F-doped O3- $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ as high-performance cathode materials for sodium-ion batteries

Qin Zhang, Yangyang Huang, Yi Liu, Shixiong Sun, Kun Wang, Yuyu Li, Xiang Li, Jiantao Han* and Yunhui Huang*

ABSTRACT The F-doped O3-type $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{F}_x$ ($x = 0, 0.005, 0.01, 0.02$ and noted as NFM-F0, NFM-F0.005, NFM-F0.01, NFM-F0.02, respectively, united as NFM-Fs) cathode materials were investigated systematically. The rate performance and capacity retention of the O3-type cathode materials are significantly improved as a function of specific F-doping levels. Optimum performance is achieved in the NFM-F0.01 material having a capacity of $\sim 110 \text{ mA h g}^{-1}$ at a current density of 150 mA g^{-1} after 70 cycles. The results indicate that the binding energy of oxygen changes as a result of F-doping, and in addition, F-doping results in changes to the stoichiometry of $\text{Mn}^{3+}/\text{Mn}^{4+}$, which stabilizes the O3-type layered structure, thus allowing cycling performance to be improved. However, NFM-F0.02, having a higher F-doping level, retains a high capacity retention, although a slight loss is observed. The results suggest there is an optimum F-doping level for the NFM-F system to deliver enhanced cycling performance.

Keywords: O₃-type, $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$, F-doping, sodium-ion batteries

INTRODUCTION

In the past decades, lithium-ion batteries (LIBs) have been widely used in mobile electronic devices ascribed to their higher energy and power density when compared with various secondary batteries [1]. However, LIBs are not expected to meet future requirements of large-scale energy storage applications because of the scarcity of the lithium resource and cost considerations [2]. Therefore, there is a demand to develop alternative energy storage technologies to meet the need of the rapid development of electric vehicles (EVs), hybrid electrical vehicles (HEVs), smart grid and clean-energy industries [3,4].

Recently, sodium-ion batteries (SIBs) have attracted a

wealth of interdependent research because of the abundant and cheap sodium resources [5]. The cathode materials of SIBs such as layered Na_xMO_2 ($\text{M} = \text{Cr}, \text{Mn}, \text{Ti}, \text{Ni}, \text{Co}, \text{Fe}$, etc.) [6–12], polyanion compounds [13–15], and Prussian blue analogues [16] have been widely studied. Particularly, the layered cathode Na_xMO_2 received significant attention because of its high specific capacity, low cost, and facile preparation methods. These layered materials are classified as O3- and P2-type phases, where O and P represent the octahedral and trigonal prismatic sites, based on the location of the Na ion at octahedral and prismatic sites, respectively [11]. While the numbers 3 and 2 indicate the number of transition metal layers in the periodic cell unit [17]. The O3-phase layered oxide material has higher first discharge capacity, which is attributed to a higher Na content. However, the O3-phase suffers from an intrinsic problem of Fe migration when in the desodiated state with a voltage of $\sim 3.8 \text{ V}$ vs. Na/Na^+ , which results in structural collapse. Therefore, significant research efforts have focused on suppressing the irreversible Fe migration in the O3-type layered structure by Ni and Mn substitution into the Fe sites [11,18]. Recently, $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{NaNi}_{0.25}\text{Fe}_{0.5}\text{Mn}_{0.25}\text{O}_2$ were investigated as high capacity cathodes, which all crystallized into an O3-type layered structure. More recently, the effect of Ni and Fe substitution in O3-type layer systems and their optimal production were obtained with a high capacity and respectable capacity retention [19]. In this work, fluorine is introduced into O3-type layered cathodes for SIBs for the first time to investigate their electrochemical and related structural properties. Finally, the optimized ratio of fluorine in the cathode material was found to be $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_{1.99}\text{F}_{0.01}$.

School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

* Corresponding authors (emails: jthan@hust.edu.cn (Han J)); huangyh@hust.edu.cn (Huang Y))

EXPERIMENTAL SECTION

Material Synthesis

All chemical reagents were of analytical grade specification and were used as received. $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{F}_x$ ($x = 0, 0.005, 0.01, 0.02$ and noted as NFM-F0, NFM-F0.005, NFM-F0.01, NFM-F0.02, respectively, united as NFM-Fs) cathode materials were synthesized by a simple solid-state reaction method. Stoichiometric amounts of NaCO_3 (Aladdin, purity $\geq 99.8\%$), NiO (Aladdin, purity 99.0%), Fe_2O_3 (Aladdin, purity 99.0%), MnO_2 (Aladdin, purity 99%), and NaF (Aladdin, purity $\geq 99\%$) were mixed and ground together in an agate mortar for 1 h to obtain the precursor powders. The precursor powders were heated in a muffle furnace at 1000°C for 12 h at a heating rate of 3°C s^{-1} before cooling naturally to room temperature.

