A high-capacity P2 $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ cathode material for sodium ion batteries with oxygen activity

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HIGHLIGHTS

- This work reports a P2 $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ cathode material for Na-ion batteries.
- The material delivers a discharge capacity of 228 mAh g^{-1} between 1.5 and 4.5 V.
- The high capacity is due to the redox couples of transition metal and oxygen.
- Utilizing an ionic liquid electrolyte improves the material's cycling stability.

GRAPHICAL ABSTRACT
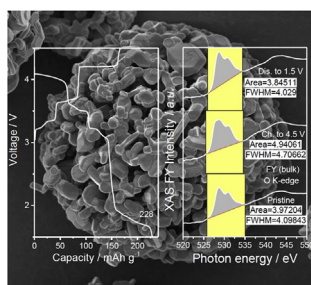
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ABSTRACT

$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ with a P2 phase is investigated as a cathod material for sodium ion batteries. It delivers a high discharge capacity of 228 mAh g^{-1} within 1.5–4.5 V in half cells, which is much higher than the theoretical value of 172 mAh g^{-1}. Metal K-edge X-ray absorption near edge spectroscopy results show that the Mn ions remain in 4 + oxidation state during sodiation/desodiation and the charge compensation is due to the Ni^{2+}/Ni^{4+} redox. Soft X-ray absorption spectroscopy results reveals a gradient in the valence state of Ni ions from bulk to surface for the charged electrode, and a change in the integrated intensity of O K-edge peak after charging, strongly suggesting that part of the charge compensation takes place at the oxygen sites. In addition, the reduction of Mn ions on the surface is observed on the discharged electrode, which indicates that the carbonate-based electrolyte reacts with the cathode material, resulting in a fast capacity drop. By utilizing an ionic liquid (IL) electrolyte (1 M NaTFSI in Pyr$_{14}$TFSI) to reduce the interfacial reactions, the discharge capacity of ~ 200 mAh g^{-1} is retained.

1. Introduction

Sodium ion batteries (SIBs) are considered as a promising alternative to lithium ion batteries (LIBs) when it comes to large-scale energy storage [1–3]. Although SIBs might not compete with LIBs in terms of energy densities, they eventually offer a potential cost

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advantage over LIBs, which is a crucial aspect for large-scale application. This cost advantage originates from the widespread and abundant sodium itself, from the possibility to use Co-free layered cathode materials (unlike the case of LIBs, where a minimum of Co is necessary for structural stabilization) [4,5], and from the possibility to replace the copper current collector on the anode side by the much cheaper and lighter aluminum, which is also used on the cathode side [6,7]. The key issue for developing SIBs rests with the development of appropriate electrode materials. Over the last decades, much effort has been devoted to searching new sodium intercalation cathode materials, such as NaTMO_2 (TM = transition metal = Fe, Co, Mn, Ni, Ti $etc.$) [8–19], polyanion-type materials [20,21], Prussian blue [22] $etc.$, and anodes such as hard carbon [23], $Na_2Ti_3O_7$ [24], $Na[FeTi]O_4$ [25], carboxylate-based materials [26] and so on.

Layered Na_xMnO_2 derivatives are considered as excellent candidates due to the low cost and environmental sustainability of Mn [19,27,28]. The layered Na_xMnO_2 derivatives can be generally categorized into two structural groups: P2 and O3 [11,27]. Compared to O3 phase, P2 phase has more open prismatic paths with a lower Na^+ ions diffusion barrier, which makes it a promising structure with higher reversible capacity and better rate capability [29]. However, when stored in (moist) air, P2-type Na_xMnO_2 is unstable. And water molecules as well as carbonate ions can insert into the structure, due to the high-spin Jahn-Teller active Mn^{3+} centers [30]. One strategy to improve the storage stability is to introduce Ni ions into P2-type Na_xMnO_2 to increase the valence state of Mn ions to 4 + [10,16,31–42]. By utilizing this strategy, the obtained materials exhibit enhanced stability when exposed to moist air. Therefore, Ni substituted P2-Na_xMnO_2 materials, such as P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$, attract more and more attention.

Prof. Dahn's group reported the P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ material in the 2000's [10,43–45]. The P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$, material has shown a high discharge capacity of ~ 170 mAh g^{-1} in the voltage range of 2.0–4.5 V [16,32]. By setting the lower cut-off voltage at 1.5 V, a discharge capacity, far exceeding the theoretical value of 172 mAh g^{-1} calculated based on the Ni^{2+}/Ni^{4+} redox reaction, can be obtained [34]. However, this material exhibits fast capacity drop in this voltage range. Applying a narrower voltage range of 2.0–4.0 V can solve this issue, but it decreases the reversible capacity to ~ 80 mAh g^{-1} [14]. The substitution by inert elements in the P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ material also improves the capacity retention, but the compromise still sacrifices the high discharge capacity of the material [31,35–37,46,47]. Thus, it is of primary concern to achieve high and stable discharge capacities for the P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ cathode. And the priority is to understand the mechanisms of the high discharge capacity over the theoretical capacity and the fast capacity drop.

