Revealing and suppressing surface Mn(II) formation of Na_{0.44}MnO₂ electrodes for Na-ion batteries

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Abstract:

Understanding and controlling the surface activities of electrode materials is critical for optimizing the battery performance, especially for nanoparticles with high surface area.

Na_{0.44}MnO₂ is a promising positive electrode material for large-scale sodium-ion batteries.

However, its application in grid-scale energy storage requires improvements in cycling stability at high rate. Here, we performed comprehensive surface-sensitive soft x-ray

spectroscopic studies of the Na_{0.44}MnO₂ electrode. We are able to quantitatively determine the Mn evolution upon the potentials and cycle numbers. We reveal the Mn²⁺ formation on the top 10 nm of Na_{0.44}MnO₂ particles when the electrochemical potential is below 2.6V, which does not occur in the bulk. A portion of the surface Mn²⁺ compounds become electrochemically inactive after extended cycles, contributing to the capacity fading. Based on the spectroscopic

discoveries, we demonstrate that cycling $\text{Na}_{0.44}\text{MnO}_2$ above 3 V could efficiently suppress the Mn^{2+} formation.

Keywords: Sodium Ion Batteries, soft x-ray absorption spectroscopy, $\text{Na}_{0.44}\text{MnO}_2$, Surface reactions

1. Introduction

The growing global concerns on the climate change and environmental deterioration have created a pressing demand to develop sustainable energy applications, which rely on efficient energy storage systems. Especially, high-performance energy storage with low-cost and long-lifetime is yet to be developed for utilizing the intermittent renewable energy resources. Although Lithium-ion batteries, which are ubiquitous in portable electronics, remain promising candidates for these large-scale energy storage,[1] concerns on the lithium supply and cost have motivated recent investigations of batteries based on sodium and other multivalent elements. Sodium-ion batteries (SIBs) utilize sodium that is earth-abundant and low-cost. Developing high performance SIBs has become a new research frontier in energy storage.[2-4] One of the challenges for advancing SIB technologies is to develop and optimize electrode materials that can accommodate sodium ions and allow rapid reversible ion insertion and extraction.[5, 6] In particular, the cycling stability is of critical importance for the applications of SIBs in grid-scale energy storage.

$\text{Na}_{0.44}\text{MnO}_2$ is a promising positive electrode material for sodium ion batteries.[7-12] In principle, it has the wide tunnel structure suitable for fast sodium ion incorporation.[13-16] The $\text{Na}_{0.44}\text{MnO}_2$ structure is energetically stable, and could be cycled in the sodium composition range from 0.22 to 0.66,[17, 18] providing the high capacity of 121mAh g^{-1} as a SIB cathode material.[8, 10] It is also applicable in aqueous electrolyte, indicating a substantial reduction of cost and improvement in safety.[9, 12, 19-21] Therefore, extensive

efforts have been made to understand and optimize $\text{Na}_{0.44}\text{MnO}_2$ as a SIB cathode material through various synthesis methods,[8-11] characterization,[15] and theoretical calculations.[18] It is generally believed that the electrochemical cycling involves the $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple.[15, 18] Sauvage et al. firstly demonstrated the high capacity of $\text{Na}_{0.44}\text{MnO}_2$, however the cyclability was poor.[8] Cao et al. reported significantly improved cyclability but with low rate performance.[10] Hosono et al. prepared $\text{Na}_{0.44}\text{MnO}_2$ nanowires following a hydro-thermal approach. Their material displays relatively high rate capability within 20 cycles.[11] Xu et al. reported high-capacity (120 mAh/g) cycling at a low 0.1C rate of ultra-long $\text{Na}_{0.44}\text{MnO}_2$ slabs. No high rate data was reported and the ion diffusion coefficient is low ($2.6 \times 10^{-14} \text{ cm}^2\text{S}^{-1}$). [22] At this time, the application of $\text{Na}_{0.44}\text{MnO}_2$ in practical SIBs is still hindered by its electrochemical performance, especially the rate capability and cycling stability. On the other hand, the cycling and capacity-fading mechanism of $\text{Na}_{0.44}\text{MnO}_2$ based electrodes is yet to be clarified.