Characterization

The crystal structure of NFM-Fs was characterized by X-ray diffraction (XRD) using a PANalytical X'pert PRO MRO equipped with $\text{Cu K}\alpha$ radiation. Morphology, element composition and distribution were observed by scanning electron microscopy (SEM, Nova nanoSEM 450) under an accelerating voltage of 10 kV coupled to an energy dispersive X-ray spectroscopy (EDS) detector. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) observations were performed using a JEOL JEM-2100F microscope.

The binding energy of the materials was characterized by X-ray photo electron spectroscopy (XPS) (AXIS-ULTRA DLD-600W). Raman spectra were measured using a Renishaw Invia spectrometer with a laser wavelength of 514.5 nm. The XRD patterns were refined using the GSAS program based on the Rietveld method [20,21].

Electrochemical measurements

Electrochemical tests were performed in CR2032 coin cells with Na metal as the counter electrode. The cathode consisted of 70 mg active material, 20 mg Super-P conductive carbon, and 10 mg polyvinylidene fluoride (PVDF), which was dispersed in *N*-methyl-2-pyrrolidone (NMP). The obtained slurry was pasted onto aluminum foil acting as a current collector before drying under vacuum at 120°C for 12 h. The 2032-type coin cells were assembled comprising a working electrode, sodium counter electrode, glass fiber separator and sufficient electrolyte in an argon-filled glovebox. The electrolyte was 1 mol L^{-1} sodium perchlorate (NaClO_4 , Sigma-Aldrich) dissolved in propylene carbonate (PC, Sigma-Aldrich). The cells were left for 10 h before

testing in order to make the electrolyte fully-permeating active materials. The galvanostatic charge/discharge cycling was performed using a LAND CT2001A system (Wuhan Land Electronic Co. Ltd., China) at room temperature. Cyclic voltammetric (CV) tests were performed using an electrochemical working station (PARSTAT MC, Princeton Applied Research, US) with varying scan rates. Electrochemical impedance spectroscopy (EIS) was conducted on a PARSTAT MC potentiostat by sweeping the frequency from 0.01 to 10^5 Hz with an alternating current amplitude of 5 mV.

RESULTS AND DISCUSSION

The crystallographic structures of NFM-Fs with different F-doping levels were analyzed by XRD and the patterns are shown in Fig. 1a. All the diffraction peaks are indexed to the O3-type phase having the $\text{R}\bar{3}\text{m}$ space group (standard card JCPDS 25-0819). The XRD patterns show a slight difference among NFM-Fs, which is attributed to a relatively low F-doping ratio. As shown in Fig. 1a, the (003) peak has a slight left shift followed by a right shift with increasing F-doping content from 0.005 to 0.02, which suggests successful F ion substitution into the crystal lattice inducing structural change. Fig. 1b shows the schematic structure of NFM in which Na ions occupy the octahedral sites of the NaO_2 layer, while Fe, Ni and Mn ions are located at the octahedral sites of MO_2 . Lattice parameter variation as a function of F-doping content, which is obtained from the results of the XRD Rietveld refinement (see Fig. 2 and Table S1), is shown in Fig. 1c. As can be seen from Fig. 1c, the lattice parameter is first observed to decrease as a function of increased F-doping as the radius of F^- (1.33 Å) is smaller than that of O^{2-} (1.40 Å) [22] when the doping amount is less than 1%. However, further increasing the F-doping levels above 1% results in a lattice parameter increase, which is attributed to an elevated proportion of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and the larger ion radius of Mn^{3+} (0.645 Å) than Mn^{4+} (0.53 Å) [23]. To observe the crystal structure, HRTEM and SAED measurements were performed. In Fig. 1d, the lattice fringes with a d -spacing of $\sim 0.57\text{ nm}$ is assigned to the (003) planes.

