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In operando Synchrotron XRD/XAS Investigation of Sodium Insertion into the Prussian Blue Analogue Cathode Material $Na_{1.32}Mn[Fe(CN)_6]_{0.83}\cdot z\ H_2O$

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ABSTRACT

Prussian Blue Analogues (PBAs) with general formula $Na_xM_A[M_B(CN)_6]_y\cdot z\ H_2O$ (M_A, M_B = transition metal) are promising low cost, high rate and high capacity cathodes for sodium ion battery (SIB) technology. Here, we have studied the PBA $Na_{1.32}Mn[Fe(CN)_6]_{0.83}\cdot z\ H_2O$ (z = 3.0 and 2.2) with varying structural modifications (monoclinic and cubic) using *in operando* quasi-simultaneous X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). We observed a series of reversible structural phase transitions which accompany Na insertion/extraction during electrochemical cycling. The samples show pronounced differences in their galvanostatic charge and discharge profiles which could be linked to structural and electronic response. Different desodiation and sodiation mechanisms were identified. The influence of $[Fe(CN)_6]$ vacancies and water content on the electrochemical performance was investigated.

1. Introduction

Efficient energy storage is essential for the implementation of intermittent renewable energy sources into the electrical grid. Rechargeable battery technology can be used to balance electricity supply and demand. Today lithium ion battery (LIB) technology dominates the portable devices and electric vehicle market. Unlike Li, Na is relatively cheap and readily available worldwide which might make sodium ion battery (SIB) technology a viable option for large scale stationary storage. The realisation of the market potential of SIBs has boosted a large research effort into rechargeable, low-cost SIBs with reasonable energy density, high charge/discharge rate and durability [1,2].

Ideal cathode materials for SIBs offer host-guest interactions in their 6-fold octahedral or prismatic coordination sites with negligible volume changes. Prominent examples are layered oxide materials and poly-anionic frameworks based on phosphates or sulphates [1–3].

Prussian blue analogues (PBAs), also referred to as metal hexacyanoferrates, with general formula, $Na_xM[Fe(CN)_6]_y\cdot zH_2O$ (M = transition metal, $x = 4y\text{-}2$, $y \leq 1$) have attracted substantial interest as promising cathode materials for SIBs. Generally, when M is Mn, Fe, Co or Ni, $M^{2+/3+}$ and $Fe^{2+/3+}$ reside on alternate corners of 8 sub cubes of corner-shared octahedra linked by linear $(C\equiv N)^-$ bridges in the face centred cubic (*fcc*) unit cell (*Fm*-3*m*, *Z* = 4). The low-spin (LS) $Fe^{2+/3+}$ bonds with C atoms while the high-spin (HS) $M^{2+/3+}$ bonds with N atoms. Coordinating water resides in the randomly distributed $[Fe(CN)_6]$ vacancies (6 H_2O molecules per vacancy), while zeolitic water and Na-ions can be found in the nanosized voids of the framework structure. The Na-ions diffuse across the faces of the sub cubes formed by the $(C\equiv N)^-$ ligands which compared to O^{2-} ions interact less with Na^+ [4].

High specific capacities can be achieved in these compounds due to a potential two-electron per formula unit redox reaction. Reversible Na insertion/extraction into PBA has been demonstrated for M = Mn, Fe, Co, Ni, Cu and Zn [4]. For M = Fe promising high rate performance and high specific capacity of up to 170 mAh/g with good cycling stability were obtained by controlling water content, number of vacancies and crystallite size [5–7]. For M = Mn similar high rate capability, but lower capacity were found [8–10]. Wang et al. [9] reported 134 mAh/g initial discharge capacity for a distorted PBA structure with composition $Na_{1.72}Mn[Fe(CN)_6]_{0.99}\cdot 2.3H_2O$. After 30 cycles 90% of the initial discharge capacity was retained. For a non-distorted PBA cubic structure with