In this work, we aim to tackle both the fundamental understanding and the practical optimization of $\text{Na}_{0.44}\text{MnO}_2$ as the positive electrode material for SIBs. We first show that Polyvinylpyrrolidone (PVP)-assisted combustion is an effective synthesis process to achieve superior electrochemical performance of $\text{Na}_{0.44}\text{MnO}_2$ materials, in particular the high rate performance and the Coulombic efficiency. This also provides us the opportunity to clarify the intrinsic cycling mechanism of $\text{Na}_{0.44}\text{MnO}_2$. We then employ the soft x-ray absorption spectroscopy (sXAS) to achieve a quantitative analysis of the Mn oxidation states in Na_xMnO_2 ($0.22 \leq x \leq 0.66$) electrodes at different stages of the electrochemical operation. While the electrochemical cycling in the bulk of the electrode is confirmed to be dominated by $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple, as revealed by hard x-ray Raman spectroscopy (XRS), we discovered the formation of Mn^{2+} below certain potential on the electrode surface. Our analysis shows that this surface Mn^{2+} formation is associated with the capacity fading. We further demonstrate that cycling $\text{Na}_{0.44}\text{MnO}_2$ electrodes above 3V could eliminate the surface

Mn²⁺ formation, leading to greatly improved cycling stability with the remaining energy density of 147 Wh kg⁻¹.

2. Material and methods

2.1 Na_{0.44}MnO₂ Synthesis: Na_{0.44}MnO₂ was prepared by poly (vinyl pyrrolidone) (PVP) - assisted gel combustion method. In detail, NaHCO₃, Mn(OAc)₂·4H₂O (Na : Mn = 0.44 : 1), and PVP (the molar ratio of PVP monomer to total metal ions was 2.0) were dissolved in deionized water and pH = 3 was achieved by adding 1:1 HNO₃. The mixture was stirred at 120 °C to obtain dried gel. The dried gel was ignited on a hot plate to induce a combustion process which lasted for several minutes. The resulting precursor was preheated at 400 °C for 2 h and then calcined at 900 °C for 6 h with the heating rate of 5 °C min⁻¹. After heat treatment, the oven was switched off and the sample was cooled down naturally. The whole process was performed in air.

2.2 Morphology and crystal structure characterization: The morphology was examined using a JEOL 7500F scanning electron microscope (SEM). High-resolution transmission electron microscopy (HRTEM) analysis was carried out via a Philips CM200FEG at the National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory (LBNL) and the acceleration voltage was 200 kV. X-ray powder diffraction (XRD) was done using a Bruker D2 PHASER diffractometer equipped with Cu K α radiation that was operated over a 2θ range of 10~70° in a continuous scan mode with a step size of 0.004°.

2.3 Electrochemical tests: The Na_{0.44}MnO₂ cathode was prepared by mixing 80 wt.% active material, 10 wt.% acetylene black (AB) and 10 wt.% polyvinylidene fluoride (PVdF) binder in N-methylpyrrolidone (NMP) to form a slurry. The slurry was doctor-bladed onto aluminum foil, dried at 60 °C, and then punched into electrode discs with a diameter of 12.7 mm. The prepared electrodes were dried at 130 °C for 12 h in a vacuum oven and show typically an active material loading of about 2 mg. The electrochemical cells were fabricated with the Na_{0.44}MnO₂ cathode, sodium foil anode, 1 mol L⁻¹ NaClO₄ in propylene carbonate

(PC) as electrolyte, and glass fiber as separator in an argon-filled glove box. Electrochemical performances were evaluated using CR2325 coin cells. Galvanostatic charge-discharge tests were performed using Maccor 4000. The potential intermittent titration technique (PITT) test was conducted using Bio-Logic VMP-3 multichannel electrochemical Analyzer. A small potential step size (20 mV) and a low enough cutoff current (C/50) were adopted to ensure the equilibrium states were achieved at every potential step.