The SAED pattern (inset of Fig. 1d) shows a perfect lattice structure, which consists with the XRD results. The SEM images of NFM-Fs (see Fig. S1) show that the morphology consists of irregular bulk particles $\sim 20\text{--}100\text{ }\mu\text{m}$ in size, which indicates that F-doping has little influence over the NFM-Fs morphology. Fig. S2 gives the EDS element mapping images of NFM-Fs and clearly demonstrates homogeneous distribution of the F element, which confirms

Figure 1 (a) XRD patterns for $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{F}_x$ ($x = 0, 0.005, 0.01, 0.02$ and noted as NFM-F0, NFM-F0.005, NFM-F0.01, NFM-F0.02, respectively, united as NFM-Fs) and enlarged view in the range of 14–19 degrees. (b) The schematic structure of NFM. (c) Lattice parameter variation as a function of F-doping amount; (d) the HRTEM image of NFM-F0.01, the inset is the SAED pattern of NFM-F0.01.

Figure 2 Rietveld refinement of NFM-Fs XRD patterns.

the successful introduction of F in the O3-type structure.

In Fig. 3a, Raman spectra of NFM-Fs exhibit three bands located at 600, 490, and 220 cm^{-1} , which are assigned to the anti-symmetric stretching vibration (B_{2g}), stretching vibration $A_1(g)$, and stretching vibration $A_2(g)$ mode of O, respectively. $A_2(g)$ reveals changes to the Mn-O bond angle, $A_1(g)$ and $B_{2g}(1)$ indicate changes to Mn-O bond distance. The peak at 490 cm^{-1} attributed to $A_1(g)$, right shifts, which suggests an increase of Mn^{3+} amount [24], which is in good agreement with the XPS results. In Fig. 3b, the O 1s band of NFM-F0.01 shows the highest binding energy across the NFM-Fs materials, which confirms the electrochemical results that a high capacity retention is associated with a stable crystal structure.

Fig. 4 shows the XPS of the Mn 2p regions for NFM-Fs and the peaks located at 655 and 643 eV are assigned to Mn^{3+} and Mn^{4+} , respectively, which indicates that the Mn oxidation state is between +3 and +4, and the valence change of Mn verifies the charge compensation effect resulting from F-doping. The Mn^{3+} to Mn^{4+} ratio is obtained by the respective peak areas as shown in Table 1. The results indicate that Mn^{3+} concentration increases as a function of increasing F-doping levels [23,25,26]. It is known that the more Mn^{3+} present in the system, the better electrochemical performance is achieved. However, excessive Mn^{3+} causes rapid capacity fading because of the John-Teller distortion of Mn^{3+} .

To investigate the electrochemical performance of the NFM-Fs, the discharge curves were performed at various

current densities across a potential range of 2.0–4.0 V. As shown in Fig. 5, the NFM-Fs voltage plateaus at ~ 2.8 V, which suggests no obvious changes to the operating voltage as a function of F-doping. Furthermore, the reversible capacities of NFM-Fs are practically identical when subjected to a small current of 30 mA g^{-1} . At high current densities of 150 and 300 mA g^{-1} , NFM-F0.01 shows the best rate performance. Fig. 6 displays the cycle performance of NFM-Fs in the voltage range of 2.0–4.0 V at a current density of 150 mA g^{-1} . F-doped NFM-Fs show superior cyclicity compared with F-free NFM. The F-free NFM-F0 suffers from severe capacity fading, only retaining a capacity of $\sim 60 \text{ mAh g}^{-1}$ after 70 cycles. In comparison, the 70th discharge capacity of NFM-F0.01 is $\sim 110 \text{ mAh g}^{-1}$ with a retention of $\sim 85\%$. Additionally, the results show that excessive F-doping plays a negative role on capacity retention, as shown in NFM-F0.02. As reported, excessive Mn^{3+} causes rapid capacity fading because of the John-Teller effect [27], but the appropriate content of Mn^{4+} can maintain the stability of the structure, which suggests there is an optimal F-doping level in the NFM-Fs system to enhance cycle performance.

Fig. 7a shows the CV curves of F-free NFM-F0 and NFM-F0.01 in the voltage range of 2.0–4.0 V at 0.1 mV s^{-1} . A pair of sharp peaks at 2.85 and 3.05 V are observed, which mainly correlate to the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox reaction. It is evident that the redox/oxidation peaks of NFM-F0.01 are higher than that of NFM-F0, indicating a lower degree of polarization in the NFM-F0.01 cathode material, which means Na^+ diffusion in NFM-F0.01, is higher than that of NFM-F0.

