Conversion-type Anode Materials for Alkali-Ion Batteries: State of the Art and Possible Research Directions

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ABSTRACT: In this study, the potential of conversion-type anode materials for alkali-ion batteries has been examined and analyzed in terms of the parameters of prime importance for practical alkali-ion systems. Issues like voltage hysteresis, discharge profile, rate stabilities, cyclic stabilities, irreversible capacity loss, and Columbic efficiencies have been specifically addressed and analyzed as the key subjects. Relevant studies on achieving a better performance by addressing one or more of the issues have been carefully selected and outlook has been presented on the basis of this literature. Mechanistic insights into the subject of conversion reactions are discussed in light of the use of recent and advanced techniques like in situ transmission electron microscopy, in operando X-ray diffraction, and X-ray absorption spectroscopy. Three-dimensional plots depicting the performance of different materials, morphologies, and compositions with respect to these parameters are also presented to highlight the systematic of multiparameter dependencies. Inferences are drawn from these plots in the form of a short section at the end, which should be helpful to the readers, especially young researchers. We believe that this study differs from others on the subject in being focused toward addressing the practical limitations and providing possible research directions to achieve the best possible results from conversion-type anode materials.

INTRODUCTION

Conversion materials are being researched in parallel to alloying and intercalation materials as possible ideal anodes for future alkali-ion batteries. The simple conversion electrochemistry of transition-metal oxides (TMOs), sulfides, phosphides, and similar compounds of p-block metalloids shares some interesting and useful electrochemical features with other anode materials. As already well understood, different types of anode electrochemistries that qualify the required norms set for the said application, namely, the operating potential versus Li/Na <2, are categorized as intercalation, alloying, and conversion types. Figure 1 plots all of the set of available anode categories with respect to this defining parameter along X axis and another primary quantitative parameter i.e., capacity, along the Y axis. Although intercalation and alloying materials have received the preferred focus, conversion materials have thus far been left out for any type of practical industrial applications owing to certain specific shortcomings.

This category of materials lacks seriously in terms of cyclic stability, flat charge–discharge behavior, round-trip energy efficiency, and desirable operating voltages with respect to Li and Na. In this article, we analyze various conversion chemistries with regard to these parameters and attempt to provide an outlook based on the work that has addressed some of these specific issues.

We first compare the performance of these material types with the other anode types that have shown commercial promise i.e., alloying and intercalation. Table 1 portrays the comparison in the best possible way by considering the performance parameters of real importance for both Li and Na cases. Among conversion materials, the operating potentials show considerable variation, which is mostly guided by the transition metal (TM) and counteranion. The operating potential is also seen to considerably differ for the Na and Li cases. Figure 2 depicts these observations in a more systematic
way. Despite these unresolved issues on the practical front in the present form, a lot of high-impact papers are still being constantly published pertaining to their use as anodes in Li- and Na-ion batteries in view of the specific positive aspects mentioned above, and efforts are on to make them industrially attractive and viable with a variety of strategies.

Mechanistic Insights into the Conversion Mechanism. For the broad class of conversion materials, the conversion redox reactions ultimately result in the formation of the metallic phase, as depicted in Scheme 1. The presence of metallic and alkali oxide phases has been probed by different characterization techniques. Indeed, in situ X-ray diffraction and X-ray absorption spectroscopy (XAS) have revealed interesting stages of lithiation and sodiation during the course of the overall conversion. The formation of multiple phases at different stages of lithiation and sodiation has been tracked by X-ray absorption spectroscopy (XAS) and other in operando techniques. In situ imaging techniques have further enhanced the level of our understanding and have revealed that the conversion reactions are associated with the breakdown of long-range crystalline order. Thus, lithiation and sodiation invariably involve breakdown of single-crystalline parent material to polycrystalline metallic particles dispersed in amorphous alkali oxide matrix. Electron energy loss spectroscopy analysis of some conversion materials has revealed that the back conversions are incomplete and thus could be mainly responsible for inconsistent cycling capacity.

Problems Associated with Conversion Materials. The major issues that need to be addressed if the conversion materials are to invoke a potential commercialization claim are voltage hysteresis, long sloping regions in discharge profile (voltage-dependent redox reaction), inconsistent cycling stability, rate instability, and higher first-cycle capacity loss. Figures 3 and 4 portray some of these issues based on some relevant literature reports. Before going into the full analysis and possible ways out, we present a brief discussion about each of these.

Voltage Hysteresis. A major factor that hinders the practical application of conversion anodes is the low round-trip energy efficiency due to the voltage hysteresis between the charging and discharging profiles, i.e., charging occurs at a higher voltage compared to discharging, indicating that the amount of energy retrieved back is less than the energy stored in each cycle. Figure 3a presents the voltage–capacity profile showing the voltage hysteresis in conversion anodes. Different reasons have been proposed for the drastic difference in the charging and discharging potentials. Although there has been a large volume of research on this subject, the origin of the voltage hysteresis in conversion anodes is still not clearly understood. The first and most obvious reason for the existence of voltage hysteresis lies in the conversion process itself. The lithiation-mediated conversion to metallic phase and amorphous alkali oxides does possess a lower activation barrier than the back conversion to single-phase parent material from these two evenly distributed phases. Thus, electronegativities of the anions holding Li play a critical role. Indeed, some preliminary studies by Oumellal et al. have revealed that oxides show higher hysteresis and hydrides show the least. The voltage hysteresis has other contributions; notable among them is the contribution from electronic conductivity of the material.

Table 1. Comparison of Voltage Hysteresis, Cyclic Stability, and High Current Performance of Different Types of Negative Electrodes for Na- and Li-Ion Batteries

| anode type       | composition | voltage hysteresis (V) | Li   | Na | % capacity retention at 10 times higher current density (Li) | Na | cyclic stability (%) retention after 100 cycles (Li) | Na | first cycle Coulombic efficiency (%) |
|------------------|-------------|------------------------|------|----|-------------------------------------------------------------|----|---------------------------------------------------------|----|-------------------------------------|
| alloying type    | Si          | 0.2                    | 85   | 92 | 100                                                         | 91 | 69                                                      | 81.7|                                     |
|                  | Sn          | 0.2                    | 97   | 51 | 100                                                         | 91 | 69                                                      | 81.2|                                     |
| conversion materials | Fe2O3      | 0.8                    | 56   | 62.5 | 77                                                          | 60 | 69                                                      | 81.2|                                     |
|                  | FeS2        | 0.6                    | 65   | 90 | 73                                                          | 91 | 63.5                                                    | 61.6|                                     |
|                  | FeP         | 0.6                    | 56   | 48 | 67                                                          | 71 | 74                                                      | 66 |                                     |
| intercalation type | LTO         | <0.1                   | 87   | 43 | ~100                                                        | 83 | 95                                                      | 50 |                                     |

Figure 2. Comparison of operating potentials of Li- and Na-ion batteries for different conversion material compositions.

