Structural water and disordered structure promote aqueous sodium-ion energy storage in sodium-birnessite

Xiaoqiang Shan1, Fenghua Guo1, Daniel S. Charles1, Zachary Lebens-Higgins2, Sara Abdel Razek2, Jinpeng Wu3, Wenqian Xu4, Wanli Yang3, Katharine L. Page5, Joerg C. Neuefeind5, Mikhail Feygenson5,6, Louis F.J. Piper2 & Xiaowei Teng1*

Birnessite is a low-cost and environmentally friendly layered material for aqueous electrochemical energy storage; however, its storage capacity is poor due to its narrow potential window in aqueous electrolyte and low redox activity. Herein we report a sodium rich disordered birnessite (Na0.27MnO2) for aqueous sodium-ion electrochemical storage with a much-enhanced capacity and cycling life (83 mAh g−1 after 5000 cycles in full-cell). Neutron total scattering and in situ X-ray diffraction measurements show that both structural water and the Na-rich disordered structure contribute to the improved electrochemical performance of current cathode material. Particularly, the co-deintercalation of the hydrated water and sodium-ion during the high potential charging process results in the shrinkage of interlayer distance and thus stabilizes the layered structure. Our results provide a genuine insight into how structural disordering and structural water improve sodium-ion storage in a layered electrode and open up an exciting direction for improving aqueous batteries.
Electrochemical energy storage (EES) using earth-abundant materials has become attractive for storing electric energy generated by solar and wind.1 Aqueous EES using sodium (Na)-ion as charge carrier is promising alternative to non-aqueous lithium (Li)-ion batteries (LIBs) owing to low cost, high safety and the availability of Na sources in terrestrial reserves.6 However, Na-ion storage is challenging for its large radius. One is to replace oxygen anions (O\textsubscript{2−}) with anions having weaker bonding with metal cations so that cations are sufficiently mobile in the electrode. Recent studies show promise of hexacyano (C\textsubscript{6}≡N\textsubscript{6})\textsuperscript{−} based electrode materials for Na- and K-ion storage due to the weakened bonding between cyanide (C≡N\textsuperscript{−}) and cations. Cui and co-workers have demonstrated that potassium copper hexacyanoferrate and its analogues can function as stable electrode materials for aqueous K- and Na-ion storage. Sodium-manganese hexacyanoferrate reported by Goodenough’s group showed good energy performance and cycling life in a non-aqueous electrolyte.8 Another approach is to use a large interstitial host framework, especially layered structure. Layered materials with planar or zigzag layers show different polymorphs (P\textsubscript{2}, P\textsubscript{3} or O\textsubscript{2}, O\textsubscript{3} phase) with respect to the sites of intercalated Na-ion by simply altering the stacking of transition-metal-oxygen octahedra.9–11 Pioneer works on studying Na-ion intercalation in layered Na\textsubscript{x}MnO\textsubscript{2} were reported by Hagenmuller in the 1980s.12,13 However, the mechanistic understanding of Na-ion storage inside various host materials is still not settled. Size difference between Na-ion and Li-ion gives rise to different intercalation chemistries,14 so that the understanding obtained from Li-ion storage may not be directly applied to the Na-ion electrode.15–18 In addition, layered Na\textsubscript{x}MnO\textsubscript{2} especially P-type materials where Na-ions occupy trigonal prismatic site suffer from P\textsubscript{2}-O\textsubscript{2} phase transition during charging with a large lattice collapse and up to 23% of volume shrinkage, resulting in an increased Na-ion diffusion barrier and rapid capacity decay.19,20

Birnessite (δ-MnO\textsubscript{x}) is a layered structure comprised of two-dimensional sheets of edge-sharing MnO\textsubscript{6} octahedra with intercalated cations and/or water in the interlayer.21–25 Although birnessite has a large interlayer distance (~7 Å), its storage capacities for Na-ion were low due to the limited thermodynamically stable potential window (~1.23 V) of an aqueous electrolyte and ineffective redox process.26–28 Recent studies showed that a concentrated Li-bis(trifluoromethane sulfonyl) imide salt in water electrolyte helped the formation of an electrode-electrolyte interphase on a Mo\textsubscript{5}S\textsubscript{8} anode that prevented the direct contact between anode and water, thus achieved potential window of 3.0 V for aqueous EES.29 A similar wide potential window was reported for aqueous electrolyte using hydrate-melt of Li salts.30,31 However, little work has been reported to date on how to widen the potential window of birnessite electrode materials in aqueous electrolytes.

Here we present an effective strategy to significantly improve the discharge capacity and cycle life of birnessite (full-cell capacity of 83 mAh g\textsuperscript{−1} at 1 A g\textsuperscript{−1} after 5000 cycles) through increasing the stable potential window and promoting redox charge transfer process towards aqueous Na-ion storage. Our results demonstrate that Na-rich and disordered birnessite structure can afford a stable potential window of 2.5 V in an aqueous electrolyte with high overpotential towards the gas evolution reactions. Moreover, co-deintercalation of water molecules along with Na-ion at the high potential charging, evidenced by in situ XRD, can stabilize the layered structure from over-expansion of the interlayer distance.

**Results**

**Structural characterizations and formation mechanism.** Different from wet chemistry synthesis of birnessite\textsuperscript{24,25,27,28}, disordered and Na-rich birnessite were prepared at 270 °C in air via a solid-state reaction between NaOH and Mn\textsubscript{3}O\textsubscript{4} nanoparticles (Mn\textsubscript{3}O\textsubscript{4} particles were synthesized using a method reported previously\textsuperscript{33}). By altering the molar ratios between NaOH and Mn\textsubscript{3}O\textsubscript{4}, sodium-intercalated manganese oxides (Na\textsubscript{δ}Mn\textsubscript{3}O\textsubscript{4}; δ: 0.10, 0.17, and 0.27) were prepared, verified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Supplementary Table 1). The Na/Mn ratio remained around 0.27 even when a higher NaOH/Mn\textsubscript{3}O\textsubscript{4} ratio of 4 was used (Supplementary Figure 1). The Na/Mn ratio of 0.27 is higher than those of birnessite materials reported (Supplementary Table 2).\textsuperscript{21–25} Figure 1a and Supplementary Fig. 2 show that as Na concentrations increased from 0.10 to 0.27, the morphologies of resulting Na–Mn–O materials evolved from a mixture of faceted particles and planar structures to a complete planar structure. The atomic ordering of the resulting Na–Mn–O materials was analyzed using neutron total scattering and the atomic pair distribution function (PDF) (Fig. 1b), from which both the Bragg and diffuse scattering were analyzed to provide local structural details such as defects, mismatch or disorder at the atomic level. The structural parameters of various Na\textsubscript{x}Mn\textsubscript{3}O\textsubscript{4} materials obtained from refinement are summarized in Supplementary Fig. 3 and Supplementary Table 3–6. The neutron PDF showed that the coherent length of

