

Short Communication

## Synthesis of $\text{Na}_2\text{MnFe}(\text{CN})_6$ and its Application as Cathode Material for Aqueous Rechargeable Sodium-ion Battery

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**Abstract:** Prussian Blue type  $\text{Na}_2\text{MnFe}(\text{CN})_6$  was prepared by direct precipitation method and a subsequent drying procedure as a cathode material for aqueous rechargeable sodium-ion batteries. XRD patterns showed that  $\text{Na}_2\text{MnFe}(\text{CN})_6$  has a typical Prussian Blue structure with space group  $Fm\bar{3}m$ .  $\text{Na}_2\text{MnFe}(\text{CN})_6$  presents good electrochemical behaviors at  $10 \text{ mA g}^{-1}$  discharge current density with specific capacity  $73.1 \text{ mAh g}^{-1}$  after 30 cycles. The results show that  $\text{Na}_2\text{MnFe}(\text{CN})_6$  could be a potential cathode material for aqueous Sodium-ion battery.

**Keywords:** Aqueous Sodium-ion battery; Cathode Material;  $\text{Na}_2\text{MnFe}(\text{CN})_6$ ; Prussian blue analogue

### 1. INTRODUCTION

Due to limited storage in the world and negative impact on environment of coal and oil, the need of clean energy is increasingly high for persistent power supply. In order to solve discontinuous and instable problems of renewable electricity (such as solar arrays and wind farms), energy storage systems can be used. The advanced new batteries are needed to have not only high energy density, but also good safety and affordable electric storage systems that enable better use of the intermittent renewable energy sources [1-3]. Because of superior performance in various electrochemical aspects, Li-ion batteries are often viewed as an energy storage device. However, limited resource and high price of lithium salts restrict its application in this area.

Following the achievements in the field of lithium-ion batteries, there have been more and more attempts over the years to develop aqueous rechargeable sodium-ion battery (ASIBs), due to its natural abundance, relatively low price, and higher expected safety [4-6]. The vital issue for developing aqueous sodium ion battery is the availability of cathode materials. Cathode materials of ASIBs have been widespread studied for accelerating the large-scale applications of ASIBs, which is the critical aspect of high rate capability and cycling stability in a whole cell [7].

Recently, Prussian blue and its analogues can provide three-dimensional framework structure and large enough channels for

sodium ion insertion/extraction [8,9]. This structure demonstrated good performance for sodium ion batteries. In this study,  $\text{Na}_2\text{MnFe}(\text{CN})_6$  was prepared by direct precipitation method and its electrochemical behavior in  $1.0 \text{ mol}\cdot\text{L}^{-1}$   $\text{Na}_2\text{SO}_4$  aqueous solution is discussed.