Scheme 1. Li/Na-Storage Mechanism in Conversion-Type Anodes

Conversion reactions of TM, oxides Sulfides, and Phosphides with Li/Na.

\[
\{M_xR_y + (y \cdot n) A -> x M + y A_nR\}
\]

Where, A = Li, Na and M is transition metal, R is O, S, Se, P, H.
the lithiation-mediated phase breakdown generates non-conducting alkali compounds, the $iR$ drop related to hysteresis will also be invariably present. In addition to this, the voltage hysteresis contributions from the solid electrolyte interphase (SEI) layer and the surface stresses also contribute significantly.

However, the lack of a more detailed research in this context has limited our understanding of the exact origin of the voltage hysteresis in conversion anodes. Further, the relative contributions from the different underlying factors also need to be ascertained through a more fundamental research.

**Inconsistent Cycling Stability.** Another important issue that has been associated with conversion materials is the inconsistent cycling performance. Figure 3b,c shows two observations in this respect from the relevant literature. Both the huge capacity fading and the constant increase in capacity have been observed for some initial cycles. Although the exact mechanism behind the capacity fading is unexplored in any significant details, the phase conversion followed by aggregation of the metallic domains may be cited as the underlying reason for the long-term cyclic instability.

The gradual increase in the size of metallic particles upon cycling may decrease the kinetic availability of the material for Li storage. This can consequently lead to massive capacity fading with cycling. Although some theoretical studies have been directed toward understanding this, there is a lack of enough experimental research in this respect. These theoretical studies have hinted that the small irreversibility inherently associated with the conversion process at individual steps ultimately leads to cyclic failures. The first-principle calculations on Co$_3$O$_4$ and NiO reveal that the reaction proceeds by insertion mechanism until the incorporation of three Li per formula unit and can be cycled completely if the Li insertion is restricted to this value. But the inclusion of further Li leads to actual conversion and hence capacity fading upon cycling can be related to this basic conversion process. Additionally, the reversible growth of a polymeric gel-like film that grows on the surface of electrolyte decomposition on progressively crumbled anode particles can further add to the problem.

As far as the capacity increase upon cycling for some conversion oxides, sulfides, and selenides is concerned, the lithiation-based reactivation can be cited as a possible reason. Again, no conclusive work exists in the literature that can be cited as the exact reason behind these observations. However, the findings have been partly attributed to a slow release of Li$^+$ that gets trapped in amorphous Li$_2$R (R = O, S, P, H, Se) during the first conversion. Incomplete first conversion due to the formation of isolated islands in amorphous matrix can participate in subsequent cycles by generation of new ionic and electronic connections therein.

To address the capacity fade because of the formation of larger metallic domains that in turn make the material kinetically unavailable for the rest of cycles, prior addition of excess metallic grains can help solve the issues. The extra metallic sites can act as fresh reaction sites during the charging and can compensate for the unavailable metal for the rest of the reaction. However, the lack of proper understanding in this respect has hindered the progress of research for resolving the issue.

**Sloping Regions in Charge−Discharge Profile.** One of the major hurdles for the conversion materials is the sloping region in the charge−discharge profiles. The sloping charge−discharge voltage profiles in electrochemical terms imply that the charge storage and delivery occur over a range of potentials.
and not at one fixed voltage, but the industrial demands are otherwise. For commercial applications, a material with flat or nearly flat voltage plateau is sought so as to have less voltage fluctuations during the working of the full cell. Sloping regions owe their origin to a number of factors, including incomplete initial reduction, reaction kinetics, the formation of various metastable phases during the course of discharge, and ion diffusion within the material.\textsuperscript{40} For example, the sloping region in the discharge profile of Mn\textsubscript{3}O\textsubscript{4} owes its origin to slow diffusion of Li in the intermediate LiMnO\textsubscript{3} phase compared to fast movement in the channels of Mn\textsubscript{3}O\textsubscript{4}.\textsuperscript{40,41} The entire sloping discharge profile in the ternary spinel oxides arises due to the progressive movement of constituent ions while the spinel structure converts to rock-salt type.\textsuperscript{42,43} In the case of sulfides (representative: FeS\textsubscript{2}), the sloping regions are attributed to the conversion into various metastable Li phases along the reaction coordinate, whereas the plateau regions owe their origin to the initial intercalation that proceeds before the complete conversion.\textsuperscript{42} This issue is the least talked about in the literature, but counts as the major drawback for these materials not being considered for practical applications. It needs to be addressed so as to bring the voltage profile to the plateau form or nearly plateau regime. Partial conversion can be an option, but in that case, full benefits of conversion reaction are nonachievable. Further insights are needed into the mechanism of conversion in terms of identification of various metastable states, different doping strategies that can enhance the kinetic diffusion within the material, catalyst supports, and conductive supports as viable alternatives.

Different conversion materials have different contributions to the total capacity. Additionally, the same conversion material in different morphologies and compositions has been seen to display different contributions to the total capacity. Figure 3d lists various conversion materials with varying contributions from the sloping region and plateau regions.

**Columbic Efficiency.** The very low Columbic efficiencies (even less than 75\%) and higher first cycle losses have questioned their industrialization claims since their inception.\textsuperscript{1} Figure 3e shows the huge capacity loss observed in the case of Fe\textsubscript{2}O\textsubscript{3}. Various underlying phenomena can be associated with these adversities, three of which need a mention here. They are: (1) irreversible electrolyte decomposition, (2) incomplete back conversions, and (3) the back conversion to the phases that can permit less Li/Na uptake than the original one.\textsuperscript{44} In some cases, the Columbic efficiency is remarkably improved after the few initial cycles, but in some cases, the conditions can become worse if the polymeric coating of SEI layer breaks.\textsuperscript{36,45} Again, enough studies have not been carried out to look for the pedigrees behind the issue, which need to be addressed. The kinetic path of the back conversion reactions needs to be tracked to devise suitable strategies that can catalyze smooth and desired conversions. The future of conversion material research shall be more focused on fundamental studies like...
understanding their failure rather than devising new conversion materials.