It is known that Na^+ diffusion is related to the peak shape and peak current evolution of the CV curves at different sweep rates. Fig. S3 shows the CV curves of NFM-Fs at various scan rates from 0.1 to 1.0 mV s^{-1} across a voltage

Table 1 The $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratios of NFM-Fs

Sample	$x=0$	$x=0.005$	$x=0.01$	$x=0.02$
Mn^{3+}	41.89%	42.36%	43.00%	43.17%
Mn^{4+}	58.11%	57.64%	57.00%	56.83%

Figure 3 (a) Raman spectra of NFM-Fs samples. (b) XPS collected at O of NFM-Fs.

Figure 4 XPS collected at Mn 2p regions of NFM-Fs: (a) NFM-F0, (b) NFM-F0.005, (c) NFM-F0.01, (d) NFM-F0.02.

Figure 5 Discharge curves of NFM-Fs at different current densities: (a) NFM-F0, (b) NFM-F0.005, (c) NFM-F0.01, (d) NFM-F0.02.

Figure 6 Cycling stability of the NFM-Fs at 150 mA g⁻¹.

Figure 7 (a) The first CV curves at a scan rate of 0.1 mV s⁻¹ of NFM-F0 and NFM-F0.01. (b) The relationship of peak current (i_p) and the square root of scan rate ($\nu^{1/2}$) of NFM-Fs.

range of 2.0–4.0 V. The peak currents (i_p) of the oxidation and reduction peaks increase with increasing scan rates. The diffusion coefficient (D) of Na⁺ can be estimated according to Equation (1):

$$i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} \nu^{1/2} C_0, \quad (1)$$

where i_p is the peak current (mA), n is the number of electrons per reaction species (1.0 for Na⁺), A is the area between both electrodes (here the area of the electrode is ~ 0.64 cm²), D is the diffusion coefficient of Na⁺, ν is the scan rate (mV s⁻¹) and C_0 is the concentration of Na⁺. As shown in Fig. 7b, i_p has a linear relationship with the square root of the scan rate. According to the slope of the straight lines acquired from the plots of i_p vs. $\nu^{1/2}$, the diffusion coefficients D of NFM-Fs are: 1.037×10^{-12} , 3.076×10^{-12} , 6.796×10^{-12} , and 1.742×10^{-12} cm² s⁻¹, respectively [28], which reveals that the Na⁺ diffusion coefficients of NFM-Fs are enhanced greatly as a result of F-doping, with the highest coefficient observed in NFM-F0.01.

Furthermore, the EIS spectra (see Fig. 8) of NFM-F0 and NFM-F0.01 were measured before the charge/discharge test. The results show that both the EIS spectra consist of a small intercept on the horizontal axis located in the high frequency region, a semicircle at the intermediate frequency region, and an oblique line present at the low frequency region. The intercept corresponds to ohmic resistance (R_s). R_s mainly includes the electrolyte resistance, particle-particle contact resistance, and the resistance between the electrode and current collector. The semicircle in the high and middle frequency range is ascribed to the charge transfer resistances (R_{ct}) and its corresponding constant-phase-angle element (Q_{ct}) at the electrode/electrolyte. The oblique line at the low frequency is attributed to Warburg impedance (W_o), which results in Na⁺ diffusion resistance in the electrodes.

Our results show that the R_{ct} values are 140.7, 127.4, 100.2 and 118.3 Ω for NFM-F0, NFM-F0.005, NFM-F0.01 and NFM-F0.02, respectively, which verifies the above CV results that NFM-F0.01 has a higher ionic conductivity than that of F-free NFM-F0.

Figure 8 EIS plots of the NFM-Fs samples.

CONCLUSIONS

In summary, the F-doped O3-type NFM cathode materials were successfully synthesized *via* a one-step solid-state reaction method. F-doping greatly improves the electronic and Na⁺ conductivity of NFM-Fs. NFM-F0.01 exhibits the best cycling stability and rate performance with a discharge capacity of ~110 mAhg⁻¹ after the 70th cycle at a current density of 150 mA g⁻¹ with a capacity retention ratio of ~90%. The enhanced cycling stability is attributed to two effects: (i) F-doping adjusts the binding energy of oxygen and the ratio of Mn³⁺/Mn⁴⁺, which can suppress the Jahn-Teller effect of Mn³⁺ and consequently facilitate NFM-F electrochemical performance; (ii) F-doping allows a higher Na⁺ diffusion rate, resulting in improved rate performance.

