Insights into the Enhanced Cycle and Rate Performances of the F-Substituted P2-Type Oxide Cathodes for Sodium-Ion Batteries

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Insights into the Enhanced Cycle and Rate Performances of the F-Substituted P2-Type Oxide Cathodes for Sodium-Ion Batteries

Abstract
A series of F-substituted Na2/3Ni1/3Mn2/3O2−xFx (x = 0, 0.03, 0.05, 0.07) cathode materials have been synthesized and characterized by solid-state 19F and 23Na NMR, X-ray photoelectron spectroscopy, and neutron diffraction. The underlying charge compensation mechanism is systematically unraveled by X-ray absorption spectroscopy and electron energy loss spectroscopy (EELS) techniques, revealing partial reduction from Mn4+ to Mn3+ upon F-substitution. It is revealed that not only Ni but also Mn participates in the redox reaction process, which is confirmed for the first time by EELS techniques, contributing to an increase in discharge specific capacity. The detailed structural transformations are also revealed by operando X-ray diffraction experiments during the intercalation and deintercalation process of Na+, demonstrating that the biphasic reaction is obviously suppressed in the low voltage region via F-substitution. Hence, the optimized sample with 0.05 mol f.u.−1 fluorine substitution delivers an ultrahigh specific capacity of 61 mAh g−1 at 10 C after 2000 cycles at 30 °C, an extraordinary cycling stability with a capacity retention of 75.6% after 2000 cycles at 10 C and 55 °C, an outstanding full battery performance with 89.5% capacity retention after 300 cycles at 1 C. This research provides a crucial understanding of the influence of F-substitution on the crystal structure of the P2-type materials and opens a new avenue for sodium-ion batteries.

Keywords
charge compensation mechanism, F-substitution, long cycle stability, P2-type oxide, sodium battery

Disciplines
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Abstract: P2-type layered transition metal oxides as one of the most promising candidates for sodium-ion batteries (SIBs) have been extensively investigated, but they still need improvement in both cycling stability and rate performance. Herein, a series of F-substituted Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$-$xF_x$ (x=0, 0.03, 0.05, 0.07) cathode materials have been synthesized and confirmed by solid state $^{19}$F and $^{23}$Na NMR, X-ray photoelectron spectrometer and Neutron diffraction. The underlying charge compensation mechanism is systematically unraveled by X-ray absorption spectroscopy and electron energy loss spectroscopy techniques, indicating F-substitution induces a small quantity of reduction from Mn$^{4+}$ to Mn$^{3+}$. Surprisingly, not only nickel but also manganese element participates in the redox reaction process, which is confirmed for the first time by electron energy loss spectroscopy techniques, contributing to an extra discharge specific capacity. The detailed structure transformations are also revealed by an in-situ XRD experiment during the intercalation and de-intercalation process of Na$^+$, which demonstrates the biphasic reaction, is obviously suppressed in the low voltage region. Hence, the optimized sample with 0.05 fluorine substitution delivers an ultrahigh specific capacity of 61 mAh g$^{-1}$ at 10 C after 2000 cycles at 30 °C, an extraordinary cycling stability with a capacity retention of 75.6 % after 2000 cycles at 10 C and 55 °C, an outstanding full batteries performance with 89.5 % capacity retention after 300 cycles at 1 C. This research provides a profound understanding on the influence of F-substitution on the crystal structure of the P2-type materials and opens a new avenue for SIBs.

