SO₃Na dissolved in diglyme/graphite cell at a current density of 37.2 mA g⁻¹. Reprinted with permission from Ref. 59. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) Charge/discharge curves of hard carbon electrodes, derived from sucrose carbonized at 1300°C, at a rate of 25 mA g⁻¹ in 1 mol dm⁻³ NaClO₄ dissolved in PC:FEC (98:2 in vol %), and its capacity retention is also shown in the inset. Reprinted with permission from Ref. 64. Copyright 2014 PCCP Owner Societies.

though graphite can be used as a negative electrode material in Na cells with excellent cycle stability, reversible capacity is limited to less than 150 mAh g⁻¹ and large irreversible capacity is observed at an initial cycle. Further investigation on Na⁺-solvent co-intercalation and optimization of electrodes and electrolyte solution is thought to be necessary for practical use.

On the contrary, reversible Na intercalation/de-intercalation into/from hard carbon, prepared by carbonization of glucose, at room temperature was reported by Stevens and Dahn in 2000.⁶⁰ They described that the Na/hard carbon cell delivered ca. 300 mAh g⁻¹ of reversible capacity. The reversible capacity of hard carbon was much higher than that of graphite in Na cells but cycle stability was insufficient. In 2009, we first achieved sufficient cyclability for hard carbon in Na cells as reported at the ECS Japan meeting in Kyoto⁶¹ and then the ECS meeting in Vienna.⁶² The points of the improved cyclability are as follows: (i) very low contamination of water and volatile organics from Ar atmosphere into the Na cells during cell assembly, and (ii) high purity of electrolyte and solvent (as battery grade chemicals), supplied by the Japanese company. Actually, when we first summarized the results of sufficient cyclability of Na full cells and submitted our manuscript to a peer-reviewed journal,⁶³ reviewing researchers doubted our results and pointed out the inevitable problem of water contamination from commercially-available reagent of NaClO₄, which is not battery grade. Recently, our group reported that hard carbon electrodes prepared from sucrose delivered ca. 300 mAh g⁻¹ with good cycle stability over more than 50 cycles as

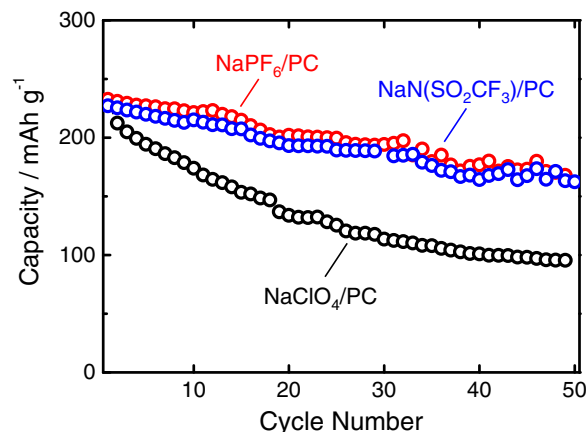


Figure 3. Capacity retention for hard carbon electrodes in the coin-type cells with PC-based electrolyte solvent containing different Na salts; 1 mol dm⁻³ NaPF₆, NaN(SO₂CF₃), and NaClO₄ at a rate of 25 mA g⁻¹. Reprinted with permission from Ref. 64. Copyright 2014 PCCP Owner Societies.

shown in Fig. 2b.⁶⁴ Similar results of Na insertion properties for various hard carbons are reported in recent papers.^{65–87} Clear differences in irreversible capacity and cycle stability between the Dahn's pioneering results⁶⁰ and ours originate from difference in the contamination, purity of electrolyte solution, and binder as described below.

Electrolyte Salts, Solvents, Additives and Binders

Looking back on the history of LIBs, a 1 mol dm⁻³ LiBF₄/propylene carbonate (PC) solution was used for the first electrochemical study of LiCoO₂ in Li cells by Mizushima, Goodenough, and coworkers.⁸⁸ They reported only the first cycle of Li/LiCoO₂ cycle due to the insufficient cyclability. Dr. Mizushima personally commented us in 2014 that he could not believe long cycle life of the Li/LiCoO₂ cell because he observed anodic decomposition of electrolyte solution in the Li cells when they tested the cell in 1970s. As is known presently, the decomposition can be avoided by higher purity electrolyte solution as well as suitable selection of solvents, Li salts, and electrolyte additive etc., and these knowledge resulted in the practical Sony's Li-ion battery. For NIBs, cyclability is also achieved by designing electrolyte solutions with much higher purity.⁶³ To utilize graphite as a negative electrode material in LIB, passivation surface layer, so-called solid electrolyte interphase (SEI), is required for good battery performance, which is adequately formed in high purity electrolyte consisting of Li salts, solvents, and additives.⁸⁹ Nowadays, electrolyte solution for LIBs is developed and custom-designed for required performance, applications, and electrode materials, such as operation temperature, voltage limit, power capability, alloy electrode, LiMn₂O₄ and manganese dissolution, and so on. Consequently, the practical electrolyte in LIB is known to be a complex mixture containing multi additives.

The electrolyte first reported for Na batteries is 1.1 mol dm⁻³ NaI/PC and 0.86 mol dm⁻³ NaPF₆/PC solution in Na/TiS₂ cells in 1980.⁷ Then, for P2-Na_xCoO₂ as a positive electrode material, 1 mol dm⁻³ NaClO₄/PC solution was used in the Na cells in 1980.⁸ In Na-ion full cells, 1 mol dm⁻³ NaPF₆/dimethyl ether (DME) was reported to be used for poly(*p*-phenylene)-Na_xPb alloy composite//P2-Na_xCoO₂ and Na_xPb alloy//P2-Na_xCoO₂ cells.^{9,10} Dependency of electrolyte salts on electrochemical properties of carbonaceous materials of negative electrode in Na cells was previously studied and reported by Alcántara et al. in 2002.⁹⁰ Na/soft carbon cells with NaClO₄/ethylene carbonate (EC) : dimethyl carbonate (DMC) (= 50:50 vol%) solution showed larger reversible capacity than that in the cells with NaPF₆/EC:DMC (= 50:50 vol%) solution. Ponrouch et al. similarly reported larger capacity, smaller initial irreversible capacity, smaller polarization for

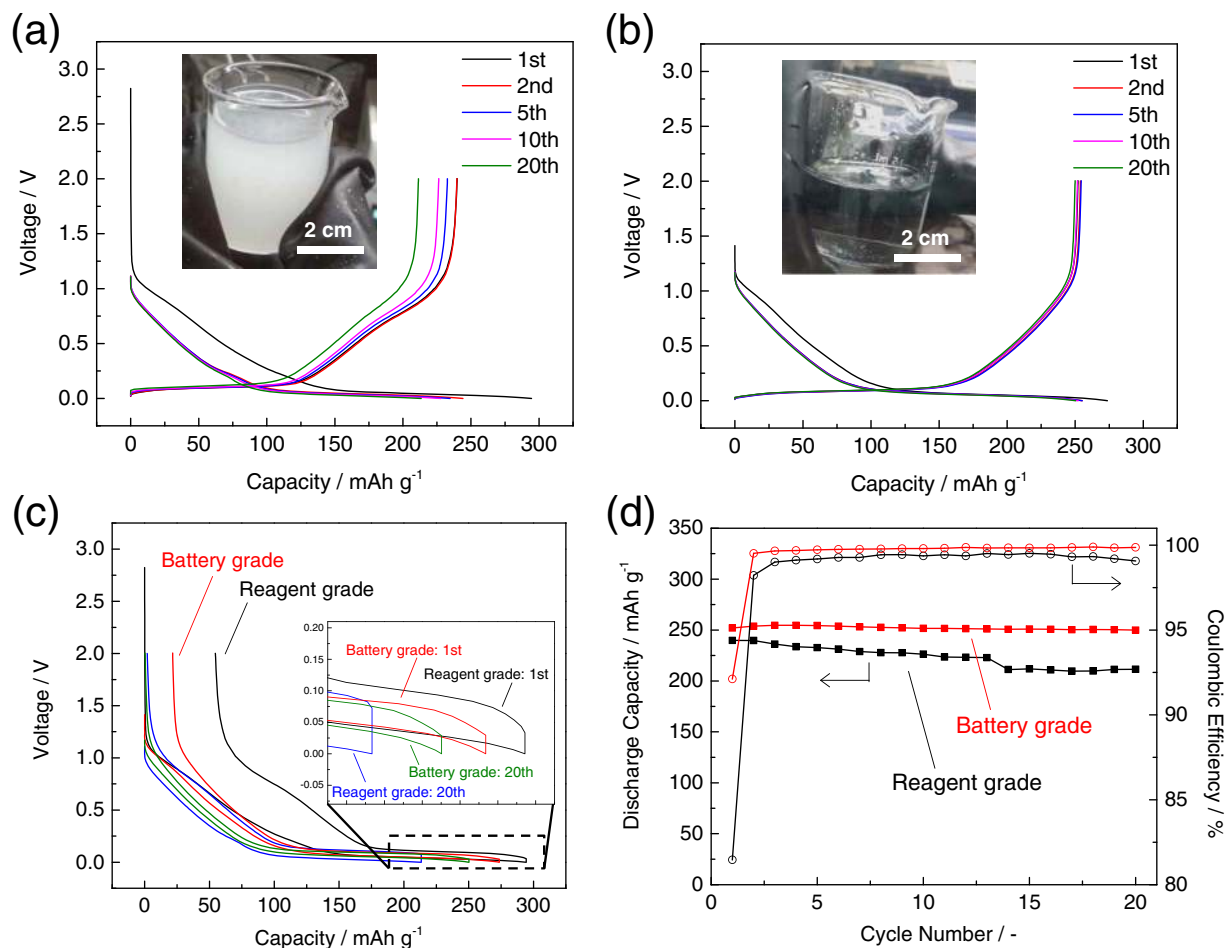


Figure 4. Charge/discharge curves of hard carbon electrodes at a rate of 25 mA g^{-1} in 1 mol dm^{-3} (a) reagent grade and (b) battery grade NaPF_6 PC solution, (c) comparison of the curves and polarization at the end of sodiation and (d) their capacity retention. Photographs of the electrolyte solution use are inserted in (a) and (b).

1 mol dm^{-3} $\text{NaClO}_4/\text{EC}:\text{PC}$ ($= 50:50 \text{ wt}\%$) solution than those for 1 mol dm^{-3} $\text{NaPF}_6/\text{EC}:\text{PC}$.⁹¹ On the other hand, our group obtained opposite results that the coin-type cell with 1 mol dm^{-3} NaPF_6/PC and $\text{NaN}(\text{SO}_2\text{CF}_3)_2/\text{PC}$ solutions exhibited larger reversible capacity and better cycle performance than those for 1 mol dm^{-3} NaClO_4/PC solution.^{63,64} As mentioned above, the research groups tested using different-grade electrolyte solutions under different conditions including contamination level in glove box, therefore, the results should not be simply compared in our understanding. In general, purity of the electrolyte salts is known to significantly influence on the battery performances of LIBs. Water contamination in LiPF_6 generates HF and worse the electrochemical performances in LIBs.⁸⁹ Bhide and Adelmhelm et al. proved the presence of NaF in NaPF_6 (99.0%, Alfa Aesar) using X-ray diffraction and the observation of the insoluble fraction in $\text{NaPF}_6/\text{EC}:\text{DMC}$ solution by eyes.⁹² Detailed study on influence of impurities contained in NaPF_6 salts on sodium insertion properties is required for further understanding. Therefore, influence of the NaPF_6 salts with different purity on electrochemical properties has been investigated using the salts supplied different companies.