**Rate Instabilities.** Conversion materials, in general, are associated with lower rate performance in comparison to the intercalation and alloying materials (Figure 3f). The massive reorganizations and the gradual movements of ions have an impact on the overall kinetics of conversion reactions apart from the diffusion limitations posed by the electrolyte. In addition to the sluggish ion movements in the material, the lower electronic conductivity associated with these also imposes kinetic limitations and thus influences power delivery. Thus, two approaches that can be adopted to achieve the gain in terms of power density are either to increase the diffusion coefficient of alkali ion in the material or to reduce the diffusion path length. No conclusive work exists, which could explain the rate instabilities in the materials. However, on the basis of the existing understanding, a few strategies can be suggested. The diffusion of ions can be enhanced by doping of foreign atoms in the material, whereas the diffusion path lengths can be reduced by fabricating nanomaterials.

**Other Issues.** Although a variety of conversion materials have been studied with enhanced electrochemical performance, there are other challenges to be addressed for commercialization. These include earth abundance, processing cost, supply chain, and environmental friendliness. Here, we provide a brief insight into the challenges for commercialization of conversion anodes other than the need for enhancement in their electrochemical performance. Earth abundance of the elements of interest and their regional distribution over earth are the key factors that are highly influential for cost considerations. Transition-metal oxides, such as iron oxide, manganese oxide, etc., are earth-abundant, need minimum processing cost, and show good electrochemical performance. However, their lower electrical conductivity may restrict their use in high-power devices. With conductivity management with dopants or additives, these elements may stand a good chance for possible commercialization. Although chalcogenide- and phosphide-based materials have better capacity and electrical conductivity compared to oxides, their complex synthesis protocols, toxicity, high reactivity under ambient conditions, and high processing cost may limit their commercialization at the industrial level. Further remarks on commercialization aspects are out of the scope of this article and beyond the expertise of the authors.

**Synopsis of Relevant Literature.** Figure 4 surveys the most researched conversion materials with different reported morphologies and architectures in light of the voltage hysteresis, discharge profile, and irreversible capacity loss. These data invite some interesting analyses and potential conclusions with regard to the issues associated with conversion materials. The voltage hysteresis plot of relevant conversion materials is shown in Figure 4a. Among the various conversion types, phosphides have been seen to render the lowest voltage hysteresis. The voltage hysteresis values in the case of the reported CoP nanoarrays and phosphorus-rich CuP2 drop down to ∼0.4 V, which lies close to the Li hysteresis in successful alloying materials. Oxides, on the other hand, are associated with very high voltage hysteresis. The voltage hysteresis is inherent to a material, and synthetic tuning like size and morphology engineering has only a small effect. However, making composites with carbon may help reduce the iR hysteresis.

Higher plateau capacity contributions have been seen from oxides like Fe2O3 and Co3O4 in comparison to Mn3O4 (Figure 4b). Again, phosphides have rendered higher plateau capacity than sulfides. Phosphorus-rich CuP2 and high-temperature-treated NiP2 have delivered high proportion of their capacity, 77 and 75, respectively, at a constant voltage, i.e., major contribution emanating from the plateau region.

Phosphides and sulfides of transition metals have performed better as far as irreversible capacity loss is concerned (Figure 4c). However, upon forming composites with carbon, the irreversible capacity losses have been seen to increase considerably. Thus, optimization of the carbon percentages along with suitable choice of conversion material is a must to have minimum losses.

**Brief Review of the Research on Improving the Performance of Conversion Anodes.** Particle size has a huge impact on the overall electrochemical performance. Some comparative studies on the effect of particle size have revealed a better performance of nanosized particles than micron-sized particles. This better performance is due to shortening of insertion path length that Li has to traverse. Tarascon and co-workers in one of their earlier works had studied the effect of particle size on the insertion of Li ion into α-Fe2O3. Their finding revealed that nanosized Fe2O3 renders 3 times better performance in terms of specific capacity than the micron-sized particles. Xie and co-workers have studied the effect of the diameter of Fe2O3 nanorods on the overall performance. Their measurements revealed a capacity increase from 450 to 700 mAh g−1 when the particle diameter changed from 60−90 to 2−16 nm.

It is useful to point out that the voltage hysteresis and the sloping profiles have been seen to be associated with inherent materials properties and that the control over particle size alone does not address these issues. But positive effects like capacity enhancement and cyclic stability warrant the studies toward optimization of particle size because the change in size in itself is associated with a variety of other challenging issues like extensive electrode decomposition through SEI layer formation, larger volume changes, loss of intrinsic conductivity, and low volumetric capacity. The nanosize can also have a considerable influence on increasing the rate and stability of conversion materials. The rate improvement may mainly be effected by decreasing the diffusion paths and hence making the material accessible at higher mass transfer rates. On the other hand, the stability improvement in the nanosize regime may be related to complete conversion.

The above findings reveal that the particle size impacts the overall performance and needs to be researched for the threshold particle size for the optimal performance.

**Morphological Control.** The effects of morphology on the capacity have already been well studied in the literature. Utilization of the bulk of the material upon nanostructuring leads to considerable capacity enhancements. Ultraslim nanoparticles, nanoneedles, nanorods, nanospindles, nanosheets, and other nanoscale architectures have resulted in the enhancement of capacity by the complete utilization of material, harnessing the benefits associated with the nano-morphologies, in general.

Other issues like cyclic stability and rate stability have also been addressed by employing suitable morphologies. The suitably exposed facets mediate a faster Li/Na transport, thereby minimizing the effects associated with sluggish kinetics. Improvements in the overall discharge profile, rate stability, cyclic stability, and even voltage hysteresis have indeed been observed. The (001) facets of Fe2O3 nanosheets have been seen
to mediate faster Li diffusion than the (010) facets of Fe$_2$O$_3$ nanorods owing to higher packing density of Fe$^{3+}$ and O$^{2-}$ along this facet. The enhancement in the rate has mostly been attributed to a higher diffusion coefficient for Li along this facet compared to the other. Similarly, studies on the electrochemical performance of different morphologies of Co$_3$O$_4$ have revealed that the capacity and cyclic stability of nanoflowers were higher compared to those of nanodisks and nanocubes. This result was attributed to better diffusion paths in the former. The control on pore size and wall thickness in some cases has been seen to boost the rate performance. The study of Li storage in the mesoporous Mn$_2$O$_3$ has revealed that although both the pore size and wall thickness have a profound effect on the overall rate performance, the effect of pore size variations is more significant. Wall thickness increase from 5 to 8 nm was seen to bring the rate performance down considerably. The effect of pore size distribution was more prominent. Larger pore diameters (intermediate and higher mesoporous range; 10−30 nm) and the higher proportions of even smaller mesopores (<10 nm) were seen to increase the rate performance considerably.