Keyword: P2-type oxide; F-substitution, charge compensation mechanism, long cycle stability, sodium battery.
The energy resources and environment pollution crisis have seriously hampered the development of the world economy in the past few decades.\textsuperscript{1-3} As a result, extensive research has been focused on seeking sustainable green energies from renewable sources such as wind and solar.\textsuperscript{4-6} Lithium-ion batteries as the most promising candidates to store those renewable energies have achieved enormous success in view of their high work voltage, extraordinary specific capacity, and outstanding energy density and so on.\textsuperscript{7-9} However, the limited reserves of lithium with inhomogeneous distribution in the earth and ever-increasing consumption have anxiously urged researchers to explore alternative sustainable substitutions in large-scale energy storage devices. Sodium-ion batteries (SIBs) as one of the most suitable candidates have recently received tremendous interest owing to the advantages of intrinsic abundance and relatively low-cost of sodium resources.\textsuperscript{10-12} Cathode materials as the heart of SIBs dominate the level of energy density and manufacturing costs. Exploiting a new cathode material with satisfactory characteristics will be an imminent challenge.\textsuperscript{13-15} Currently, different types of cathode materials, including transition metal oxides,\textsuperscript{16-17} polyanion phosphides\textsuperscript{18-19} and hexacyanoferrate derivatives\textsuperscript{20-21}, have been widely investigated. Among different cathode materials, the layered metal oxides with high output voltage and easy synthesis have become the most promising candidate for SIBs.

Considering the different sodium occupation sites and stacking sequences indicated by Delmas et al,\textsuperscript{22} sodium-based oxide materials are primarily presented into two styles, namely P2-type and O3-type.\textsuperscript{23-26} Unlike the O3-type compounds with octahedral structure accompanied by ABC oxygen cumulate, P2-type materials display an open trigonal prismatic peculiarity with ABBA oxygen stacking. This unique characteristic endows adequate space for storage of sodium ions, lowers phase transition and sodium ion diffusion obstacle for P2-type cathode materials than O3-type compounds.\textsuperscript{27-28} Recently, Manganese-based P2-type materials (Na\textsubscript{x}Mn\textsubscript{y}M\textsubscript{1-y}O\textsubscript{2}; M: Ni, Cu, Mg, etc.) have achieved prominent development with primary focus on enhancing its cycle stability by adopting different cationic dopants to suppress the notorious phase transition (P2-O2) and improving the kinetics of the cathode materials and specific capacity at high voltage, particularly for Na\textsubscript{2/3}Ni\textsubscript{1/3}Mn\textsubscript{2/3}O\textsubscript{2}.\textsuperscript{29-31} However, many research works have indicated that external cationic substitution usually decreased specific capacity with the expense of redox center and didn't achieve the desired cycle and rate performances.\textsuperscript{32-33} In addition, SIBs are targeted for grid-based energy storage that usually prefers the long cycle stability to high specific capacity, as previously demonstrated that reducing the charge cut-off voltage could effectively hamper the occurrence of
obnoxious OP4 and ameliorate the cycling and rate performances. Furthermore, although anion doping has been proposed as a significant way to improve the specific capacity of the materials by evoking more redox centers, the detailed regulation mechanism on which anion substitution enhancing the electrochemical characteristics of the SIBs is still obscure. Thus, tailoring reasonable cut-off voltage range with suitable anion doping coupled with clear elucidation of structural mechanism are crucial to realize long cycling stability and excellent rate performances of the next generation SIBs.

In this work, a series of F-substituted Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$-xF$_x$ (x = 0.03, 0.05, 0.07) cathode materials were synthesized by a simple solid-state high-temperature reaction. The incorporation of F into the crystal texture was confirmed by solid state nuclear magnetic resonance (ssNMR) and X-ray photoelectron spectroscopy (XPS) and the corresponding oxidation-reduction charge compensation mechanisms were illustrated for the first time by X-ray absorption near edge structure (XANES) and electron energy loss spectroscopy (EELS). This result indicated the F doping induced the reduction of Mn$^{4+}$ to Mn$^{3+}$, which altered the single redox center of Ni$^{2+}$ and promoted the increase of specific capacity for SIBs. Meanwhile, the detailed crystal structure evolution of prepared samples is demonstrated by neutron diffraction (ND). The phase transformations of the targeted materials were followed by in-situ XRD during the charge-discharge process, which implied that the Jahn-Teller induced disproportionation reactions were effectively suppressed in the F-substituted samples at the low voltage region. Once being assembled in half/full cells, the optimized cathode delivered remarkable long cycle stability with high rate performance at both 30 °C and 55 °C.

