Synthesis of Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ and its application as cathode material of sodium ion battery

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Abstract. The Prussian blue cathode material with a unique three-dimensional structure in sodium ion batteries had great potential. Na$_2$MnFe(CN)$_6$ and Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ cathode materials were prepared by the improved co-precipitation method of chelating agent, and the electrochemistry of the half-cell was tested. The results showed that the first discharge capacity of the two materials can reached 152.4mAh/g and 119.5mAh/g respectively at 0.1C (1C=170mA/g). The capacity retention rate of Na$_2$MnFe(CN)$_6$ was only 43.2% after 100 cycles at 0.2C current density, but Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ can reached 70%. The capacity retention of Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ can still reached 69.8% after 100 cycles at 0.5C current density. The discharge specific capacity fluctuation of Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ was smaller than that of Na$_2$MnFe(CN)$_6$.

1. Introduction

With the intelligent of modern industry and the rapid development of the energy storage industry, rechargeable batteries are widely used in mobile electronic devices and electric vehicles, and have become an indispensable part of today's society. Among various energy storage systems, compared with other traditional energy storage devices, lithium-ion batteries have the advantages of high energy density and long service life. However, the scarcity and uneven distribution of lithium resources have gradually increased the production cost of lithium-ion batteries, limiting the application of lithium-ion batteries in large-scale energy storage[1,2,3]. Therefore, it is necessary to develop a new type of inexpensive energy storage equipment to meet large-scale energy storage applications. Because sodium resources are richer than lithium resources, they are more widely distributed and lower in cost, and sodium shows similar electrochemistry to lithium, which makes sodium ion batteries have received extensive attention in recent years[4,5]. The Prussian blue analogue(PBA) has become a popular cathode material for sodium ion batteries in recent years due to its excellent electrochemistry and unique open frame structure. The general formula of Prussian blue analogues is A$_x$M$_AM_B$(CN)$_6$, where M$_A$ and M$_B$ is usually a transition metal element, A is an alkali metal element[6]. It can be seen from the general formula that it takes transition metal elements as the central atom, CN$^-$ as ligands, and alkali metal elements to fill it to form a three-dimensional face-centered cubic structure with unique open frame characteristics[7,8]. In theory, redox reaction of 2e$^-$ can be completed and migration of two Na$^+$ can be achieved in Mn-based Prussian blue analogue (Mn-PBA) sodium ion battery. So it has a higher theoretical specific capacity(170mAh/g)[9]. Studies have shown that Mn-PBA prepared under different preparation conditions has different material properties. The Mn-PBA after high-vacuum
drying has fewer lattice defects, and the first discharge capacity at 0.1C reaches 150mAh/g[10]. MnNi-PBA obtained by doping Ni$^{+1}$ can improve its structural stability[11]. Mn-PBA has excellent cycle performance and rate performance by covering conductive polymer material[12]. Therefore, modifying Mn-PBA to improve its electrochemical has far-reaching research significance. In this work, the Prussian blue cathode material Na$_2$MnFe(CN)$_6$ with high capacity was prepared by improving the solution co-precipitation method by chelating agent, and then Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ was prepared by doping 20% Fe$^{+2}$. Their electrochemical performance was measured.

2. Experimental

2.1. Materials
The raw materials used in this experiment included Na$_4$Fe(CN)$_6$·10H$_2$O, MnCl$_2$·4H$_2$O, NaCl, FeCl$_2$·4H$_2$O, C$_6$H$_5$Na$_3$O$_7$ and absolute ethanol. All the above chemical materials were analytically pure and had not been processed.

2.2. Sample preparation

2.2.1. Preparation of Na$_2$MnFe(CN)$_6$.
First, 14g NaCl and 0.003mol Na$_4$Fe(CN)$_6$·10H$_2$O were added to 100ml deionized water to obtain solution A, and then 14g NaCl, 0.006mol MnCl$_2$·4H$_2$O and 0.006mol C$_6$H$_5$Na$_3$O$_7$ were added to 100ml of deionized water to obtain solution B. B dropped into A (the dropping rate is 1mL/min) at 80°C, and continued to react for 4 hours after the addition was complete. Finally, the obtained precipitate was washed and dried in a vacuum drying oven at 60°C for 12 hours. The sample was shown in figure 1.