We examined galvanostatic charge-discharge test of Na/hard carbon cells with different NaPF_6 salts dissolved in PC as compared in Fig. 4. When we tried to dissolve anhydrous NaPF_6 (98%, reagent grade from Sigma-Aldrich) without drying treatment, 1 mol dm^{-3} NaPF_6 was not completely dissolved in PC (99.5%, battery grade from Kishida Chemical) resulting in the white-turbid solution as seen in Fig. 4a. The solution was used as an electrolyte solution as it is. On the other hand, 1 mol dm^{-3} NaPF_6/PC solution (battery grade, Kishida Chemical) was colorless and transparent because of complete dissolu-

tion of 1 mol dm^{-3} NaPF_6 , and was used for Na/hard carbon cells. As anticipated from the coloration, the cell with the white-turbid solution by dissolving the reagent grade NaPF_6 showed a smaller reversible capacity, a lower coulombic efficiency at the initial cycle, larger polarization and an insufficient cycle stability compared to those of the cell with a colorless and transparent solution by dissolving battery grade NaPF_6 (Kishida Chemical Co. Ltd.), as shown in Fig. 4. In the both cells, sodium polyacrylate was used as a binder with hard carbon in the working electrodes.⁶⁴ Surface of the hard carbon is covered with the polyacrylate binder, and surface passivation is highly improved in comparison to poly(vinylidene fluoride) (PVDF) binder⁷⁴ as discussed latter. Of course, the electrolyte solution influences on electrochemical properties not only of negative electrode but also of positive electrode and Na metal counter electrode. From these results, high purity NaPF_6 salt should be used for the research on aprotic NIBs instead of low purity NaPF_6 and potentially explosive NaClO_4 salt. It is also worth noting that more than 2 mol dm^{-3} of NaPF_6 salt is dissolved in PC solvent at room temperature when we use the highly pure NaPF_6 . The electrochemical properties of Na/hard carbon cells with more than 2 mol dm^{-3} of NaPF_6 electrolyte are under investigation. The results will be reported in the future elsewhere.

Dependency of electrolyte solvents on electrochemical properties in Na cells was reported by Alcántara et al. in 2005 using EC:DMC, DME, tetrahydrofuran (THF) and EC:THF solvents containing 1 mol dm^{-3} NaClO_4 in Na/hard carbon cells.⁹³ THF-based electrolyte solution exhibited the largest reversible capacity and the most stable cycle retention. However, high oxidation current was obviously observed in $\text{NaClO}_4/\text{THF}$ solution above 4.26 V compared to PC, DMC,

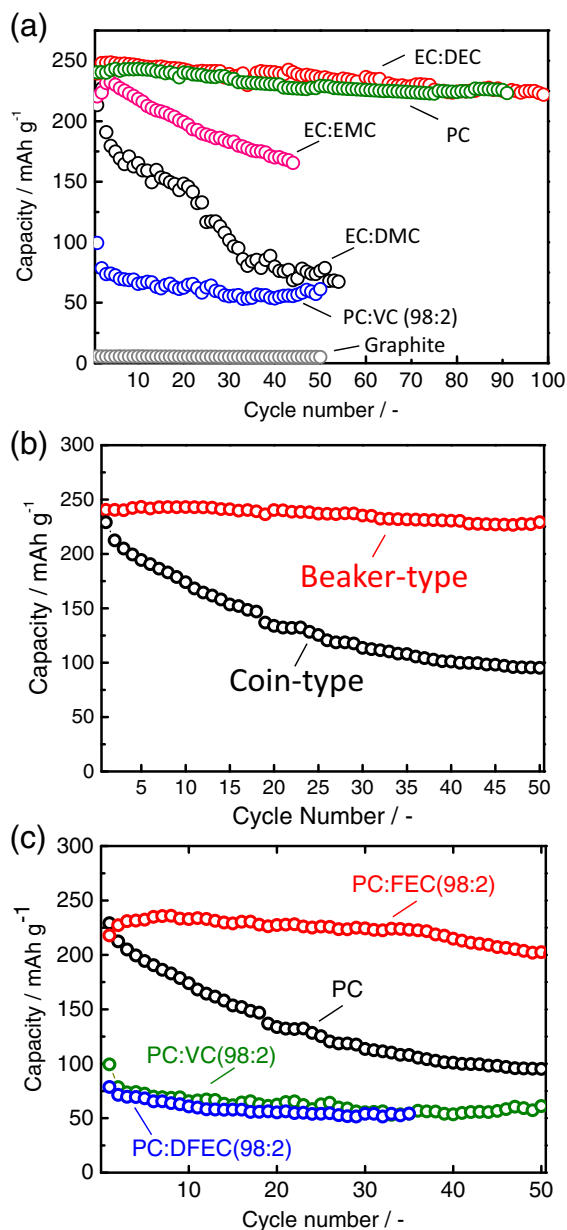


Figure 5. (a) Capacity retention for hard carbon electrodes in the beaker-type cells with $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ dissolved in different solvent mixtures. Reprinted with permission from Ref. 64. Copyright 2014 Wiley Owner Societies. (b) Reversible capacity variation for hard carbon electrodes in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ PC solution in beaker-type or coin-type Na cells at a rate of 25 mA g^{-1} . Reprinted from Ref. 96 with copyright permission from American Chemical Society. (c) Reversible capacity variation for hard carbon electrodes in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ PC solutions with and without additives at a rate of 25 mA g^{-1} in coin-type Na cells.

diethyl carbonate (DEC), DME, and triglyme solutions containing $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ in the cyclic voltammograms, suggesting instability of $\text{NaClO}_4/\text{THF}$ solution against anodic oxidation.⁹¹ Our group also evaluated the battery performances of Na/hard carbon cells with different electrolyte solvents of PC, EC:DEC (50:50 vol%), EC:EMC (50:50 vol%), EC:DMC (50:50 vol%), and PC:VC (98:2 vol%) containing $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ supplied by Kishida Chemical.⁶³ The cells with PC and EC:DEC solutions exhibited better cycle stability than those of EC:EMC, EC:DMC, and PC:VC in beaker-type cells (Fig. 5a), which would be related to the passivation stability.⁶⁴ Ponrouch et al. previously investigated the influence of various solvents with NaClO_4 salt on the physical properties of viscosity and

ionic conductivity for the solution and on the electrochemical properties in Na/hard carbon Swagelok cells.^{91,94,95} They concluded that the Na/hard carbon cells with $1 \text{ mol dm}^{-3} \text{ NaClO}_4/\text{EC:PC:DMC}$ (45:45:10 wt%) solution exhibited the largest reversible capacity and the best rate performance among the cells with PC, $\text{EC}_{0.5}:\text{PC}_{0.5}$, $\text{EC}_{0.5}:\text{DME}_{0.5}$, $\text{EC}_{0.5}:\text{DMC}_{0.5}$, $\text{EC}_{0.5}:\text{DEC}_{0.5}$, $\text{EC}_{0.4}:\text{PC}_{0.4}:\text{DEC}_{0.2}$, $\text{EC}_{0.4}:\text{PC}_{0.4}:\text{DMC}_{0.2}$, $\text{EC}_{0.4}:\text{PC}_{0.4}:\text{DME}_{0.2}$ and $\text{EC}_{0.45}:\text{PC}_{0.45}:\text{DMC}_{0.1}$ solvents with $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ salt. However, as described in the literatures, NaClO_4 -based electrolyte solution could not be used for commercial battery because of explosion hazards. Electrochemical properties of full cell, hard carbon/ $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ with $1 \text{ mol dm}^{-3} \text{ NaPF}_6$ (98%, Aldrich) $\text{EC}_{0.45}:\text{PC}_{0.45}:\text{DMC}_{0.1}$ solution, was also investigated but the cell showed severe polarization compared to those of the cell with $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ (98%, Aldrich) $\text{EC}_{0.45}:\text{PC}_{0.45}:\text{DMC}_{0.1}$ solution. The electrochemical performances might be influenced by the impurity in lower purity NaPF_6 salt as mentioned above. No report on systematic investigation of NaPF_6 -based electrolyte solution, its battery performances, and surface chemistry of electrode is found according to our knowledge. Higher purity NaPF_6 salt and its lower contamination are certainly required to be commonly used for further investigation to understand NaPF_6 -based electrolyte solution for Na-ion research. Simultaneously, we have to note that a good glove box equipped with acceptable purification and circulation of inert atmosphere is also important to avoid contamination into Na cells.

In our investigation based upon the high purity electrolyte solution in Na cells, the different cycle retention was observed for beaker-type and coin-type $\text{Na}/1 \text{ mol dm}^{-3} \text{ NaClO}_4$ PC/hard carbon cells (Fig. 5b).⁹⁶ In the coin-type cell, thin glass separator soaked with the minimal amount of electrolyte solution is sandwiched between the Na and hard-carbon electrodes. In the beaker-type cell, sodium insertion electrodes are examined in flooded electrolyte solution. When electrolyte solution is gradually decomposed and consumed in Na cells during cycles, damage to electrolyte solution in coin-type cell is much significant due to its smaller quantity of electrolyte solution. Because the beaker-type cell contained ca. 10 ml of electrolyte solution while the coin-type cell had ca. 0.2 ml of the solution, capacity degradation in coin-type cell severely occurs than that in beaker-type cells. The results imply importance of the amount of electrolyte solution.

The other important component in the electrolyte effective to battery performances is electrolyte additive. In practical LIBs, less than 5 wt% of electrolyte additives play an important role to improve the battery performances.⁸⁹ In Na cells, our group investigated the influence of additives, fluoroethylene carbonate (FEC), trans-difluoroethylene carbonate (DFEC), and vinylene carbonate (VC) on the electrochemical properties of Na/hard carbon cells using coin-type cells.⁹⁶ By the addition of ca. 2 vol% FEC in $1 \text{ mol dm}^{-3} \text{ NaClO}_4/\text{PC}$ solution, the capacity retention was remarkably improved but the other additives did not show any beneficial effects in the NaClO_4 solution (Fig. 5c). The effects of additives on the electrode performance might change in NaPF_6 solution, which is under investigation by our group.

As recently reported, FEC addition in $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ (Aldrich, $\geq 98\%$) in EC : DEC (= 1:1 v/v, PANAX ETEC, Korea), $1 \text{ mol dm}^{-3} \text{ NaPF}_6$ in EC : DEC and $1 \text{ mol dm}^{-3} \text{ NaClO}_4$ in PC (Kishida Chemical) electrolyte solutions effectively improved cycle stability of alloy compounds, Sn_4P_3 ,⁴⁶ Sb/C nanocomposite⁴¹ and phosphorus,⁵¹ respectively. Alloy compounds usually induce large volume expansion and shrinkage during Na insertion and extraction, respectively. Therefore, stable passivation surface is required and the influence of the electrolyte additive would be significant.

On the other hand, influences of the electrolyte additives in NaPF_6 (99+%, Alfa Aesar)/PC on battery performances of positive electrode materials were recently reported by Delmas' group using Na//O3- $\text{Na}_{0.82}\text{Mn}_{1/3}\text{Fe}_{2/3}\text{O}_2$ cells and the cycle stability was significantly improved by adding 2 wt% FEC or VC.⁹⁷ Although they showed clear influence of additives on the cycle performance, it is difficult to discuss based on only battery performance without considering additive effects on Na metal, and impurity of electrolyte salt, especially NaPF_6 , would be also another concern.

