

Communication



Expanded K_{0.37}Fe_{0.04}Al_{0.07}Mn_{0.89}O₂ Layered Material as a High-Performance Cathode in Sodium-Ion Batteries

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Abstract: Due to a high operating voltage and theoretical capacity, P2-type layered Mn-based metal oxides are considered to be promising cathodes in sodium-ion batteries, but their poor structural stability in the process of Na⁺ insertion/deinsertion severely hinders their practical application. Here, an interesting K⁺ pre-intercalation is used to expand the interlayer distance and enhance the electrochemical reversibility of K_sFe_xAl_yMn_zO₂. With a suitable K⁺ content, the optimized electrode shows a high specific capacity of 135 mAh g⁻¹ at 0.1 C, a good rate capability of 80 mAh g⁻¹ at 5 C and an excellent cycling performance of 76.4% capacity retention after 200 cycles at a high rate of 5 C. This work proves the feasibility of a K⁺ pre-intercalation strategy in a P2-type layered cathode.

Keywords: layered $K_{0.37}$ Fe_{0.04}Al_{0.07}Mn_{0.89}O₂ cathode; expanded interlayer spacing; good structural stability; sol–gel method; sodium-ion batteries

1. Introduction

Sodium-ion batteries (SIBs) are widely considered to be one of the most significant potential next-generation energy storage devices due to their similar working principle to lithium ion batteries, high safety and low cost [1–7]. Outstanding cathode materials with an excellent working voltage, a high specific capacity and good structural stability are key for the commercial application of SIBs [8–11]. Among the reported cathode materials, P2-type layered Mn-based metal oxides have had great attention from researchers because of their high operating voltage. However, a low discharge capacity and an unfavorable P2–O2 phase transition at a high voltage severely hinder their practical application [12–15].

To enhance the electrochemical properties of P2-type layered Mn-based metal oxides, many methods have been tested such as surface modifications and metal-ion doping [16–18]. Vanaphuti and coworkers designed a highly sustainable cobalt-free P2 Na_{0.72}Mn_{0.75}Li_{0.24}X_{0.01}O₂ (X = Ti/Si) cathode, where Ti worked as a protective layer and alleviated the side reactions in a carbonate-based electrolyte and Si regulated the local electronic structure and suppressed the oxygen redox activities, leading to good electrochemical properties [19]. Hwang et al. reported a Cu-doped Mn-based P2-type Na_{0.67}Cu_{0.125}Fe_{0.375}Mn_{0.5}O₂ cathode; the introduction of Cu generated electron holes above the Fermi level in the electronic structure and suppressed the phase transition from the P2 to the Z phase, which resulted in an improved structural stability [20]. Alkali site doping is also an effective method as well as Mn site doping; both methods have recently gained attention. Chen and coworkers prepared a novel layered K_{0.7}Mn_{0.7}Ni_{0.3}O₂ cathode with interlayer spacing of 0.69 nm, which was higher than that of a Na_{0.7}Mn_{0.7}Ni_{0.3}O₂ cathode (0.563 nm); thus, it showed a high reversible capacity of 161.8 mAh g⁻¹ at 0.1 A g⁻¹, a superior rate capability of 71.1 mAh g⁻¹ at 5 A g⁻¹ and a long-term cycling performance of 500 cycles [21]. Wang



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). et al. reported $K_{0.4}Ni_{0.2}Mn_{0.8}O_2$ with a "pillar-beam" structure and freely diffused Na⁺ in an interlayer; excellent electrochemical properties were obtained due to multiple advantages [22]. The above works reflect the feasibility and advantage of a K⁺ pre-intercalation strategy.

Mn-based metal oxides undergo severe phase transitions because of the Jahn–Teller distortion induced by Mn³⁺, resulting in distinct capacity fading. To improve stability, the partial substitution of manganese by electrochemically active and/or inactive transition metals such as Fe, Ni and Mg is considered to be an effective method. Among these metals, the introduction of Fe and Al is beneficial to suppresses the Jahn–Teller distortion. The simultaneous introduction of Fe and Al may prompt an excellent structural stability, which is rarely reported.

