Sodium-Ion Batteries



# Manganese-Based Na-Rich Materials Boost Anionic Redox in High-Performance Layered Cathodes for Sodium-Ion Batteries

Xiaoyu Zhang,\* Yu Qiao, Shaohua Guo,\* Kezhu Jiang, Sheng Xu, Hang Xu, Peng Wang, Ping He, and Haoshen Zhou\*

To improve the energy and power density of Na-ion batteries, an increasing number of researchers have focused their attention on activation of the anionic redox process. Although several materials have been proposed, few studies have focused on the Na-rich materials compared with Li-rich materials. A key aspect is sufficient utilization of anionic species. Herein, a comprehensive study of Mn-based Na1,2Mn0,4Ir0,4O2 (NMI) O3-type Na-rich materials is presented, which involves both cationic and anionic contributions during the redox process. The single-cation redox step relies on the Mn<sup>3+</sup>/Mn<sup>4+</sup>, whereas Ir atoms build a strong covalent bond with O and effectively suppress the O<sub>2</sub> release. In situ Raman, ex situ X-ray photoelectron spectroscopy, and soft-X-ray absorption spectroscopy are employed to unequivocally confirm the reversibility of  $O_2^{2-}$  species formation and suggest a high degree of anionic reaction in this NMI Na-rich material. In operando X-ray diffraction study discloses the asymmetric structure evolution between the initial and subsequent cycles, which also explains the effect of the charge compensation mechanism on the electrochemical performance. The research provides a novel insight on Na-rich materials and a new perspective in materials design towards future applications.

The pursuit of clean energy has been a broadly discussed topic during the past two decades as environmental issues become increasingly severe. Due to the rapidly developing energy and energy storage industries, multiple choices have been proposed to displace conventional energy resources. Li-ion batteries, which transform chemical energy into electric energy, are one

Dr. X. Zhang, Prof. S. Guo, K. Jiang, S. Xu, H. Xu, Prof. P. Wang,
Prof. P. He, Prof. H. Zhou
Center of Energy Storage Materials & Technology
College of Engineering and Applied Sciences
National Laboratory of Solid State Microstructures
Collaborative Innovation Center of Advanced Microstructures
Nanjing University
Nanjing 210093, China
E-mail: xy.zhang@nju.edu.cn; shguo@nju.edu.cn; hszhou@nju.edu.cn
Dr. Y. Qiao, Prof. H. Zhou
Energy Technology Research Institute
National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba 305-8565, Japan
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201807770.

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of the most attractive inventions because they have dramatically improved our daily lives by enabling portable electronics, the onset of electronic mobility and electrical vehicles.<sup>[1]</sup> With the development of materials science, anionic redox chemistry, typically O redox, has enabled more energy storage than the traditional electrochemical reactions, in which the energy and power density are solely determined by the cation redox reaction of transition metals.<sup>[2]</sup> On the other hand, the rapid growth of lithium consumption leads to continuously increasing demand for lithium. Considering the uneven distribution of lithium resources, the inherent drawbacks of lithium supply and demand are difficult to overcome.<sup>[3]</sup> Therefore, an alternative to lithium must be considered, especially for large-scale energy storage applications in the foreseeable future.

The Na-ion battery, which has a reaction pattern comparable with that of the Li-ion battery, is one of the promising alternatives

because of its low cost and the abundance of sodium resources.<sup>[4]</sup> Currently, the study of Na-ion batteries is focused on improving their energy density. Considering the successful study of Lirich materials, one of the possible solutions to improve the capacity of Na-ion batteries is to develop Na-rich materials. It is very important to involve reversible O redox and expand the material series from the material design point of view.