Our group has demonstrated that Fe-based MOFs can be used to generate porous nanostructures of Fe$_2$O$_3$. Another phase of iron oxide, Fe$_3$O$_4$, is considered to be promising due to its better cyclic stability and high current performance, although the theoretical capacity 928 mAh g$^{-1}$ is lower. In another report from our group, magnetically separated Fe$_3$O$_4$ from red mud was used as an anode material in Li-ion battery and showed 61% retention after 2000 cycles in a full-cell assembly with LiMn$_2$O$_4$ as cathode.

Several studies on the morphology tuning for performance enhancement have been mostly restricted to well-known shapes and morphologies yielding only some broader picture lacking deeper insights. This situation invites the use of interesting new experimental strategies to specifically address multiple parametric issues simultaneously.

**Composition Control.** Composition has a marked influence on the overall performance of material. Although the oxides have been more robust and stable, they have been found to be lacking in terms of voltage hysteresis. On the other hand, phosphides and hydrides have shown a lower voltage hysteresis, but are seen to be lacking in terms of stability.

Different transition-metal compounds with different anion species with formula M$_x$X$_y$, where X = F, O, S, P, and H, have been shown to exhibit Li/Na insertion by reversible conversion reaction with a theoretical capacity that is a factor of three higher than that of commercial graphite. Among different conversion anodes, transition-metal oxides are the most explored, which include both binary and ternary oxides of 3d transition metals, such as Cr, Mn, Fe, Co, Ni, and Cu. Various phases of different binary oxides of 3d transition metals, including Cr$_2$, Mn$_2$, Fe$_2$, Co$_2$, and Ni$_2$, and 4d transition metals, including Nb and Mo, have been studied for their suitability as negative electrode in Li-ion battery. Similarly, transition-metal oxides store Na-ion through conversion reaction and are considered to be the potential choices of anode materials for Na-ion battery as well.

Among different oxides studied, iron oxide (Fe$_2$O$_3$) is one of the well-studied systems because of its many advantages, including high capacity (1011 mAh g$^{-1}$), earth abundance, and stability. Hence, there are enormous efforts to improve its performance by engineering the morphology, size, precursors, and synthesis protocols. Oxide systems with more than one electrochemically active transition metal with formula AB$_2$O$_4$ have also been studied as hosts for Li/Na-ion batteries. During lithiation, the metal ions are reduced into individual metal nanoparticles in the Li$_2$O matrix. However, during delithiation, metal nanoparticles are converted into corresponding oxides rather than mixed transition-metal oxide. Similar to binary oxides, ternary transition-metal oxides also exhibit low electronic conductivity and cyclic stability. In the case of binary transition-metal oxides, the conversion from spinel to cubic phases has been observed. However, the back conversion has been seen to be sometimes restricted because of the lesser tendency of one of the constituent ions to switch the oxidation states.

In addition to the oxides, other transition-metal chalcogenide compounds (sulfides and selenides), phosphides, hydrides, and ternary chalcogenides have also attracted much attention as anodes in Li- and Na-ion batteries. During discharge, Li/Na reacts with metal chalcogenides to form metal nanoparticles in the sulfide matrix, resulting in high theoretical capacity (>800 mAh g$^{-1}$). Compared to oxides, sulfides possess better electrical conductivity. Dissolution of the discharge product, however, leads to low Coulombic efficiency and cycle life. Although there has been a considerable progress along this direction, achieving high practical capacity and cycle life still needs further improvement. This can be achieved through tuning the size and morphology of the compound, protecting the material to avoid a direct contact with the electrolyte so as to avoid dissolution of polysulfides, and tuning the electrolyte. Transition-metal phosphides can also store Li or Na ion through conversion reactions, which yield Li$_2$P/Na$_2$P and metal nanoparticles as discharge products. Phosphides of transition metals including Mn, Fe, Co, Ni, and Cu have been studied for Li/Na-storage properties. Recently, ternary compounds with more than one anion species have also shown promise as anode materials for alkali-ion batteries. This includes MS$_2$Se$_2$ and MP$_2$S$_2$. The reaction mechanism involves the reaction of both anions with Li/Na, which leads to higher theoretical capacity.

**Composite with Carbon.** Composites of conversion anodes with polymers and carbon materials have been shown to enhance the electrochemical performance of the active component. Carbon-based composites seem to be more promising as they possess high electrical conductivity, high surface area, and good mechanical strength. In addition to improving the high current performance by reducing the electronic resistance, the carbon support absorbs the strain due to the volume expansion in the electrode which renders better cyclic stability. Different carbon forms have been employed to make composites with the active material of the electrode. This includes carbon nanostructures such as carbon nanotubes (both multiwalled and single-walled), carbon nanofibers, graphene, carbon nanohorns, etc. This is generally achieved by adding functionalized carbon nanostructures along with the metal precursor during synthesis. A thin layer of conductive carbon-coated nanoparticle with core−shell structure has also shown to improve the electrochemical performance. Such coating protects the electrode from direct contact with the electrolyte and avoids side reactions, facilitating stable SEI formation. This can be obtained by hydrothermal or solvothermal treatment of the electrode material or metal with carbonaceous materials, such as glucose, sucrose, and polymers, followed by high-temperature annealing in inert atmosphere. Although this strategy has been shown to enhance the stability and high current performance, the main
disadvantage of this method is the formation mixed-phase/metallic form along with oxide or sulfide due to high-temperature treatment in the argon atmosphere. Chemical vapor deposition is another method to obtain thin carbon coating on the electrode surface.92 Instead of adding the carbon source externally, direct use of metal precursor containing carbonaceous molecules has been shown to be another promising strategy to develop carbon composite of metal oxide or sulfide nanostructures. This includes metal−organic frameworks, metal complexes, and organic salts.93 Heteroatom doping in the carbon matrix can be achieved by adding an external source or carbonaceous compounds containing heteroatoms.94