### 2. EXPERIMENTAL

#### 2.1. Preparation of $\text{Na}_2\text{MnFe}(\text{CN})_6$

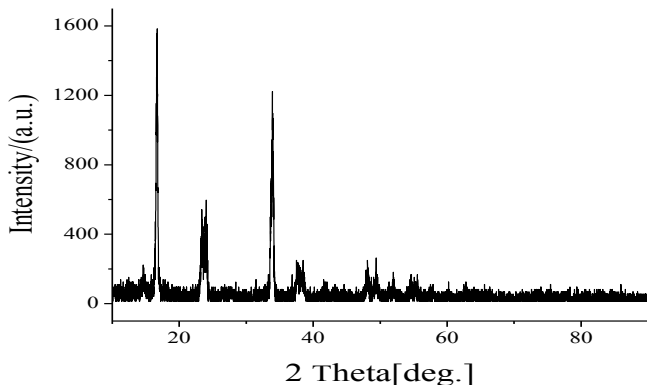
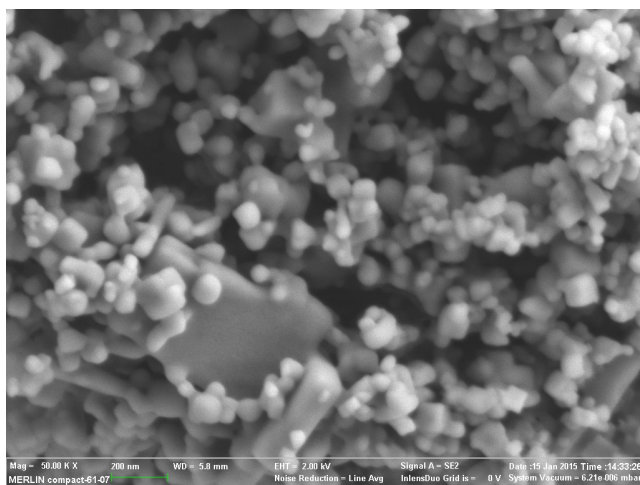
$\text{Na}_2\text{MnFe}(\text{CN})_6$  was synthesized via direct precipitation method and a subsequent drying procedure. First, the starting materials of sodium ferrocyanide ( $\text{Na}_4\text{Fe}(\text{CN})_6\cdot 10\text{H}_2\text{O}$ ) and manganese acetate ( $\text{MnAc}_2\cdot 4\text{H}_2\text{O}$ ) in a stoichiometric ratio were dissolved in a beaker with water and the mixture was magnetically stirring. After a residence time of 6 hours, the resulting precipitate was separated from the solution by high speed centrifuge. Next, the precipitate was washed with deionized water and ethanol, and then dried in vacuum oven at  $60^\circ\text{C}$ . The final product was  $\text{Na}_2\text{MnFe}(\text{CN})_6$ .

#### 2.2. Characterization and Electrochemical Measurements

##### 2.2.1. XRD and SEM

X-ray diffraction (XRD) was performed on a Bruker D8A25 X-Ray diffractometer, the X-ray beam was nickel-filtered Cu  $K\alpha$  ( $\lambda=0.15406 \text{ nm}$ ) radiation operated at 40 kV and 30 mA; and the data were collected from  $10^\circ$  to  $80^\circ(2\theta)$  at a scanning rate of  $5^\circ/\text{min}$ .

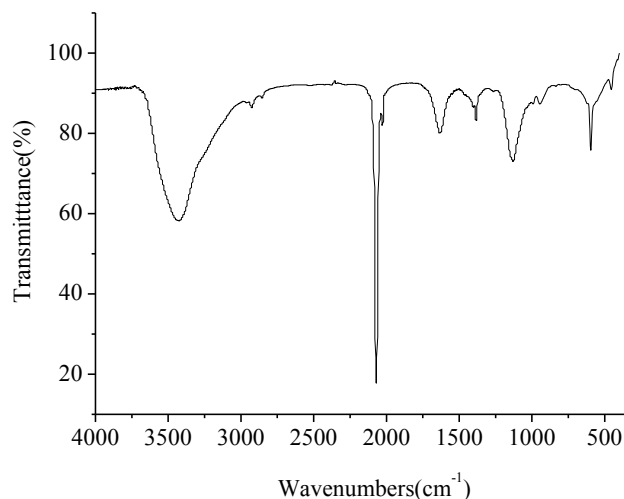
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Figure 1. The XRD patterns of  $\text{Na}_2\text{MnFe}(\text{CN})_6$  sampleFigure 2. SEM image of  $\text{Na}_2\text{MnFe}(\text{CN})_6$ 

The morphology of the samples was observed by JEOL JSM-5600LV SEM.