Recent research disclosed, the increasing of the Li(Na) content within layered structure materials can effectively influence the local atom coordination around oxygen atoms which could improve O redox upon cycling and lead to a higher capacity.<sup>[5]</sup> As demonstrated by Tarascon and Ceder et al., increasing the Li(Na) ratio can shift the O 2p nonbonding band gradually up near the Fermi level. This labile nonbonding O offers an extra way for electrons to move away, hence increasing the capacity by triggering an extra redox process.<sup>[2e,5c,6]</sup> This explanation has been successfully applied to Li<sub>2</sub>MnO<sub>3</sub> Li-rich materials<sup>[7]</sup> and is widely agreed upon. Benefitting from the established Li<sub>2</sub>MnO<sub>3</sub> Li-rich prototype, Li-rich material development has highly improved during the past decades, achieving additional capacity.<sup>[8]</sup> For the counterpart Na-ion battery design, although anionic redox was recently realized in the Mn-based







**Figure 1.** a,b) Schematic illustration of the DOS for chosen potential doping species (a) and Ir-doped  $Na_{1.2}Mn_{0.4}Ir_{0.4}O_2$  (b). The O-2p band and Mn 3d band are depicted in red and blue, respectively. The Cd Ru and Ir doped Mn-based Na-rich system has a tendency for increasing O redox improvement as the Mn 3d band increases from the deep part, which refers to a suppression of O<sub>2</sub> release.

Na-deficient P-type layered structure materials,<sup>[9]</sup> Na-rich materials with both anionic and cationic redox reactions have only been found with Ru and Ir based O3-type layered structure materials.<sup>[10]</sup> Mn-based Na-rich materials, to the best of our knowledge, have not been reported until now. Considering the inherent advantage of Na-ion batteries with low cost, developing a suitable prototype of the Mn-based Na-rich materials is imperative for potential improvement.

Although O redox is anticipated, the established of TM-O covalence bond is weak when only a 3d transition metal is involved, which could lead to  $O_2$  release in the high voltage regions. Experimental and theoretical studies revealed that 4d and 5d transition metals effectively reduced the possibility of  $O_2$  release via the formation of the strong covalent TM-O bond.<sup>[2d,10a,11]</sup> All of these factors should be seriously considered in material design for the practical use.

Herein, the Mn-based Na-rich material Na<sub>1,2</sub>Mn<sub>0,4</sub>Ir<sub>0,4</sub>O<sub>2</sub>, which exhibits additional capacity, is reported and relies on both cationic and anionic redox processes upon cycling. Density functional theory (DFT) calculations were performed to confirm the advantage of the utilization of Ir doping, and the calculations also explicitly disclosed the potential O redox. The in operando Raman and X-ray diffraction (XRD) techniques were employed as the implements to monitor structure evolution. The peroxorelated O-O bonding was unambiguously observed, which has good reversibility during electrochemical cycling and was further confirmed by X-ray photoelectron spectroscopy (XPS) tests. No obvious O2 release was detected from the in situ gas chromatography-mass spectrometry (GC-MS) measurement. Moreover, the significant structure distortion upon cycling would also lead to the partial redox reaction of Mn, making more O involved in the electrochemical process. Our research proposes a novel perspective on anionic redox Na-rich batteries that is imperative for advanced energy storage as well as the improvement of material design.

To confirm a suitable doping element for Mn-based Na-rich materials, DFT calculations were performed for several alternative doping species according to previous research on other noblemetal-based Na-rich materials.<sup>[10d,12]</sup> A schematic of the DOS results is displayed in Figure 1a. As shown in Figure 1a, the calculation clearly sketched all of the doped (Cd, Ru, and Ir) Mnbased Na-rich materials and showed that the O 2p band was the top valance band. This result indicates that O could be successfully involved in the oxidation process. The difference between the doped elements was the O involvement mode. For the Cddoped system, the Mn 3d band was deep in the band structure, which referred to the formation of O<sub>2</sub> upon cycling and led to an irreversible redox process with poor anionic utilization.<sup>[2a,e]</sup> However, for the Ir-doped case (see Figure 1b), the Mn 3d band was embedded within the O 2p band with increasing energy levels, which reduced the possibility of O<sub>2</sub> evolution, leading to an improvement in the O redox involvement. This result could be ascribed to the strong metallic character of Cd relative to that of Ir. As reported in previous research, the high covalence of the 5d TM-O band would have a tendency to suppress O<sub>2</sub> release.<sup>[2a,6,10a,13]</sup> To obtain further information, a comparison of the reaction energy for O2 release was performed for the Ir, Ru, and Cd surfaces. The results showed that Ir has the lowest adsorption energy corresponding to the most favorable oxygen absorption (see Figure S1 in the Supporting Information). In addition, the large hybridization of the Ir 5d band with O 2p as well as an increasing in the Mn 3d band would also reduce the possibility of O<sub>2</sub> release. Therefore, the high covalence of the 5d TM-O band could be considered for the suppression of O<sub>2</sub> release (detailed calculation can be found in Figure S2 in the Supporting Information). Therefore, Ir was chosen as the doping element.