2.4 Soft X-ray absorption spectroscopy (sXAS): $\text{Na}_{0.44}\text{MnO}_2$ cathodes were electrochemically cycled to certain stages in Swagelok cells. Afterwards, they were disassembled and the cathodes were rinsed with DMC thoroughly and dried in vacuum to remove any residue. The cathode materials were then pressed onto conducting carbon tapes and loaded into our special sample transfer chamber inside the argon glove box. The sample transfer chamber was sealed and mounted directly onto the ultra-high vacuum sXAS characterization chamber to avoid any air exposure effects.[23] Soft x-ray absorption spectroscopy was performed at Beamline 8.0.1 of the Advanced Light Source (ALS) in LBNL.[24] The undulator and spherical grating monochromator supply a linearly polarized photon beam with resolving power up to 6000. The experimental energy resolution is about 0.15eV. Experiments were performed at room temperature and with the linear polarization of the incident beam 45° to sample surfaces. All the spectra have been normalized to the beam flux measured by the upstream gold mesh. . Total florescence yield signals are also collected but suffer serious spectral distortions due to self-absorption effect, especially for Mn-L edges.[25]

For the test on Mn evolution upon different electrochemical potentials (figure 3), in order to precisely determine the biphasic transition voltages indicated in figure 1c, differential capacity (dQ/dV) plots were obtained during the first cycle discharge, considering the complexity of the voltage profiles of $\text{Na}_{0.44}\text{MnO}_2$ with the presence of seven biphasic transitions in narrow domains. All the tested electrodes were then prepared at the

corresponding voltages during the second discharge. The good reversibility assures the accuracy of this controlled experimental procedure.

2.5 Hard X-ray Raman Scattering: Hard x-ray Raman Scattering (XRS) measurements were carried out at beamline 6-2b at Stanford Synchrotron Radiation Lightsource (SSRL).[26] The x-ray Raman signals were collected with Si-660 reflection of the 40-crystal XRS spectrometer at 9694.8 eV with a bandwidth of 0.55 eV and the incident photon energy was selected with a double-crystal monochromator Si(311) around 10.3 keV to have the Raman offset corresponding to Mn L_{2,3}-edges. XRS spectra were recorded with samples kept in helium atmosphere during measurements. Each XRS spectrum reported here is an accumulation of data collected for about two hours.

3. Results and discussion

3.1 PVP-Assisted Synthesis and Electrochemical Performance: It has been demonstrated that polymer-pyrolysis is an efficient method to synthesize high-quality Na_{0.44}MnO₂ materials.[10] In order to further improve the properties of the material, we introduce PVP to aid the combustion process in this work. PVP is an excellent stabilizing agent that has been employed for synthesizing metal colloids. It prevents the aggregation of metal particles and retains a uniform colloidal dispersion.[27] Previously, we have utilized PVP-assisted combustion method to synthesize the high-quality cathode material for Li-ion batteries with outstanding electrochemical performance, including LiMn₂O₄ nanoparticles,[28, 29] micrometer-sized LiMn₂O₄,[30] and LiNi_{0.5}Mn_{1.5}O₄[31, 32]. There are several remarkable advantages of PVP-assisted combustion method over other polymer-pyrolysis methods. First, it provides a precursor solution with a homogeneous distribution of the constituents at the atomic level, as both Na⁺ and Mn²⁺ ions are strongly chelated by the amide groups on the polymeric chains. Second, the precursor that contains PVP and NO₃⁻ is pyrolyzed violently, and therefore burns quickly and completely when it is heated. This enables a simple, fast, and clean sample synthesis process. Third, although the detailed functionality of PVP in the

combustion process is complicated and deserves further studies, we found that PVP helps improving the crystallization, purity and homogeneity of $\text{Na}_{0.44}\text{MnO}_2$, as presented below.