Although coating of amorphous carbon layer protects the electrode material from degradation due to volume expansion, its poor electrical conductivity limits the high current performance of the composite. This can be compensated by the addition of carbon forms with high electrical conductivity, such as CNT and graphene. On the other hand, the addition of CNT's alone fails to stabilize the electrode material unless it is protected properly. Hence, making composites of metal oxides (MOs)/metal sulfides (MSs) with more than one carbon matrix can overcome the limitations of using a single carbon matrix.95

Distribution of electrode materials on high-surface-area conducting carbon matrix shows improved performance. Increasing the amount of carbon in the composite reduces the total capacity if the specific capacity of the carbon is less. Xu and co-workers have shown96 that the presence of conducting graphene support promotes core−shell conversion in the CoS2/graphene composite instead of side-to-side conversion observed in bare single-crystalline CoS2. Core−shell conversion is benign for the overall lithiation and delithiation process. Figure 5 depicts the stable conversion process in CoS2/graphene composite in comparison to the bare CoS2 conversion. Additionally, the high surface area of the composite reduces the volumetric capacity and increases the irreversible capacity loss in the first cycle because of the SEI formation. Hence, optimizing the form and amount of carbon content in the composite is the most challenging task to achieve the best performance of the electrode material.

**CONCLUSIONS**

In this study, we have evaluated the conversion materials in terms of different key parameters that are of interest in the context of their performance as technologically viable anode materials for alkali-ion batteries. We recognize that apart from general limitations like volume expansion and irreversible capacity loss, the conversion anodes need to perform well in crossing over various other important hurdles like larger voltage hysteresis, low cyclic stability, low rate performance, and lower Columbic efficiency, if they are to receive any industrial attention. We have presented the best of the lot among the state-of-the-art materials and proposed some possible solutions for realizing their enhanced performance. A multipronged approach, based on the available literature and new findings, is required to address these diverse issues.

In light of previous literature and the new insights obtained from in situ techniques, we present below some thoughts on...
the research directions that could fuel constructive future research on the conversion materials.

1. The research is still open toward understanding issues like voltage hysteresis, inconsistent cyclic performance, and origin of sloping regions in the discharge profiles (voltage-dependent conversion) as these issues have not been properly understood as yet. The kinetics of the conversion processes, in particular, needs a specific attention in this respect. The multistep kinetics of conversion reaction needs to be fully explored to locate the reaction intermediates and various metastable states. Use of techniques such as in situ solid-state NMR, in situ XAS, in situ transmission electron microscopy electron tomography, atomic force microscopy, and other dynamic characterization approaches may be central for battery research in the next decade as far as conversion materials are concerned.

2. The issue of irreversible capacity loss in the conversion materials in full-cell assembly can aggravate into serious failures. Thus, a variety of prefabrication strategies may be required to undo the associated problems, although their commercial viability may have to be concurrently established. Some of these include prelithiation/sodiation, short circuit, adding stabilized lithium nanoparticles, and use of different electrolyte additives. However, none of these has thus far solved the issue uniquely and completely. Thus, synthetic and engineering strategies that account for these issues in advance shall be the main component of future research on conversion types.

3. At the material level, novel synthesis, fabrication, and postsynthesis processing strategies can be of real value in terms of directly addressing the issues, but have surprisingly been less explored in the present context. Architectural control through the use of patterned electrodes and the use of thin-film deposition techniques to construct heterostructures through techniques like pulsed laser deposition, atomic layer deposition, and other deposition methods may lead to the resolution of some specific issues related to the conversion-type materials.

4. Certain facets of oxides like Fe$_2$O$_3$ and Co$_3$O$_4$ have been seen to promote better diffusion of Li and Na than others. Thus, exposure of suitable facets is important as far as the kinetic stability (rate performance) is concerned. So far, these findings have been taken rather less seriously and attempts toward targeted synthesis of the morphologies that can have suitably exposed facets are needed to be intensified. Additionally, there is need for theoretical calculations (predictive modeling) for the recognition of specific phases that can kinetically promote faster diffusion.

5. The diffusion of Li/Na is a very important factor for better power delivery. It has been observed that elemental or defect doping could enhance the diffusion coefficient of Li/Na within oxides. Thus, novel valence-controlled doping strategies should be adopted so as to have enough defects in the materials, which in turn could mediate better diffusion of alkali ions within the material. The proper choice of conversion materials, with optimized size and morphology, and their composites with optimized amounts of specific carbon forms can help achieve the best for this class of materials.

6. The use of micro- and nanopatterned electrodes and the direct growth of aligned one-dimensional structures that has been tried in the case of alloying materials may fit the bill for engineering conversion-type anodes as well. The benefits of nanostructuring with reduced diffusion paths, better material utilization, better accommodation of volume expansion, and better material connectivity with the substrate can be achieved by employing strategies such as photolithography, patterning, and laser writing techniques.

7. Self-discharge and memory effects in the Li/Na-ion batteries are less known and have been neglected. However, very recent findings have revealed the existence of memory-type effects in cathode materials, i.e., LiFePO$_4$. Similarly, self-discharge has been observed in some Li$_x$Mn$_{2−x}$O$_4$/C Li-ion batteries. High temperature and thermal history of battery have also been reported to mediate the self-discharge in the LiCoO$_2$ cathode. Thus, in full-cell configurations for applications other than mobile electronics, where the battery can get exposed to higher thermal conditions, the occurrence of these additional issues cannot be overlooked. Memory effects and self-discharges in anode materials have so far not been reported in their half-cell configurations, to the best our knowledge. However, in full-cell configurations involving conversion materials, these issues have to be addressed, especially in the context of potential commercialization.