**Figure 2.** Structure characterization of  $Na_{1.2}Mn_{0.4}Ir_{0.4}O_2$  (NMI). a) XRD pattern and Rietveld refinement of the as-synthesized NMI sample with experimental data in black dots, calculated data in red line, difference curve in blue, and standard Bragg diffraction peaks in pink vertical bars. b) EDS mappings of different element distributions; c) nanobeam diffraction patterns of typical O3 phase; d) corresponding HAADF image of a single typical  $Na_{1.2}Mn_{0.4}Ir_{0.4}O_2$  particle viewed on the c axis. Scale bar, 5 nm.

The frame of our Na-rich material contains 0.2 mol excess Na in the transition metal layers with the chemical formula Na<sub>1.2</sub>Mn<sub>0.4</sub>Ir<sub>0.4</sub>O<sub>2</sub> (NMI). The as prepared Na-rich compound was first characterized by XRD followed by Rietveld refinement to confirm its crystal structure. The results are shown in Figure 2a, and the NMI structure can be assigned as the O3 phase with the space group R  $\overline{3}$  m in which sodium ions occupy the octahedral (O) site according to the classification by Delmas et al.<sup>[14]</sup> The lattice parameters were a = b = 3.02429(7) Å and c = 16.39287(6) Å according to the Generalized Structure and Analysis Software (GSAS) refinement<sup>[15]</sup> (see Table S1 in the Supporting Information). It is well accepted that Li-rich anionic redox materials could be viewed as a biphase compound described as xLiMO2 · (1-x)Li[Li1/3M2/3]O2. The shortrange ordered Li<sub>2</sub>MO<sub>3</sub>, which accounts for the anionic redox process, has a remarkable diffraction peak at approximately 20°.<sup>[8a,16]</sup> However, as shown in Figure 2a, the XRD patterns did not exhibit obvious impurity diffraction lines or any shortrange ordered superstructure patterns, which indicates that our Na-rich compound has a well-arranged long-range ordering in contrast to the Li-rich compounds. In addition, the diffraction peaks did not show pronounced asymmetric broadening which means that the large stacking faults found in the Ir based Na-rich Na<sub>2</sub>IrO<sub>3</sub> did not show up in our pristine materials.<sup>[10a]</sup> Hence, the crystal structure of Na<sub>1.2</sub>Mn<sub>0.4</sub>Ir<sub>0.4</sub>O<sub>2</sub> can be depicted simply as a hexagonal O3 phase, where all the cations occupied the octahedral sites. The excess Na atoms are in the transition metal layers and are arranged along with the Ir and Mn atoms. (see the insertion of Figure 2a). The atom positions were also obtained from the GSAS refinement to describe the crystal structure in detail (see Table S2 in the Supporting Information). This result was further confirmed through nanobeam diffraction (Figure 2c) and high-angle annular dark field (HAADF-STEM) (Figure 2d).<sup>[17]</sup> As showing in Figure 2c, the diffraction patterns refer to the structure of the O3 phase with no biphase patterns. Meanwhile, for the HAADF images shown in Figure 2d, the bright spots, due to the Z contrast, represent the transition metal ions viewed from the [001] axis, showing







**Figure 3.** Electrochemical tests and in operando X-ray diffraction of NMI electrode. a) Electrochemical performance of NMI in the first cycle. b) Cycling performance of NMI. The red and blue dots represents columbic efficiency and capacity retention respectively. c) Left: in operando XRD patterns collected at a constant current rate of 20 mA  $g^{-1}$ . Middle: Schematic of phase evolution upon cycling where the pristine O3 phase, O1' and O1 coexistence biphase and O1' sole phase areas are depicted in green, orange with blue and blue color bars respectively. Right: the corresponding electrochemical performance during XRD measurement.

no obvious stacking faults or cation migration. Moreover, the results from the energy dispersive X-ray spectroscopy (EDS) mapping revealed a uniform distribution of all the elements in the particles.