The morphology and crystal structure of the as-prepared $\text{Na}_{0.44}\text{MnO}_2$ are characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (**Figure 1a-1b**). Most $\text{Na}_{0.44}\text{MnO}_2$ particles grow anisotropically into stick-shaped crystals with a diameter of about 200 nm, and a length around 10 μm (Figure 1a). Its excellent crystallinity is shown by the high-resolution TEM (Figure 1b). A selected-area electron diffraction (SAED) pattern (inset of Figure 1b) indicates that the particles are single-crystalline and along the [001] direction. The X-ray diffraction pattern is shown in figure S1. XRD confirms the formation of well-crystallized $\text{Na}_{0.44}\text{MnO}_2$ (JCPDS No. 27-0750). All diffraction peaks can be indexed as an orthorhombic structure with *Pbam* space group. The cell parameters, $a = 9.080(3)$, $b = 26.37(1)$, $c = 2.827(1)$, are consistent with the previous reports.[8, 9]

Sodium ion extraction/insertion properties of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes are investigated by galvanostatic charge/discharge cycling. Figure 1c shows the charge/discharge profiles of the first two cycles tested at C/5 in the potential range of 2 to 4 V (vs Na^+/Na). The profiles display many short voltage plateaus (arrows), which are in good agreement with previous reports and indicate multiple biphasic transitions of the $\text{Na}_{0.44}\text{MnO}_2$ electrode during electrochemical Na^+ ion insertion/exaction.[8, 10, 11] The complex phase transitions observed in $\text{Na}_{0.44}\text{MnO}_2$ could be attributed to the coupling between sodium and charge (on the manganese sites) orderings,[15, 18] which have also been reported in other Na-intercalation systems.[33, 34] The initial charge capacity at C/5 is 60 mAh g^{-1} , corresponding to 0.22 Na^+ ions extracted from $\text{Na}_{0.44}\text{MnO}_2$, forming $\text{Na}_{0.22}\text{MnO}_2$. The following discharge/charge cycles provide the reversible discharge/charge capacity of 122 mAh g^{-1} , suggesting that the total of 0.44 Na^+ ion insertion/extraction takes place in the full-range Na_xMnO_2 cycling, i.e., $0.22 \leq x \leq 0.66$.

The electrodes demonstrate superior rate capability and high-rate cycling stability. Figure 1d shows the discharge capacity tested at different C rates, with the same C rate used for both charge and discharge processes. Even at 20C, the electrode delivers reversible capacity of 99 mAh g⁻¹, corresponding to 82% of the theoretical capacity. As shown in Figure 1e, after 700 cycles at 10C, the electrode still display a discharge capacity of 88mAh g⁻¹, corresponding to 83% capacity retention. The Coulombic efficiency of the electrode at 10C is as high as 99.8% during the initial cycle and further increases to above 99.9%.

To the best of our knowledge, our Na_{0.44}MnO₂ material exhibits by far the best electrochemical performance in terms of high capacity, high rate and excellent cycling stability (table S1). We believe the outstanding electrochemical properties are related with the high quality Na_{0.44}MnO₂ nanoparticles generated from the optimized PVP-assisted combustion method, which display improved crystallinity, purity, homogeneity and facile Na⁺ ion diffusion. The Na⁺ ion diffusion coefficient is obtained through potentiostatic intermittent titration technique (PITT) measurements with Na counter electrode. Note that the diffusivity value from a two-electrode measurement tends to yield a lower number than that from a more reliable three-electrode measurement. Still, our diffusivity of 3×10⁻¹² cm² s⁻¹ (Figure S1) is higher than those in previous reports, [10, 20] which is consistent with the high rate performance. [30] While there have been controversial results on the rate capability of Na_{0.44}MnO₂ in previous reports,[8, 10, 11] our results directly show that fast Na⁺ ion diffusion and phase transformation could be realized in Na_{0.44}MnO₂.