Only a few studies on Na_xTMO_2 materials have suggested the participation of oxygen ions in the redox processes upon Na (de)intercalation [15,46]. Ma et al. provided experimental evidences by electron energy loss spectroscopy (EELS) and soft X-ray absorption spectroscopy (sXAS) when reporting on a high sodium content and TM-deficient P2-$Na_{0.78}Ni_{0.23}Mn_{0.69}O_2$ material [15]. The authors claim that the TM deficiency is the key to activate the oxygen anion redox. Then, the question is to know whether or not the oxygen ions participate in the charge compensation in stoichimetric $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$. Understanding this question would definitely help to find a suitable way to improve the electrochemical performance of P2-Na_xTMO_2 materials.

In this work, a spherical P2-type $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ was synthesized by a combination of co-precipitation, spray drying and solid-state reaction methods. It exhibits a very high discharge capacity of 228 mAh g^{-1} at 10 mA g^{-1} in the voltage range of 1.5–4.5 V. The mechanisms of the high discharge capacity and the fast capacity drop are examined by *ex situ* hard and soft X-ray absorption spectroscopy (XAS) measurements. Furthermore, the effect of the substitution of the carbonate electrolyte by an IL electrolyte on cycle life is also investigated.

2. Experimental

2.1. Synthesis of $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ material

All chemicals were used as received without further purification. The synthesis was duplicated at least twice to ensure reproducibility. For the preparation of $(Ni_{1/3}Mn_{2/3})(OH)_2$ precursor, an aqueous solution containing stoichiometric amounts of $NiSO_4\cdot6H_2O$ and $MnSO_4\cdot4H_2O$ was co-precipitated with an aqueous solution of NaOH. The pH value of the slurry was kept at 11, and the slurry was continuously stirred at 60 °C for 12 h in Ar atmosphere. The resultant powder was filtered, washed with water, and dried in air at 100 °C. Thereafter, stoichiometric amounts of the dried $(Ni_{1/3}Mn_{2/3})(OH)_2$ powder, Na_2CO_3 and a (polyacrylic acid based) dispersing agent (Dispex AA 4040, BASF) were thoroughly mixed in water by using a ball-milling method. Then a spray drying method followed by high-temperature treating was used to produce $Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ material. The spray drying process was carried out under air atmosphere at a temperature of 110 °C. The spray-dried precursor was then calcined at 500 °C for 5 h, then at 900 °C for 15 h, with a heating rate of 5 K min^{-1}, using an open-air muffle oven. Afterwards the sample was cooled down naturally to room temperature.

2.2. Physical characterizations

The crystal structure was determined by X-ray diffraction (XRD) with Cu Kα radiation on the Bruker D8 Advance (Germany) in the 2θ range from 10° to 90°. The morphology was evaluated by a high-resolution scanning electron microscopy (SEM; EVO MA 10 microscope, Zeiss). Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) images and selected-area electron diffraction (SAED) patterns were taken by a FEI Tecnai G2 F20 TEM at an accelerating voltage of 200 kV.

2.3. Electrochemical measurements

In order to prepare electrodes, the obtained material together with a conductive carbon (TIMCAL Super P) and a binder, polyvinylidene difluoride (PVdF, ARKEMA KYNAR®) (weight ratio 80:10:10) was mixed in 1-methyl-2-pyrrolidinone (NMP, ACROS Organics) and casted onto Al foil. After being dried, electrode tapes were punched into Ø12 mm discs, pressed by a hydraulic press, and dried at 120 °C under vacuum overnight. 2032-type coin cells were assembled in a dry room using 1 M $NaPF_6$ in 1/1 wt ratio of ethylene carbonate to dimethyl carbonate (EC/DMC) as electrolyte. The mass loading of the active material was approximately 3 mg cm^{-2}. Metallic sodium foil served as the counter electrode. The cells were galvanostatically charged and discharged on Maccor series 4000 battery testers (USA) at different C rates (nominal current density 1 C = 200 mA g^{-1}) between 1.5 and 4.5 V at 20 °C.

2.4. X-ray absorption spectroscopy (XAS)

The pristine, charged (4.5 V) and discharged (1.5 V) electrodes protected with adhesive Kapton tape were used for the XAS measurements [48]. XAS analysis at the Ni and Mn K-edge was carried out in transmission mode at the KMC-2 beamline of the synchrotron BESSY at Helmholtz-Zentrum Berlin, Germany, using a graded Si–Ge (111) double-crystal monochromator. In order to eliminate the high order harmonics, about 65% of the maximum possible intensity of the beam is transmitted through the sample during the measurements. Pure Mn and Ni foil were measured simultaneously with each sample for energy calibration. The data were processed by using the software ATHENA and ARTEMIS of the package IFEFFIT as reported in the literature [49,50]. Each spectrum was energy-calibrated with respect to the first