In this work, novel P2-type $K_sFe_xAl_yMn_zO_2$ layered cathodes are prepared by a solgel method followed by high-temperature calcination. By adjusting the content of K⁺, the structural stability and diffusion rate are optimized. Thus, the $K_{0.37}Fe_{0.04}Al_{0.07}Mn_{0.89}O_2$ cathode shows a high reversible capacity, an excellent rate capability and a long cyclic life. This work proves the feasibility of a K⁺ pre-intercalation strategy in P2-type layered Mn-based metal oxides.

2. Materials and Methods

2.1. Material Preparation

 $K_sFe_xAl_yMn_zO_2$ was synthesized by the sol–gel method followed by calcination in air. Typically, 8.2/9.0/10.1 mmol CH₃COOK, 0.8 mmol Fe(NO₃)₃·9H₂O, 0.8 mmol Al(NO₃)₃·9H₂O and 13.5 mmol (CH₃COO)₂Mn were dissolved in distilled water then 37.5 mmol citric acid was added to the solution with continuous stirring. The solution was kept in an oven at 90 °C for 12 h to obtain a fluffy porous substance. After grinding, the precursor was calcined at 350 °C in air for 5 h and cooled down to room temperature. The obtained material was ground and finally annealed at 900 °C for 10 h to obtain the target product. The products were denoted as KFAM-1, KFAM-2 and KFAM-3, which corresponded with 8.2, 9.0 and 10.1 mmol CH₃COOK in the raw materials, respectively.

2.2. Characterization

The morphologies of the materials were viewed using a scanning electron microscope (SEM, S4800, Hitachi, Japan). The crystal structure and compositions of the materials were studied using X-ray diffraction (XRD, D-MAX 2200 VPC, Rigaku, Japan).

2.3. Electrochemical Tests

The electrochemical performances of the KFAM-X were tested by CR2032 coin-type cells using Na foil as working and reference electrodes. Whatman glass fiber (GF/D) acted as a membrane. The electrolyte consisted of 1 mol L⁻¹ NaClO₄ in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 in volume) with the addition of 5 vol.% fluoroethylene carbonate (FEC). The charge and discharge tests were performed by an Arbin BT2000 system at 25 °C. The positive electrode consisted of 80 wt.% active materials, 10 wt.% conductive carbon (super P) and 10 wt.% polyvinylidene fluoride (PVDF) binder. A ball mill was used to mix the materials and was rotated at 700 rpm for 30 min. The obtained slurry was cast onto an Al foil and dried at 90 °C overnight in a vacuum drying oven. The mass loading was about 1.5 mg cm⁻².

3. Results and Discussion

The X-ray diffractometry (XRD) pattern was collected to analyze the crystal structure of the KFAM-X (Figure 1). The characteristic peaks of the KFAM-X were similar to previously reported $K_{0.7}Mn_{0.7}Ni_{0.3}O_2$. Its peaks at 12.8°, 25.8°, 36.6°, 37.2°, 47.8°, 51.1° and 57.7° were assigned to (003), (006), (101), (102), (105), (107) and (108) planes, which indicated the layered structure of the KFAM-X [21,22]. Its *d*-spacing was 6.95 Å, distinctly higher than the diameter of Na⁺. We noted that the peaks of KFAM-2 were stronger than those of KFAM-1. There were several impurity peaks of K₂O (JCPDS no. 77-2176) and K(H₂O)OH

(JCPDS no. 77-1221) for KFAM-3, reflecting that excessive K^+ could not intercalate to the interlayer (Figure S1). Thus, all potassium ions of KFAM-1 and KFAM-2 were included in the P2 structure; a part of K^+ in KFAM-3 was not included in the P2 structure. The results of XRD indicated that the P2-type KFAM-2 layered cathode could show a good electrochemical performance.



Figure 1. XRD patterns of KFAM-X.