3.2 sXAS and Quantitative Analysis: The crystalized Na_{0.44}MnO₂ particle with the superior electrochemical performance is an excellent candidate for studying the intrinsic reaction mechanism in Na_{0.44}MnO₂ associated with the electrochemical sodium insertion/extraction process. For a systematic study of the Mn oxidation states on the surface and in the bulk of Na_{0.44}MnO₂ electrodes, synchrotron-based soft x-ray sXAS and hard x-ray XRS are performed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory

and Stanford Synchrotron Radiation Lightsource (SSRL), respectively. Below we first clarify the critical Mn oxidation state evolution on the electrode surface through sXAS, and then discuss the contrast between surface and bulk.

sXAS provides a direct and sensitive measurement of transition metal (TM) $3d$ states through strong dipole $2p$ - $3d$ transitions.[35] The sensitivity and accuracy of sXAS for probing TM- $3d$ states allows the quantitative analysis of the transition metal oxidation states through a straightforward linear combination fitting.[36] In particular, for Mn L -edge sXAS spectra, we have found that the overall lineshape is insensitive to the different chemical configurations with the local octahedral structure, which is adopted by many battery materials.[23] Additionally, we have recently demonstrated that a quantitative definition of the Mn valence distribution is possible through a straightforward linear combination of the sXAS results.[37] Based on the same methodology, here, we first focus on the surface activities of the electrode that are quantitatively defined by sXAS through the total electron yield (TEY) mode with a probe depth of about 10 nm.

Figure 2 shows the Mn L -edge sXAS spectra (solid lines) collected on reference samples with different formal Mn valences, including MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}) and Li_2MnO_3 (Mn^{4+}), as well as on Na_xMnO_2 electrodes, including pristine ($\text{Na}_{0.44}\text{MnO}_2$, P), after the initial charge ($\text{Na}_{0.22}\text{MnO}_2$, 1Ch) and discharge ($\text{Na}_{0.66}\text{MnO}_2$, 1D).. The spectra consist of well-separated absorption features in two regions, L_3 (638-646eV) and L_2 (649-656eV), resulting from the $2p$ core-hole spin-orbital splitting. The spectra of the three standard manganese oxides with different Mn oxidation states display dramatically different absorption features, especially on L_3 edge. Therefore, the Mn- L spectral lineshape fingerprints the different oxidation states of manganese.[23] As shown in Figure 2, it is evident that the spectra of the Na_xMnO_2 electrodes are composed of features corresponding to the contribution from Mn^{4+} , Mn^{3+} and possibly Mn^{2+} . Note that the existence of Mn^{2+} in the discharged $\text{Na}_{0.66}\text{MnO}_2$ sample is directly indicated by the sharp peak at 640eV. By virtue of the high-resolution and

high-sensitivity of sXAS for detecting Mn oxidation states, we are able to perfectly fit the experimental data through a simple linear combination of the three reference spectra (dot lines).[37] The excellent fitting provides a fairly precise measurement of the concentration of Mn^{4+} , Mn^{3+} and Mn^{2+} in Na_xMnO_2 electrodes at different cycling states.

3.3 Mn Evolution upon Electrochemical Potentials: **Figure 3a** displays the Mn L -edge sXAS results of Na_xMnO_2 electrodes that are electrochemically cycled to different voltages between 4V and 2V ($0.22 \leq x \leq 0.66$). The intermediate voltages were elaborately selected so they correspond to all the biphasic transitions indicated in Figure 1c. The sXAS data presented in the main text are collected from the side of the electrodes facing current collector, unless otherwise mentioned. The data collected on the other side of the electrodes, i.e. the side facing the separators, are shown in Figure S3 and display identical behavior. The spectra with the full energy range, including both L_3 - and L_2 -edges, are shown in Figure S4. Figure 3a focus on the Mn L_3 -edge, which displays a systematic evolution upon sodium insertion. Generally, the electrode at charged state (4V) displays mainly Mn^{4+} . From 4V to 2.6V, the intensity of the Mn^{3+} sXAS features between 641 and 642.6 eV increases, suggesting the formation of Mn^{3+} during this discharge process. However, when the voltage drops below 2.6V, the Mn^{2+} peak at 640V is enhanced significantly until the electrode is fully discharged (2V).