---

**Fig. 1 TEM and neutron PDF analysis of sodium-manganese oxides.** a TEM image of Na\textsubscript{0.27}Mn\textsubscript{2}O\textsubscript{3} materials; scale bar, 50 nm; b Experimental neutron PDFs of Na\textsubscript{x}Mn\textsubscript{3}O\textsubscript{4} materials, where coherent lengths, defined as the longest interatomic distance of the material, decreased as the Na concentration increased; c Phase percentage of Na\textsubscript{0.27}Mn\textsubscript{2}O\textsubscript{3} in Na\textsubscript{δ}Mn\textsubscript{3}O\textsubscript{4} materials obtained from neutron PDF analysis.
Na0.27MnOx materials (a distance at which the peaks of atomic pairs vanished) decreased from ~50 Å to ~30 Å as δ increases, indicating more confined crystalline order. Namely, Na0.27MnOx materials cannot sustain long-range crystallinity and became more disordered when more Na-ions are incorporated into the structure. Figure 1c shows that as Na concentration (δ) increased, Na0.27MnOx materials showed pure phase MnO2 (δ = 0), mixture of MnO2 and layered MnO2 (δ = 0.10 and 0.17). When δ reached 0.27, a pure triclinic birnessite structure formed with an interplanar distance of 7.19 Å. The chemical formula was determined as Na0.27MnO2·0.63H2O, where the Na+ and structural water (determined from thermal gravimetric analysis shown in Supplementary Fig. 5) occupied the interlayers.

Neutron PDF studied the evolution of local structure during the transition from MnO2 to MnO2, and finally to MnO2 birnessite (Fig. 2). The PDF data were normalized by the intensity of the peak at 1.9 Å to see the comparative changes of the structural details as δ increased, and the original coherent scattering and structure factor data can be found in Supplementary Fig. 6. The peaks of PDF can be indexed as O–H bond (0.95 Å, P1) from water (a), one Mn–O pair (1.9 Å, P2) from the MnO2 octahedral unit and another Mn–O pair (2.2 Å, P3) from Mn atoms in prismatic sites, Mn–Mn or O–O pair (2.8 Å, P4), and Mn–O pair (3.5 Å, P5) from the nearest neighbors of MnO2 octahedral units, respectively. The contribution of individual pairs such as Mn–O, Mn–Mn, O–O, and Mn–Na, to the overall PDF of the materials can be found in Supplementary Figure 7. Notably O–H pair (P1) and Mn–O pairs (P2, P3, P5, and P7) showed negative peaks due to negative coherent neutron scattering lengths of H and Mn atoms (~3.74 and ~3.73 femtometer, respectively). The Mn–O pair (1.9 Å, P2) is attributed to Mn-O octahedral coordination in both MnO2 (b) and layered Na0.27MnO2 (c) structures. The Mn–O pair (2.2 Å, P3) is attributed to Mn(II)–O from MnO2 phase (d), which decreased relatively to Mn(IV)–O pair at P2 as δ increased, congruent with the decreasing phase fractions of MnO2. The positive peaks at 2.8 Å (P4) are attributed to Mn–Mn or O–O bonding from adjacent [MnO6] octahedral units in MnO2 (e) and Na0.27MnO2 (f) relative to the Mn(IV)–O pair, which did not change significantly as δ increased. A similar trend can be found in the Mn–O pair at 3.5 Å (P5) from adjacent [MnO6] in Mn4O8 (g) and Na0.27MnO2 phases (h). The peaks at ~4.0 Å (P6 and P7) showed a rather interesting transition from positive to negative direction as δ increased. The positive peak at 3.96 Å (P6) is related to O–O pairs (i) in MnO2 either within the same [Mn(IV)O6] octahedral unit or [Mn(II)–O] units where Mn2+ is located in the trigonal prismatic site. In contrast, the negative peak at 4.0 Å (P7) is attributed to Mn–Na pair at 4.11 Å (h) from the interaction between Na-ions in interlayers and Mn2+ from [MnO3] octahedra or Mn–O–O pair (Ow from structural water in the interlayer) at 3.73 Å (h) from the interaction between H2O in interlayers and Mn4+–O2−, both from Na0.27MnO2 layered phase. The interplay between negative peaks of Mn–Na and Mn–O–O in Na0.27MnO2 and the positive peak of O–O in MnO2 at around 4.0 Å explains the overall peak change from positive to negative directions when δ increased. This suggests that phase transition from MnO2 to Na0.27MnO2 birnessite was driven by Na-ion insertion during solid-state annealing.

From neutron PDF and in situ XRD during the thermal treatment (Supplementary Fig. 8), a formation mechanism of Na0.27MnO2 birnessite is proposed in Fig. 3. MnO2 nanoparticles were first converted into MnO2 materials through oxidation of [Mn(III)O3] octahedra of MnO2 into [Mn(IV)O4] units, followed by Na-ion driven conversion from MnO2 to Na0.27MnO2 birnessite during the thermal annealing in air. MnO2 and Na0.27MnO2 share similar structural characteristics: MnO2 has a layered structure and consists of sheets of [Mn3+O6]− in the bc plane. The Mn4+O4− sheets resemble the structure of Na2MnO2 birnessite comprised of infinite [MnO3] octahedral layers with intercalated Na cations in between. The transition from MnO2 to Na0.27MnO2 birnessite is an equivalent process to the ion-exchange of Mn2+ ions in the Mn2+O2−/C138, Mn4+O4−/C0 units, driven by the formation of Li-MnO2 via the ion-exchange between Ca2Mn3O8 (Ca2+/C138) and Na0.27MnO2 phases (Fig. 10). Figure 4a shows the CVs of disordered Na-rich MnO2 (CV) between the oxidation of Mn2+ to the [Mn4+O4−/C138]− layers, and drove the formation of Na0.27MnO2·0.63H2O. XRD showed that anhydrous Na0.27MnO2 has an interlayer distance of 5.6 Å (Supplementary Fig. 9), similar to that of MnO2 (5.2 Å). Upon water intercalation, Na0.27MnO2·0.63H2O showed an increased interlayer distance of 7.19 Å, Na-ion driven conversion from MnO2 to Na0.27MnO2 reported here contrasts the formation of Li-MnO2 via the ion-exchange between Ca2MnO2·0.63H2O and Na0.27MnO2·0.63H2O, isomorphic structure of MnO2 (Mn2+/C22·Mn4+O4−/C0), and molten lithium nitrate.35 In the formation of Li-MnO2, Li-ions occupied all the available octahedral sites between the [Mn4+O4−]− layers rather than the trigonal prismatic sites occupied by Ca2+ in the parent Ca2MnO2 compound due to much smaller size of Li+ compared with Ca2+, resulting in the complete conversion to layered LiMnO2 with R3m or O3 symmetry.