The electrochemical performance of the as-prepared NMI is shown in Figure 3a,b. The batteries were assembled using sodium metal as the anode part. The tests were performed galvanostatically at a 0.1C rate ( $1C = 203 \text{ mAg}^{-1}$  based on full desodiation of the NMI) within a voltage window from 1.5 to 4.4 V. For the Na-ion battery, the voltage window cannot be too high to avoid severe decomposition of the electrolyte.<sup>[18]</sup> In principle, the complete extraction of 1.2 mol Na in the NMI would lead to a total capacity of 203 mAhg<sup>-1</sup>. However, in our cases, only Mn<sup>3+</sup> in the TM layers can be oxidized upon charging, which contributes a capacity of  $\approx 68 \text{ mAhg}^{-1}$ . Although Ir<sup>4+</sup> atoms could be further oxidized to Ir5+ state,[2d,10a] this was not the case in our experiment (see discussion on XPS analysis). Therefore, the extra capacity originating from the O<sup>2-</sup> oxidation should be expected and is around 0.6 mol Na removal upon the first cycle of charging. The excess Na should be responsible for O<sup>2-</sup> oxidation and shift of the O 2p nonbonding band up to the Fermi level. This was further confirmed by the DFT calculations (see Figure S3 in the Supporting Information).

As seen in Figure 3a, the first discharge cycle rendered an irreversible capacity loss of about 30 mAhg<sup>-1</sup>, resulting in a low columbic efficiency (see Figure 3b). To investigate the irreversible capacity fading, in situ GC-MS was performed for the first charging process to examine whether the released gases behaved as Li-rich materials. The results can be seen in Figure S4 in the

Supporting Information. The GC-MS measurement verified that there was merely no O2 release upon charging. However, CO2 release was detected. The existence of CO2 was found both in Li-rich and Na-rich materials,[2f,10a,b] which is wildly believed to be the decomposition of carbonate electrolyte solvents. Notably, unlike most of the Li-rich materials, although Mn<sup>3+</sup> was involved in our case, no O<sub>2</sub> was detected during the charging operation. This result can be ascribed to the existence of Ir atoms, which have a stronger covalent bond with O atoms and effectively reduce the possibility of O<sub>2</sub> release.<sup>[2a,e,10a]</sup> The cyclability tests were performed galvanostatically at a 0.5 C rate (see Figure 3b). The capacity retention was greater than 60% after 50 cycles. Compared with the reported Na-rich materials, such as  $Na_3RuO_4^{[10b]}$  and  $Na_2IrO_3^{[10a]}$  the suppression of the  $O_2$ evolution up cycling was the key factor. Although only a small amount of O2 was detected in Na2IrO3, this Na-rich material still suffered from poor capacity retention which can be ascribed to the severe structure changes during electrochemical cycling.<sup>[10a]</sup>

To disclose the structural evolution of NMI during electrochemical performance, in operando XRD was performed. Figure 3c depicts the evolution of the XRD pattern for the NMI electrode over the first two cycles between 1.5 and 4.4 V at a constant current rate of 20 mAg<sup>-1</sup>. As a whole, the results in Figure 3c show that the NMI underwent a phase transition between O3 O1' and O1 stacking patterns during the first cycle, whereas the O1 phase was absent during subsequent cycling, leaving only O3 and O1' transformations (see Figures S5 and S6 in the Supporting Information). The O3–O1'–O1 structural transformation is quite similar to that of Na<sub>2</sub>IrO<sub>3</sub> as reported by







**Figure 4.** In situ Raman characterization of the  $Na_{1,2}Mn_{0,4}Ir_{0,4}O_2$  cathode during the initial two cycles. The original capacity/time-dependent Raman spectra collected from the cathode surface are offset for clarity (left). The newly-observed Raman peaks are specifically assigned to the corresponding products. Note that, the peak position shift of the peroxo-related O–O stretching peaks (around 850 cm<sup>-1</sup>) is highlighted for clarity. The capacity dependence of the relative peak area and position are directly read from the in situ spectra (middle).