The crystal patterns of different F-substituted P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$-xF$_x$ (x=0, 0.03, 0.05, 0.07) cathode materials were confirmed by X-ray powder diffraction (XRD). As shown in the Figure 1a, all samples display definite and sharp diffraction peaks that belong to the P6$_3$/mmc space group with the P2-type layered structure. No trace impurities are detected in the F-substituted samples as compared to those of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$, indicating that F substitution doesn’t alter the bulk structure of the materials. However, the clear shift of (002) peak towards lower angle as displayed in the zoom-in spectra implies that the lattice cell of the c direction is enlarged, which is beneficial to enhance the kinetics of Na$^+$ during cycling. This is in direct conflict with the Vegard’s rule in view of the smaller ionic diameter of fluorine than that of oxygen and
the detailed charge compensation mechanism will be discussed in the following XANES and EELS discussions.39-40

Figure 1. a) X-ray powder diffraction patterns. b) 19F direct-polarization magic-angle spinning (DPMAS) of the F-substituted materials and NaF reference. All spectra were normalized to the 19F content in the rotor for quantitative comparison. Background signals were subtracted (the distortion around -40 ppm arose from the background subtraction). Asterisks represent spinning sidebands. c) 23Na DPMAS spectra of a series of F-substituted materials. All spectra were normalized to the 23Na content in the rotor for quantitative comparison. d) XPS spectra of F1s. e) Rietveld refined neutron diffraction spectrum of Na2/3Ni1/3Mn2/3O1.95F0.05 with corresponding structure module and SEM image. f) Raman profiles of Na2/3Ni1/3Mn2/3O2 and Na2/3Ni1/3Mn2/3O1.95F0.05.

To further elucidate the fluorine being incorporated into the bulk structure of the cathode materials rather than being deposited as NaF on the cathode surfaces, Figure 1b shows the background-subtracted 19F ssNMR spectra of the samples with NaF as a reference (all spectra were normalized to the 19F content). A sharp signal appeared at -119 ppm in the NaF reference, while no detectable signals were observed in the cathode samples (note that the negative intensity observed in the Na2/3Ni1/3Mn2/3O1.95F0.05 results from the background subtraction process and is not a real signal). Most likely, the complete disappearance of 19F signal results from strong paramagnetic interactions between the 19F nuclei and the unpaired d electrons of the Mn ions,
corroborating the incorporation of F into the cathode materials.\textsuperscript{41} Figure 1c shows the $^{23}$Na DPMAS spectra with Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ as a reference. It is mainly consisted of manifolds of spinning sidebands, further demonstrating that the $^{23}$Na ssNMR signal is strongly perturbed by the paramagnetic interactions with Mn ions. Meanwhile, the noteworthy shift of the main signals toward higher field as shown in the zoom-in spectra indicates that the valence state and structure of the Mn ions with identical stoichiometry have also been altered.\textsuperscript{4, 42} This is mainly ascribed to the decrease of average unpaired electron density on the Mn$^{4+}$ by fluorine substitution, which affects the Na$^+$ environment.

Figure 1d shows the XPS spectra of F1s in different cathode materials. Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.93}$F$_{0.07}$ exhibit obvious fluorine signal, confirming the existence of F element in the materials. The fluorine signal for Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.97}$F$_{0.03}$ is not detected, mainly due to the low content of fluorine beyond the probe limitation of the XPS equipment. The XPS spectra of Ni 2p and Mn 2p from all the samples are shown in Figure S1a & S1b, which can be divided into two peaks, namely 2p$_{3/2}$ and 2p$_{1/2}$ peaks with different satellite peaks, suggesting the valence state of Ni and Mn is mainly located in the +2 and +4, respectively. The formation of fluorinated transition metal bonds is supported by the shifting of both Ni 2p and Mn 2p peaks to higher binding energy with increasing the amount of fluorine.\textsuperscript{43} However, the Mn 2p peak shifts much larger than the Ni 2p peak does, suggesting Mn ion is more favorable to form the bond with F, as further confirmed later. In addition, the Mn 3s spectrum displays another distinction between Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ in Figure S 1c, which implies the valence state of Mn is slightly reduced in the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ sample.\textsuperscript{44}