2.2.2. Preparation of Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$.
The synthesis steps were the same as before, except that 0.006mol MnCl$_2$·4H$_2$O in solution B was replaced by 0.0012mol FeCl$_2$·4H$_2$O, and 0.0048mol MnCl$_2$·4H$_2$O, and the final sample was shown in the figure 2.

2.3. Electrochemical measurements
First, take the active material (sample), conductive agent (acetylene black), and binder (PVDF) according to the mass ratio of 7:2:1 and add them to the agate mortar. Then add an appropriate amount of 1-methyl-2-pyrrolidone (NMP) to the inside for grinding. After grinding and stirring for 1 hour, slowly pour the uniform slurry on a 30cm*20cm aluminum foil and dried at 80°C under vacuum for 12h to ensure that all NMP evaporates cleanly. The dried pole piece film is cut into 10mm round electrode pieces. Finally, put electrode sheet (positive electrode), Sodium tablets (negative electrode), diaphragm (glass fiber whatman1825-047), electrolyte(1mol/L NaClO$_4$, PC:EC=1:1, 5% FEC), positive case, negative case, gasket, and shrapnel in a glove box filled with argon to assemble button batteries. The assembled half-cell was tested by Land CT2001A tester.
3. Results and discussion
Tested cycle performance and rate performance of Na$_2$MnFe(CN)$_6$ and Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$, and the result is as follows.

![Figure 3. First charge and discharge curve at 0.1C (1C=170mAh/g)](image)

![Figure 4. Discharge capacity at 0.2C](image)

![Figure 5. Rates capacity](image)

![Figure 6. Cycle performance at 0.5C](image)

In figure 3, the charging curve of Na$_2$MnFe(CN)$_6$ had two platforms, which correspond to 3.5V (Fe$^{2+}$$\rightarrow$Fe$^{3+}$) and 3.7V (Mn$^{2+}$$\rightarrow$Mn$^{3+}$) respectively. The discharge capacity can reached 152.4mAh/g. The Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ cathode material prepared by doping with iron ions only showed a voltage plateau, and the first-lap discharge capacity was 119.5mAh/g. Figure 4 showed the two materials were charged and discharged for 100 cycles at 0.2C. The cycle curve of Na$_2$MnFe(CN)$_6$ is relatively steep and the capacity decays quickly, the discharge capacity was less than 60mAh/g, and the capacity retention rate was only 43.2% after 100 cycles, while the cycle curve of Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ is relatively flat, the discharge capacity remained to 71.3mAh/g after 100 cycles, and the capacity retention rate can reached 70%. Figure 5 shows the rate capacity of the Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ material was significantly higher than that of the Na$_2$MnFe(CN)$_6$ material. The discharge ratio of the Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ material was smaller than the capacity fluctuation. When the current density increased from 0.1C to 5C, and the discharge capacity can reached 40mAh/g at 2C. The Na$_2$MnFe(CN)$_6$ material attenuates more severely at a small current density of 0.1C to 0.2C, and the discharge capacity fluctuates greatly at different rates. The discharge capacity of Na$_2$Mn$_{0.8}$Fe$_{0.2}$Fe(CN)$_6$ material remained 70.5mAh/g, and the capacity retention rate was 69.8% after 100 cycles at 0.5C in figure 6. The above data showed that the doping of Fe$^{2+}$ changes the crystal structure of the material. Although the initial charge and discharge capacity was slightly reduced, the Fe$^{2+}$ contained in the crystal made the crystal structure difficult to collapse during the charge and
discharge process. The constant current charge and discharge can maintained better electrochemical at 0.2C and 0.5C.

4. Conclusion
The Na₂Mn₀.₈Fe₀.₂Fe(CN)₆ cathode material was prepared by the co-precipitation method with Fe²⁺ doping was subjected to constant current charge and discharge test and the reversible capacity was still 71.3mAh/g after 100 cycles at 0.2C, and the retention rate can reached 70%. The reversible capacity remained 70.5mAh/g, and the capacity retention rate was 69.8% after 100 cycles at 0.5C. The discharge capacity fluctuates less and the rate capacity was more stable when the current density rose from 0.1C to 5C. In summary, the Na₂Mn₀.₈Fe₀.₂Fe(CN)₆ cathode material is prepared by Fe²⁺ doping can effectively improve the cycle performance and rate capacity of the Mn-PBA cathode material. This will be of great significance to the study of Prussian blue materials as cathode materials for sodium ion batteries.

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