Received 8 March 2017; accepted 28 April 2017;
published online 2 June 2017

- Peng L, Zhu Y, Chen D, *et al.* Two-dimensional materials for beyond-lithium-ion batteries. *Adv Energ Mater*, 2016, 6: 1600025
- Zhu YE, Qi X, Chen X, *et al.* A P2-Na_{0.67}Co_{0.5}Mn_{0.5}O₂ cathode material with excellent rate capability and cycling stability for sodium ion batteries. *J Mater Chem A*, 2016, 4: 11103–11109
- Wang J, He X, Zhou D, *et al.* O3-type Na[Fe_{1/3}Ni_{1/3}Ti_{1/3}]O₂ cathode material for rechargeable sodium ion batteries. *J Mater Chem A*, 2016, 4: 3431–3437
- Zhu Y, Peng L, Chen D, *et al.* Intercalation pseudocapacitance in ultrathin VOPO₄ nanosheets: toward high-rate alkali-ion-based electrochemical energy storage. *Nano Lett*, 2016, 16: 742–747
- Buchholz D, Chagas LG, Vaalma C, *et al.* Water sensitivity of layered P2/P3-Na_{0.22}Co_{0.11}Mn_{0.66}O₂ cathode material. *J Mater Chem A*, 2014, 2: 13415–13421
- Yu CY, Park JS, Jung HG, *et al.* NaCrO₂ cathode for high-rate sodium-ion batteries. *Energ Environ Sci*, 2015, 8: 2019–2026
- Billaud J, Clément RJ, Armstrong AR, *et al.* β-NaMnO₂: a high-performance cathode for sodium-ion batteries. *J Am Chem Soc*, 2014, 136: 17243–17248
- Wu D, Li X, Xu B, *et al.* NaTiO₂: a layered anode material for sodium-ion batteries. *Energ Environ Sci*, 2015, 8: 195–202
- Vassilaras P, Ma X, Li X, *et al.* Electrochemical properties of monoclinic NaNiO₂. *J Electrochemical Soc*, 2013, 160: A207–A211
- Sathiyam M, Hemalatha K, Ramesha K, *et al.* Synthesis, structure, and electrochemical properties of the layered sodium insertion cathode material: NaNi_{1/3}Mn_{1/3}Co_{1/3}O₂. *Chem Mater*, 2012, 24: 1846–1853
- Yabuuchi N, Kajiyama M, Iwatate J, *et al.* P2-type Na_x[Fe_{1/2}Mn_{1/2}]O₂ made from earth-abundant elements for rechargeable Na batteries. *Nat Mater*, 2012, 11: 512–517
- Yuan DD, Wang YX, Cao YL, *et al.* Improved electrochemical performance of Fe-substituted NaNi_{0.5}Mn_{0.5}O₂ cathode materials for sodium-ion batteries. *ACS Appl Mater Interfaces*, 2015, 7: 8585–8591
- Kim H, Park I, Lee S, *et al.* Understanding the electrochemical mechanism of the new iron-based mixed-phosphate Na₄Fe₃(PO₄)₂(P₂O₇) in a Na rechargeable battery. *Chem Mater*, 2013, 25: 3614–3622
- Chen H, Hautier G, Ceder G. Synthesis, computed stability, and crystal structure of a new family of inorganic compounds: carbonophosphates. *J Am Chem Soc*, 2012, 134: 19619–19627
- Jian Z, Han W, Lu X, *et al.* Superior electrochemical performance and storage mechanism of Na₃V₂(PO₄)₃ cathode for room-temperature sodium-ion batteries. *Adv Energ Mater*, 2013, 3: 156–160
- Lu Y, Wang L, Cheng J, *et al.* Prussian blue: a new framework of electrode materials for sodium batteries. *Chem Commun*, 2012, 48: 6544–6546
- Han MH, Gonzalo E, Singh G, *et al.* A comprehensive review of sodium layered oxides: powerful cathodes for Na-ion batteries. *Energ Environ Sci*, 2015, 8: 81–102
- Wang X, Liu G, Iwao T, *et al.* Role of ligand-to-metal charge transfer in O3-type NaFeO₂-NaNiO₂ solid solution for enhanced electrochemical properties. *J Phys Chem C*, 2014, 118: 2970–2976
- Hwang JY, Myung ST, Aurbach D, *et al.* Effect of nickel and iron on structural and electrochemical properties of O3 type layer cathode materials for sodium-ion batteries. *J Power Sources*, 2016, 324: 106–112
- Toby BH. EXPGUI, a graphical user interface for GSAS. *J Appl Crystall*, 2001, 34: 210–213
- McCusker LB, Von Dreele RB, Cox DE, *et al.* Rietveld refinement guidelines. *J Appl Crystall*, 1999, 32: 36–50
- Milović M, Jugović D, Cvjetičanin N, *et al.* Crystal structure analysis and first principle investigation of F doping in LiFePO₄. *J Power Sources*, 2013, 241: 70–79
- Deng YF, Zhao SX, Xu YH, *et al.* Impact of P-doped in spinel LiNi_{0.5}Mn_{1.5}O₄ on degree of disorder, grain morphology, and electrochemical performance. *Chem Mater*, 2015, 27: 7734–7742
- Wang PF, You Y, Yin YX, *et al.* Suppressing the P2-O2 phase transition of Na_{0.67}Mn_{0.67}Ni_{0.33}O₂ by magnesium substitution for improved sodium-ion batteries. *Angew Chem Int Ed*, 2016, 55: 7445–7449
- Biesinger MC, Payne BP, Grosvenor AP, *et al.* Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl Surface Sci*, 2011, 257: 2717–2730
- Tang D, Sun Y, Yang Z, *et al.* Surface structure evolution of LiMn₂O₄ cathode material upon charge/discharge. *Chem Mater*, 2014, 26: 3535–3543
- Mortemard de Boisse B, Cheng JH, Carlier D, *et al.* O3-Na_xMn_{1/3}Fe_{2/3}O₂ as a positive electrode material for Na-ion batteries: structural evolutions and redox mechanisms upon Na⁺ (de)intercalation. *J Mater Chem A*, 2015, 3: 10976–10989
- Yu H, Rui X, Tan H, *et al.* Cu doped V₂O₅ flowers as cathode material for high-performance lithium ion batteries. *Nanoscale*, 2013, 5: 4937–4943