Tarascon et al.<sup>[10a]</sup> Specifically, as shown in Figure 3c, there were some pronounced asymmetric diffraction patterns, especially within the O1'-O1 region. This asymmetric broadening was due to the potential stacking faults that were caused by the systematic shifting of the TM layers. Similar phenomena were also reported by Yamada et al. in the Na2RuO3 systems,<sup>[10c]</sup> yet have seldom been found in Li-rich materials. This difference can be ascribed to the larger radius of Na atoms versus Li atoms, which increase the distance of the interlayer and reduce the interaction between the slabs. Moreover, unlikely the normally existing O3-P3 phase transition, the Na-rich materials exhibit opposite lattice transformations along the c-axis, as can be found in the shift tendency of the (003) peak. The explanation can also be attributed to the shifting of the slabs. The difference between O1' and O1 was the distortion degree. The suppression of the TM slab shifting in the O1' structure leads to the rearrangement of the metallic layers towards an ordered stacking sequence.<sup>[10a]</sup> However, the ordered stacking O1 phase was not found after the 2nd cycle, which was guite different from the Na<sub>2</sub>RuO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> systems. The difference should indicate the large incomplete redox of Mn<sup>4+</sup>, which hindered continuous rearrangement of the metallic atoms with each other. Further evidence will be presented in the discussion below. The O1 phase, which could further transform to the O1\* phase,<sup>[10a]</sup> disappeared and decreased the possibility of layered collapse, thereby improving the cycling performance of the NMI.

To trace the O redox evolution process, in situ Raman spectroscopy was further employed as a powerful tool to reveal the oxygen-related redox behavior in both Li-O2 batteries as well as the Li/Na-rich battery systems.<sup>[10b,19]</sup> As shown in Figure 4, as the voltage increased to 3.8 V during the first charging process, pronounced peaks arose at  $\approx 1109$  cm<sup>-1</sup>, which can be ascribed to the O–O stretching mode within the superoxide related species  $(O_2^{-})$ .<sup>[20]</sup> Considering that propylene carbonate (PC) was used as the electrolyte solvent, the  $O_2^-$  species will inevitably attack the PC molecule resulting in decomposition of the carbonate-based electrolyte. This also coincides with the observation of Na<sub>2</sub>CO<sub>3</sub> species (CO<sub>3</sub> stretching mode, 1085 cm<sup>-1</sup>), i.e., a typical decomposition product derived from superoxo-related nucleophilic attack of carbonate-based electrolytes. Moreover, the observation of superoxo and Na<sub>2</sub>CO<sub>3</sub> related Raman signals was also consistent with the in situ GC-MS information obtained with Na2CO3 (Figure S2, Supporting Information), and the CO<sub>2</sub> emitted from Na<sub>2</sub>CO<sub>3</sub> decomposition increased in the superoxo-related range at the end of the initial charging process.<sup>[10a]</sup> However, the strong Raman peak of Na<sub>2</sub>CO<sub>3</sub> can be ascribed to the formation of a passivation surface film on the cathode surface (derived from the decomposition of the carbonate-based electrolyte solvent). Thus, the signal of Na<sub>2</sub>CO<sub>3</sub> can be easily collected by surfaceenhanced Raman spectroscopy technology. However, due to the different absorption coefficients of varying observed species (e.g., peroxo-related O–O stretching around 850 cm<sup>-1</sup>,  $Na_2CO_3$ -related  $CO_3$  in-plane stretching around 1080 cm<sup>-1</sup>), specific peak intensities do not represent the corresponding component ratio.





**Figure 5.** a,b) XPS analysis of Mn-2p (a) and O1s (b) peaks. The peak fitting includes both pristine materials and the first two cycles. The results show that the oxidation of  $Mn^{3+}$  was not fulfilled at the end of charge and that the  $Mn^{4+}$  species increased at the end of the 2nd discharge cycle. The  $(O_2)^{n-}$  species exist upon charging with good reversibility, as indicated by the disappearance at the end of discharge.