The quantitative analysis of the evolution of the manganese oxidation states is obtained by fitting the experimental data using a linear combination of the three reference spectra in Figure 2.[37] The fitting results (dotted lines in Figure 3a) again show excellent agreement with the experimental data. The calculated concentrations of the Mn^{4+} , Mn^{3+} and Mn^{2+} are display in Figure 3b-d. The Mn^{4+} composition decreases monotonously with the sodium insertion. When the electrodes are discharged from 4V to 2.6V ($0.22 \leq x \leq 0.49$), Mn^{3+} increases almost linearly with the sodium insertion, with negligible amount of Mn^{2+} . However, the Mn^{2+} concentration increases rapidly once the cycling voltage drops below 2.6V. At fully

discharged state (2V), the Mn^{2+} concentration is as high as 14%. Note this quantitative analysis is consistent with the overall sXAS lineshape evolution of the raw sXAS data. Within the 10 nm probe depth of the sXAS experiments, this result clearly reveals the evolution of Mn^{2+} at electrochemical potentials below 2.6 V.

Figure 4 shows the Mn *L*-edge sXAS spectra collected on a series of $\text{Na}_{0.44}\text{MnO}_2$ electrodes at fully charged (4V) and discharged (2V) states from the 1st to 100th cycles. Again, both sides of the electrodes display identical behavior (see Figure S5). The reversible Mn cycling is well demonstrated by the sXAS spectra through the periodic lineshape change of the L_3 - features and the zig-zag shift of the central energy positions of the L_2 - humps.[23] In addition, the intensity of the Mn^{2+} peak at 640eV is evidently increased in the discharged state after 20 cycles. This Mn^{2+} feature can be seen even in the charged state of the 100th cycle (100Ch).

The fitting results of the Mn^{4+} , Mn^{3+} and Mn^{2+} concentrations are displayed in Figure 4b-d. The charge/discharge process of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes within 4–2 V is accompanied by the cycling of Mn^{4+} versus both Mn^{3+} and Mn^{2+} . Besides the reversible behavior, it is found that the overall amount of Mn^{2+} on the electrode surface increases after extended cycles. After 100 cycles, the amount of Mn^{2+} in the charged sample (100Ch) reaches 12%, which corresponds to the capacity loss of the $\text{Na}_{0.44}\text{MnO}_2$ electrode tested at the rate of 1C. It is well known that the Mn^{2+} on the electrode surface is detrimental to the battery performance due to its dissolution and shuffling in the electrolyte.[38] Our results show directly that part of the surface Mn^{2+} does not participate in the electrochemical reaction after extended cycles, and thus contributes to the capacity fading of the electrodes. Note that Mn^{2+} formation has been observed on the surfaces of many manganese oxide cathode materials for Li-ion batteries. In particular, it is found that Mn^{2+} tends to form at the charged states in high-voltage manganese spinel [37, 39, 40]. Our finding that Mn^{2+} forms at a low voltage in Na_xMnO_2 is an interesting contrast and indicates a different mechanism of Mn^{2+} formation. Recently, Ti-substituted

$\text{Na}_{0.44}\text{MnO}_2$ material is demonstrated to be a promising anode material for Na-ion batteries. The material could be cycled at very low potential, 1.5V [41]. Consistent with this work, stronger Mn^{2+} formation is found at the very low discharge potential. Therefore, proper surface treatment is necessary to prevent the Mn^{2+} evolution in both the cathode and anode at low electrochemical potentials.

3.4 Hard X-ray XRS and the Contrast between Surface and Bulk: In order to clarify whether the Mn^{2+} formation is only from the surface reactions, or it is a bulk behavior of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes, we performed hard x-ray XRS at SSRL.[26] XRS at low momentum transfer geometry is principally analogous to the sXAS but with a probe depth of several micrometers. As shown in **Figure 5**, it is obvious that the Mn^{2+} content in the discharged Na_xMnO_2 electrodes (1D and 100D) is much less in XRS than that in sXAS spectra. The quantitative spectral fitting results (Table S2) show that the redox reaction in the bulk of the Na_xMnO_2 electrode during the full-range (4-2V) electrochemical cycling is predominantly between Mn^{3+} and Mn^{4+} . The calculated total cation valences based on the Na content (0.22 - 0.66) through bulk-sensitive XRS is close to 4. Therefore, the Mn^{2+} formation revealed by sXAS takes place only on the surface of the Na_xMnO_2 electrodes.

