

# A sodium manganese ferrocyanide thin film for Na-ion batteries

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## 1 Introduction

Rechargeable lithium ion batteries (LIBs) are essential for the development of smart phones, laptop computers, and many other consumer products. The next targets of LIBs are considered to be automotive applications and huge energy storage systems. However, lithium resources are limited, and the cost of lithium-based raw materials has roughly doubled from the first practical application in 1991 to now, and it will increase more when the demand for lithium increases as a result of the commercialization of large-scale LIBs. In contrast, sodium resources are inexhaustible everywhere around the world. Furthermore, the electrochemical standard potential of sodium is the second most favorable for aprotic battery applications after lithium. Hence, the search for the materials for sodium ion batteries (SIBs) is quite important for the next generation energy storage systems.

From the structural point of view, coordination polymers, which consist of a covalently bonded transition metal framework with micro cavities and channels for alkali cations, are suitable cathode materials for SIBs. Prussian blue analogues (PBAs), represented as  $A_{4-x}M_A[M_B(CN)_6]_x \cdot zH_2O$  ( $M_A$  and  $M_B$  are transition metal ions, and  $A$  is an alkali metal ion), are one of the most studied coordination polymers, which include guest alkali cations and water molecules at the interstitial sites of the framework. Recently, Goodenough et al.[1] showed that the  $KFe_2(CN)_6$  PBA exhibits a high discharge capacity ( $\approx 100$  mAh/g) as a cathode material for SIBs, even though the coulombic efficiency ( $\approx 60\%$  at the initial cycle) is not good.

Here, we investigated the cathode property of the  $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$  thin film for SIBs. We found that the electrode exhibits reversible and fast sodium ion intercalation–deintercalation without any structural phase transition of the host framework. We further compared the intercalation–deintercalation properties into/from the PBA host framework for the sodium and lithium ions.

## 2 Experiment

A thin film of  $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$  was electrochemically synthesized on an indium tin oxide (ITO) transparent electrode under potentiostatic conditions at  $-0.50$  V vs. a standard Ag/AgCl electrode in an aqueous solution containing 1.0 mM  $K_3[Fe(CN)_6]$ , 1.5 mM  $MnCl_2 \cdot 6H_2O$ , and 1.0 M NaCl. The obtained film was transparent with a thickness of  $1\mu m$ . Chemical compositions of the films were determined using the inductively coupled plasma (ICP) method. The mass of

each film was measured using a conventional electronic weighing machine after the film was carefully removed from the ITO substrate using a microspatula. The experimental error for the mass, and hence, the capacity, is 10%.

The electrochemical properties of the film against Na were investigated with a beaker-type cell. The cathode was the thin film and the anode was Na spread on a stainless steel mesh. The electrolyte was propylene carbonate solution containing 1 M  $NaClO_4$  (Kishida Chemical). The cut-off voltage was from 2.0 to 4.0 V.

We further investigated the crystal structure of  $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$  against the Na concentration ( $x$ ) by the ex situ powder X-ray diffraction (XRD) measurements, performed at the 8B beamline at KEK-PF. The partially charged films were carefully removed from the ITO glass in air, and the obtained powder samples were filled into 0.3 mmf glass capillaries. The wavelength of the X-ray ( $= 0.73283$  Å) was calibrated by the lattice constant of standard  $CeO_2$  powders. The lattice constants ( $a$ ) were refined by the Rietveld method (Rietan-FP program).

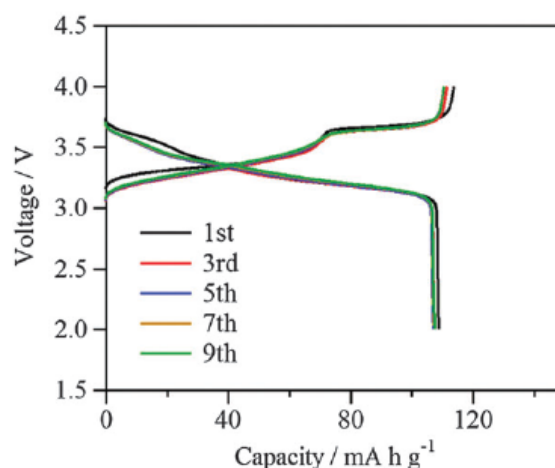


Fig. 1: Charge–discharge curves of a thin film electrode of  $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$  against Na at 0.5 C.

## 3 Results and discussion

Fig. 1 shows the charge–discharge curves of the thin film electrode of  $Na_{1.32}Mn[Fe(CN)_6]_{0.83} \cdot 3.5H_2O$  against Na at the first to the ninth cycles at 0.5 C. The discharge capacity ( $\approx 109$  mAh/g) is nearly the same as the ideal value ( $\approx 109$  mAh/g) for the two site reaction. The coulombic efficiency ( $>95\%$ ) was good. The charge curve showed two plateaus at 3.3 and 3.6 V. The first and the

second plateaus are ascribed to the oxidization process of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $\text{Mn}^{2+}$ , respectively. We investigated the cyclability of the thin film electrode of  $\text{Na}_{1.32}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.83}3.5\text{H}_2\text{O}$  against Na at a constant charge–discharge rate of 0.9 C. The discharge capacity at the 100th cycle is 90% of the initial value.

Fig. 2 shows the XRD patterns of  $\text{Na}_{1.32}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.83}3.5\text{H}_2\text{O}$  ( $x = 0.00, 0.50, \text{ and } 1.32$ ) for the first charge process. The whole reflections could be indexed with the face-centered cubic ( $\text{Fm}\bar{3}\text{m}; Z = 4$ ) setting, indicating that the framework is robust against Na deintercalation.

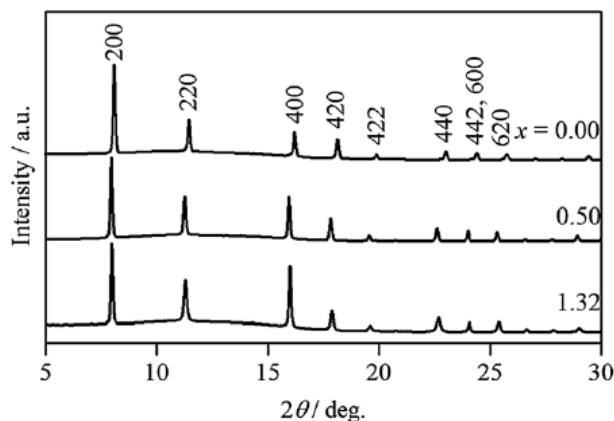


Fig. 2: The XRD patterns of  $\text{Na}_{1.32}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.83}3.5\text{H}_2\text{O}$  ( $x = 0.00, 0.50, \text{ and } 1.32$ ) for the first charge process. The wavelength of the X-ray is 0.73283Å.

#### Acknowledgement

This work was supported by the Mitsubishi foundation, Cannon foundation, and also by the Grant-In-Aid (21244052) for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. The synchrotron-radiation XRD experiments were performed at KEK-PF under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2010G502 and 2013G001).

#### References

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