To further investigate the fluorine effect on the crystal structure of the cathode materials, Neutron diffraction (ND) was carried out on both Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$. The specific crystal structure and the structure module of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ is depicted in Figure S2 and Figure S3a & S3c, whereas those of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ is shown in the inset of Figure 1e (1) & 1e (3), respectively. The fitting results of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ are shown in Figure 1e and Figure S 4, respectively. Fluorine substitution causes noticeable Na redistribution: overall reduction in Na stoichiometry was particularly predicted at the Na2 site (Table S1). In addition, the difference in Na occupancies amongst the Na1 sites becomes minimal, suggesting less degree of Na ordering. The diffraction patterns also support the refinement results:
closer examination of the diffraction pattern reveals fractional index, namely \( \frac{4}{3}00 \) and \( \frac{4}{3}01 \), in the larger hexagonal cell, with \( d = 3.283 \ \text{Å} \) and \( 3.145 \ \text{Å} \) respectively. These numbers correspond to the Mn and Ni (the nearest neighbors) distance between the neighboring Na ions, and is an indication of the in-plane Na ordering.\(^{45-47}\) The F substitution decreases the intensity of these reflections, confirming a less ordered Na layer. Furthermore, an overall increased Ni/Mn mixing was observed in the \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{2} \) sample, showing reduced TM ordering with F substitution (Table S1). Therefore, the calculated BVS at TM1 and TM2 sites drift away from the ideal 4+ valence. Although it is not feasible to identify the F positions due to its low concentration, it can be clearly seen from Table S2 that the introduction of fluorine has resulted in changes in bond length, that is, a slight contraction of the lattice parameters within the ab plane and a slight increase along c.

The morphology characteristics of both samples are revealed by scanning electron microscopy (SEM) in the inset of Figure 1e (4) and Figure S 4, demonstrating the layer samples are constituted of different sizes of primary particles. The corresponding of energy-dispersive spectroscopy (EDS) mapping for \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{2} \) and \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{1.95}\text{F}_{0.05} \) are illustrated in Figure S5a & S5b, which manifest the uniform distribution of all elements in the samples. The morphologies of other P2-type \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{2-x}\text{F}_x \) (\( x = 0.03, \ 0.07 \)) materials are shown in Figure S6a & S6b. Meanwhile, the specific surface area of all samples shown in Figure S 7 is very similar, confirming F-substitution does not affect the specific surface area of materials. To explore the alteration of short-range structure of the targeted materials upon fluorine substitution, Raman spectroscopy is collected on the \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{2} \) and \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{1.95}\text{F}_{0.05} \) samples. As shown in Figure 1f, two intense bands at 583 (\( \text{A}_{1g} \)) and 472 (\( \text{E}_g \)) cm\(^{-1} \) attributed to unsymmetrical stretching vibration of M-O bond (M: Ni, Mn) and bending vibration of O-M-O bond are observed for both samples, indicating they have the same space group.\(^{48}\) Nevertheless, the \( \text{A}_{1g} \) value exhibits obviously shift between \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{2} \) and \( \text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_{1.95}\text{F}_{0.05} \), which indicates the local interatomic distance has been altered. This result further demonstrates F atom has been doped into the crystal structure of the materials.
Figure 2. a) TEM images and the corresponding SAED of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ particles. b) Cross-sectional TEM images and c) the corresponding HRTEM. d) SAED. e) EDS mapping of various elements for Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$.