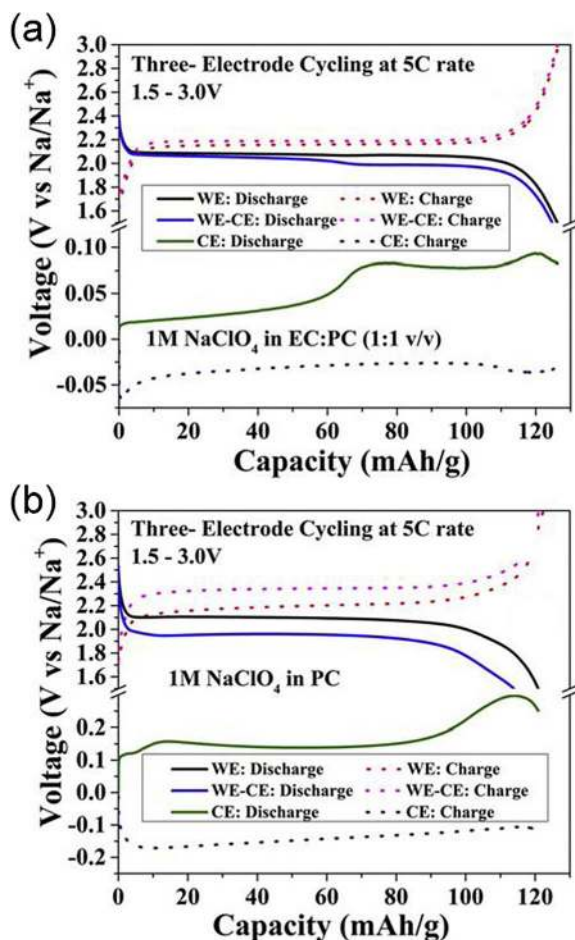


Figure 6. Charge/discharge curves of three electrode cells with $\text{NaTi}_2(\text{PO}_4)_3$ as working electrode, Na metal as counter and reference electrodes at a rate of 5C in 1 mol dm^{-3} in NaClO_4 in (a) EC:PC and (b) PC. Reprinted with permission from Ref. 98, Copyright 2014, with permission from Elsevier.

The influence of additives on electrochemical properties was reported for not only positive but also negative electrodes and metallic Na electrode. However, electrolyte salts used are different in the literatures and no description on Na metal as a counter electrode is seen. Therefore, overall studies on the influence of electrolyte salts, solvents, and additives on electrode performances of positive and negative electrodes as well as Na metal are necessary and would be reported elsewhere.

In addition, the quality of electrolyte solution influences on Na metal as a counter electrode in half cells. Rudola and Aurbach et al. recently reported that a clear voltage polarization-step was observed around 65 mAh g^{-1} for $\text{NaTi}_2(\text{PO}_4)_3$ electrode during Na stripping at 5C rate in 1 mol dm^{-3} NaClO_4 EC:PC (= 50 : 50 vol%) solution (Fig. 6a) due to an increase in polarization of Na metal counter electrode while the voltage step is absent in 1 mol dm^{-3} NaClO_4 PC solutions (Fig. 6b), which has never observed in Li half cells.⁹⁸ Furthermore, polarization of Na metal counter electrode is remarkable at 5C rate in both PC and EC:PC solutions, dissimilar to Li metal. As they pointed out, electrochemical properties should be carefully evaluated especially at high current density and for the materials showing very low operating voltage at around 0 V vs. Na/Na^+ such as hard carbon.⁶³

Another important key component to exploit the electrode performance is binder used for powdery active materials. It is well known and widely studied that binder significantly influences on the electrode performances of Si and alloy compounds as negative electrode materials, involving a huge volume exposition during lithiation.⁹⁹ In

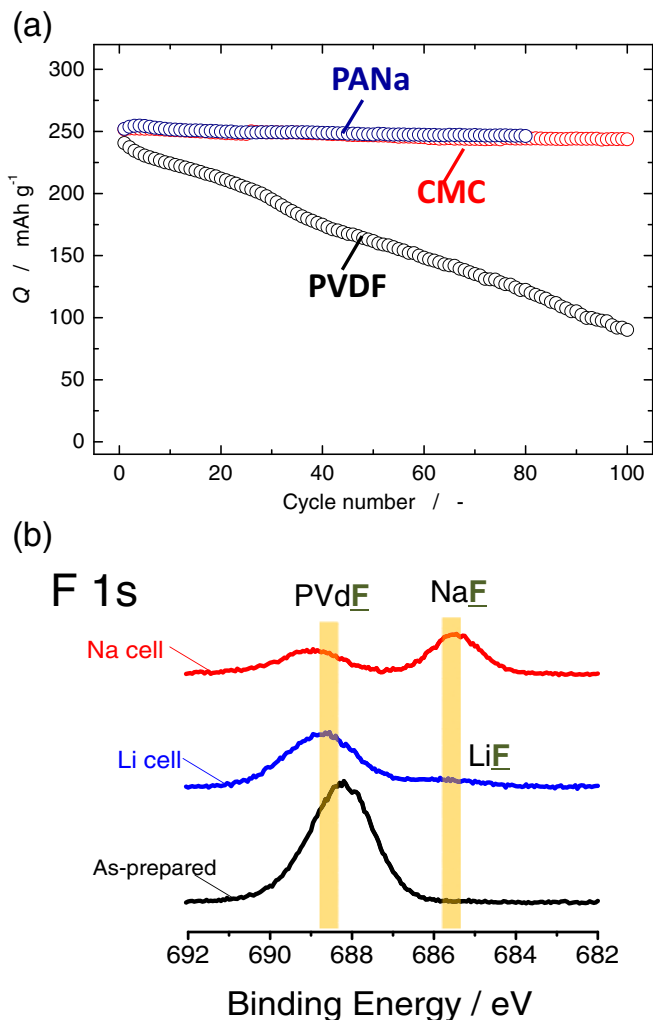


Figure 7. (a) Cycle performance of hard-carbon electrodes with CMC, PANa and PVdF binders in 1 mol dm^{-3} NaPF_6 PC solution. (b) HAXPES spectra of F 1s for hard carbon electrode as prepared and after 1st cycle in NaClO_4 or LiClO_4 PC solution in Li- or Na-cell, respectively. Reprinted with permission from Ref. 74, Copyright 2014, with permission from Elsevier.

Na cells, PVdF binder in the hard carbon electrode is gradually defluorinated, resulting in carbon and NaF formation, accompanied with capacity degradation during repeated Na insertion and extraction into hard carbon. Fig. 7a shows capacity retention of hard carbon electrodes with different binders in 1 mol dm^{-3} NaPF_6 in PC solution. In the case of PVdF without FEC additive, the reversible capacity significantly decayed during cycles. In contrast, the hard carbon electrodes with sodium carboxymethyl cellulose (hereafter denoted as CMC for simplicity) and sodium polyacrylate (PANa) binders exhibited excellent capacity retention in coin-type cells. Furthermore, the initial and averaged coulombic efficiencies were improved by using CMC and PANa binders. As clear difference in capacity retention was observed and fluorine-containing salts, NaPF_6 and $\text{NaN}(\text{SO}_2\text{CF}_3)_2$ showed better cycle stability than that of fluorine-free electrolyte solution as shown in Fig. 3, fluorine-containing salts would be preferentially decomposed instead of PVdF binder, leading to good passivation. The defluorination of PVdF and following formation of NaF in the Na cell with fluorine-free electrolyte solution, 1 mol dm^{-3} NaClO_4/PC , were clearly evidenced by X-ray photoemission spectroscopy as shown in Fig. 7b. On the other hand, formation of LiF was not observed for the hard carbon electrode with PVdF binder in Li cell, which is due to the better passivation in Li insertion negative electrodes than Na ones.⁶⁴ PVdF is electric insulator, therefore, the electrochemical

decomposition of PVdF requires both electron/ion connection from hard carbon/electrolyte respectively. This means that the three phase interface of hard carbon/PVdF/electrolyte influences the degree of electrochemical defluorination of PVdF, and that SEI formation on hard carbon should influence the connection between hard-carbon/PVdF interface.

The previous studies on electrolyte salts, solvents, additives and binders in Na cells are conducted mainly for hard carbon electrodes. The optimum combination of those components must depend on electrode materials and test conditions. For example, some transition metal oxides show electrocatalysis behavior and accelerate electrolyte decomposition on the surface. Therefore, suitable passivation on the electrode surface with effective binder and additive is very important to suppress the electrolyte decomposition. Controlling the surface reaction, electrolyte decomposition, and SEI formation is necessary to further improve the performance of NIBs.

Ionic liquid is also utilized as electrolyte solution in NIBs. Ionic liquid generally has negligibly low volatility, nonflammability, and high thermal and electrochemical stability. Recently, NIBs with ionic liquid can be operated at room temperature¹⁰⁰ and Sumitomo Electric Industries Ltd. has studied to realize practical NIBs with ionic liquid. Although the NIBs exhibit sufficient cycle stability¹⁰¹ and are relatively safe, cost reduction of ionic liquid, increase in energy density, and further safety tests are required for practical use. LIBs with ionic liquid have been also studied broadly, therefore, we have to carefully consider merits and demerits of ionic liquids for the LIBs and NIB for practical applications.

Operation Potential of Negative Electrodes

In order to increase the operation voltage of NIBs, the materials operating at lower-potential for negative electrode materials are important which is essential to increase the energy density. Although hard carbon exhibits more than 550 mAh g⁻¹ of reversible capacity by CC-CV lithiation in Li cells,¹⁰² the redox potential in plateau region during insertion process into nanopores is almost 0 V vs. Li/Li⁺ and utilization of the plateau region at high current density has a high risk for the formation of metallic Li metal dendrite. Fig. 8a compares charge and discharge curves for Li//graphite, Li//hard carbon and Na//hard carbon cells in detail. Hard carbon electrodes in both Li and Na half cells show slope and plateau regions during (de)intercalation⁶³ while graphite exhibited stepwise potential variation due to the formation of staging structure. Fig. 8b shows dQ/dV curves of the charge and discharge curves in the potential region between 0–0.3 V. The voltages of reduction and oxidation peaks are the lowest in Li//hard carbon cell and the highest in Li//graphite cell from Fig. 8b when optimized hard carbon for LIBs was used in both Li and Na cells. Interestingly, the voltages for Na//hard carbon was intermediate between Li//hard carbon and Li//graphite cells. A risk for the formation of dendrite metal in Na//hard carbon cell is, therefore, insignificant compared to that in Li//hard carbon cell. It is thought that both of the slope and plateau capacity of hard carbon can be utilized as a negative electrode material for Na-ion cell to deliver larger capacity with less risk of alkali metal deposition than those of Li-ion cells.