3.5 Suppressing Surface Mn^{2+} to Improve Cycling Stability: The revealed Mn^{2+} formation on the surface and its association with the capacity fading provide valuable insight into rational approaches to improve the cyclability of Na_xMnO_2 electrodes. Based on our quantitative analysis of the sXAS results (Figure 3), the formation of Mn^{2+} could be suppressed if we limit the electrochemical cycling with the discharge cut-off voltage higher than 2.6 V. Note that this is very close to the chemical potential of the stable $\text{Na}_{0.44}\text{MnO}_2$ phase that is typically the pristine electrode material (about 3V in potential). This naturally leads to another benefit if we cycle the battery cells above 3V: the cell could become independent from an extra sodium source, typically from the anodes. Cycling in such high voltage range still retains about a half of the energy density.

Figure 6a shows that, with the electrochemical cycling in the potential range of 4-3 V (red), the $\text{Na}_{0.44}\text{MnO}_2$ electrode displays negligible capacity loss until 100 cycles at 1C rate. This is in sharp contrast with the obvious capacity drop if the electrode is cycled within the typical 4-2 V range (black). The remaining energy density of $\text{Na}_{0.44}\text{MnO}_2$ electrodes cycling in the range of 4-3V is 147 Wh kg^{-1} . Mn *L*-edge sXAS data (Figure 6b) and the fitting results (Figure 6c) clearly show that the crucial change by cycling above 3V is the absence of Mn^{2+} on the Na_xMnO_2 electrode surfaces. Although cycling with a shallow voltage range may generally improve the cycling stability and we cannot rule out other factors that affects the cycling stability, especially the irreversible structural changes, we argue that the suppressed Mn^{2+} formation on the electrode surface at least partially contributes to the improvement of the cycling stability.

Although the energy density of the Na_xMnO_2 electrode cycling within 4-3 V is compromised (147 Wh kg^{-1}), Na-ion batteries are under scrutiny mainly due to the needs of grid-scale storage, where cost and stability is more important than energy capacity[3, 42]. As discussed earlier, cycling Na_xMnO_2 electrode above 3V naturally avoid the manufacture complication of introducing extra Na source, which will dramatically lower the cost. Furthermore, cycling above 3 V does eliminate the surface Mn^{2+} formation and improves the cycling stability. So, such a rational approach of limiting the cycling potential to 4-3V is an advisable method even from the practical point of view.

4. Conclusions

This work provides both the synthesis improvements and fundamental insights of $\text{Na}_{0.44}\text{MnO}_2$ based electrodes for SIBs. Our materials display superior rate performance through the optimized synthesis method. More importantly, we reveal a significant concentration of Mn^{2+} on the surface (top 10 nm) of the Na_xMnO_2 electrodes at low electrochemical potential. This finding indicates the critical role of the surface activities of battery electrodes on the electrochemical performance, and provides the rationality of

regulating the cycling voltages for improving the electrochemical cycling stability. Besides the demonstration of the suppressed Mn^{2+} formation by regulating the discharge cut-off voltage, revealing the Mn^{2+} on the surface of $\text{Na}_{0.44}\text{MnO}_2$ electrodes suggests that modifying and controlling the surface of the $\text{Na}_{0.44}\text{MnO}_2$ electrodes, e.g., through surface coating, could be another key to optimize its electrochemical performance.

Acknowledgements

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy. Battery fabrication, testing and analyses were funded by the assistant Secretary for Energy Efficiency, Office of Vehicle Technologies of the US Department of Energy, under the Batteries for Advanced Transportation Technologies (BATT) Program. Both are under Contract No. DE-AC02-05CH11231. The material synthesis is supported by the Fundamental Research Funds for the Central Universities of China (N110802002) and the National Natural Science Foundation of China (51204038). K.D. is financially supported by the China Scholarship Council (201208210038). The Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. R.Q. is supported by the LDRD program at the Lawrence Berkeley National Laboratory. R.Q. and K.D. contributed equally to this work.