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**Notes**

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**REFERENCES**

(1) Cabana, J.; Monconduit, L.; Larcher, D.; Palacín, M. R. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting through Conversion Reactions. *Adv. Mater.*, 2010, 22, E170–E192.
(2) Klein, F.; Jache, B.; Bhide, A.; Adelhelm, P. Conversion Reactions for Sodium-Ion Batteries. *Phys. Chem. Chem. Phys.*, 2013, 15, 15876–15887.
(3) Kang, H.; Liu, Y.; Cao, K.; Zhao, Y.; Jiao, L.; Wang, Y.; Yuan, H. Update on Anode Materials for Na-Ion Batteries. *J. Mater. Chem. A*, 2015, 3, 17899–17913.
(4) Aravindan, V.; Lee, Y. S.; Madhavi, S. Best Practices for Mitigating Irreversible Capacity Loss of Negative Electrodes in Li-Ion Batteries. *Adv. Energy Mater.*, 2017, 7, No. 1602607.
(23) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. J. Am. Chem. Soc. 2013, 1167.
(24) Li, L.; Jacobs, R.; Gao, P.; Gan, L.; Wang, F.; Morgan, D.; Jin, S. Origins of Large Voltage Hysteresis in High-Energy-Density Metal Fluoride Lithium-Ion Battery Conversion Electrodes. J. Am. Chem. Soc. 2016, 138, 2838–2848.
(25) Ye, J.; Zhao, D.; Hao, Q.; Xu, C. Facile Fabrication of Hierarchical Manganese-Cobalt Mixed Oxide Microspheres as High-Performance Anode Material for Lithium Storage. Electrochem. Acta 2016, 222, 1402–1409.
(26) Bhardwaj, M.; Suryawanshi, A.; Fernandes, R.; Tonda, S.; Banerjee, A.; Kothari, D.; Ogale, S. CuCo2O4 nanowall Morphology as Li-Ion Battery Anode: Enhancing Electrochemical Performance through Stoichiometry Control. Mater. Res. Bull. 2017, 90, 303–310.
(27) Puthussery, D.; Aravindan, V.; Madhavi, S.; Ogale, S. 3D Interconnected Porous Graphene Sheets Loaded with Cobalt Oxide Nanoparticles for Lithium-Ion Battery Anodes. Energy Technol. 2016, 4, 816–822.
(28) Hong, J.-E.; Oh, R.-G.; Ryu, K.-S. Li4Ti3O12/Co3O4 Composite for Improved Performance in Lithium-Ion Batteries. J. Electrochem. Soc. 2015, 162, A1978–A1983.
(29) Kim, H.; Kim, H.; Kim, J.; Yoon, G.; Lim, K.; Yoon, W.-S.; Kang, K. Understanding Origin of Voltage Hysteresis in Conversion Reaction for Na Rechargeable Batteries: The Case of Cobalt Oxides. Adv. Funct. Mater. 2016, 26, 5042–5050.
(30) Oumellal, Y.; Rougier, A.; Nazri, G. A.; Tarascon, J. M.; Aymard, L. Metal Hydrides for Lithium-Ion Batteries. Nat. Mater. 2008, 7, 916–921.
(31) Lu, B.; Song, Y.; Zhang, Q.; Pan, J.; Cheng, Y.-T.; Zhang, J. Voltage Hysteresis of Lithium Ion Batteries Caused by Mechanical Stress. Phys. Chem. Chem. Phys. 2016, 18, 4721–4727.
(32) Kitaura, H.; Takahashi, K.; Mizuno, F.; Hayashi, A.; Tadana, K.; Tatsumisago, M. Mechanochemical Synthesis of α-Fe2O3 Nanoparticles and Their Application to All-Solid-State Lithium Batteries. J. Power Sources 2008, 183, 418–421.
(33) Yao, Z.; Kim, S.; Aykol, M.; Li, Q.; Wu, J.; He, J.; Woltverton, C. Revealing the Conversion Mechanism of Transition Metal Oxide Electrodes during Lithiation from First-Principles. Chem. Mater. 2017, 29, 9011–9021.
(34) Zhao, B.; Ran, R.; Liu, M.; Shao, Z. A Comprehensive Review of Li4Ti3O12-Based Electrodes for Lithium-Ion Batteries: The Latest Advancements and Future Perspectives. Mater. Sci. Eng., R 2015, 98, 1–71.
(35) Xiao, Y.; Lee, S. H.; Sun, Y.-K. The Application of Metal Sulfides in Sodium Ion Batteries. Adv. Energy Mater. 2017, 7, No. 1601329.
(36) Shaju, K. M.; Jiao, F.; De, Y.; Li, Q.; Li, L.; Tanaka, M.; Hiyama, S.; Fujita, T.; Maiti, S.; Li, Y.; Wang, Z. A Novel Three-Dimensional Graphene Encapsulated with Hollow FeP@Carbon Nanocomposite as High-Performance Anode Material for Lithium-Ion Batteries. ACS Nano 2017, 11, 11602–11616.
(37) Prakash, A. S.; Manikandam, P.; Ramesha, K.; Sathiya, M.; Tarascon, J. M.; Shukla, A. K. Solution-Combustion Synthesized Nanocrystalline Li4Ti5O12 as High-Rate Performance Li-Ion Battery Anode. Chem. Mater. 2010, 22, 2857–2863.
(38) Wang, X.; Chen, K.; Wang, G.; Liu, X.; Wang, H. Rational Design of Three-Dimensional Graphene Encapsulated with Hollow FeP@Carbon Nanocomposite as Anode Material for Lithium-Ion Batteries. ACS Nano 2017, 11, 10453–10462.
(39) Lin, F.; Fujii, Y.; Lu, C.; Cheng, L.; Singer, A.; Shpyrko, O. G.; Xie, H. L.; Tamura, N.; Tian, C.; Weng, T. C.; et al. Synchrotron X-Ray Analytical Techniques for Studying Materials Electrochemistry in Rechargeable Batteries. Chem. Rev. 2017, 117, 13123–13186.
(40) Lowe, M. A.; Gao, J.; Abriñu, H. D. In Operando X-Ray Studies of the Conversion Reaction in Mn3O4 Lithium Battery Anodes. J. Mater. Chem. A 2013, 1, 2094–2103.
(41) Zhang, L.; Sun, D.; Kang, J.; Feng, J.; Bechtel, H. A.; Wang, L.-W.; Cairns, E. J.; Guo, J. Electrochemical Reaction Mechanism of the MoS2 Electrode in a Lithium-Ion Cell Revealed by in Situ and Operando X-Ray Absorption Spectroscopy. Nano Lett. 2018, 18, 1466–1475.