In general, Na containing transition metal oxides show lower redox potential (vs. Na/Na⁺) compared to Li containing ones (vs. Li/Li⁺). In LIBs, spinel-type Li₄Ti₅O₁₂ has been extensively studied and is already utilized in practical LIB since Li₄Ti₅O₁₂ exhibits excellent cycle performance due to the negligible volume change and high thermal stability.^{103–105} Its redox potential of 1.55 V vs. Li/Li⁺ is higher than the reduction potential of electrolyte decomposition occurring at approximately 0.8 V vs. Li/Li⁺, resulting in the stable cycle life and high rate performance without apparent passivation layer such as SEI. NASICON-type titanium phosphate negative electrode material, NaTi₂(PO₄)₃ having higher redox potential than the decomposition potential of ca. 1.1 V vs. Na/Na⁺ are thought to be good candidates for high-rate NIBs.¹⁰⁶ However, negative electrode materials showing the relatively high operating potential would provide NIB batteries with very low operating voltage

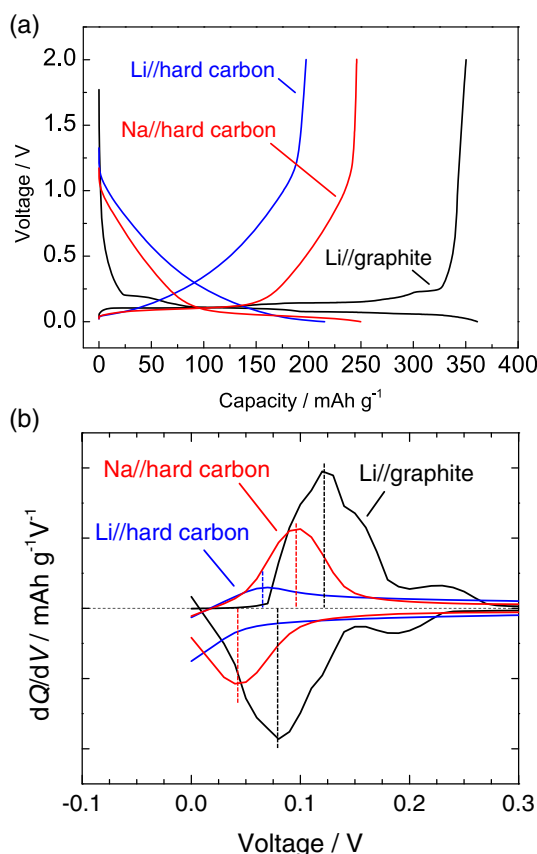


Figure 8. (a) Charge/discharge curves (corresponding to lithiation/delithiation or sodiation/desodiation, respectively) at 2nd cycle for Li/1 mol dm⁻³ LiPF₆ EC:DMC (= 50:50 vol%)/graphite, Li/1 mol dm⁻³ LiPF₆ EC:DMC (= 50:50 vol%)/hard carbon, and Na/1 mol dm⁻³ NaPF₆ PC/hard carbon cells tested at a current density of 25 mA g⁻¹ in the voltage range of 0.0–2.0 V using coin-type cells. (b) Comparison of the dQ/dV curves between 0 and 0.3 V.

at 1.5–2.5 V. Therefore, high-potential negative electrode materials could not be targets for high energy NIBs but possibly suitable for high safety and lower cost NIBs. Various titanium oxides as negative electrode materials for Na-ion application have been reported so far.⁶⁴

The materials map of reversible capacity and average voltage plots are represented in Fig. 9. To calculate the energy density that is based upon the active material mass only, reversible capacity and average discharge potential of P2-type Na_{2/3}Ni_{1/3}Mn_{1/2}Ti_{1/6}O₂ are hypothetically used for the calculation for Na-ion full cells. In Figure 9, sodium titanium oxides such as Na₂Ti₃O₇,¹⁰⁷ P2-Na_{0.66}Li_{0.22}Ti_{0.78}O₂¹⁰⁸ and Li₄Ti₅O₁₂¹⁰⁹ show lower averaged potential below 1.1 V vs. Na/Na⁺ unlike 1.55 V vs. Li/Li⁺ for Li₄Ti₅O₁₂. Some materials, NaTi₂(PO₄)₃¹⁰⁶ and Li_{0.5}Na_{0.5}Ti₂(PO₄)₃¹¹⁰ show higher potential of 2.1 and 2.2 V, respectively but the potential is too high to utilize as negative electrode materials in high-energy Na full cells, which may be applicable for aqueous battery. As we described in the literature,¹¹¹ operating voltage is an important parameter to demonstrate high-energy NIBs. Sn⁴⁵ and P^{49–51} show anomalous capacity of ca. 700 and 1600 mAh g⁻¹, respectively, but almost same energy density of 350 mWh g⁻¹ was obtained for Sn and P cases from the calculation of Fig. 9. To further increase the energy density of Na full cells, development of the negative materials showing lower potential and larger capacity is necessary otherwise new positive electrode materials exhibiting larger capacity at higher potential are required to deliver the higher energy density in Fig. 9. Note that the available capacity of positive electrode materials is usually lower than that of the negative electrode in NIBs as well as LIBs. Therefore, higher-

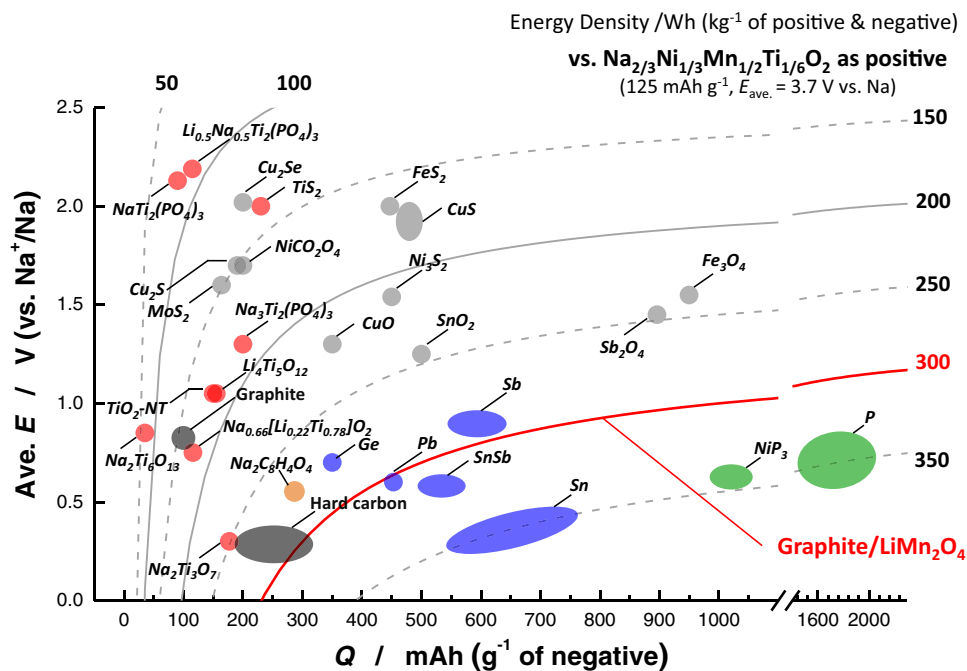


Figure 9. Average voltage (V) and energy density (Wh kg^{-1}) versus gravimetric capacity (mAh g^{-1}) for negative electrode materials for Na-ion batteries: (black circles) carbonaceous materials, (red circles) oxides and phosphates as sodium insertion materials, (blue circles) alloy, (green) phosphide/phosphorus, and (gray circles) oxides and sulfides with conversion reaction. Energy density based on weight of active materials in positive and negative electrodes is calculated using their reversible discharge capacity. Positive electrode is assumed to be $\text{Na}_{2/3}[\text{Ni}_{1/3}\text{Mn}_{1/2}\text{Ti}_{1/6}]\text{O}_2$ for the calculation. Reprinted from Ref. 111 with copyright permission from American Chemical Society.

capacity positive electrode materials are more important to achieve higher energy battery.

Layered Positive Electrode Materials

Studies on Na batteries operable at room temperature had been started using layered TiS_2 and Na_xCoO_2 materials. Our group has also studied the electrode performance of the layered transition metal oxides as positive electrode materials for NIBs since 2004. One of the authors had a very good opportunity to study layered sodium oxides as a postdoctoral researcher in Dr. Delmas and Dr. Croguennec research group in 2003. In the next year, Okada's group also reported excellent and surprising data of 3.3 V operation of $\alpha\text{-NaFeO}_2$ in NaClO_4 PC solution supplied by Tomiyama Pure Chemical Industries, Ltd.¹¹² One of the authors previously examined sodium salt as an efficient electrolyte additive to improve graphite negative electrode for Li-ion cells in 2002.¹¹³ This is another reason why the author has been much interested in sodium insertion into carbon materials as a component of Na-ion system since 2003.

Figure 10a compares charge and discharge curves of Li//LiCoO₂ and Na//NaCoO₂ cells. Although both samples have the same crystal structure consisting of CoO₂ slabs alternately accommodating Li⁺ or Na⁺ ions between the slabs along *c*-axis as shown in Fig. 10b, the operating potential of LiCoO₂ for the region at the end of discharge (start of charge) is >1.0 V higher than that of NaCoO₂. Lower capacity with stepwise potential change is obtained for the NaCoO₂. Consequently, the energy density is much lower for Na system when the same framework structure and elements with the Li system is used as the comparison between LiCoO₂ and NaCoO₂ in Fig. 10a. Therefore, increase in the operating potential has been targeted by changing structure and composition in not only layered oxides but also polyanionic compounds to demonstrate comparable energy density to LIB.^{15,28,29,111,114}

Na system has clear difference from Li one in the crystal polymorphism of layered oxides. The most common layered structures such as $\alpha\text{-NaFeO}_2$ are built up by stacking sheets of edge-sharing

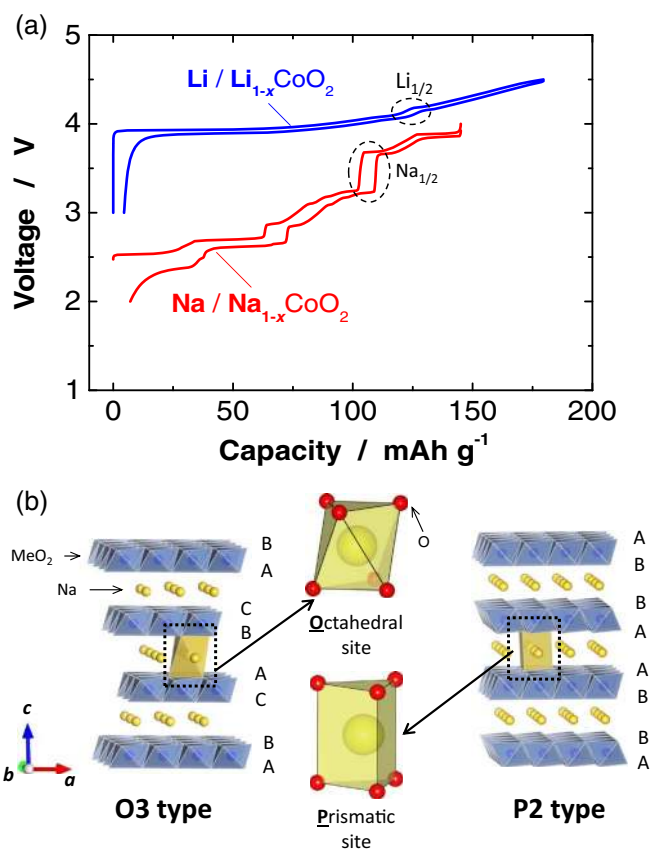


Figure 10. (a) Comparison of charge/discharge curves of Li//LiCoO₂ and Na//NaCoO₂ cells. (b) Schematic illustrations of crystal structures for O3 and P2 type Na_xMeO_2 (Me = transition metals). Reprinted from Ref. 111 with copyright permission from American Chemical Society.

MeO₆ octahedra. Polymorphs are generated by stacking the sheets of edge-sharing MeO₆ octahedra with different orientations along *c*-axis. Sodium-containing layered oxides can be categorized into two main groups using the classification proposed by Delmas et al.:¹¹⁵ O3-type or P2-type, in which the sodium ions are occupied at octahedral and prismatic sites, respectively, as shown in Fig. 10b. Although O3-type LiMeO₂ is synthesized directly by solid state reaction or through Li⁺/Na⁺ ionic exchange process from NaMeO₂, P2-type phases are not seen in Li-containing compounds because larger sodium ions can be located at trigonal prismatic sites where the smaller lithium ions cannot stabilize the P2 structure. From next section, experimental and practical issues on O3- and P2-type layered oxides in Na cells are reviewed.