To better understand the morphologies and microstructures information of targeted materials, Figure 2a and Figure S8a show the transmission electron microscopy (TEM) of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ particles, respectively. The selected area electron diffraction (SAED) on both sample surfaces along different crystal axis is shown on the lower right corner of the TEM pattern, which confirms that the two samples have identical transition metal atom arrangement of typical hexagonal layered structure. Meanwhile, the TEM patterns of the particle interior fabricated by focused ion beam (FIB) technology are displayed in Figure 2b and Figure S9a and the corresponding HRTEM and SAED are exhibited in Figure 2c (Figure S9b) and Figure 2d (Figure S9c), indicating that F-substitution doesn’t affect the crystal texture indexed to P2-types layered hexagonal symmetry structure. Besides, energy dispersive X-ray spectroscopy
(EDS) mapping shows homogeneous distribution of all elements on the interior of the samples in Figure 2e and Figure S10, further validating the fluorine element being incorporated into the bulk materials.

**Figure 3.** a) Ni K-edge XANES spectra. b) Corresponding the EXAFS spectra of Ni K-edge. c) Mn K-edge XANES spectra. d) 1st derivative of normalized absorption spectra of Mn K-edge. e) The EXAFS spectra of Mn K-edge. f) The relevant fit results of different samples.

To reveal the detailed charge compensation mechanism induced by F-substitution, X-ray absorption near-edge spectroscopy (XANES) is measured on the pristine and F-doped samples (Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$-$xF_x$, x=0, 0.03, 0.05 0.07). As shown in Figure 3a, the normalized Ni K-edge XANES of all the samples using Ni foil and NiO as the references exhibit similar adsorption peaks, suggesting both oxidation states and local structure environment of the Ni ions have not been altered. This is consistent with the extended X-ray absorption fine structure (EXAFS) spectra of Ni as shown in Figure 3b. Compared with the pristine sample, the Ni-O and Ni-Ni coordination of the F-doped samples do not change at all, indicating F-substitution does not induce valence change of Ni. In contrast, the Mn K-edge XANES spectra using Mn$_2$O$_3$ and MnO$_2$ as the references display conspicuous differences as shown in Figure 3c, especially for the pre-edge absorption peaks standing for the electron excitation from the core state of the 1s orbital to the unfilled 3d orbital of the high spin state of Mn$^{4+}$. Figure 3d shows the 1st derivative of the normalized Mn
K-edge absorption spectra, which exhibits an obvious shift from higher energy position to lower energy position, especially for Na_{2/3}Ni_{1/3}Mn_{2/3}O_{1.93}F_{0.05} and Na_{2/3}Ni_{1/3}Mn_{2/3}O_{1.93}F_{0.07}, suggesting the oxidation states of the Mn ions being reduced. Although Na_{2/3}Ni_{1/3}Mn_{2/3}O_{1.97}F_{0.03} displays similar absorption peaks to those of Na_{2/3}Ni_{1/3}Mn_{2/3}O_{2}, the detailed peak feature is clearly different, suggesting the little amount of doped F near Mn still causes difference in its electronic structure. The corresponding pre-edge, shoulder and main edge position of different samples are listed in Table S 3. Besides, the EXAFS spectra of the Mn K-edge in Figure 3e for F-doped samples exhibit a decreased peak intensity and an increased interatomic distance for Mn-O and Mn-Mn coordination shell than those for the pristine Na_{2/3}Ni_{1/3}Mn_{2/3}O_{2} sample, implying the reduction of Mn ion due to the bigger ionic diameter of Mn^{3+} than that of Mn^{4+}. The relevant fit results in Figure 3f are highly consistent with the experiment data and the obtained structure parameters are listed in Table S4.

Figure 4. EELS spectra of Na_{2/3}Ni_{1/3}Mn_{2/3}O_{2} from surface (point 1) to interior (point 5). a) Ni L-edge signals. b) Mn L-edge signals. EELS spectra of Na_{2/3}Ni_{1/3}Mn_{2/3}O_{1.95}F_{0.05} from surface (point 1) to interior (point 6). c) Ni L-edge
signals. d) Mn L-edge signals. EELS spectra of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ during Na$^+$ extraction/insertion process. e) Ni L-edge signals. f) Mn L-edge signals.