**Electrochemical properties.** Electrochemical performance of various Na0.27MnO2 materials was tested in a 0.1 M Na2SO4 electrolyte in a three-electrode half-cell using cyclic voltammetry (CV) between −1.25 V and 1.25 V (vs Ag/AgCl) (Supplementary Fig. 10). Figure 4a shows the CVs of disordered Na-rich Na0.27MnO2, where distinct redox peaks can be observed at all the tested scan rates. Figure 4a shows that when scan rate increased, Na0.27MnO2 shows small peak shifts in the anodic process (0.12 V) and the cathodic process (0.14 V), compared with the other Na0.27MnO2 materials (Supplementary Fig. 11), indicating Na-ion transport in Na0.27MnO2 required a lower
overpotential at higher charging rates. Further quantitative evaluation of Na-ion transport in all NaMnO$_x$ materials was obtained using a current-pulse relaxation method$^{13}$, where the Na$_{0.27}$MnO$_2$ material showed a highest diffusion coefficient of 38.7 (relative to Mn$_3$O$_4$) than the other NaMnO$_x$ materials (Supplementary Figure 12). This result was congruent with CV data, where Na$_{0.27}$MnO$_2$ had the lowest energy barrier for Na-ion intercalation since it had a more dominant phase of layered birnessite.

Figure 4b shows the galvanostatic chronopotentiometry (CP) tests of Na$_{0.27}$MnO$_2$ materials in half-cell at 0.6 A g$^{-1}$ under the potential window between −0.75 V and 1.25 V (vs Ag/AgCl), demonstrating a high discharge capacity of 138 mAh g$^{-1}$ (1st cycle) and a capacity of 94 mAh g$^{-1}$ after 4th cycle. A highest discharge capacity of 144 mAh g$^{-1}$ was observed for Na-ion storage at a current density of 0.3 A g$^{-1}$ (Supplementary Fig. 13), although additional capacity could be attributed to the hydrogen evolution reaction (HER). It is suggested that discharge capacity of 144 mAh g$^{-1}$ could be the highest capacity of Na$_{0.27}$MnO$_2$ materials measured at three-electrode half-cell conditions, corresponding to 0.47 Na-ion transfer per Mn atom. As Na$_{0.27}$MnO$_2$ electrode materials was initially charged to 1.25 V from open circuit voltage of ~0.5 V with the 1st cycle charge capacity of 71 mAh g$^{-1}$, indicating a roughly 0.23 Na-ion removal. In the
following 1st cycle discharge process, the MnO$_2$ birnessite electrode displayed a discharge capacity about 144 mAh g$^{-1}$, pointing to 0.47 Na-ion insertion. Figure 4c shows CPs of Na$_{0.27}$MnO$_2$ in the three-electrode half-cell at current densities from 0.6 A g$^{-1}$ to 2 A g$^{-1}$. As current densities increased, discharged capacities decreased from 115 to 61 mAh g$^{-1}$. Moreover, Supplementary Figure 14 shows that the charge and discharge potential differences at the midpoint of the capacity increased from 0.65 V to 0.75 V as current densities increased, suggesting an increasing polarization for Na-ion transport, comparable to the values reported in Zn-MnO$_2$36–38, Na–MnO$_2$39, and Li$_2$Mn$_{2/3}$Nb$_{1/3}$O$_2$F system40, reflecting the intrinsic redox barrier for the MnO$_2$ based electrode systems.

Supplementary Figure 15 shows X-ray photoelectron spectroscopy (XPS) spectra of Na$_{0.27}$MnO$_2$. The pristine state Mn showed a dominant Mn$^{4+}$ state with characteristic Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ features at 654.2 eV and 642.5 eV, and less distinct but discernable Mn$^{3+}$ features at 642.2 eV and 653.3 eV, respectively (Supplementary Fig. 16). The ratio between Mn$^{4+}$ and Mn$^{3+}$ was calculated to be 0.72:0.28. Since the Mn$^{3+}$ resulted from the intercalated Na-ion in interlayers of MnO$_2$, a Mn$^{4+}$/Mn$^{3+}$ ratio of 0.72:0.28 suggested a Na/Mn ratio of 0.28, nearly identical to the ICP-MS result (Na:Mn = 0.27). At charged state (1.25 V) Na$_{0.27}$MnO$_2$ showed a Mn$^{4+}$/Mn$^{3+}$ ratio of 0.97:0.03, and a Mn$^{4+}$/Mn$^{3+}$ ratio of 0.62:0.38 at discharged state (−1.25 V). Although the exact determination of Mn$^{2+}$/Mn$^{4+}$/Mn$^{3+}$ ratio is challenging from the Mn 2p core region due to the multiplet structure and significant overlap between different oxidation states, XPS results confirmed that Na$_{0.27}$MnO$_2$ materials had a Mn$^{4+}$/Mn$^{3+}$ redox couple during insertion and extraction of Na-ions.

We also analyzed the current (i) at different scan rates (v) at a given potential, assuming that the total current (i) at a particular potential contains both capacitive current ($i_1$ = $k_1v$) and diffusion-limited redox current ($i_2$ = $k_2v^{1/2}$).41

$$i = i_1 + i_2 = k_1v + k_2v^{1/2} \text{ or } i/v^{1/2} = k_1v^{1/2} + k_2$$

The values of $k_1$ and $k_2$ and the relative current response from $i_1$ and $i_2$ can be obtained. The CVs marked with capacitive and diffusion-limited redox contributions at scan rates ranging from 5 to 1000 mV s$^{-1}$ can be found and summarized in Supplementary Figs. 17 and 18.

Long-term performance of Na$_{0.27}$MnO$_2$ was tested in symmetric full-cells in a potential window of 2.5 V. Toray paper was used as the current collector without causing gas evolution reactions (Supplementary Fig. 19). Figure 4d and Supplementary Fig. 20 show that voltage-capacity profiles are nearly linear at all the tested current densities, pointing to a single-phase solid solution reaction. Accordingly, electrode capacities were calculated to be 83 mAh g$^{-1}$ to 1000 mAh g$^{-1}$ at corresponding discharge times ranging from 160 s to 4.5 s. Moreover, Na$_{0.27}$MnO$_2$ exhibits an excellent cycle stability up to 5000 cycles without obvious capacity loss, as well as nearly 100% coulombic efficiency and high energy efficiency at various current densities (Fig. 4e). Figure 4f compares the energy and power performance of Na$_{0.27}$MnO$_2$ materials with several aqueous or non-aqueous EES devices, including Panasonic (17500) Li-ion battery42, α-MnO$_2$, δ-MnO$_2$ or amorphous birnessites32,43–45, and tunnel-structured Na$_{0.44}$MnO$_2$ and O3 type Na$_2$MnO$_2$39,46. Notably, energy and power densities of our reported system were obtained after 5000 galvanostatic cycles, higher than those found in commercial products and recent literature. Comparisons between current works with other Mn-based electrode materials in aqueous storage are summarized in Supplementary Table 7.43,46–48.

Proton (H$^+$) insertion has been reported in aqueous EES in mild acidic aqueous electrolytes$^{36,37}$. Current work used a neutral Na$_2$SO$_4$ electrolyte, thus the H$^+$ concentration was very low and H$^+$ intercalation may not contribute to overall storage capacity. In addition, Na$_{0.27}$MnO$_2$ materials showed continuously increasing capacities during the initial cycling especially at the low current densities. The electrochemical impedance spectroscopy measurements (Supplementary Fig. 21) demonstrate decreasing solution resistance during the initial electrochemical cycling, congruent with I-R drop in the discharge curves (Supplementary Fig. 22). It suggested that the increasing capacities in early cycles can be attributed to the slow building-up of a transport before the electrode reached its best electrochemical condition. Similar behaviours were also observed in Na$_2$S, Na$_{0.67}$Ni$_{1/6}$Co$_{1/6}$Mn$_{2/3}$O$_2$, and LiFe$_{0.3}$P$_{0.95}$O$_4$49–51.