O3-type Layered Oxides

O3-type sodium-containing layered transition metal oxides generally exhibit reversible Na intercalation/extraction into/from the structure even if O3-type lithium-containing layered oxides consisting of the same 3*d* transition metal oxides are electrochemically inactive in Li cells such as NaFeO₂ and NaCrO₂ except for NaScO₂. In order to obtain large reversible capacity and high operating voltage for high energy density NIBs, reversibly available range of Na extraction in NaMeO₂ (Me = transition metals) and adequately high voltage avoiding anodic decomposition of electrolyte solution are very important. However, the available reversible capacity is usually limited to the capacity corresponding to 0.5 moles of Na extraction from NaMeO₂. By further Na extraction, O3-type oxides show large irreversible capacity and finally lose the reversibility of Na intercalation as shown for Na/O3-NaFeO₂ cells in Fig. 11.¹¹⁶ The capacity decay is mainly due to irreversible structural changes accompanied by migration of transition metal ions, for example, iron, chromium, and titanium ions, from octahedral site in the slab to tetrahedral site and then to face-shared octahedral site in interslab space.¹¹⁶⁻¹¹⁹ Even though O3-type structure transforms into P3-type one by moderate Na extraction, having no tetrahedral sites in interslab space, another O3-type phase having tetrahedral sites appears again when the electrode is charged beyond 0.5 moles of Na extraction.¹¹⁸ Despite, NaFe_{1/2}Co_{1/2}O₂,¹²⁰ NaNi_{1/3}Fe_{1/3}Co_{1/3}O₂,¹²¹ NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂,¹²² and NaNi_{1/4}Fe_{1/4}Co_{1/4}Mn_{1/4}O₂¹²³ demonstrate larger reversible capacity corresponding to more than 0.6 moles of Na extraction. The metal doping in NaFeO₂ effectively suppresses the irreversible migration of iron and extends the available range of Na extraction. Appropriate selection of transition metals and the composition to control the structural changes and to increase operating potential is important for O3-type layered oxides in Na system.

Furthermore, when we test battery performance of electrode materials, slurry mixture is prepared by mixing active materials with carbon additive, binder and solvent, and the slurry has to be uniformly pasted on aluminum foil as a current collector by “doctor blade” to make a composite electrode for assembling cells. These mixing and coating operation are usually conducted in air which is well established for LIB production. Fig. 12 compares the photographs of electrode sheets for (a) O3-type LiCoO₂ and (b) O3-type NaNi_{0.5}Mn_{0.5}O₂ composites before drying treatment. Smooth and homogeneous features were found for LiCoO₂. In contrast, heterogeneously agglomerated particles, scratched line by the large agglomerated particle and rough surface were observed for NaNi_{0.5}Mn_{0.5}O₂. According to our experiences, most of O3-type NaMeO₂ are hygroscopic. In detail, Na⁺ ions are readily exchanged with H⁺ ions by uptaking H₂O from atmosphere, that is,



Additionally, OCV of some pristine NaMeO₂s is mostly about 2 V vs. Na/Na⁺ as seen in Fig. 10a. Such low OCV support the fact that NaMeO₂ act as reducing agent against oxygen and/or water as follows:

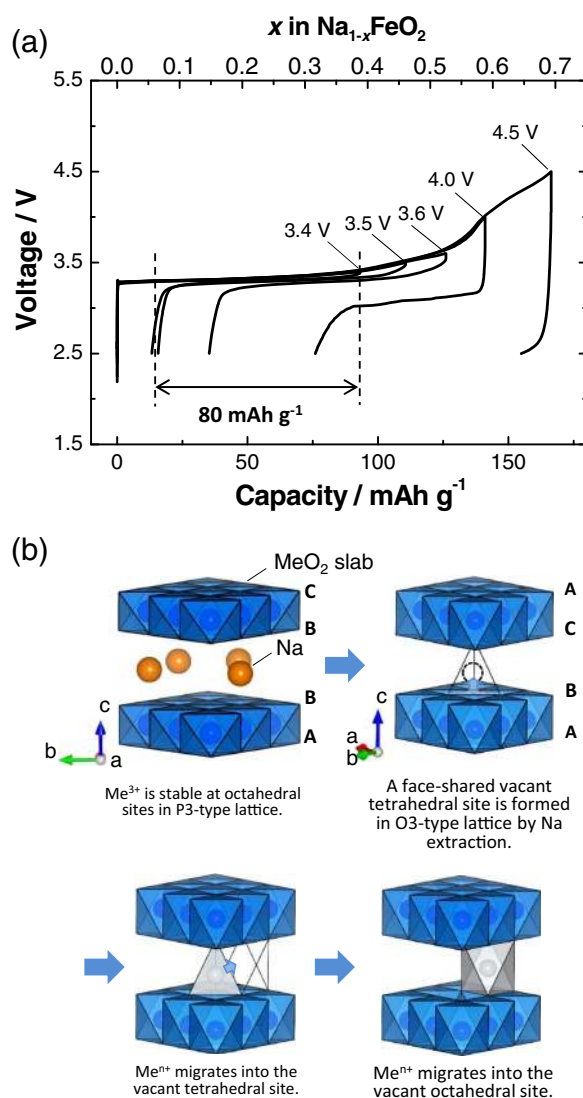


Figure 11. (a) Galvanostatic charge/discharge curves of Na/NaFeO₂ cell. (b) Proposed mechanism for the migration process of transition metal ion on sodium extraction. (a) Reprinted from Ref. 116 with permission of The Electrochemical Society of Japan. Copyright 2012. (b) Reprinted from Ref. 118 with copyright permission from American Chemical Society.



NaOH, formed in Equation 1, is partially dissolved in NMP. Furthermore, Na₂O, produced in Equations 2 and 3, will change into NaOH in atmosphere in Equation 4, and NaOH will be contained in NMR slurry.

To simulate the influence of the NaOH contamination from NaMeO₂ on slurry condition, we made slurry with TiO₂ and small portion of NaOH additive. The reason why we select TiO₂ is that TiO₂ is not hygroscopic, non-reactive with NaOH, water, and air, and white color which allows us to visually distinguish coloration of slurry. TiO₂ white powder and PVdF were mixed with or without NaOH powder at a molar ratio of 1:1 (= TiO₂ : NaOH) in NMP solvent by our assuming that NaOH formation in slurry mixture of NaTiO₂ and PVdF by air-exposure, as shown in the above equations.

From Fig. 12c, no change was visually observed for the mixture of TiO₂ white powder and PVdF without NaOH and NMP. On the other hand, very slight coloration into light brown was observed for

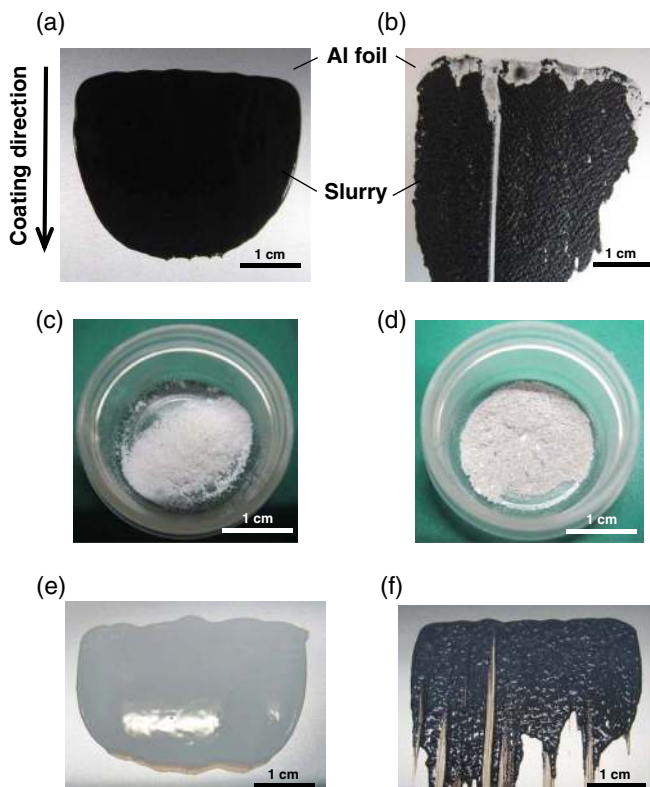


Figure 12. Photographs of the slurry just pasted on Al foil (without drying) in atmosphere for (a) LiCoO_2 and (b) $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ composites, powder mixtures of (c) TiO_2 and PVdF and (d) TiO_2 , PVdF and NaOH at a molar ratio of $\text{TiO}_2 : \text{NaOH} = 1 : 1$, and the slurry just pasted on Al foil (without drying) in inert atmosphere inside glove box for TiO_2 and PVdF with NMP (e) without and (f) with NaOH.

the mixture of TiO_2 and PVdF with NaOH powder and without NMP in Fig. 12d, supporting a slight reaction between PVdF and NaOH in power state in atmosphere. More obvious difference was observed by mixing with NMP under Ar-filled glove box. No coloration was observed for the sheet of TiO_2 and PVdF slurry free from NaOH. However, black coloration and agglomeration were observed for TiO_2 and PVdF slurry mixed with NaOH powder, indicating a chemical reaction between PVdF and NaOH in the slurry, because no significant coloration was seen for the powder mixture of TiO_2 and NaOH. The coloration is due to defluorination for PVdF in NaOH solution.^{124,125} Clearly, the worse condition of the NaOH-added slurry is similar to the case of $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as seen in Figs. 12b and 12f.

If hygroscopic O3- NaMeO_2 slurry is exposed to moist atmosphere, the extraction of Na^+ and NaOH formation, as described in Eqs. 1, 2, 3 and 4, result in the increase in alkalinity of the slurry due to NaOH formation and its dissolution into NMP, leading to defluorination of PVdF binder in the NaOH-containing slurry, and then the agglomerated particles gradually appear. Furthermore, if we pasted the slurry on aluminum foil, the NaOH containing slurry should corrode aluminum foil, because aluminum is an amphoteric element. During handling O3-type NaMeO_2 product, dry condition is required to avoid the damage to PVdF binder, Al foil, and also NaMeO_2 product. This problem is similarly found in LiNiO_2 and layered oxides containing Ni^{3+} in the Li system because of their hygroscopicity. The developed techniques for practical use for the hygroscopic Li-containing oxides would be applied to Na system.

Recently, the research group of Sumitomo Chemical Co., Ltd. reported to synthesize Ca-doped $\text{NaFe}_{0.4}\text{Ni}_{0.3}\text{Mn}_{0.3}\text{O}_2$ and successfully suppressed the hygroscopic character by Ca doping.¹²⁶ Metal doping in the active materials, surface coating of the particles, addition of self-sacrificial agents to absorb alkali ions in slurry and so on are

expected to overcome the deterioration of slurry. Consequently, materials design considering control the hygroscopic character, phase transition, and operating potential is required for O3-type layered oxides.

P2-type Layered Oxides

In constant to O3-type layered oxides, P2-type oxides generally exhibit high operating voltage.¹⁵ The fact probably originates from the off-stoichiometry of sodium and the difference in oxygen stacking sequence in the structure: ABCABC in O3-type and ABBA in P2-type, resulting in suppression of irreversible structural change and almost all Na ions can be extracted from the structure without collapse of the crystal structure. As described above in Fig. 10a, lowering redox potential is significant in Na-rich region in Na cells. Utilizing the Na-poor region for $x = 2/3 \sim 0$ in Na_xMeO_2 leads to relatively high operating potential and P2-type layered oxides provide higher energy density of Na cells than that for O3-type layered oxides. Additionally, such higher potential in as-prepared materials is advantageous to suppression of hygroscopic damage.