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Figure 1. Morphology, crystal structure and electrochemical performance of $\text{Na}_{0.44}\text{MnO}_2$. (a) SEM image. (b) High-resolution TEM image and SAED pattern (inset). (c) Charge/discharge profiles for the first two cycles at $C/5$. C/n rate corresponds to the applied current to fully charge/discharge a cell in n hours. Arrows indicate the short voltage plateaus and the potentials of the samples measured by sXAS in Figure 3. (d) Galvanostatic cycling performance at different C rates. The same C rate is used for both charge and discharge processes. (e) Cycling performance at 10C rate.

Figure 2. Mn *L*-edge sXAS spectra (solid lines) collected on references with different formal Mn valences, including MnO (Mn²⁺), Mn₂O₃ (Mn³⁺) and Li₂MnO₃ (Mn⁴⁺), as well as on Na_{*x*}MnO₂ electrodes, which are pristine (Na_{0.44}MnO₂, P), after the initial charge (Na_{0.22}MnO₂, 1Ch) and discharge (Na_{0.66}MnO₂, 1D). The calculated spectra (dot lines) for the electrode samples are obtained through a simple linear combination of the three reference spectra, which agree perfectly with the experimental data. This provides a direct measurement of the Mn^{*n*+} concentration (*n*=2,3 and 4) in the Na_{*x*}MnO₂ electrodes.

Figure 3. Mn valence evolution upon the electrochemical potentials. (a) Comparison of the experimental (solid lines) and calculated (dotted lines) Mn L-edge sXAS data collected on Na_xMnO_2 electrodes at different electrochemical potentials as marked by the arrows in figure 1c. (b-d) Evolution of Mn^{4+} , Mn^{3+} and Mn^{2+} concentration in Na_xMnO_2 electrodes plotted as a function of the sodium concentration. The values of the concentration are obtained directly from the fitting parameters of the calculated (dotted lines) spectra in (a) (see text).

Figure 4. Mn valence evolution upon electrochemical cycles. (a) Experimental (solid lines) and calculated (dotted lines) Mn *L*-edge sXAS spectra of Na_xMnO_2 electrodes at fully-charged (4V) and fully-discharged (2V) states of different cycles. (b-d) Evolution of the concentration of Mn^{4+} , Mn^{3+} and Mn^{2+} in Na_xMnO_2 electrodes as a function of their charge/discharge states and cycle numbers.

Figure 5. Hard x-ray XRS compared with sXAS. Experimental (solid lines) and calculated (dash lines) hard x-ray XRS spectra of the charged and discharged Na_xMnO_2 electrodes of the 1st and 100th cycles. For comparison, sXAS spectra are plotted as the dot lines on top.

Figure 6. Optimizing the cycling stability of Na_xMnO_2 electrodes by suppressing the surface Mn^{2+} evolution. (a) Capacity retention as a function of the cycle number at a current density of 120 mA g^{-1} (1C rate) with different discharge cut-off voltages, i.e., 4-2 V (dark) and 4-3 V (red). The initial specific capacity of cycling in the range of 4-2 V and 4-3 V is 122.3 mAh g^{-1} and 45 mAh g^{-1} , respectively. (b) Experimental (solid lines) and calculated (dot lines) Mn *L*-edge sXAS spectra of discharged (3V) $\text{Na}_{0.44}\text{MnO}_2$ electrodes cycled within 4-3 V for 1, 20, and 100 cycles. The sXAS spectrum of the electrode that is cycled within 4-2V for 100 cycles and discharged to 2V is also shown for comparison. (c) Evolution of the Mn^{2+} content at the discharged state as a function of the cycle number. Black data points are the same in figure 4d.

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Mn L-edge sXAS Intensity (a.u.)

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