The morphology of the KFAM-X was studied by scanning electron microscope (SEM) images. As shown in Figure 2, the KFAM-X consisted of many nanoparticles with an irregular shape and a size of 300–500 nm. There were no obvious differences between the KFAM-X samples with different K⁺ contents. To further determine the compositions of the KFAM-X, energy dispersive X-ray (EDX) spectra and elemental mapping were collected (Figure 3, Figures S2 and S3). The EDX spectra proved the presence of elemental K, Fe, Al, Mn and O (Figure 3b, Figures S2b and S3b). According to the elemental ratios, the chemical formulas of the KFAM-X were determined to be K_{0.34}Fe_{0.04}Al_{0.07}Mn_{0.89}O₂, K_{0.37}Fe_{0.04}Al_{0.07}Mn_{0.89}O₂ and K_{0.42}Fe_{0.04}Al_{0.07}Mn_{0.89}O₂. The elemental mapping showed the uniform distribution of K, Fe, Al, Mn and O, even reflecting K⁺ pre-intercalation (Figure 3c, Figures S2c and S3c).



Figure 2. SEM images of (a,d) KFAM-1, (b,e) KFAM-2 and (c,f) KFAM-3.



Figure 3. (a) ADF image, (b) EDX spectrum and (c) elemental mapping of KFAM-2.

The electrochemical properties of the KFAM-X were tested in a 2020 coin-type cell. The electrochemical impedance spectra (EIS) were then compared (Figure 4a). The charge transfer and interfacial resistances could not be separated; thus, they were denoted as R_{ct+int} . The ohmic resistance (R_o) and R_{ct+int} of KFAM-2 were 16 and 440 Ω , respectively, smaller than those of KFAM-1 (21 and 710 Ω , respectively) and KFAM-3 (35 and 570 Ω , respectively). The slope of the line at the low-frequency area of KFAM-2 was also larger than that of KFAM-1 and KFAM-3, indicating the fastest Na⁺ transfer rate of KFAM-2 from the electrolyte to the electrode surface. The excellent conductivity of KFAM-2 was attributed to its high crystallinity and purity. Figure 4b-d exhibits the charge-discharge curves of the KFAM-X and their curves showed a similar shape. The 1st and 2nd discharge capacities of KFAM-2 were 61 and 141 mAh g⁻¹, respectively, larger than those of KFAM-1 (59 and 113 mAh g^{-1} , respectively) and KFAM-3 (60 and 113 mAh g^{-1} , respectively). Previous studies have found that sodium ions enter the structure of KFAM-X by both an ion exchange and electrochemical intercalation during the 1st discharge process and Na⁺ can be extracted after the 1st charge process, which leaves a greater number of vacancies for the next discharge [21,22]. The EDX spectra of the KFAM-X after cycling were collected (Figures S4–S6). Both Na and K elements could be found, proving the above-mentioned mechanism. The cyclic life of the KFAM-X was further compared. At a current density of 0.1 C, KFAM-2 displayed a good coulombic efficiency and the highest discharge capacity (Figure 4e). After 50 cycles, the discharge capacity of KFAM-2 was 124 mAh g^{-1} , higher than that of KFAM-1 (114 mAh g^{-1}) and KFAM-3 (83 mAh g^{-1}). Furthermore, a cyclic life at 2 C was performed. After 200 cycles, the capacity retention of KFAM-2 (78%) was obviously higher than that of KFAM-1 (58%) and KFAM-3 (26%) (Figure 4f). At the beginning of cycling, a part of K^+

ential (V vs. Na/Na[†])

3.

3.0

2.0

Specific Capacity (mAh·g⁻¹)



(¹.2.4K

apacity

120

80

40

escapes from the interlayer and results in a greater number of active sites for Na⁺ storage, which leads to an initial capacity increase [22].

Figure 4. (a) EIS plots of KFAM-X. The 1st and 2nd charge–discharge curves of (b) KFAM-1, (c) KFAM-2 and (d) KFAM-3. Cyclic life of KFAM-X at (e) 0.1 and (f) 2 C.