For example, P2-type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ exhibits large reversible capacity of ca. 160 mAh g^{-1} close to theoretical capacity of 173 mAh g^{-1} with high operating potential of 3.63 V.^{127,128} Figure 13a shows the charge curve of Na//P2-type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cell. Structure of P2-type $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ changes into O2-type having octahedral sites in interslab space by Na extraction and almost Na-free O2-type phase is formed at 4.5 V (Fig. 13b). However, almost all Na extraction induces a significant lattice shrinkage accompanied by the P2–O2 phase transition. The large volume change results in the insufficient capacity retention due to the loss of electronic conducting path and isolation of the active materials from carbon and current collector.¹²⁸ Water dispersible/soluble binders are very effective to improve their battery performance involving the large volume change, which have

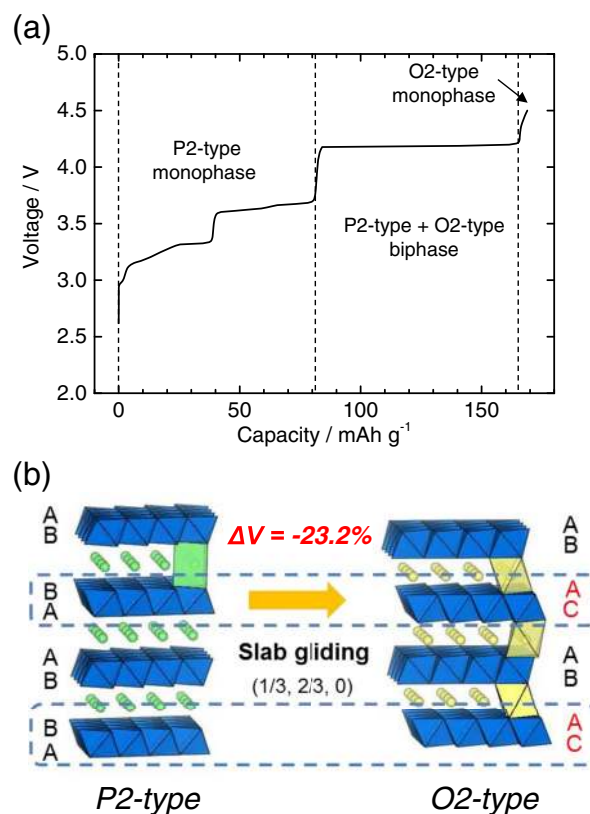


Figure 13. (a) Charge curve of Na//P2- $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$ cells with indication of phase evolution region. (b) Schematic illustration for the reversible structural change from P2- to O2-type phase by the slab gliding.

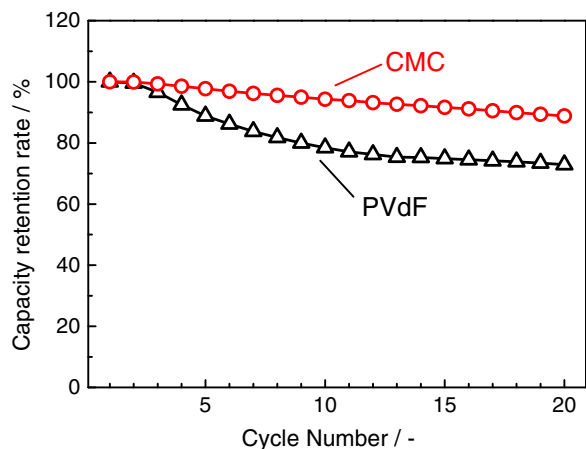


Figure 14. Comparison of capacity retention rate of P2-Na_{2/3}Ni_{1/3}Mn_{2/3}O₂ electrodes with PVdF and CMC binder.

been developed for silicon negative electrode material in Li cells to keep the connection between active materials, carbon additive and current collector.⁹⁹ P2-type Na_{2/3}Ni_{1/3}Mn_{2/3}O₂ is not hygroscopic and does not uptake water as crystal water in the structure.^{85,129} Therefore, no significant damage to the active materials during aqueous slurry process is expected and water-soluble CMC binder can be used for P2-type Na_{2/3}Ni_{1/3}Mn_{2/3}O₂, which differs from O3-type materials. CMC binder electrode exhibited remarkably improved capacity retention compared to that of PVdF electrode in the voltage range of 2.0–4.5 V at rate of 13 mA g⁻¹ as shown in Fig. 14. Binder significantly influences on the electrode performance of not only negative electrode materials but also positive ones in Na batteries. Although stability of positive electrode materials against moisture and water is not often discussed by academic researchers, the stability is essential to use water dispersible/soluble binders for the materials, especially involving large volume change such as P2-type layered oxides.

As described above, most of Na containing layered transition metal oxides evidently react with moisture and water, resulting in H⁺/Na⁺ exchange and/or Na extraction from the structure on the basis of oxidation. Recently, Buchholz and Passerini et al. investigated water sensitivity of layered Na_xNi_{0.22}Co_{0.11}Mn_{0.66}O₂ and found that a hydrated phase, having long interslab distance, is formed at low sodium contents below 0.33 in the composition.¹³⁰ Indeed, our group also observed the phases with long *c* lattice parameter after charge for *x* < 0.4 in Na_xNi_{1/2}Mn_{1/2}O₂.¹³¹ Even a laboratory made attachment of sample holder was used to avoid air exposure, extra peaks attributed to the hydrated phase was observed by ex-situ X-ray diffraction.¹³¹ The Na extracted phases should be highly reactive and promptly entrap water molecules through the tiny interstices of the holder. Ex-situ measurements such as X-ray and neutron diffraction after disassembling cells should be carefully conducted without air exposure otherwise in-situ measurements is required to obtain reliable data.

Operation Potential of Positive Electrodes

In order to achieve high energy density of NIBs, large reversible capacity and low and high potential materials as negative and positive electrode, respectively, are required. In the recent five years, high-potential positive electrode materials have been explored. The capacity and averaged discharge potential of selected materials, oxides and polyanionic compounds, are plotted in Fig. 15a. Specific energy density based on weight of active materials only was estimated by calculation with the assumption of 300 mAh g⁻¹ for hard carbon as a negative electrode material as full cells. Combined with hard carbon, the estimated energy density of NIBs with some of the electrode materials reaches and/or exceeds 300 Wh kg⁻¹ based on the mass of active materials and is now competitive to the graphite/

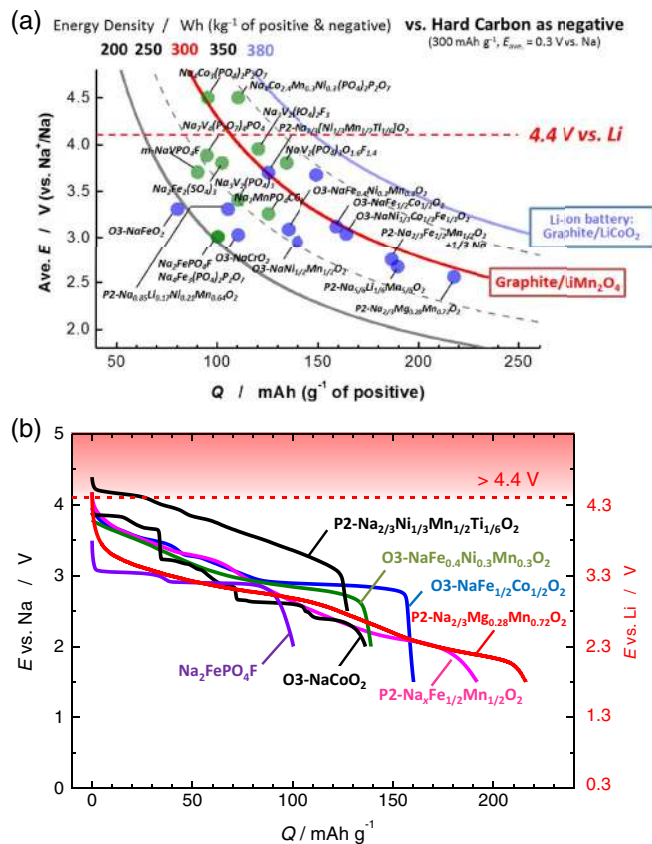


Figure 15. Average voltage (V_{ave}) and energy density (Wh kg^{-1}) versus gravimetric capacity (mAh g^{-1}) for selected positive electrode materials for Na-ion batteries. Energy density was calculated by hypothesizing the hard carbon (reversible capacity of 300 mAh g^{-1} with $V_{ave} = 0.3 \text{ V vs. Na/Na}^+$, see Figure 2b) as negative electrode materials. Reprinted from Ref. 111 with copyright permission from American Chemical Society.

LiMn₂O₄ system. However, available voltage window without electrolyte decomposition at high voltage should be taken into account. Similar electrolyte solutions to those in practical LIBs are used for NIBs; therefore, anodic restriction of voltage to avoid the decomposition of electrolyte solution, leading to gas evolution and swelling of battery, could be identical in both battery system. As generally known among battery engineers, state-of-the-art LIB is charged up to 4.4 V vs. Li/Li⁺. Because the difference in standard electrode potentials between Li/Li⁺ and Na/Na⁺ is about 0.3 V, anodic cutoff voltage in Na cells should be limited to approximately 4.1 V vs. Na/Na⁺.

Figure 15b compares discharge curves of selected layered oxides. In the figure, charging beyond a red dotted line at 4.1 V will suffer from gas evolution in practical full cells of NIB. Our group recently reported that P2-type Na_{2/3}Ni_{1/3}Mn_{1/2}Ti_{1/6}O₂ delivered 127 mAh g⁻¹ of reversible capacity and the average voltage of 3.7 V at first discharge with good capacity retention, originating from successful suppression of the large volume change during charge and discharge.¹²⁸ However, these performances are obtained by charge up to 4.5 V vs. Na/Na⁺. It is thought that the charge up to 4.5 V will lead to gradual decomposition of electrolyte solution, resulting in gas generation and short cycle life. To achieve the practical NIBs with high energy density and satisfactory cyclability, further developments of electrolyte or improving passivation for positive electrode are necessary. Recently, a computational chemistry has been applied to investigate the interphase between electrode/electrolyte with an additive in an atomic scale in the Li system.¹³² New findings from the calculations would be helpful to understand SEI in detail and further improve the electrochemical stability of the electrolytes.

On the basis of research and development of LIBs, NIBs have been rapidly developed since 2010. Simultaneously, we are facing with the drawbacks and issues: unstable SEI on the surface of negative electrode materials, anodic electrolyte decomposition at high charge voltage, degradation by contamination into battery and so on. Optimization of electrolyte solution is still required for NIBs especially for understanding dependency of the NaPF₆ purity and suitable electrolyte additive(s) for NIBs. Contrary to the similar intercalation reaction in NIBs and LIBs, battery chemistry in NIB is totally different from that in LIB as observed for the differences in electrochemical activity of graphite, silicon and AMeO₂ (A = Li and Na, Me = Fe, Cr, Co etc.), and the stability of crystal structure such as P2- and P3-type phase. Material design to exploit the advantages of NIBs consisting without any costly metals is further required to realize practical NIBs.

Conclusions

Recent progress, practical issues, and future perspective of Na-ion batteries are reviewed on the basis of recent literatures and our achievement. Theory, principle, material synthesis, and experimental methods for research and development of Na-ion batteries should be further established and understood with consideration of both similarity and differentia to Li-ion batteries. It is therefore no surprise that research on Na-ion batteries faces the same challenge as Li system, for example, electrolyte decomposition at high voltage and capacity fading upon cycling. However, as to further investigation, simultaneous developments of all materials for Na-ion batteries with those of Li-ion batteries are highly required, that is, electrode active materials, carbon additives, binders, electrolyte salts, solvents, current collectors, and so on. We believe that new finding and understanding in Na-ion chemistry, including materials science and surface chemistry, will synergistically affect acceleration of further developments of electrochemical energy devices, such as Li-ion batteries, Mg batteries, Al batteries, and redox capacitors.