(42) Zhao, Z.-W.; Wen, T.; Liang, K.; Jiang, Y.-F.; Zhou, X.; Shen, C.-C.; Xu, A.-W. Carbon-Coated Fe2O3/V2O5 Hollow Microboxes Derived from Metal–Organic Frameworks as a High-Performance Anode Material for Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2017, 9, 3757–3765.
(43) Su, X.; Wu, Q.; Li, J.; Xiao, X.; Lott, A.; Lu, W.; Sheldon, B. W.; Wu, J. Silicon-Based Nanomaterials for Lithium-Ion Batteries: A Review. Adv. Energy Mater. 2014, 4, No. 1300882.
by X-Ray Absorption Spectroscopy. *Electrochim. Acta* 2017, 246, 699–706.
(43) Permien, S.; Indris, S.; Schüttmann, U.; Kienle, L.; Zander, S.; Doyle, S.; Bensch, W. What Happens Structurally and Electronically during the Li Insertion Reaction of CoFe2O4 Nanoparticles: An Operando XAS and XRD Investigation. *Chem. Mater.* 2016, 28, 434–444.
(44) Debart, A.; Dupont, L.; Poizot, P.; Leriche, J.-B.; Tarascon, J. M. A Transmission Electron Microscopy Study of the Reactivity Mechanism of Tailor-Made CuO Particles toward Lithium. *J. Electrochem. Soc.* 2001, 148, A1266–A1274.
(45) Taberna, P. L.; Mitra, S.; Poizot, P.; Simon, P.; Tarascon, J. M. High Rate Capabilities Fe2O3-Based Cu Nano-Architected Electrodes for Lithium-Ion Battery Applications. *Nat. Mater.* 2006, 5, S567–73.
(46) He, K.; Yao, Z.; Hwang, S.; Li, N.; Sun, K.; Gan, H.; Du, Y.; Zhang, H.; Wolverton, C.; Su, D. K. D. Kinetically-Driven Phase Transformation during Lithiation in Copper Sulfide Nanoflakes. *Nanoscale* 2012, 4, 7572–7579.
(47) Bhardwaj, M.; Patrike, A.; Naphade, R.; Tonda, S.; Gavli, Y.; Ogale, S. Porous CuCo2O4 Nanotubes for Li-Ion Battery Anode. *ChemistrySelect* 2017, 2, 2922–2926.
(48) Li, H. H.; Zhou, L.; Zhang, L. L.; Fan, C. Y.; Fan, H. H.; Wu, X. L.; Sun, H. Z.; Zhang, J. P. Co3O4 Nanospheres Embedded in a Nanocomposite Membrane as Advanced Anodes for Li-Ion Batteries. *Nano Energy* 2017, 39, 3848–3855.
(49) Bhardwaj, M.; Patrike, A.; Naphade, R.; Tonda, S.; Gavli, Y.; Ogale, S. Porous CuCo2O4 Nanotubes for Li-Ion Battery Anode. *ChemistrySelect* 2017, 2, 2922–2926.
(50) Li, H. H.; Zhou, L.; Zhang, L. L.; Fan, C. Y.; Fan, H. H.; Wu, X. L.; Sun, H. Z.; Zhang, J. P. Co3O4 Nanospheres Embedded in a Nanocomposite Membrane as Advanced Anodes for Li-Ion Batteries. *Nano Energy* 2017, 39, 3848–3855.
(51) Guo, H.; Li, T.; Chen, W.; Liu, L.; Yang, X.; Wang, Y.; Guo, Y. General Design of Hollow Porous CoFe2O4 Nanocubes from Metal–organic Frameworks with Extraordinary Lithium Storage. *Nano Scale* 2014, 6, 15168–15174.
(52) Chen, Y.; Zhu, J.; Qu, B.; Lu, B.; Xu, Z. Graphene Improving Lithium-Ion Battery Performance by Construction of NiCo2O4/graphene Hybrid Nanosheet Arrays. *Nano Energy* 2014, 3, 88–94.
(53) Gillot, F.; Boyanov, S.; Dupont, L.; Doublet, M. L.; Morcrette, M.; Monconduit, L.; Tarascon, J. M. Electrochemical Reactivity and Design of NiP2 Nanoparticles Anchored on Carbon Nanotubes as Ultra-Long-Life Anodes for Reversible Lithium Storage. *Nano Energy* 2017, 11, 3705–3715.
(54) Boyanov, S.; Bernardi, J.; Gillot, F.; Dupont, L.; Womes, M.; Tarascon, J. M.; Monconduit, L.; Doublet, M. L. FeP: Another Attractive Anode for the Li-Ion Battery Enlisting a Reversible Two-Step Insertion/conversion Process. *Chem. Mater.* 2006, 18, 3531–3538.
(55) Yan, N.; Hu, L.; Li, Y.; Wang, X.; Zheng, H.; Hu, X.; Kong, X.; Chen, Q. CoO Nanocubes for High-Performance Anode Material in Lithium-Ion Batteries. *J. Phys. Chem. C* 2012, 116, 7227–7235.
(56) Guo, H.; Liu, L.; Li, T.; Chen, W.; Liu, J.; Guo, Y.; Guo, Y. Accurate Hierarchical Control of Hollow Crossed NiCo2O4 Nanocubes for Superior Lithium Storage. *Nano Scale* 2014, 6, 5491–5497.
(57) Jeong, J.-M.; Choi, B. G.; Lee, S. C.; Lee, K. G.; Chang, S.-J.; Han, Y.-K.; Lee, Y. B.; Lee, H. U.; Kwon, S.; Lee, G.; et al. Hierarchical Hollow Spheres of Fe3O4@Polyaniline for Lithium Ion Battery Anodes. *Adv. Mater.* 2013, 25, 6250–6255.
(58) Wang, J.-G.; Jin, D.; Zhou, R.; Li, X.; Liu, X.; Shen, C.; Xie, K.; Li, B.; Kang, F.; Wei, B. Highly Flexible Graphene/Mn3O4 Nanocomposite Membrane as Advanced Anodes for Li-Ion Batteries. *ACS Nano* 2016, 10, 6227–6234.
(59) Zhou, J.; Qin, J.; Zhang, X.; Shi, C.; Liu, E.; Li, J.; Zhao, N.; He, C. 2D Space-Confined Synthesis of Few-Layer MoS2 Anchored on Carbon Nanosheet for Lithium-Ion Battery Anode. *ACS Nano* 2015, 9, 3837–3848.
(78) Jo, M. R.; Jung, J.; Lee, G.-H.; Kim, Y.; Song, K.; Yang, J.; Chae, J. S.; Roh, K. C.; Kim, Y.-I; Yoon, W.-S.; et al. Fe2O3 nanoparticles Encapsulated in One-Dimensional LiTi3O8 nanomatrix: An Extremely Reversible Anode for Long Life and High Capacity Li-Ion Batteries. Nano Energy 2016, 19, 246–256.