Electron energy loss spectroscopy (EELS) with point analysis from sample surface to interior is used to further substantiate the charge balance mechanism induced by F-substitution. The selected analytic points for Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ are specified on Figure S 11a & S 11b with the corresponding Ni L-edge and Mn L-edge spectra are shown in Figure 4. As shown in Figure 4a & 4b, the Ni L-edge spectra and the Mn L-edge spectra of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ from surface (point 1) to interior (point 5) exhibit almost the same feature, confirming the valence states of Ni and Mn being the same from point 1 to point 5, respectively. It also suggests that the synthesized materials maintain coherent texture pertaining to the P2-type layered structure. Figure 4c exhibits the Ni L-edge spectra of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ from surface (point 1) to interior (point 6) with pristine Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ as a reference and designated as point 0. All points show almost identical spectra, suggesting the Ni ion does not participate in the charge compensation process. On the contrary, the Mn L-edge spectra of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ shown in Figure 4d exhibits conspicuous shift with respect to that of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ (point 0), that is, from 650 eV to 652 eV and 661 eV to 662 eV for Mn L$_3$ and Mn L$_2$, respectively. This confirms the decrease of the oxidation state of Mn ion, consistent with the XANES results. Meanwhile, the energy positions of the Mn L-edge spectra of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ from point 1 to point 6 remain the same, revealing the coherent reduction of the Mn ion by homogeneous F-substitution from the surface to the interior of the particles to maintain the electro-neutrality. To further illustrate the charge compensation mechanism during the intercalation and de-intercalation process of Na$^+$, Figure 4e displays distinct variations of the Ni L-edge spectra at different voltage conditions, which demonstrates the Ni$^{2+}$/Ni$^{3+}$ redox couple being mainly responsible for the charge compensation during cycling as previously reported. Surprisingly, the Mn L$_{2,3}$-edge spectra also exhibit an visible shift during the charge-discharge process, which implies for the first time that the Mn$^{3+}$/Mn$^{4+}$ redox couple is also participated in the charge compensation process during cycling. The corresponding EDS line scanning at different voltages, as illustrated in Figure S12a & S12d, further confirms uniform distributions of all elements during the cycling process.

The electrochemical evaluation of the pristine and the F-substituted cathodes are carried out in Na half/full cells at both 30 °C and 55 °C (1 C=170 mA g$^{-1}$). As exhibited in Figure 5a, the constant
current charge-discharge curves of the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode display obvious four pairs of voltage plateaus at 3.3/2.95 V, 3.39/3.26 V, 3.68/3.56 V, and 3.73/3.6 V corresponding to the redox couples of Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$, which is consistent with the CV profiles in Figure S13 in the voltage range of 2 - 4 V at a scanning rate of 0.2 mv s$^{-1}$. Remarkably, a more pronounced voltage plateau emerges at about 2.25 V corresponding to the Mn$^{3+}$/Mn$^{4+}$ redox reactions for Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$, contributing to an extra specific capacity of 10 mAh g$^{-1}$. Meanwhile, the F-substitution reduces the polarization voltage from 0.36 V to 0.31 V, mainly ascribed to the higher electronic conductivity of the F-substituted materials. Figure 5b shows the cycle performances of the pristine and F-substituted samples between 2 V and 4 V at 2 C. Among all the samples, Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ exhibits the best cycling performance with the highest specific capacity of 95.4 mAh g$^{-1}$ and the best capacity retention of 89 % after 400 cycles. The stability of the electrodes after 400 cycles were further evaluated by CVs as illustrated in Figure S 14a & 14b, all exhibiting the same redox peaks as those of fresh samples shown in Figure S13. In addition, the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ sample displays an extraordinary long-term cycle stability with a capacity retention of 70 % after 2000 cycles and a high coulombic efficiency of 99.9 % at a high rate of 10 C at 30 °C (Figure S15). The SEM images of the pristine and F-doped samples after 2000 cycles shown in Figure S 16 exhibit similar morphology but the former electrode clearly has much larger cracks than the latter one. Furthermore, the pristine and F-doped samples were evaluated in a wider voltage range of 1.5 - 4.0 V. Figure S17a & S17b show the long cycling performances at 2 C and the initial CVs for Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$, respectively. Although the capacities decay faster than those cycled in the voltage range of 2 - 4.0 V, they are much better than those reported in the literature, especially for the F-substituted material.
Figure 5. Electrochemical performances of different F-substituted samples. a) Charge-Discharge curves of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode at 0.1 C. b) Cycle stability performance of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$-xF$_x$ (x= 0.03, 0.05, 0.07) cathode at 2 C. c) Rate performance of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$-xF$_x$ (x= 0.03, 0.05, 0.07) cathode at various current densities. d, e) EIS spectra of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode after different cycles, respectively. f, g) Corresponding the CV profiles of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode at various scan rates, respectively. h) High temperature performance (55 ℃) of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode at 10 C. i) Full cell performance of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode at 1 C.