Acknowledgments

The authors acknowledge the students, collaborators, and industrial partners who have contributed to this series of research over the past ten years. This work was partially granted by the Japan Society for the Promotion of Science (JSPS) through the "Funding for NEXT Program", initiated by the Council for Science and Technology Policy (CSTP), by MEXT program "Elements Strategy Initiative to Form Core Research Center" (since 2012), MEXT; Ministry of Education Culture, Sports, Science and Technology, Japan, and by Adaptable and Seamless Technology Transfer Program (A-STEP) through Target-driven R&D from Japan Science and Technology Agency, JST.

References

- J. M. Tarascon, *Nature Chemistry*, **2**, 510 (2010).
- B. Nykvist and M. Nilsson, *Nat Clim Change*, **5**, 329 (2015).
- D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, and E. Levi, *Nature*, **407**, 724 (2000).
- J. Muldoon, C. B. Buecr, and T. Gregory, *Chem. Rev.*, **114**, 11683 (2014).
- N. Jayaprakash, S. K. Das, and L. A. Archer, *Chem. Commun.*, **47**, 12610 (2011).
- M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, and H. Dai, *Nature*, **520**, 324 (2015).
- G. H. Newman and L. P. Klemann, *J. Electrochem. Soc.*, **127**, 2097 (1980).
- J. J. Braconnier, C. Delmas, C. Fouassier, and P. Hagemuller, *Mater. Res. Bull.*, **15**, 1797 (1980).
- L. W. Shacklette, J. E. Toth, and R. L. Elsenbaumer, Conjugated polymer as substrate for the plating of alkali metal in a nonaqueous secondary battery, in, Allied Corp., USA (1985).
- T. Shishikura and M. Takeuchi, *Secondary batteries*, in, Showa Denko K. K. Hitachi, Ltd., Japan (1987).
- N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada, and S. Komaba, *Nat. Mater.*, **11**, 512 (2012).
- R. Berthelot, D. Carlier, and C. Delmas, *Nat. Mater.*, **10**, 74 (2011).
- Y. S. Wang, R. J. Xiao, Y. S. Hu, M. Avdeev, and L. Q. Chen, *Nat. Commun.*, **6** (2015).
- K. W. Nam, S. Kim, S. Lee, M. Salama, I. Shterenberg, Y. Gofer, J. S. Kim, E. Yang, C. S. Park, J. S. Kim, S. S. Lee, W. S. Chang, S. G. Doo, Y. N. Jo, Y. Jung, D. Aurbach, and J. W. Choi, *Nano Lett.*, **15**, 4071 (2015).
- K. Kubota, N. Yabuuchi, H. Yoshida, M. Dahbi, and S. Komaba, *MRS Bull.*, **39**, 416 (2014).
- J. F. Whitacre, A. Tevar, and S. Sharma, *Electrochem. Commun.*, **12**, 463 (2010).
- Y. H. Liao, K. S. Park, P. H. Xiao, G. Henkelman, W. S. Li, and J. B. Goodenough, *Chem. Mater.*, **25**, 1699 (2013).
- E. Lee, S. Sahngong, C. S. Johnson, and Y. Kim, *Electrochim. Acta*, **143**, 272 (2014).
- I. D. Gocheva, M. Nishijima, T. Doi, S. Okada, J. Yamaki, and T. Nishida, *J. Power Sources*, **187**, 247 (2009).
- C. L. Li, C. L. Yin, L. Gu, R. E. Dinnebier, X. K. Mu, P. A. van Aken, and J. Maier, *J. Am. Chem. Soc.*, **135**, 11425 (2013).
- C. L. Li, C. L. Yin, X. K. Mu, and J. Maier, *Chem. Mater.*, **25**, 962 (2013).
- Y. Kawabe, N. Yabuuchi, M. Kajiyama, N. Fukuhara, T. Inamasu, R. Okuyama, I. Nakai, and S. Komaba, *Electrochem. Commun.*, **13**, 1225 (2011).
- Z. L. Jian, L. Zhao, H. L. Pan, Y. S. Hu, H. Li, W. Chen, and L. Q. Chen, *Electrochem. Commun.*, **14**, 86 (2012).
- H. Kim, I. Park, D. H. Seo, S. Lee, S. W. Kim, W. J. Kwon, Y. U. Park, C. S. Kim, S. Jeon, and K. Kang, *J. Am. Chem. Soc.*, **134**, 10369 (2012).
- M. Nose, S. Shiotani, H. Nakayama, K. Nobuhara, S. Nakanishi, and H. Iba, *Electrochem. Commun.*, **34**, 266 (2013).
- P. Moreau, D. Guyomard, J. Gaubicher, and F. Boucher, *Chem. Mater.*, **22**, 4126 (2010).
- S. M. Oh, S. T. Myung, J. Hassoun, B. Scrosati, and Y. K. Sun, *Electrochem. Commun.*, **22**, 149 (2012).
- P. Barpanda, G. Oyama, S.-i. Nishimura, S.-C. Chung, and A. Yamada, *Nat. Commun.*, **5**, 4358 (2014).
- P. Serras, V. Palomares, A. Goni, I. G. de Muro, P. Kubiak, L. Lezama, and T. Rojo, *J. Mater. Chem.*, **22**, 22301 (2012).
- Y. U. Park, D. H. Seo, H. S. Kwon, B. Kim, J. Kim, H. Kim, I. Kim, H. I. Yoo, and K. Kang, *J. Am. Chem. Soc.*, **135**, 13870 (2013).
- J. C. Lu, S. C. Chung, S. Nishimura, and A. Yamada, *Chem. Mater.*, **25**, 4557 (2013).
- Y. H. Lu, L. Wang, J. G. Cheng, and J. B. Goodenough, *Chem. Commun.*, **48**, 6544 (2012).
- H. W. Lee, R. Y. Wang, M. Pasta, S. W. Lee, N. Liu, and Y. Cui, *Nat. Commun.*, **5** (2014).
- L. Wang, J. Song, R. M. Qiao, L. A. Wray, M. A. Hossain, Y. D. Chuang, W. L. Yang, Y. H. Lu, D. Evans, J. J. Lee, S. Vail, X. Zhao, M. Nishijima, S. Kakimoto, and J. B. Goodenough, *J. Am. Chem. Soc.*, **137**, 2548 (2015).
- R. R. Zhao, L. M. Zhu, Y. L. Cao, X. P. Ai, and H. X. Yang, *Electrochem. Commun.*, **21**, 36 (2012).
- W. W. Deng, X. M. Liang, X. Y. Wu, J. F. Qian, Y. L. Cao, X. P. Ai, J. W. Feng, and H. X. Yang, *Sci Rep-Uk*, **3** (2013).
- D. Su, S. Dou, and G. Wang, *Nano Energy*, **12**, 88 (2015).
- V. L. Chevrier and G. Ceder, *J. Electrochem. Soc.*, **158**, A1011 (2011).
- C. Yue, Y. J. Yu, S. B. Sun, X. He, B. B. Chen, W. Lin, B. B. Xu, M. S. Zheng, S. T. Wu, J. Li, J. Y. Kang, and L. W. Lin, *Adv. Funct. Mater.*, **25**, 1386 (2015).
- J. Liu, Y. R. Wen, P. A. van Aken, J. Maier, and Y. Yu, *Nano Lett.*, **14**, 6387 (2014).
- J. F. Qian, Y. Chen, L. Wu, Y. L. Cao, X. P. Ai, and H. X. Yang, *Chem. Commun.*, **48**, 7070 (2012).
- A. Darwiche, C. Marino, M. T. Sougrati, B. Fraisse, L. Stievano, and L. Monconduit, *J. Am. Chem. Soc.*, **135**, 10179 (2013).
- A. Abouimrane, D. Dambournet, K. W. Chapman, P. J. Chupas, W. Weng, and K. Amine, *J. Am. Chem. Soc.*, **134**, 4505 (2012).
- L. D. Ellis, T. D. Hatchard, and M. N. Obrovac, *J. Electrochem. Soc.*, **159**, A1801 (2012).
- S. Komaba, Y. Matsuura, T. Ishikawa, N. Yabuuchi, W. Murata, and S. Kuze, *Electrochem. Commun.*, **21**, 65 (2012).
- Y. Kim, Y. Kim, A. Choi, S. Woo, D. Mok, N. S. Choi, Y. S. Jung, J. H. Ryu, S. M. Oh, and K. T. Lee, *Adv. Mater.*, **26**, 4139 (2014).
- Y. Kim, Y. Kim, Y. Park, Y. N. Jo, Y.-J. Kim, N.-S. Choi, and K. T. Lee, *Chem. Commun.*, **51**, 50 (2015).
- Z. Hu, L. X. Wang, K. Zhang, J. B. Wang, F. Y. Cheng, Z. L. Tao, and J. Chen, *Angew Chem Int Edit*, **53**, 12794 (2014).
- Y. Kim, Y. Park, A. Choi, N. S. Choi, J. Kim, J. Lee, J. H. Ryu, S. M. Oh, and K. T. Lee, *Adv. Mater.*, **25**, 3045 (2013).
- J. F. Qian, X. Y. Wu, Y. L. Cao, X. P. Ai, and H. X. Yang, *Angew Chem Int Edit*, **52**, 4633 (2013).
- N. Yabuuchi, Y. Matsuura, T. Ishikawa, S. Kuze, J. Y. Son, Y. T. Cui, H. Oji, and S. Komaba, *ChemElectrochem*, **1**, 580 (2014).
- A. Abouimrane, W. Weng, H. Eltayeb, Y. J. Cui, J. Niklas, O. Poluektov, and K. Amine, *Energ Environ. Sci.*, **5**, 9632 (2012).
- Y. Park, D. S. Shin, S. H. Woo, N. S. Choi, K. H. Shin, S. M. Oh, K. T. Lee, and S. Y. Hong, *Adv. Mater.*, **24**, 3562 (2012).
- S. Wang, L. Wang, Z. Zhu, Z. Hu, Q. Zhao, and J. Chen, *Angew. Chem. Int. Ed.*, **53**, 5892 (2014).
- M. Moshkovich, Y. Gofer, and D. Aurbach, *J. Electrochem. Soc.*, **148**, E155 (2001).
- M. Wakihara and O. Yamamoto, *Lithium Ion Batteries: Fundamentals and Performance*, WILEY-VCH Verlag GmbH, Weinheim (2008).
- M. M. Doeff, Y. P. Ma, S. J. Visco, and L. C. Dejonghe, *J. Electrochem. Soc.*, **140**, L169 (1993).
- R. C. Asher and S. A. Wilson, *Nature*, **181**, 409 (1958).
- B. Jache and P. Adelhelm, *Angew Chem Int Ed Engl*, **53**, 10169 (2014).
- D. A. Stevens and J. R. Dahn, *J. Electrochem. Soc.*, **147**, 1271 (2000).