The existence of  $O_2^-$  species should also be responsible for the irreversible capacity decay during the first cycle. It is noteworthy that the  $O_2^-$  species disappeared at the end of the first charging cycle, and this superoxo-related irreversible influence element never showed up appeared in the subsequent cycle, which can be viewed as preactivation of O redox as claimed for the Li-rich materials.

Additionally, the results in Figure 4 unequivocally indicated the reversible anionic redox of O species with the appearance of serial peaks within the peroxo-related O–O stretching region (see the green and blue area in Figure 4). Unlike the superoxo-related O–O stretching, this peroxo-species displayed high reversibility upon cycling, which enabled extra capacity from an electronic point of view. During the charging process, these peaks gradually moved towards a higher wavenumbers and then reverted back at the end of discharging, which is also consistent with the reversible variation trend of the O–O bond length during de-/sodiation. More importantly, while the peroxo species formed around the same time as the superoxo species in the first cycle ( $\approx$ 3.8 V), they showed up much earlier during the 2nd cycle, i.e., at about 3.2 V. This difference suggested that a more dynamic anionic redox was involved in the electrochemical performance once the anion was activated. This can be better understood from charge compensation and electronic aspects as discussed below.

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The unique behavior and unambiguous difference between the initial cycle and subsequent cycle observed in the in operando XRD and Raman tests were further discussed from a charge compensation aspect.

XPS and synchrotron based argon etching assisted XPS were employed as the implement to investigate the charge compensation mechanism at different electrochemical stages. The results are displayed in **Figure 5**. In contrast to Na-rich Na<sub>2</sub>IrO<sub>3</sub>, there was no obvious peak shifting or peak broadening of the Ir<sup>4+</sup> 4f state after two cycles, which suggested that Ir does not contribute to the redox process (see Figure S7 in the Supporting Information). According to the experimental results, only Mn participates in the cation redox reaction over the whole electrochemical reaction. Therefore, the detailed analysis focused on the valence evolution of both Mn and O atoms.

For the Mn atoms, the spin-orbit coupling leads to the splitting of the main peak. In our experiment, the Mn2p core

spectra showed Mn2 $p_{3/2}$  and Mn2 $p_{1/2}$  binding energies located at 641.5 and 653 eV respectively, which are consistent with Mn<sup>3+</sup> for pristine NMI. Upon charging, both the Mn2 $p_{3/2}$  and Mn2 $p_{1/2}$  peaks shifted towards higher binding energies and indicated the emergence of the Mn<sup>4+</sup> state (located at ~642.5 and 654 eV for Mn2 $p_{3/2}$  and Mn2 $p_{1/2}$  respectively<sup>[21]</sup>). However, the oxidation of Mn<sup>3+</sup> was not complete at the end of the charge cycle as evidenced by the coexistence of both Mn<sup>3+</sup> and Mn<sup>4+</sup>. This unusual performance was similar to that of the reverse oxidation in Ru based Li-rich material<sup>[2c]</sup> and Na<sub>3</sub>RuO<sub>4</sub> Na-rich material.<sup>[10b]</sup> A explanation is significant modification of the Mn environment. As demonstrated in the in operando XRD, a continuous lattice distortion existed upon desodiation, which induced strong electronic redistributions along the Mn–O bonds.

During the sodiation process, although the intensity and broadening of the Mn<sup>3+</sup> peaks increased, the Mn<sup>4+</sup> peaks were still present and were more pronounced at the end of the 2nd cycle of discharging. One possible explanation is the large distortion during the charge process leads to the residual of inactive Mn species due to the rearrangement of the chemical environment. Calculation of Mn<sup>3+</sup>/Mn<sup>4+</sup> at the end of the second discharge cycle revealed that the fraction of inactive Mn<sup>4+</sup> increased due to the significant TM slab shifting upon cycling (see Figure S5 in the Supporting Information). The accumulation of redox inactive Mn4+ also suppressed the distortion towards the O1 phase transformation, where all the TM layers are stacked exactly on top of each other. Moreover, the existence of a large amount of Mn<sup>4+</sup> also alleviates the Jahn–Teller effect caused by the Mn<sup>3+</sup> species, which would also have a positive effect on the cyclability.