**Water co-deintercalation during high potential charging.**

Supplementary Figure 23 shows in situ XRD measurements conducted along with the CV test at a scan rate of 0.75 mV s$^{-1}$, where diffraction peaks at the 2θ angles of ~5.8° and ~29° can be attributed to (001) basal diffraction peak and (020) Bragg diffraction plane and the contour plot peak variation of (001) plane during the charging (black) and discharging (blue) processes.

**Water co-deintercalation during high potential charging.**

Supplementary Figure 23 shows in situ XRD measurements conducted along with the CV test at a scan rate of 0.75 mV s$^{-1}$, where diffraction peaks at the 2θ angles of ~5.8° and ~29° can be attributed to (001) basal diffraction peak and (020) Bragg diffraction plane and the contour plot peak variation of (001) plane during the charging (black) and discharging (blue) processes.
to 7.02 Å) between fully charged and discharged states, more significant than previously reported MnO2 birnessite (1.7%) with a potential window of 1.2 V and a low capacity of 36 mAh g\(^{-1}\). The contour plot in Fig. 5 reflects peak shifts of the (001) basal diffraction peak of Na\(_{0.27}\)MnO2 during charging and discharging process. The observed continuous and reversible peak shifting without a staged structural transformation indicates high structural stability of Na\(_{0.27}\)MnO2 during the charging and discharging processes, which explains the good cycle life of Na\(_{0.27}\)MnO2 materials.

In situ XRD also revealed water trafficking, for the first time, along with Na-ions insertion and extraction during the charging and discharging process. Figure 6 shows that when the potential increased from −1.250 V to −0.106 V, d\(_{001}\) and the corresponding electrochemical current remained relatively constant, suggesting a non-Faradaic capacitive charge storage process (e.g., desorption of Na-ions from electrode surface) without extracting Na-ions from interlayers. When the potential increased from −0.106 V to 0.914 V, d\(_{001}\) increased rapidly from 7.02 Å to 7.33 Å, indicating a large amount of Na-ions were extracted from the interlayers, concurrent with the increasing Faradaic current; as the potential continuously increased from 0.914 V to 1.25 V, d\(_{001}\) decreased from 7.33 Å to 7.30 Å. Interlayer collapse at higher potential is likely attributed to the removal of structural water along with Na-ion extraction, since a mere Na-ion removal alone would only cause an increase in d\(_{001}\). Notably, such compression at high potential only happened in the interlayer distance (along c-direction) because d\(_{020}\) decreased continuously indicating continued oxidation of Mn\(^{3+}\) into Mn\(^{4+}\) when the potential increased from −0.106 V to 1.25 V. Although it is possible that when the potential increased from −0.106 V to 0.914 V the extracted Na-ions would also bring structural water out of the interlayer region, it was obvious that weakened electrostatic interaction caused by the Na-ion removal offsets the water removal effect if any, so that the overall interlayer distance still significantly increases. This means that extracted Na-ions at lower anodic potential range (from −0.106 V to 0.914 V) brought much less (or none) hydrated water molecules out of the interlayer region compared with the ones extracted at higher anodic potential (from 0.914 V to 1.25 V). In other words, hydrated Na-ions required higher overpotential to be removed from interlayer region than less hydrated ones. It is possible that O ions (from water) in the solvation shell of the intercalated Na-ions could interact with Mn ions from Mn–O octahedral layer, especially when there are local defects (e.g., anion defect) and Mn cations are under-coordinated as previously reported interaction between V\(_2\)O\(_5\) and structural water\(^{32}\). Such interaction could increase the energy barrier for Na-ion migration at charging process, and thus a higher overpotential will be needed to extract these hydrated Na-ion from host material. It is also possible that water molecules in the solvation shell of Na-ion could form hydrogen bonding in the interlayer region. This argument is also supported by a recent X-ray and neutron total scattering study of the birnessite materials, where hydrogen bonding among the interlayer water molecule and adjacent Mn–O layer oxygen ion was found to play an important role in maintaining the intermediate and long-range stacking of Mn–O octahedral layer\(^{33}\). Therefore, hydrogen bonding between structural water could also stabilize the Na-ions inside the interlayer region, thus extraction these hydrated Na-ion out of interlayer region (charging) might become more difficult. Likewise, during the reduction process quite symmetric changes of d\(_{001}\) were observed: d\(_{001}\) slightly increased from 7.30 Å to 7.33 Å as the potential decreased from 1.25 V to 0.951 V, and then sharply decreased from 7.33 Å to 7.02 Å as the potential continued to decrease from 0.951 V to −0.682 V. This suggests that inserted Na-ions in the higher cathodic potential range (from 1.25 V to 0.951 V) brought more hydrated Na-ions into the interlayer region compared with ones inserted at lower anodic potentials (from 0.998 V to −0.682 V). Congruent with the observation of the water trafficking during the anodic scan, fully hydrated Na-ions preferred to be inserted into the interlayer region than less hydrated ones during the cathodic scan.

In conventional LIB layered oxide cathodes, a decrease in the c-lattice is widely observed at higher degrees of delithiation, even when there is no phase transformation\(^{34}\). Recent work on a variety of LiNi\(_{1−x−y}\)Co\(_x\)Mn\(_y\)O\(_2\) (NMC) compounds found the
onset of this decrease in the c-lattice when around 50–60% lithium has been removed from the structure with limited dependence on Ni, Co, or Mn content. In those LIB cathodes, strong nickel/cobalt-oxygen covalency is expected to facilitate charge transfer from the O 2p orbitals, decreasing the negative-charge on the oxygen. This effectively weakens electrostatic repulsions between neighboring oxygens across the Li-layer leading to a decrease in the interlayer spacing and thereby a decrease in the c-lattice. Upon reliethiation, the c-lattice expands, and can symmetrically match the collapse observed during delithiation. Density functional theory (DFT) calculations have shown this effect occurs for the LiMnO₂ system and may need to be considered for other Mn(IV)-systems.

We performed XPS measurements for pristine, rinsed, and charged Na₀.₂₇MnO₂ in conjunction with DFT calculations, shown in Fig. 7. In this case, the charged Na₀.₂₇MnO₂ is binder-free, which allowed for increased sensitivity to the Na₀.₂₇MnO₂ compound (Supplementary Fig. 24). When charged to 1.25 V, there is a decrease in the intensity of the Na peak due to the removal of Na-ions from the interlayer (Fig. 7a). The corresponding valence band XPS measurements display only a slight change in the lineshape of the charged electrode compared to the pristine and rinsed samples likely related to the depopulation of states upon the removal of Na-ions. DFT calculations of the total density of states (TDOS) Na₀.₂₇MnO₂ system weighted by the X-ray photoionization cross-section match well with the experimental spectra suggesting these calculations can be used to comment on Mn 3d-O 2p covalency (Fig. 7b). When looking at the weighted O 2p and Mn 3d partial density of states, we find O 2p states contribute at the top of the valence band (0 eV to 2 eV). At 1486 keV, the Mn 3d photoionization cross-section is over 10%, which is inversely correlated to the square of the interlayer distance (r²). Thus, it is evident that structural water co-intercalation with Na-ions plays promotional roles in electrochemical performance.