Acknowledgments This work was supported by the National High-Tech R&D Program of China (2015AA034601, 2016YFB010030X, and 2016YFB0700600). The authors also thank the State Key Laboratory of Materials Processing and Die & Mould Technology and the Analytical and Testing Center of Huazhong University of Science Technology.

Author contributions Huang Y and Han J designed and guided the work; Zhang Q, Huang YY, Liu Y projected the experiments. Zhang Q and Wang K performed the experiments. All authors contribute to the analysis of data and general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Zhang Qin received her BSc degree from Qingdao University of Science and Technology (QUST). She is now a Master candidate at Huazhong University of Science and Technology (HUST), and her research focuses on sodium-ion batteries.

Jiantao Han received his BSc and MSc degrees from Liaoning University and PhD degree from Fudan University. He worked as postdoctoral researcher at the University of Texas at Austin from 2007 to 2010. He worked as a research scientist in Los Alamos National laboratory from 2010 to 2012 and also worked as senior scientist in Pellion Technologies. Now he is a professor of materials science in Huazhong University of Science and Technology.

Yunhui Huang received his BSc, MSc and PhD degrees from Peking University. In 2000, he worked as a postdoctoral researcher at Peking University. From 2002 to 2004, he worked as an associate professor at Fudan University and a JSPS fellow at Tokyo Institute of Technology, Japan. He then worked in the University of Texas at Austin for more than three years. His research group works on batteries of energy storage and conversion. For details please see the lab website: <http://www.sys-doing.com.cn>.

氟元素掺杂O3-NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂正极材料的储钠性能研究

张芹, 黄洋洋, 刘义, 孙世雄, 王坤, 李煜宇, 李翔, 韩建涛*, 黄云辉*

摘要 本文通过固相法制备出NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_{2-x}F_x ($x = 0, 0.005, 0.01, 0.02$) 正极材料. 该材料的电化学性能表明F元素的掺杂有利于提高其循环性和稳定性. 其中当F元素的掺杂量为0.01时, 材料的电化学性能最为优异, 在150 mA g⁻¹的电流密度下, 循环70圈容量仍保持在110 mAh g⁻¹. 通过XPS、Raman等表征方法研究了F元素掺杂提高材料电化学性能的机理. 本工作对于F元素掺杂钠电层状正极材料研究具有一定的参考意义.