### 2.2.2. Electrochemical measurements

Electrochemical characterization of the  $\text{Na}_2\text{MnFe}(\text{CN})_6$  sample was carried out using three-electrode cells, in which a  $\text{NaTi}_2(\text{PO}_4)_3$  and a SCE (saturated calomel electrode) served as a counter and reference electrodes. The working electrodes were prepared by pressing a  $1 \text{ cm}^2$  thin film onto nickel net. Electrochemical Sodium-ion intercalation performances of the samples were evaluated in test cells using  $\text{Na}_2\text{MnFe}(\text{CN})_6$  cathode and  $\text{NaTi}_2(\text{PO}_4)_3$  anode. The sample electrode pellet was prepared by pressing the 75:15:10 (in wt.) mixture of active materials, acetylene black and Polytetrafluoroethylene (PTFE). The glass fibers were used as separators. The electrolyte was 1.0 mol/L  $\text{Na}_2\text{SO}_4$  solution purged with Nitrogen before use. The cell assembly was carried out and maintained at  $20^\circ\text{C}$  for 24 h in order to establish the equilibrium state of the electrodes with the electrolyte. Cyclic Voltammetry (CV) measurements were performed on a Gamry Reference 600 Electrochemical Analyst multichannel workstation manufactured by the Gamry Echem Analyst. Galvanostatic charge/discharge was recorded with

Figure 3. IR spectrum of  $\text{Na}_2\text{MnFe}(\text{CN})_6$ 

a Land battery measurement system (Wuhan, China) with the cut-off voltage of 1.5/0.1 V, at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of sample

The results of the X-ray diffraction study have shown that  $\text{Na}_2\text{MnFe}(\text{CN})_6$  powder is mainly a single phase material. The corresponding X-ray powder diffraction pattern obtained at room temperature is presented in Fig. 1. The  $\text{Na}_2\text{MnFe}(\text{CN})_6$  compounds belong to the face-centered cubic structures with space group  $\text{Fm}\bar{3}\text{m}$  and the cell parameters:  $a=0.929 \text{ nm}$ ,  $\alpha=\beta=\gamma=90^\circ$ . In the face-centered cubic lattice, the Mn(II) ions are 6-fold coordinated to nitrogen atoms, and the Fe(II) ions are octahedrally surrounded by carbon atoms of the CN ligands, forming large ionic channels along the  $\langle 100 \rangle$  directions for facile insertion and extraction of alkaline cations. It can provide three-dimensional framework structure and large enough channels for sodium ions insertion/extraction.

SEM: Fig. 2 shows the microspheres of  $\text{Na}_2\text{MnFe}(\text{CN})_6$ . The particle size distribution is narrow, and most of the particles are approximately 70 nm on average.

Infrared spectra: Infrared absorption spectra of the sample is presented in Fig. 3. The spectra are dominated by intense, overlapping intramolecular  $\text{C}\equiv\text{N}$  stretching modes at  $2068.84 \text{ cm}^{-1}$ . Two bands detected at  $1647.73$  and  $2924.50 \text{ cm}^{-1}$  of  $\text{Na}_2\text{MnFe}(\text{CN})_6$  are ascribed to the hydroxyl(-OH), so the compound contains coordinating water molecule. The Fe-CN vibrations occur at  $594.90 \text{ cm}^{-1}$ .

### 3.2. Electrochemical properties

Fig. 4 shows the CV of  $\text{Na}_2\text{MnFe}(\text{CN})_6$  electrode in aqueous  $\text{Na}_2\text{SO}_4$  electrolyte in the potential range of 0.0–0.8 V (vs  $\text{Na}/\text{Na}^+$ ) at a scan rate of 0.1 mV/s. As shown in Fig. 4, the main CV feature appears as a pair of broad and symmetric redox peaks between 0.35 and 0.65 V (vs.  $\text{Hg}/\text{Hg}_2\text{Cl}_2$ ). In the light of the well-documented intercalation chemistry of Prussian Blue lattices [14], the CV peaks in Fig. 4 can be attributed to the reversible redox reactions of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couples in the  $\text{Na}_2\text{MnFe}(\text{CN})_6$  lattice with insertion/extraction of  $\text{Na}^+$  for charge counterbalance, whereas, the  $\text{Mn}^{2+}$