As for the corresponding O 1s spectra, the emergence of a new peak around 530.7 eV at the end of the charge stage indicated the oxidation of  $O^{2-}$  with the formation of peroxo-related species  $(O_2^{2-})$  upon desodiation.<sup>[2c,22]</sup> This peak disappeared at the end of discharging demonstrating that peroxo-related species  $(O_2^{2-})$  displayed high reversible activity. The activated proportion of  $O_2^{2-}$  can be roughly estimated from the  $O_2^{2-}$  peak area divided by the  $O^{2-}$  peak. The results (see Figure S8 in the Supporting Information) show that the activated proportion was 31% in the first cycle and 48% for the second cycle. This result was in accordance with the Raman spectra, which suggested that more O was involved in the early stage of charging. In addition, the existence of inactive Mn species leads to a reduction in cationic redox, which could result in high participation of oxygen during the redox reaction.

To confirm our findings on the anionic redox process, O K-edge near edge X-ray absorption fine structure (NEXAFS) soft X-ray absorption spectroscopy (sXAS) spectra were measured. The results are shown in Figure S9 in the Supporting Information. The data were collected using total electron yield (TEY) mode, which can obtain the information at around 5 nm from the surface. Information under 300 nm was collected using argon etching assisted sXAS. As shown in Figure S9 (Supporting Information), all spectra displayed a sharp peak at around 532 eV and a broader peak in the high energy rage. The most interesting states were in the low energy region. There are two main peak areas at about 530 and 534 eV, which refer to O with a transition metal and vacancy O, respectively.

Recent research has shown that the edge peak around 530 eV arises from the transitions between  $O_{2p}$  and the transition metal d band; therefore, this peak can indicate the oxygen redox in a system.<sup>[2f,23]</sup> From Figure S9a (Supporting Information) we can see that the edge of the peaks of the charged samples shift towards the lower energy region and revert back to the initial position after discharge. This change can be ascribed to electron filling and extraction of the  $O_{2p}$  band, which refers to oxygen redox. A similar tendency was observed in the argon etched samples. The main distinction was the etching-induced the increase in the O vacancies, which led to a shift in the O vacancy peak to the high energy area. Nevertheless, these results confirmed that the oxygen redox was not limited to the surface but also occurred inside the samples.

In summary, a comprehensive study was performed on newly designed Na-rich battery materials. Na12Mn04Ir04O2 was proposed as the O3 phase layered structure Na-rich material that can deliver a capacity of 179 mAhg<sup>-1</sup> upon charging to 4.4 V. The small capacity fading during the first discharge can be ascribed to the formation of the superoxo-related O species, which results in CO<sub>2</sub> emission by attracting the carbonatebased electrolyte. Subsequent experiments demonstrated that the NMI electrode exhibited a good capacity retention which was greater than 60% after 50 cycles. The extra capacity that was generated from the anionic redox reaction was further confirmed through XPS, in operando Raman spectroscopy technique as well as the sXAS measurements. During the first charge process, the cationic oxidation was completely ascribed to the  $Mn^{3+}/M^{4+}$  reaction without the involvement of the Ir atoms. Both XPS, in operando Raman and sXAS tests confirmed the high level participation of  $O^{2-}/O_2^{2-}$  oxidation during charging. Subsequent measurements revealed that this anionic redox originating from the O species was highly reversible. The presence of Ir atoms resulted in strong covalence with O, which effectively suppressed O<sub>2</sub> release. Notably, the unusual existence of partially inactive Mn4+ can be ascribed to the significant distortion of the structure, which was successfully characterized using the in situ XRD as the implement. The irreversible phase transition during the second cycle can be related to the existence of electrochemically inactive Mn4+ which redistributions the electronic environment along the Mn–O bonds.

Our research has successfully created a the prototype Mnbased Na-rich material, which will inspire a new perspective for the Na-rich materials with the inherent advantages of sodiumion batteries with low cost and could be helpful for creating advanced energy storage materials.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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### **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

anionic redox, in situ characterization, Ir doping, Mn based Na-rich materials, Na-ion batteries

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