Different from c-lattice collapse in charged LIB layered oxide, where the irreversible and large lattice collapse (up to 5%) results in the pulverization of electrode material and impairs their full utilization for Li-ion storage, the reversible co-deintercalation of structural water in Na₀.₂₇MnO₂ benefits Na-ion storage. Notably, repetitive insertion and extraction of cations and thus drastic changes of the interlayer distance during prolonged cycling can cause the degradation of the electrode material. Figure 6 showed that as the c-lattice contracted, the b-lattice distance and c-axis continue to increase (d₀₀₁ and d₀₂₀ decreased). This indicates that the co-deintercalation of water molecules along with Na-ions stabilizes the layered structure against further expansion of the interlayer distance at higher voltages while sustaining an intensive redox process. To the best of our knowledge, this new safety mechanism has never been reported in aqueous energy storage. Notably, previous investigations of intercalation cations (e.g., Na⁺ and Mg²⁺) in aprotic electrolytes in layered materials have reported a similar water-assisted cation insertion, where insertion kinetics can be greatly improved since a water solvation shell partially shields the charge of cations within the cation/water co-intercalation compound.
The disordered structure widens the voltage window. Although MnO₂ and Na₀.₂₇MnO₂ materials showed a 2.5 V stable voltage window for aqueous Na-ion storage (Supplementary Figs. 10, 28), the mechanisms underlying their high resistance toward HER and OER were completely different. Figure 8a shows that O-K sXAS spectra of Na₀.₂₇MnO₂ and Mn₂O₄ have similar sharp features below 534 eV from the hybridization between the O 2p band and Mn 3d states. However, only the Mn₂O₄ material showed distinct fingerprint water-features at the 535 and 537 eV, indicating the formation of a highly ordered hydroxylated interphase on the surface as we reported previously. To understand role of disordered structure in mitigating the water decomposition, we synthesized ordered Na₀.₁₉MnO₂ birnessite via thermal decomposition of NaMnO₂ materials at 800 °C and conducted the Tafel analysis for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on ordered Na₀.₁₉MnO₂, ordered Na₀.₁₉MnO₂ and commercial MnO₂ materials in a 0.1 M Na₂SO₄ electrolyte. XRD and X-ray PDF were conducted to compare the structural difference of three materials (Supplementary Fig. 29–30, Supplementary Tables 8–10), showing that disordered Na₀.₂₇MnO₂ had a triclinic (C-1) birnessite structure. Though disordered Na₀.₂₇MnO₂ and ordered Na₀.₁₉MnO₂ both show the birnessite layered structure, Na₀.₂₇MnO₂ has a smaller crystalline size and a shorter coherence length (Supplementary Fig. 29b) compared to Na₀.₁₉MnO₂. On the other hand, commercial MnO₂ showed a highly crystalline and ordered β-MnO₂ phase. Supplementary Figure 30 demonstrated the difference of local structures between disordered Na₀.₂₇MnO₂ and ordered Na₀.₁₉MnO₂ birnessite and commercial MnO₂, where the former showed a more disordered lattice structure.

Figure 8b shows the CVs of disordered Na₀.₂₇MnO₂, ordered Na₀.₁₉MnO₂ and commercial β-MnO₂ and a scan rate of 5 mV s⁻¹ (CVs tested at other scan rates are shown in Supplementary Fig. 31). Though all three materials were tested in a 2.5 V potential window, ordered Na₀.₁₉MnO₂ and commercial β-MnO₂ materials displayed obvious gas evolution features at lower and higher potential ranges. The Tafel analysis showed that disordered Na₀.₂₇MnO₂ displayed a much weaker HER current at potentials up to −1.25 V (overpotential of 0.63 V towards HER) and higher Tafel slopes at various scan rates (Fig. 8c, Supplementary Fig. 31), suggesting sluggish HER kinetics. It is notable that three materials were inactive towards OER even at a potential of 1.25 V (overpotential of 0.63 V towards OER), however, only disordered Na₀.₂₇MnO₂ has high overpotential for both HER and OER, suggesting that the disordered nature leads to high resistance to the gas evolution reactions, thus a kinetically stable potential window of 2.5 V. Although ordered Na₀.₁₉MnO₂ and commercial β-MnO₂ materials showed a great capacity enhancement at a lower potential range close to −1.25 V, probably benefiting from hydrogen insertion, disordered Na₀.₂₇MnO₂ still showed much superior capacities at all tested scan rates. The inferior capacities from ordered Na₀.₁₉MnO₂ and commercial β-MnO₂ might be due to the parasitic gas evolution reactions especially HER that degraded the electrode and causes capacity loss at prolonged cycles. Previous DFT calculations demonstrated that the thermodynamically unstable edge sites of the layered transition-metal dichalcogenide nanocrystals were catalytically active for HER. Previous studies showed that HER current was proportional to the length of edges rather than the coverage area of catalysts, but these catalytically active sites were located on the thermodynamically unstable planes (edges of the layers), which are difficult to be exposed preferentially. In this study, disordered MnO₂ layered structures have highly exposed (001) planes that are thermodynamically stable plane but...
catalytically inert, while the ordered Na0.13MnO2 birnessite possesses a large grain size with a long coherent length, therefore the edges of the layers that are more active toward gas evolution are likely exposed.

Discussion
In this work, we have integrated detailed structural analysis with electrochemical measurements to understand the observed high capacity and good structural stability found in the disordered and Na-rich Na0.27MnO2 birnessite layered materials. In situ XRD has revealed the role of water co-intercalation in mitigating interlayer expansion during the high potential charging. Investigations of solvent co-intercalation properties in other layered materials will be useful in designing high capacity rechargeable aqueous batteries. In addition to water trafficking, our results also manifest the promotional effects of the disordered structure on aqueous Na-ion storage: disordered Na0.27MnO2 structure allows continuous and smooth structural evolution during the charging and discharging processes without phase transitions and possesses highly exposed (001) planes with low density of active edge sites for gas evolution reactions, and thus yields a large aqueous Na-ion storage capacity and long cycling life. The reported results have provided the insight underlying the promotional roles of structural water and disordered electrode structure for aqueous Na-ion storage. Especially, the structural water trafficking at high potential charging discovered here may provide a fundamental leap forward in current understanding how water molecules stabilize the electrode structure during redox processes.