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composition $Na_{1.40}Mn[Fe(CN)_6]_{0.97}\cdot 3.3H_2O$ they observed lower initial discharge capacity (123 mAh/g) but improved capacity retention (96% after 30 cycles). The capacity degradation was therefore ascribed to the expected phase transitions between distorted and cubic structure when Na is extracted from and inserted into the structure during the electrochemical cycles. Starting from non-distorted manganese hexacyanoferrate thin films depending on the initial composition ($y = 0.83$, 0.87 and 0.93) Moritomo et al. observed different structural changes against Li content [11]. For $Na_{1.32}Mn[Fe(CN)_6]_{0.83}\cdot 3.5H_2O$ they report a single cubic phase with different lattice parameters for different Na content. The discharge profiles of Na and Li analogues ($y = 0.83$) show different features (two well separated flat plateaus for Li and only slightly separated sloped plateaus for Na) and thus different sodiation and lithiation mechanisms might be expected.

A fundamental understanding of extraction/insertion processes (single phase vs. two-phase), structural stability and voltage-composition profiles is pivotal for optimisation of electrode materials. In addition to X-Ray Diffraction (XRD) which probes the long range order, X-ray Absorption Spectroscopy (XAS) can be used to determine changes in oxidation state and fine structural details such as C≡N bond length and M_A-C≡N-M_B orientation in metal hexacyanoferrates [11–14]. *In operando* quasi-simultaneous powder XRD and XAS where the structural and electronic response of the electrodes is constantly monitored during continuous cycling are therefore powerful techniques for understanding a materials electrochemical performance.

Here we report the first *in operando* quasi-simultaneous XRD and XAS investigation of the PBAs $Na_{1.32}Mn[Fe(CN)_6]_{0.83}\cdot z\ H_2O$ (z = 3.0 and 2.2) with varying structural modifications (distorted and non-distorted PBA structures similar to those observed by Wang et al. [9]) as cathode material for SIBs. Contrary to the previous findings [11] we observed a series of reversible structural phase transitions that are clearly linked to the galvanostatic charge and discharge profiles. The influence of the different water content on the electrochemical performance was also studied. Our data give a deeper insight into the possible reasons for capacity degradation in this family of materials.

2. Experimental

2.1. Material Synthesis and Characterization

Both samples were prepared by a simple precipitation method: First, 14 g NaCl (Sigma Aldrich) were dissolved in 100 ml of 0.1 M $Na_4Fe(CN)_6\cdot 10\,H_2O$ (Alfa Aesar) aqueous solution. Then 50 ml of 0.2 M $Mn(NO_3)_2\cdot 4H_2O$ (Sigma Aldrich) aqueous solution was added dropwise to the $Na_4Fe(CN)_6$ and NaCl solution under continuous stirring. The final solution was left to age at room temperature overnight. Further, filtering and washing with deionized water was carried out. The sample was then divided into two batches and dried for 6 hours: the first batch was dried at 60 °C (sample **I**), and the second at 120 °C (sample **II**).