61. W. Murata, T. Ozeki, and S. Komaba, in *76th spring meeting of the electrochemical society of Japan*, Kyoto (2009).
62. S. Komaba, W. Murata, and T. Ozeki, in *216th ECS Meeting*, Vienna, Austria (2009).
63. S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, and K. Fujiwara, *Adv. Funct. Mater.*, **21**, 3859 (2011).
64. M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa, and S. Komaba, *Phys. Chem. Chem. Phys.*, **16**, 15007 (2014).
65. X. Xia and J. R. Dahn, *J. Electrochem. Soc.*, **159**, A515 (2012).
66. K. Gotoh, T. Ishikawa, S. Shimadzu, N. Yabuuchi, S. Komaba, K. Takeda, A. Goto, K. Deguchi, S. Ohki, K. Hashi, T. Shimizu, and H. Ishida, *J. Power Sources*, **225**, 137 (2013).
67. W. Luo, J. Schardt, C. Bommier, B. Wang, J. Razink, J. Simonsen, and X. L. Ji, *J. Mater. Chem. A*, **1**, 10662 (2013).
68. A. Ponrouch, A. R. Goni, and M. R. Palacin, *Electrochem. Commun.*, **27**, 85 (2013).
69. J. Zhao, L. W. Zhao, K. Chihara, S. Okada, J. Yamaki, S. Matsumoto, S. Kuze, and K. Nakane, *J. Power Sources*, **244**, 752 (2013).
70. R. S. Babu and M. Pyo, *J. Electrochem. Soc.*, **161**, A1045 (2014).
71. G. Y. Xu, J. P. Han, B. Ding, P. Nie, J. Pan, H. Dou, H. S. Li, and X. G. Zhang, *Green Chem.*, **17**, 1668 (2015).
72. C. Bommier, W. Luo, W. Y. Gao, A. Greaney, S. Q. Ma, and X. Ji, *Carbon*, **76**, 165 (2014).
73. T. Q. Chen, Y. Liu, L. K. Pan, T. Lu, Y. F. Yao, Z. Sun, D. H. C. Chua, and Q. Chen, *J. Mater. Chem. A*, **2**, 4117 (2014).
74. M. Dahbi, T. Nakano, N. Yabuuchi, T. Ishikawa, K. Kubota, M. Fukunishi, S. Shibahara, J. Y. Son, Y. T. Cui, H. Oji, and S. Komaba, *Electrochem. Commun.*, **44**, 66 (2014).
75. A. Fukunaga, T. Nohira, R. Hagiwara, K. Numata, E. Itani, S. Sakai, K. Nitta, and S. Inazawa, *J. Power Sources*, **246**, 387 (2014).
76. K. Gotoh and H. Ishida, *Carbon*, **78**, 633 (2014).
77. K. L. Hong, L. Qie, R. Zeng, Z. Q. Yi, W. Zhang, D. Wang, W. Yin, C. Wu, Q. J. Fan, W. X. Zhang, and Y. H. Huang, *J. Mater. Chem. A*, **2**, 12733 (2014).
78. J. Jin, B.-j. Yu, Z.-q. Shi, C.-y. Wang, and C.-b. Chong, *J. Power Sources*, **272**, 800 (2014).
79. E. M. Lotfabad, J. Ding, K. Cui, A. Kohandehghan, W. P. Kalisvaart, M. Hazelton, and D. Mitlin, *ACS Nano*, **8**, 7115 (2014).
80. E. M. Lotfabad, P. Kalisvaart, A. Kohandehghan, D. Karpuzov, and D. Mitlin, *J. Mater. Chem. A*, **2**, 19685 (2014).
81. V. G. Pol, E. Lee, D. H. Zhou, F. Dogan, J. M. Calderon-Moreno, and C. S. Johnson, *Electrochim. Acta*, **127**, 61 (2014).
82. R. Suresh Babu and M. Pyo, *J. Electrochem. Soc.*, **161**, A1045 (2014).
83. Y. Bai, Z. Wang, C. Wu, R. Xu, F. Wu, Y. C. Liu, H. Li, Y. Li, J. Lu, and K. Amine, *ACS Appl. Mater. Interfaces*, **7**, 5598 (2015).
84. Z. R. X. Guan, H. Liu, B. Xu, X. Hao, Z. X. Wang, and L. Q. Chen, *J. Mater. Chem. A*, **3**, 7849 (2015).
85. F. Legrain, J. Sottmann, K. Kotsis, S. Gorantla, S. Sartori, and S. Manzhos, *J. Phys. Chem. C*, **119**, 13496 (2015).
86. Y. M. Li, S. Y. Xu, X. Y. Wu, J. Z. Yu, Y. S. Wang, Y. S. Hu, H. Li, L. Q. Chen, and X. J. Huang, *J. Mater. Chem. A*, **3**, 71 (2015).
87. W. Luo, C. Bommier, Z. L. Jian, X. Li, R. Carter, S. Vail, Y. H. Lu, J. J. Lee, and X. L. Ji, *ACS Appl. Mater. Interfaces*, **7**, 2626 (2015).
88. K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, *Mater. Res. Bull.*, **15**, 783 (1980).
89. K. Xu, *Chem. Rev.*, **114**, 11503 (2014).
90. R. Alcantara, J. M. J. Mateos, and J. L. Tirado, *J. Electrochem. Soc.*, **149**, A201 (2002).
91. A. Ponrouch, E. Marchante, M. Courty, J. M. Tarascon, and M. R. Palacin, *Energ Environ. Sci.*, **5**, 8572 (2012).
92. A. Bhide, J. Hofmann, A. K. Durr, J. Janek, and P. Adelhelm, *Phys. Chem. Chem. Phys.*, **16**, 1987 (2014).
93. R. Alcantara, P. Lavela, G. F. Ortiz, and J. L. Tirado, *Electrochem. Solid-State Lett.*, **8**, A222 (2005).
94. A. Ponrouch, R. Dedryvere, D. Monti, A. E. Demet, J. M. A. Mba, L. Croguennec, C. Masquelier, P. Johansson, and M. R. Palacin, *Energ Environ. Sci.*, **6**, 2361 (2013).
95. A. Ponrouch, D. Monti, A. Boschini, B. Steen, P. Johansson, and M. R. Palacin, *J. Mater. Chem. A*, **3**, 22 (2015).
96. S. Komaba, T. Ishikawa, N. Yabuuchi, W. Murata, A. Ito, and Y. Ohsawa, *ACS Appl. Mater. Interfaces*, **3**, 4165 (2011).
97. B. Mortemard de Boisse, J. H. Cheng, D. Carlier, M. Guignard, C. J. Pan, S. Bordère, D. Filimonov, C. Drathen, E. Suard, B. J. Hwang, A. Wattiaux, and C. Delmas, *J. Mater. Chem. A*, **3**, 10976 (2015).
98. A. Rudola, D. Aurbach, and P. Balaya, *Electrochem. Commun.*, **46**, 56 (2014).
99. M. N. Obrovac and V. L. Chevrier, *Chem. Rev.*, **114**, 11444 (2014).
100. C. Ding, T. Nohira, K. Kuroda, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, and S. Inazawa, *J. Power Sources*, **238**, 296 (2013).
101. C.-Y. Chen, K. Matsumoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, and S. Inazawa, *J. Power Sources*, **237**, 52 (2013).
102. J. R. Dahn, T. Zheng, Y. H. Liu, and J. S. Xue, *Science*, **270**, 590 (1995).
103. K. M. Colbow, J. R. Dahn, and R. R. Haering, *J. Power Sources*, **26**, 397 (1989).
104. T. Ohzuku and A. Ueda, *Solid State Ionics*, **69**, 201 (1994).
105. E. Ferg, R. J. Gummow, A. Dekock, and M. M. Thackeray, *J. Electrochem. Soc.*, **141**, L147 (1994).
106. P. Senguttuvan, G. Rousse, M. E. A. Y. de Dompablo, H. Vezin, J. M. Tarascon, and M. R. Palacin, *J. Am. Chem. Soc.*, **135**, 3897 (2013).
107. P. Senguttuvan, G. Rousse, V. Seznec, J. M. Tarascon, and M. R. Palacin, *Chem. Mater.*, **23**, 4109 (2011).
108. Y. S. Wang, X. Q. Yu, S. Y. Xu, J. M. Bai, R. J. Xiao, Y. S. Hu, H. Li, X. Q. Yang, L. Q. Chen, and X. J. Huang, *Nat. Commun.*, **4** (2013).
109. Y. Sun, L. Zhao, H. L. Pan, X. Lu, L. Gu, Y. S. Hu, H. Li, M. Armand, Y. Ikuhara, L. Q. Chen, and X. J. Huang, *Nat. Commun.*, **4** (2013).
110. M. J. Aragon, C. Vidal-Abarca, P. Lavela, and J. L. Tirado, *J. Mater. Chem. A*, **1**, 13963 (2013).
111. N. Yabuuchi, K. Kubota, M. Dahbi, and S. Komaba, *Chem. Rev.*, **114**, 11636 (2014).
112. Y. Takahashi, T. Kiyabu, S. Okada, J. Yamaki, and K. Nakane, in *The 45th Battery Symposium in Japan*, p. 3B23 (2004).
113. S. Komaba, T. Itabashi, B. Kaplan, H. Groult, and N. Kumagai, *Electrochem. Commun.*, **5**, 962 (2003).
114. M. Nose, H. Nakayama, K. Nobuhara, H. Yamaguchi, S. Nakanishi, and H. Iba, *J. Power Sources*, **234**, 175 (2013).
115. C. Delmas, C. Fouassier, and P. Hagenmuller, *Physica B & C*, **99**, 81 (1980).
116. N. Yabuuchi, H. Yoshida, and S. Komaba, *Electrochemistry*, **80**, 716 (2012).
117. A. Maazaz, C. Delmas, and P. Hagenmuller, *J. Incl. Phenom.*, **1**, 45 (1983).
118. K. Kubota, I. Ikeuchi, T. Nakayama, C. Takei, N. Yabuuchi, H. Shiiba, M. Nakayama, and S. Komaba, *J. Phys. Chem. C*, **119**, 166 (2015).
119. C. Didier, M. Guignard, C. Denage, O. Szajwaj, S. Ito, I. Saadoune, J. Darriet, and C. Delmas, *Electrochem. Solid-State Lett.*, **14**, A75 (2011).
120. H. Yoshida, N. Yabuuchi, and S. Komaba, *Electrochem. Commun.*, **34**, 60 (2013).
121. P. Vassilaras, A. J. Toumar, and G. Ceder, *Electrochem. Commun.*, **38**, 79 (2014).
122. N. Yabuuchi, M. Yano, H. Yoshida, S. Kuze, and S. Komaba, *J. Electrochem. Soc.*, **160**, A3131 (2013).
123. X. Li, D. Wu, Y. N. Zhou, L. Liu, X. Q. Yang, and G. Ceder, *Electrochem. Commun.*, **49**, 51 (2014).
124. N. A. Hashim, Y. T. Liu, and K. Li, *Chem. Eng. Sci.*, **66**, 1565 (2011).
125. J. Marchand-Brynaert, N. Jongen, and J. L. Dewez, *J Polym Sci Pol Chem*, **35**, 1227 (1997).
126. H. Tanaka, S. Matsumoto, S. Kuze, and T. Yamaguchi, in *82th Spring Meeting of the Electrochemical Society of Japan*, p. 3J29, Yokohama (2015).
127. D. H. Lee, J. Xu, and Y. S. Meng, *Phys. Chem. Chem. Phys.*, **15**, 3304 (2013).
128. H. Yoshida, N. Yabuuchi, K. Kubota, I. Ikeuchi, A. Garsuch, M. Schulz-Dobrick, and S. Komaba, *Chem. Commun.*, **50**, 3677 (2014).
129. Z. H. Lu and J. R. Dahn, *Chem. Mater.*, **13**, 1252 (2001).
130. D. Buchholz, L. G. Chagas, C. Vaalma, L. M. Wu, and S. Passerini, *J. Mater. Chem. A*, **2**, 13415 (2014).
131. S. Komaba, N. Yabuuchi, T. Nakayama, A. Ogata, T. Ishikawa, and I. Nakai, *Inorg. Chem.*, **51**, 6211 (2012).
132. K. Ushirogata, K. Sodeyama, Y. Okuno, and Y. Tateyama, *J. Am. Chem. Soc.*, **135**, 11967 (2013).