Methods

Material synthesis. Mn3O4 nanoparticles were first synthesized via a solution phase method. In a typical synthesis, MnCl2·4H2O (0.7 g, Alfa Aesar, 99% metals basis) was fully dissolved by deionized water (140 mL, 18.2 MΩ; Millipore, Inc.) in a 500 mL flask under vigorous stirring at room temperature. The aqueous solution of NaOH (Alfa Aesar, 99.98% metals basis) with a concentration of 0.123 g mL−1 was injected at a rate of 0.167 mL min−1 for 30 min using an automatic syringe (HSV Inc.). After injection, the mixture continuously reacted for another 30 min till dark brown precipitate was formed. The resulting product was separated by centrifuging and then washed by deionized water and ethanol consecutively. The obtained products (MnO2 nanoparticles) were finally vacuum-dried. In the synthesis of sodium-manganese oxides, NaOH (Alfa Aesar, 99.99% metals basis) and Mn3O4 nanoparticles were ground using a mortar and pestle with the molar ratios of 0.5, 1, 1.5, 2, and 4, respectively. The resulting mixture of NaOH and Mn3O4 was heated in a tube furnace (Thermal Scientific, Inc.) in open air at 270 °C for 6 h. The obtained solids were thoroughly washed with deionized water to remove the possible NaOH residual and vacuum-dried for overnight. Ordered Na0.27MnO2 birnessite was synthesized via thermal decomposition of NaMnO2 at 800 °C for 12 h, and then washed by deionized water and ethanol, and dried in vacuum. The Mn3O4 birnessite with low sodium concentration Na0.13MnO2 was synthesized via a wet chemistry method. Aqueous MnCl2 (5 mg mL−1) precursor was injected into 20 mL NaOH solution with a concentration of 3.7 mg mL−1 at the rate of 0.167 mL min−1 for 1 h, and the obtained product was vacuum-dried after washed by deionized water and ethanol. And then the solids were annealed in air at 270 °C for 6 h.

Material characterizations. Inductively coupled plasma mass spectrometry (ICP-MS) was used to identify the elemental ratios of samples. Sample aliquots were digested in mixed concentrated HCl-HNO3 solution and then transferred into HNO3 solution for dilution in 2% HNO3 and introduction into the Nu instruments AttoM high resolution ICP-MS. Standards of known concentrations were used to correct for drift and within-instrument elemental fractionation. Triplicate runs of each sample allowed for the determination of the precision of each sample. Energy dispersive X-ray spectroscopy (EDXS) was conducted for elemental analysis by an Amray 3300FE field emission SEM with a PGT Imix-PC microanalysis system at the University of New Hampshire. Thermodiagrmatic analysis (TGA) was measured on a Mettler-Toledo instrument at the University of New Hampshire. Regular transmission electron microscopy (TEM) images were collected on Zeiss/LEO 922 Omega TEM at the University of New Hampshire. X-ray photoelectron spectroscopy (XPS) was measured using Thermo Scientific K Alpha instrument at Harvard University.

Half-cell test. Cyclic voltammetry (CV) measurements of sodium-manganese oxide were conducted using a three-electrode half-cell powered by CHI 660d single channel electrochemical workstation. The three-electrode system contained a glassy carbon rotating disc electrode (Pine Instrument) as the working electrode, platinated silver-silver chloride (Ag/AgCl) electrode as reference electrodes, and the ink material was prepared by grinding mixture of 7 mg sodium-manganese oxide and 3 mg carbon black (Alfa Aesar, > 99.9%). The resulting mixture was mixed with deionized water to make an ink solution of 0.5 mg mL−1. The resulting solution was subsequently sonicated until the materials were homogeneously dispersed. In a typical half-cell measurement, 10 μL suspension containing 3.5 μg sodium-manganese oxide and 1.5 μg carbon black was drop-cast onto the glassy carbon disc electrode (0.5 cm in diameter) and vacuum-dried. The CV measurements of electrodes were conducted in a 250 mL flat-bottom flask containing 100 mL argon-purged Na2SO4 aqueous electrolyte (0.1 M) at a rotating rate of 500 rpm. The CV data were obtained within an applied potential range from −1.25 V to 1.25 V (vs Ag/AgCl) for three cycles, and the third CV cycle was used for the calculation of storage capacity. The CP measurements of Na0.27MnO2 in a three-electrode half-cell was also conducted at the current densities of 0.3 A g−1 to 2.0 A g−1 with potential from −0.75 V to 1.25 V (vs Ag/AgCl). Na0.27MnO2 was charged to 1.25 V (vs Ag/AgCl) from open circuit voltage in 0.5 M Na2SO4 solution with a scan rate of 1 mV s−1 by using CV in half-cell, and then discharged to −1.25 V. The charged and discharged samples were washed and collected for ex-situ XPS measurements.

Diffusivity measurements. The diffusivity measurements were tested in a typical half-cell setting as described above, except 40 μg active materials sodium-manganese oxides was loaded on working electrode and 0.25 M Na2SO4 was used as the electrolyte. A constant negative current pulse of 1 μA was first applied to the working electrode and working electrode was held for 15 s to discharge the electrode from the open circuit potential. After that, the working electrode was relaxed and potential changes were collected for 1000 s.

Potential of zero charge. The potential of zero charge (pzc) of Na0.27MnO2 materials was estimated using an open circuit voltage (OCV) measurement using a three-electrode cell in 0.1 M Na2SO4 electrolyte. Supplementary Figure 32 shows that the initial potential of the electrode was 0.47 V (vs Ag/AgCl), slowly increased to a rather stable value of 0.50 V after 2 h without an external field. In this context, pzc of Na0.27MnO2 materials should be around 0.5 V vs Ag/AgCl. As a higher (or lower) external potential is applied, the materials will be oxidized (or reduced) by Na-ion extraction (or insertion).

Full-cell test. Symmetric two-electrode full-cells with Na0.27MnO2 electrodes were assembled and measured to characterize the energy/power performance and the long cycle stability as well. Electrodes were made by drop casting the slurry containing ~5 mg Na0.27MnO2 and 1.25 mg carbon black as a mass ratio of 4:1 on Toray carbon paper (E-Tek, Inc., 1.5 cm in diameter). The resulting electrodes were weighed with an accurate mass loading of active material after vacuum-dried overnight. Two symmetric electrodes were separated by cellulose-based filter paper (Whatman), and 150 μL Na2SO4 aqueous solution (1 M) was used as the electrolyte. The cell stack of electrodes and separator were tightened by stainless plate and compression spring to ensure good electrical contact and then assembled in the split-button cells (model: EQ-STC, MTI Corp.). Galvanostatic charge and discharge measurements of symmetric full-cells were conducted on the battery analyzer (model: B-TG, Arbin Instruments) within 2.5 V potential window for 5000 cycles at the constant current densities of 1, 2, 5, and 10 A g−1. All the electrochemical calculations are provided in the supporting information. Toray paper was used as current collect for symmetric full-cell measurements and stable in 2.5 V without obvious generation of hydrogen (Supplementary Fig. 17).

Electrochemical impedance measurements. Electrochemical impedance spectroscopy (EIS) measurements were conducted after each charge and discharge cycle in full cell at the open circuit potential with a perturbation of 5 mV and frequency range from 0.1 to 100 kHz, and the Nyquist plots were collected.