The rate performances of all the samples were also evaluated from 0.1 C to 10 C in the voltage range of 2 – 4.0 V. As shown in Figure 5c, Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ displays the best rate performance with high reversible specific capacities of 106.7, 104.5, 101.7, 99.1, 96, 90.9, and 86.4 mAh g$^{-1}$ at 0.1 C, 0.2C, 0.5C, 1C, 2C, 5C, and 10 C, respectively. It is noted that the capacity at 10 C is as high as 81 % of that at 0.1 C. These excellent rate performances are mainly attributed to the benign interface stability as illustrated on the electrochemical impedance spectroscopy (EIS) in Figure 5d & 5e. Clearly, under the same condition, the EIS of the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ sample is much lower than that of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$. To further distinguish the transport kinetic
characteristics of materials, Na$^+$ diffusion coefficients in both samples are measured by the CV method as shown in Figure 5f & 5g, respectively. The detailed fitting curves of peak current ($I_p$) vs. square root of scan rates ($v^{1/2}$) and the corresponding calculated results by the Randles–Sevcik formula for Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ are shown in Figure S 18a & S18d and Table S 5 & S 6, respectively. The Na$^+$ diffusion coefficients in Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ are much higher than those in Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$, consistent with its higher rate performance and lower EIS data. In addition, Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ also exhibits an extraordinary high temperature performance (55 ℃) with a capacity retention of 75.6% and an excellent coulombic efficiency of 99.9 % at a high rate of 10 C for 2000 cycles (Figure 5h). The corresponding SEM images of the electrodes after 2000 cycles shown in Figure S 19 are similar to those cycled at 30 ℃ (Figure S16). Besides outstanding half cells performance, the F-doped sample also exhibits superior full cell properties with hard carbon as the anode. To better match the synthesized cathode materials, the hard carbon anode was first investigated in the different electrolytes in half cells. As displayed in Figure S 20a & S 20b, under the same current rate of 1 C, the hard carbon anode exhibits higher capacity in the electrolyte of 1M NaPF$_6$ in EC/DMC with 2 v% FEC than that in 1M NaClO$_4$ in PC with 5 v% FEC, mainly due to the higher ionic conductivity of the former electrolyte. Figure 5i shows the full cell performance in the former electrolyte in the voltage range of 0.5 - 4 V at 1 C, exhibiting a remarkable capacity retention of 89.5 % and a high coulombic efficiency approaching to 100 % after 300 cycles. The full cell performance in the electrolyte of 1M NaClO$_4$ in PC with 5 v% FEC electrolytes is shown in Figure S 21, also exhibiting a good cycling performance but with much lower capacities due to its lower ionic conductivity. Overall, new cathode materials with a prominent long cycle stability and rate capability has been designed by optimizing the content of the substituted element and modulating the operation voltage range to significantly ameliorate the discharge specific capacity and accelerate the diffusion coefficients of Na$^+$. 
To follow the structure evolution of the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathodes during the de-intercalation and intercalation process of Na$^+$, in-situ XRD experiments were carried out at different voltages during the charge-discharge process. As demonstrated in Figure 6a & 6b, not too much distinction between Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ are observed during the charge process with continuous shift of the (100), (012), (110) and (112) diffraction peaks toward a higher angle and the shift of the (106) peak toward a lower angle, implying the occurrence of a solid solution reaction with the contraction of the ab-plane.\textsuperscript{54} However, some apparent differences are emerged during the discharge process, that is, the (100), (110) and (112) diffraction peaks split into two peaks when the voltage is below 2 V, suggesting a biphasic reactions mechanism for the Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ cathode. This is mainly attributed to the increase of Mn$^{3+}$ concentration reduced from Mn$^{4+}$, leading to the structure distortion and
formation of a new phase (orthorhombic P2' phase). Conversely, Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ cathode presents an almost total solid solution mechanism during the charge-discharge process in the voltage range of 1.5 – 4.0 V.$^{55}$ Moreover, the structure alterations of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ and Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ in the high voltage range of 2 - 4.3 V were also investigated by the In-situ XRD technique. As demonstrated in Figure S 22, the diffraction patterns of both samples exhibit noticeable differences during the charge process when the voltage is higher 4 V as compared to those in the low voltage range. It displays the formation of a new phase (O$_2$ phase) for both cathode materials, which is attributed to the glide of the transition metal oxide slabs to form octahedral sites during the deep de-intercalation process.$^{56}$ As shown in Figure S 23, the notorious formation of the O$_2$-type phase severely deteriorates the cycle performance of both batteries, though the half-cell of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{1.95}$F$_{0.05}$ still maintains a better cycling performance than that of Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$.