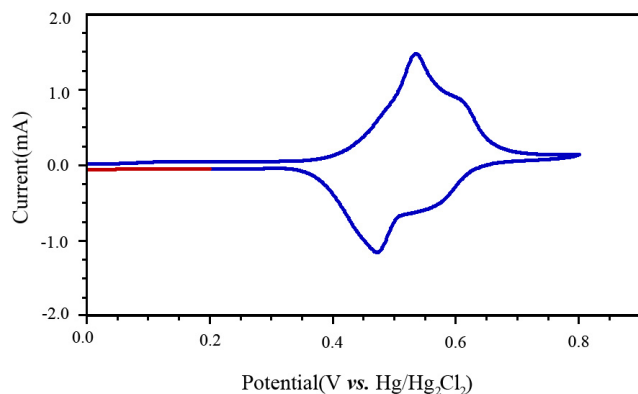


Figure 4. CV curves measured at a scan rate of 0.1 mV/s

ion is electrochemically inactive due to the limited electrochemical window of aqueous electrolyte:

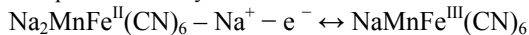


Fig. 5 shows the variation of the discharge capacity with the cycling number. This is the result of prototype Sodium-ion batteries obtained with coin-type cells comprising  $\text{NaTi}_2(\text{PO}_4)_3$  anodes and  $\text{Na}_2\text{MnFe}(\text{CN})_6$  cathodes. The discharge capacity of  $\text{Na}_2\text{MnFe}(\text{CN})_6$  is  $66.8 \text{ mAhg}^{-1}$  after 30 cycles at 1 C rate, thereby, this material seems to be a good cathode material proposed for rechargeable Sodium-ion batteries.

#### 4. CONCLUSION

In summary,  $\text{Na}_2\text{MnFe}(\text{CN})_6$  materials is prepared by direct precipitation method. The unique three-dimensional framework structure of  $\text{Na}_2\text{MnFe}(\text{CN})_6$  offers the large enough channels for sodium ions insertion/extraction. Preliminary electrochemical data demonstrated that  $\text{Na}_2\text{MnFe}(\text{CN})_6$  as a novel cathode material for aqueous rechargeable sodium-ion batteries. The aqueous rechargeable sodium-ion batteries based on the  $\text{Na}_2\text{MnFe}(\text{CN})_6$  cathode and  $\text{NaTi}_2(\text{PO}_4)_3$  anode in a  $\text{Na}_2\text{SO}_4$  electrolyte. This battery avoids the use of poisonous metals and corrosive acidic or alkaline electrolytes. In addition, the aqueous electrolyte has nonflammability, strong thermal and electrochemical stabilities. All of these advantageous features make the aqueous Na-ion battery particularly attractive for grid-scale energy storage.

#### 5. ACKNOWLEDGMENTS

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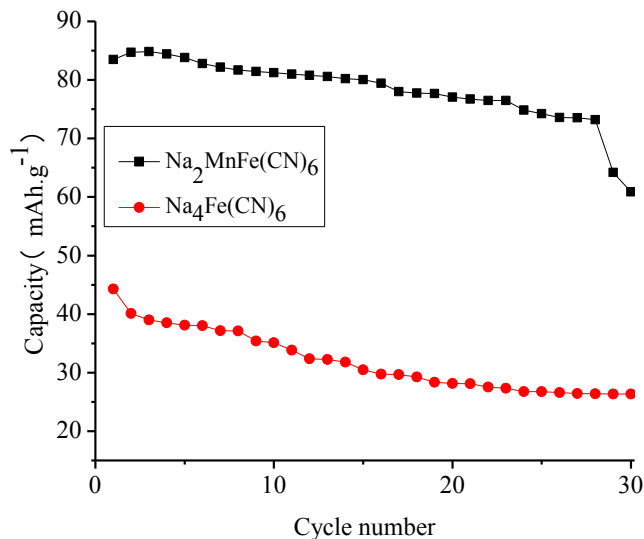


Figure 5. Cyclic performance of  $\text{Na}_2\text{MnFe}(\text{CN})_6$  tested at  $1 \text{ mA} \cdot \text{g}^{-1}$  at  $20^\circ\text{C}$ .

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