X-ray and neutron scattering characterizations. X-ray diffraction measurements were conducted at Beamline 17-RM-B at the Advanced Photon Source at the Argonne National Laboratory with a wavelength of λ = 0.72798 Å. In situ XRD of electrochemical half-cell measurements were conducted in a home-made cell consisted of thin carbon paper (E-Tek, Inc.) as working electrode, platinum wire and micro Ag/AgCl electrode as counter and reference electrodes, respectively. The Na2SO4 aqueous electrolyte (1 M) was used as the electrolyte. The suspension of a mixture of Na0.27MnO2 and carbon black was drop-cast on the thin carbon paper and dried naturally in air. The cellulose-based filter paper was used as a separator. The cell was then assembled for X-ray measurements. In situ XRD tests were performed during CV scans from −1.25 V to 1.25 V (vs Ag/AgCl) at the scan rates of 0.75 mV s−1. GIXAS-II software was used to analyze the structural changes during the charge and discharge processes. The X-ray total scattering experiment was conducted at Beamline 17-BM-B using a wavelength of 0.2418 Å. The total neutron scattering experiment was conducted at the Nanoscale-Ordered Materials Diffractometer (NOMAD) beamline at Spallation Neutron Source at Oak
Ridge National Laboratory. The atom Pair Distribution Function (PDF) analysis was conducted using PDFgui software.

Theoretical methods. Density functional theory (DFT) calculations were performed using the WIEN2k software package, which uses full potential and linearized augmented plane waves with local orbitals (LAPW + lo) to self consistently solve the Kohn-Sham equations\(^6\). The generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE) was used for the exchange and correlation energies\(^6\). The plane-wave cutoff parameters \(R_{\text{MT}}\), \(K_{\text{max}}\), and \(G_{\text{max}}\) were selected as 6.5 and 12, respectively, and the cutoff energy was \(-6.0\) Ry. The k-points of the cell was \((1 \times 12 \times 4)\) and for the \(\text{NaMnO}_2\cdot\text{H}_2\text{O}\).

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files.

Received: 12 February 2018; Accepted: 12 October 2019; Published online: 31 October 2019

References

1. Yabuuchi, N. et al. P2-type \(\text{Na}_2[\text{Fe}_{17}\text{Mn}_{12}\text{O}_{42}]\) made from earth-abundant elements for rechargeable Na batteries. Nat. Mater. 11, 512–517 (2012).
2. Kim, H. et al. Aqueous rechargeable Li and Na ion batteries. Chem. Rev. 114, 11788–11827 (2014).
3. Wessells, C. D., Huggins, R. A. & Cui, Y. Copper hexacyanoferrate battery electrodes with long cycle life and high power. Nat. Commun. 2, 5 (2011).
4. Kataoka, K., Tsuchiya, H., Ong, S. P. & Ceder, G. A comparison of destabilization points of the cell was \(1\) \(\text{Na}_{10}\).
5. Kubota, K., Yabuuchi, N., Yoshida, H., Dahbi, M. & Komaba, S. Layered \(\text{Mn}_{12}\) oxide cathodes with long cycle life aqueous electrolyte battery for grid-scale energy storage. J. Electrochem. Soc. 159, A614–A622 (2004).
6. Song, J. et al. Removal of interstitial \(\text{H}_2\text{O}\) in hexacyanometallates for a pseudocapacitive cathode. J. Electrochem. Soc. 155, 14557–15758 (2012).
7. Li, X. et al. Jahn-teller assisted \(\text{Na}\) diffusion for high performance \(\text{Na}\) ion batteries. J. Phy. Chem. C. 116, 15578–15580 (2012).
8. Chen, Z. et al. Electrochemical performance of \(\text{Mn}_3\text{O}_4\) nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors. J. Phys. Chem. C. 113, 14020–14027 (2009).
9. Zhu, H. T. et al. Birnessite-type \(\text{MnO}_2\) nanowalls and their magnetic properties. J. Phys. Chem. C. 112, 17089–17094 (2008).
10. Cai, J., Liu, J. & Suib, S. L. Preparative parameters and framework dopant effects in the synthesis of layer-structure birnessite by air oxidation. Chem. Mater. 14, 2071–2077 (2002).
11. Brousse, T., Toupin, M. & Belanger, D. A hybrid activated carbon-manganese dioxide capacitor using a mild aqueous electrolyte. J. Electrochem. Soc. 151, A614–A622 (2004).
12. Atouh, L. et al. Variation of the \(\text{MnO}_2\) birnessite structure upon charge/discharge in an electrochemical supercapacitor electrode in aqueous \(\text{Na}_2\text{S}_4\text{O}_7\) electrolyte. J. Phys. Chem. C. 112, 7270–7277 (2008).
13. Liu, Y. et al. High-performance aqueous sodium-ion batteries with \(\text{K}_2\text{Mn}_3\text{O}_8\) cathode and their sodium storage mechanism. Nano Energy 5, 97–104 (2014).
14. Luo, L. M. et al. “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. Science 350, 938–943 (2015).
15. Xu, K. & Wang, C. S. Widening voltage windows. Nat. Energy 1, 16161 (2016).
16. Shao, Y. et al. Hydrotalcite-based electrolytes for high-energy-density aqueous batteries. Nat. Energy 1, 16129 (2016).
17. Peng, L. et al. Ultrathin two-dimensional \(\text{MnO}_2\)-graphene hybrid nanostructures for high-performance, flexible planar supercapacitors. Nano Lett. 13, 2151–2157 (2013).
18. Yeager, M. P. et al. Pseudocapacitive hausmannite nanoparticles with (101) facets: synthesis, characterization, and charge-transfer mechanism. ChemSusChem 6, 1983–1992 (2013).
19. Chen, R., Zavalij, P. & Whittingham, S. M. Hydrothermal synthesis and characterization of \(\text{K}_3\text{MnO}_2\cdot\text{H}_2\text{O}\). Chem. Mater. 8, 1275–1280 (1996).
20. Park, Y. J. & Doeff, M. A. Synthesis and electrochemical characterization of \(\text{M}_2\text{Mn}_3\text{O}_8\) (\(\text{M} = \text{Ca}, \text{Cu}\)) compounds and derivatives. Solid State Ion. 177, 993–990 (2006).
21. Pan, H. et al. Reversible aqueous zinc/manganese oxide energy storage from conversion reactions. Nat. Energy 1, 16039 (2016).
22. Sun, W. et al. \(\text{Zn}/\text{MnO}_2\) battery chemistry with \(\text{H}_2\) and \(\text{Zn}^{2+}\) coinjection. J. Am. Chem. Soc. 139, 9775–9778 (2017).
23. Huang, J. et al. Polyaniline-intercalated manganese dioxide nanolayers as a high-performance cathode material for an aqueous zinc-ion battery. Nat. Commun. 9, 2906 (2018).
24. Li, Z., Young, D., Xiang, K., Carter, W. C. & Chiang, Y.-M. Towards high power high energy aqueous sodium-ion batteries: the \(\text{Ti}_3\text{P}_4\text{H}_9\)/\(\text{Na}_{10}\text{MnO}_2\) system. Adv. Mater. 3, 290–294 (2013).
25. Lee, J. et al. Reversible \(\text{Mn}_2\text{O}_4\) and \(\text{Mn}_3\text{O}_4\) redox in lithium-excess cathode materials. Nature 556, 185–190 (2018).
26. Liu, T. C., Pell, W. G., Conway, B. E. & Roberson, S. L. Behavior of molybdenum nitrates as materials for electrochemical capacitors: comparison with ruthenium oxide. J. Electrochem. Soc. 145, 1882–1888 (1998).
27. Nagasubramanian, G., Jungst, R. G. & Doughty, D. H. Impedance, power, energy, and pulse performance characteristics of small commercial Li-ion cells. J. Power Sources 83, 193–203 (1999).
28. Wu, Z.-S. et al. High-energy \(\text{MnO}_2\) nanowire/graphene and graphene asymmetric electrochemical capacitors. ACS Nano 4, 5835–5842 (2010).
29. He, Y. et al. Freestanding three-dimensional graphene/MnO\(_2\) composite networks as ultralight and flexible supercapacitor electrodes. ACS Nano 7, 174–182 (2013).
30. Zhang, D., Zhang, Y., Luo, Y. & Chu, P. K. Highly porous honeycomb manganese oxide/carbon fibers core-shell nanocables for flexible supercapacitors. Nano Energy 13, 47–57 (2015).
31. Hou, Z., Li, X., Liang, J., Zhu, Y. & Qian, Y. An aqueous rechargeable sodium ion battery based on a \(\text{Na}_2\text{MnO}_2\cdot\text{Na}_2\text{Ti}_3\text{P}_4\text{O}_{12}\) hybrid system for stationary energy storage. J. Mater. Chem. A 3, 1400–1404 (2015).
32. Brousse, T. et al. Long-term cycling behavior of asymmetric activated carbon/\(\text{MnO}_2\) aqueous electrochemical supercapacitor. J. Power Sources 173, 633–641 (2007).
33. Shan, X. et al. Bivalence \(\text{MnO}_2\) with hydroxylated interphase for high-performance aqueous sodium-ion storage. Nat. Commun. 7, 8 (2016).
34. Yu, X. & Manthiram, A. Performance enhancement and mechanistic studies of room-temperature sodium–sulfur batteries with a carbon-coated functional nafion separator and a Na2S/activated carbon nanofiber cathode. Chem. Mater. 28, 896–905 (2016).
35. Zhang, J., Yan, P., Kan, W. H., Wang, C. & Manthiram, A. A spinel-integrated P2-type layered composite: high-rate cathode for sodium-ion batteries. J. Electrochem. Soc. 163, A584–A591 (2016).
51. Kang, B. & Ceder, G. Battery materials for ultrast fast charging and discharging. Nature 458, 190–193 (2009).