Powder X-ray diffraction measurements with Cu Kα1 radiation were performed in transmission mode on a Bruker D8 with samples sealed in 0.5 mm diameter thin-walled glass capillaries (Hilgenberg GmbH). Diffraction profiles collected before and after drying are shown in Fig. S1. Energy-Dispersive X-ray spectroscopy (EDX) was carried out at 15.0 kV on a Hitachi SU8200. It revealed a chemical composition of Na, Fe, Mn, C, N, O elements in the absence of any discernible Cl element. The molar ratios of Na, Mn and Fe were measured by Microwave Plasma-Atomic Emission Spectrometry (MP-AES 4100, Agilent Technologies) analysis and normalized to the Mn content. A composition of $Na_{1.32}Mn[Fe(CN)_6]_{0.83}$ was obtained for both samples. Thermogravimetric analysis (STA 1500, Scinco Co. Ltd) was conducted in an open alumina crucible in air from room temperature to 400 °C at a heating rate of 10 °C/min (Fig. S2). Water contents of 17 wt% and 13 wt% were obtained for samples **I** and **II**, respectively. Combining MP-AES and STA results gives a stoichiometry of $Na_{1.32}Mn[Fe(CN)_6]_{0.83}\cdot z\ H_2O$ with $z = 3.0$ and $z = 2.2$ for samples **I** and **II**, respectively. Sample **II** tends to absorb water with time and the samples were therefore stored in an Ar-filled glovebox (M. Braun). Magnetic susceptibility (χ_M) measurements were carried out in the temperature range 5 K to 300 K under a magnetic field of 1 T using a Magnetic Property Measurement System (MPMS, Quantum Design). The magnetic susceptibility of sample **I** was measured representatively for both samples. Paramagnetic behaviour and no phase transitions were observed over the whole temperature range (Fig. S3). The as determined effective magnetic moment (μ_{eff}) of 5.6 μ_B per formula unit is close to the theoretical value for a purely HS Mn^{2+} ($S = 5/2$) and LS Fe^{2+} ($S = 0$) configuration ($\mu_{eff} = 5.9\ \mu_B$).

2.2. Electrochemical Measurements

For the electrochemical characterization coin cells (2032) were assembled in an Ar-filled glove box with H_2O and O_2 levels less than 0.1 ppm (M. Braun). The working electrode composition was 70 wt% of sample **I** or sample **II** as active material, 20 wt% of conductive carbon black (Timcal Super P) and 10 wt% polytetrafluoroethylene (PTFE) binder. The mixture was rolled into a thin film with a mass loading of active material of about 5 mg/cm^2. The working electrode was separated from the Na metal disk as counter electrode by electrolyte soaked glass fibre. The electrolyte used was a 1 M solution of $NaClO_4$ in ethylene carbonate/diethyl carbonate (1:1 in vol.) solution. The cells were left at open circuit for at least 3 h to make sure the electrolyte was fully soaked into the electrode before galvanostatic cycling between 2 V and 4.2 V at a current rate of C/10 (1C = 120 mA/g).

2.3. In operando *Synchrotron XRD and XAS measurements*

In operando quasi-simultaneous powder X-ray diffraction and absorption measurements were performed at the Swiss-Norwegian Beam Lines (SNBL), BM01B, at the European Synchrotron (ESRF). Diffraction profiles were collected using the Dexela 2923 CMOS 2D detector. The wavelength (λ = 0.50497 Å) was calibrated by means of a Si NIST standard. For data reduction the FIT2D software [15] was used. Spotlike reflections from the Na metal were masked prior to integration. All profile fittings and Rietveld refinements were performed using TOPAS V4.2 (Bruker AXS). For each individual powder pattern zero-shift, background (13 term Chebychev polynomial), cell parameters, peak-profile parameters for the individual phases, as well as their scale factor, were refined in parallel for all powder patterns in each dataset. Reflections from the textured Al foil were fitted with a structureless phase with the lattice parameter and space group of Al metal ($a = 4.05$ Å, *Fm*-3*m*) and from the PTFE with a peak at 5.88°. For two-dimensional detectors the counting statistics of the diffraction pattern cannot be estimated by the square root of the counts as the number of pixels integrated under the diffraction rings is not constant throughout the angular range of the diffraction pattern. The refinement software will, however, assume the square root of the counts as standard deviation if not otherwise specified which results in high *Rexp* values. X-ray Absorption Near Edge Spectroscopy (XANES) were collected at the Mn K-edge (from 6460 to 6750 eV) and at the Fe K-edge (from 7050 to 7280 eV) in transmission mode using a Si-(111) channel-cut type monochromator. The second crystal was detuned at about 70% to reduce higher harmonics. The XANES data were analysed using ATHENA [16] for absorption edge determination and spectrum normalization to an edge jump of unity. The absorption edge position was