In summary, F-substituted P2-type Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_{2-x}$Fx cathode materials with x range from 0 to 0.07 have been synthesized by conventional high temperature solid-phase reactions. Different spectroscopic technologies including $^{19}$F ssNMR, $^{23}$Na ssNMR, XPS spectroscopy, Neutron diffraction (ND) have demonstrated that fluorine has been incorporated into the bulk structure of the materials. The detailed charge compensation mechanism has been elucidated by XANES and EELS spectrum, indicating F-doping induces some reduction of Mn$^{4+}$ to Mn$^{3+}$. Meanwhile, the redox reactions illustrated by EELS during the intercalation and de-intercalation process of Na$^+$ suggest that not only nickel element but also manganese participates in the charge compensation mechanism, resulting in an extra discharge specific capacity. The total structure transformations are revealed by in-situ XRD during the charge-discharge process, which demonstrates the biphasic reaction is obvious suppressed in the low voltage region. Hence, the F-doped samples deliver an ultrahigh specific capacity of 61 mAh g$^{-1}$ at 10 C after 2000 cycles, an extraordinary cycling stability with a capacity retention of 75.6 % after 2000 cycles at 10 C and a high temperature of 55 °C, an outstanding full batteries performance with 89.5 % capacity retention after 300 cycles at 1 C. This unique design concept provides a avenue for synthesis of new cathode materials for SIBs.

**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 there is no conflict of interest.

References:

4. Liu, X. S.; Zuo, W. H.; Zheng, B. Z.; Xiang, Y. X.; Zhou, K.; Xiao, Z. M.; Shan, P. Z.; Shi, J. W.; Li, Q.; Zhong, G. M.; Fu, R. Q.; Yang, Y., P2-Na0.67AlxMn1-xO2: Cost-Effective, Stable and High-Rate Sodium


31. Cao, X.; Li, X.; Qiao, Y.; Jia, M.; Qiu, F. L.; He, Y. B.; He, P.; Zhou, H. S., Restraining Oxygen Loss and Suppressing Structural Distortion in a Newly Ti-Substituted Layered Oxide P2-Na0.66Li0.22Ti0.15Mn0.63O2. *Acs Energy Lett.* **2019**, *4* (10), 2409-2417.


39. Liu, K.; Zhang, Q. Q.; Dai, S.; Li, W.; Liu, X. J.; Ding, F.; Zhang, J. L., Synergistic Effect of F- Doping and LiF Coating on Improving the High-Voltage Cycling Stability and Rate Capacity of LiNi0.5Co0.2Mn0.3O2 Cathode Materials for Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* 2018, 10 (40), 34153-34162.