0.1 C

20

Cycle Number

The electrochemical properties of KFAM-2 were surveyed further. The 1st–3rd cyclic voltammetry (CV) curves are exhibited in Figure 5a. Two pairs of main redox peaks at 2.1/2.7 and 3.1/3.5 *V* could be seen, reflecting a stepwise Na⁺ insertion/deinsertion. The charge–discharge curves at different densities showed a similar shape, suggesting the outstanding electrochemical dynamics of KFAM-2 (Figure 5b). At current densities of 0.1, 0.2, 0.5, 1, 2 and 5 C, the discharge capacities were 135, 129, 116, 107, 96 and 80 mAh g⁻¹, respectively. The cyclic life of KFAM-2 at a large current density of 5 C was tested to prove its superiority (Figure 5c). After 200 cycles, a high capacity retention of 72% was obtained. To calculate the diffusion coefficient of Na⁺, the CV curves at scan rates from 0.2 to 2 mV s⁻¹ were collected (Figure 5d). The diffusion coefficient was counted by the following Equation (1) [23]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{Na}^{1/2} C_{Na} V^{1/2} \tag{1}$$

%

Efficiency (mAh·g^{-b}

apacity

30

-KFAM.

KFAM-2 KFAM-3

80 120

Cycle Number

60

40

KFAM-2 KFAM-3

where I_p , n, A, D_{Na} , C_{Na} and V are the peak current, the number of electron transfers in the redox process, the contact area between the electrolyte and the active substance, the diffusion coefficient, the concentration of sodium ions in the lattice and the scan rate. It could be simplified to: $I_p = 6487.6D_{Na}^{1/2}V^{1/2}$. Figure 5e,f were obtained according to the reduction and oxidation peaks at different scan rates. According the plots of $I_p-V^{1/2}$, the diffusion coefficients were 3.68×10^{-11} and 4.69×10^{-11} cm² s⁻¹, respectively, reflecting the fast charge transfer and storage of KFAM-2.

The XRD patterns of the KFAM-X after 50 cycles at 1 C were tested to detect their structural stability, as shown in Figure S7. There were no obvious changes for the characteristic peaks of KFAM-1 and KFAM-2, reflecting their good structural stability. A few peaks of $Na_sFe_xAl_yMn_zO_2$ could be found in KFAM-2, revealing its poor structural stability and phase transformation.



Figure 5. (a) The 1st–3rd CV curves, (b) charge–discharge curves at different current densities, (c) cyclic life at 5 C, (d) CV curves at different scan rates and (e,f) I_p – $V^{1/2}$ plots of KFAM-2.

4. Conclusions

In summary, novel P2-type $K_xFe_{0.04}Al_{0.07}Mn_{0.89}O_2$ layered cathodes were designed by the high-temperature calcination of a precursor obtained by a sol–gel method. The inactive K⁺ enlarged the interlayer spacing to expand the diffusion channels and hindered an adverse P2–O2 phase transition. With a suitable K⁺ content, the structural stability and diffusion rate were improved. Thus, a $K_{0.37}Fe_{0.04}Al_{0.07}Mn_{0.89}O_2$ cathode with a large interlayer distance showed a high specific capacity of 135 mAh g⁻¹ at 0.1 C, a good rate capability of 80 mAh g⁻¹ at 5 C and an excellent cycling performance of 76.4% capacity retention after 200 cycles at a high rate of 5 C. In this work, we prove the feasibility of a K⁺ pre-intercalation strategy and provide a new way of designing a layered cathode in a sodium-ion battery.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/en15155659/s1, Figure S1: XRD pattern of KFAM-3; Figure S2: Elemental analysis of KFAM-1; Figure S3: Elemental analysis of KFAM-3; Figure S4: Elemental analysis of KFAM-1 after cycling; Figure S5: Elemental analysis of KFAM-2 after cycling; Figure S6: Elemental analysis of KFAM-3 after cycling; Figure S7: XRD patterns of KFAM-X after cycling.

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