52. Chatfield, D. S. et al. Structural water engaged disordered vanadium oxide nanosheets for high capacity aqueous potassium-ion storage. Nat. Commun. 8, 15520 (2017).

53. Liu, J. et al. Large-scale synthesis and comprehensive structure study of delta- MoO2. Inorg. Chem. 57, 6873–6882 (2018).

54. Radis, M. D. et al. Narrowing the gap between theoretical and practical capacities in Li-ion layered oxide cathode materials. Adv. Energy Mater. 7, 1602888 (2017).

55. Li, W., Asl, H. Y., Xie, Q. & Manthiram, A. Collapse of LiNi0.8Co0.15Al0.05O2 lattice at deep charge irrespective of nickel content in lithium-ion batteries. J. Am. Chem. Soc. 141, 5097–5101 (2019).

56. Kondrakov, A. O. et al. Charge-transfer-induced lattice collapse in Ni-Rich NCM cathode materials during delithiation. J. Phys. Chem. C. 121, 24381–24388 (2017).

57. Grenier, A. et al. Reaction heterogeneity in LiNi0.8Co0.15Al0.05O2 induced by surface layer. Chem. Mater. 29, 7345–7352 (2017).

58. Scofield J. H. Theoretical photoionization cross sections from 1 to 1500 keV. (Lawrence Livermore Laboratory, U.S. Atomic Energy Commission, 1973).

59. Spahr, M. E., Novák, P., Haas, O. & Nesper, R. Electrochemical insertion of lithium, sodium, and magnesium in molybdenum(VI) oxide. J. Power Sources 54, 346–351 (1995).

60. Levi, E., Gofer, Y. & Aurbach, D. On the way to rechargeable Mg batteries: the challenge of new cathode materials. Chem. Mater. 22, 860–868 (2010).

61. Sai Gautam, G., Canepa, P., Richards, W. D., Malik, R. & Ceder, G. Role of structural H2O in intercalation electrodes: the case of Mg in nanocrystalline Xerogel-V2O5. Nano Lett. 16, 2426–2431 (2016).

62. Lim, S. Y. et al. Lattice water for the enhanced performance of amorphous iron phosphate in sodium-ion batteries. ACS Energy Lett. 2, 998–1004 (2017).

63. Nambu, K. W. et al. Critical role of crystal water for a layered cathode material in sodium ion batteries. Chem. Mater. 27, 3721–3725 (2015).

64. Hinnemann, B. et al. Biomimetic hydrogen evolution: MoS2 Nanoparticles as catalyst for hydrogen evolution. J. Am. Chem. Soc. 127, 5308–5309 (2005).

65. Jaramillo, T. F. et al. Identification of active edge sites for electrochemical H2 evolution from MoS2 nanocatalysts. Science 317, 100–102 (2007).

66. Kong, D. et al. Synthesis of MoS2 and MoSe2 films with vertically aligned layers. Nano Lett. 13, 1341–1347 (2013).

67. Kibsgaard, J., Chen, Z., Reinecke, B. N. & Jaramillo, T. F. Engineering the surface structure of MoS2 to preferentially expose active edge sites for electrocatalysis. Nat. Mater. 11, 963 (2012).

Acknowledgements

This work was supported by the US Department of Energy (DOE), Office of Science, Basic Energy Sciences under Award # DE-SC0010286 (X.T., X.S., F.G., D.C.). The research at Binghamton University is partially supported by NSF DMREF-1627583. This research used Beamline 17BM-B of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The neutron scattering experiments were carried out at the Spallation Neutron Source, which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy, under Contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory.

Author contributions

All authors contributed to the preparation of the manuscript. X.S. contributed to the material synthesis and characterizations, electrochemical experimental measurements and analysis, X-ray analysis. F.G., X.S., and D.C. contributed to neutron PDF analysis. X.S. and W.X. contributed to X-ray measurement. Z.L.H., S.A.R., and L.F.J.P. contributed to XPS and DFT calculations. J.W. and W.Y. contributed to XAS measurement and analysis. K.P., J.N., and M.F. contributed to the neutron measurements. X.S. and X.T. wrote the manuscript. X.T. contributed to the design of the experiments.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41467-019-12939-3.

Correspondence and requests for materials should be addressed to X.T.

Peer review information Nature Communications thanks Jacob Olchowka and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019