(79) Suryawanshi, A.; Aravindan, V.; Madhavi, S.; Ogale, S. Red Mud and Li-Ion Batteries: A Magnetic Connection. ChemSusChem 2016, 9, 2193–2200.

(80) Wu, D.; Shen, R.; Yang, R.; Ji, W.; Jiang, M.; Ding, W.; Peng, L. Mixed Molybdenum Oxides with Superior Performances as an Advanced Anode Material for Lithium-Ion Batteries. Sci. Rep. 2017, 7, No. 44697.

(81) Zheng, X.; Li, J. A Review of Research on Hematite as Anode Material for Lithium-Ion Batteries. Ionics 2014, 20, 1651–1663.

(82) Luo, W.; Lin, C.-F.; Zhao, O.; Noked, M.; Zhang, Y.; Rubloff, G. W.; Hu, L. Ultrathin Surface Coating Enables the Stable Sodium Metal Anode. Adv. Energy Mater. 2017, 7, No. 1601526.

(83) Bhattacharyya, D.; Sinhamahapatra, A.; Ko, J.-J.; Yu, J.-S. High Capacity and Exceptional Cycling Stability of Ternary Metal Sulfide Nanorods as Li Ion Battery Anodes. Chem. Commun. 2015, 51, 13350–13353.

(84) Wang, X.; Kim, H.-M.; Xiao, Y.; Sun, Y.-K. Nanostructured Metal Phosphide-Based Materials for Electrochemical Energy Storage. J. Mater. Chem. A 2016, 4, 14915–14931.

(85) Liang, Q.; Zheng, Y.; Du, C.; Luo, Y.; Zhang, J.; Li, B.; Zong, Y.; Yan, Q. 2D Nanomaterials: General and Scalable Solid-State Synthesis of 2D MPS (M = Fe, Co, Ni) Nanosheets and Tuning Their Li/Na Storage Properties. Small Methods 2017, 1, No. 1700304.

(86) Zhao, Y.; Wang, L. P.; Sougrati, M. T.; Feng, Z.; Lecomte, Y.; Fisher, A.; Srinivasan, M.; Xu, Z. A Review on Design Strategies for Carbon Based Metal Oxides and Sulfides Nanocomposites for High Performance Li and Na Ion Battery Anodes. Adv. Energy Mater. 2017, 7, No. 1601424.

(87) Liu, H.; Liu, X.; Li, W.; Guo, X.; Wang, Y.; Wang, G.; Zhao, D. Porous Carbon Composites for Next Generation Rechargeable Lithium Batteries. Adv. Energy Mater. 2017, 7, No. 100283.

(88) Choi, S. H.; Lee, J. H.; Kang, Y. C. Perforated Metal Oxide-Carbon Nanotube Composite Microspheres with Enhanced Lithium-Ion Storage Properties. ACS Nano 2015, 9, 10173–10185.

(89) Shearer, C. J.; Cherevan, A.; Eder, D. Application and Future Challenges of Functional Nanocarbon Hybrids. Adv. Mater. 2014, 26, 2295–2318.

(90) Tian, H.; Liu, H.; Yang, T.; Veder, J.-P.; Wang, G.; Hu, M.; Wang, S.; Jaroniec, M.; Liu, J. Fabrication of Core−shell, Yolk−shell and Hollow Fe2O3@carbon Microboxes for High-Performance Lithium-Ion Batteries. Mater. Chem. Front. 2017, 1, 823–830.

(91) Sun, X.; Liu, J.; Li, Y. Oxides@C Core-Shell Nanostructures: One-Pot Synthesis, Rational Conversion, and Li Storage Property. Chem. Mater. 2006, 18, 3486–3494.

(92) Xiao, L.; Cao, Y.; Henderson, W. A.; Sushko, M. L.; Shao, Y.; Xiao, J.; Wang, W.; Engelhard, M. H.; Nie, Z.; Liu, J. Hard Carbon Nanoparticles as High-Capacity, High-Stability Anodic Materials for Na-Ion Batteries. Nano Energy 2016, 19, 279–288.

(93) Zhao, Z.-W.; Wen, T.; Liang, K.; Jiang, Y.-F.; Zhou, X.; Shen, C.-C.; Xu, A.-W. Carbon-Coated Fe3O4/VOx Hollow Microboxes Derived from Metal–Organic Frameworks as a High-Performance Anode Material for Lithium-Ion Batteries. ACS Appl. Mater. Interfaces 2017, 9, 3757–3765.

(94) Zhu, K.; Wang, X.; Liu, J.; Li, S.; Wang, H.; Yang, L.; Liu, S.; Xie, T. Novel Amorphous MoS2/MoO3/Nitrogen-Doped Carbon Composite with Excellent Electrochemical Performance for Lithium Ion Batteries and Sodium Ion Batteries. ACS Sustainable Chem. Eng. 2017, 5, 8025–8034.

(95) Lin, D.; Zhao, J.; Sun, J.; Yao, H.; Liu, Y.; Yan, K.; Cui, Y. Three-Dimensional Stable Lithium Metal Anode with Nanoscale Lithium Islands Embedded in Ionically Conductive Solid Matrix. Proc. Natl. Acad. Sci. 2017, 114, 4613–4618.

(96) Su, Q.; Xie, D.; Zhang, J.; Du, G.; Xu, B. In Situ Transmission Electron Microscopy Observation of the Conversion Mechanism of Fe2O3/graphene Anode during Lithiation-Delithiation Processes. ACS Nano 2013, 7, 9115–9121.

(97) Sasaki, T.; Ukyo, Y.; Novák, P. Memory Effect in a Lithium-Ion Battery. Nat. Mater. 2013, 12, 569–575.

(98) Blyr, A.; Sigala, C.; Amatucci, G.; et al. Self-Discharge of LiMn2O4/C Li-Ion Cells in Their Discharged State. J. Electrochem. Soc. 1998, 145, 194–209.

(99) Seong, W. M.; Park, K.-Y.; Lee, M. H.; Moon, S.; Oh, K.; Park, H.; Lee, S.; Kang, K. Abnormal Self-Discharge in Lithium-Ion Batteries. Energy Environ. Sci. 2018, 0–24.