



# Stabilizing Na<sub>0.7</sub>MnO<sub>2</sub> cathode for Na-ion battery via a single-step surface coating and doping process

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## HIGHLIGHTS

- Na<sub>0.7</sub>MnO<sub>2</sub> is stabilized by a one-step surface coating and doping process.
- Air-stable Na<sub>0.7</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> coating protects Na<sub>0.7</sub>MnO<sub>2</sub> against reaction with air.
- Initial discharge capacity remains the same after modification.
- Capacity retention after 50 cycles improved from 62.2% to 87.7% with modification.

## ARTICLE INFO

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## ABSTRACT

P2-type Na<sub>0.7</sub>MnO<sub>2</sub>, with high capacity and excellent Na ion conductivity, is a promising cathode material for Na-ion batteries. However, its rapid capacity decay upon repeated cycles restricts its practical application. In this study, we demonstrate a facile method to surface coat and dope P2-Na<sub>0.7</sub>MnO<sub>2</sub> with a P2-Na<sub>0.7</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> layer in a single step to enhance its cycle stability. The coating suppresses the dissolution of Mn ions into electrolyte, and the Ni dopant suppresses orthorhombic distortion, inhibits Na<sup>+</sup>/vacancy ordering and improves structural stability upon cycling. As a consequence, the coating enhances capacity retention from 62.2% (Na<sub>0.7</sub>MnO<sub>2</sub>) to 87.7% (Na<sub>0.7</sub>MnO<sub>2</sub>/20 wt% Na<sub>0.7</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub>) over 50 cycles, and from 20.7% (Na<sub>0.7</sub>MnO<sub>2</sub>) to 68.9% (Na<sub>0.7</sub>MnO<sub>2</sub>/20 wt% Na<sub>0.7</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub>) over 100 cycles without sacrificing the initial discharge capacity. In addition, the air-stable Na<sub>0.7</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> surface layer protects Na<sub>0.7</sub>MnO<sub>2</sub> against air exposure.

## 1. Introduction

As sodium is abundant and inexpensive compared to lithium, Na-ion battery (NIB) has recently regained interest within the scientific community as a promising alternative to Li-ion battery (LIB) for large-scale energy storage applications [1–4]. One of the challenges for commercialization of NIB is to develop cathode materials with high capacity and good stability. Among various NIB cathode materials reported to date, P2-type layered transition metal oxides (Na<sub>x</sub>MO<sub>2</sub>, M = one or several transition metal(s)) have received much attention because of their high theoretical capacity, superior rate performance and ease of synthesis [5,6]. In particular, P2-Na<sub>0.7</sub>MnO<sub>2</sub> with a capacity of ~200 mAh g<sup>-1</sup> and high volumetric energy density is attractive as Mn is low-cost, earth-abundant and environmentally friendly.

However, Na<sub>0.7</sub>MnO<sub>2</sub> suffers from severe capacity fading upon repeated charging/discharging due to structural and chemical issues. First, phase transformation (P2 to O2 or OP4) occurring at high voltage (low Na<sup>+</sup> content) and the transitions between different Na<sup>+</sup>/vacancy

ordered patterns formed at particular Na stoichiometries contribute largely to the capacity loss [7]. Moreover, the orthorhombic distortion of the structure induced by Jahn-Teller effective Mn<sup>3+</sup> and the disproportionation of Mn<sup>3+</sup> into Mn<sup>4+</sup> and Mn<sup>2+</sup> result in a loss of active material and an increase in battery impedance [8–10]. Thus, strategies to stabilize the structure of Na<sub>0.7</sub>MnO<sub>2</sub> and inhibit Mn dissolution are needed to improve its cycle performance for practical applications.

Previous reports have demonstrated that the capacity fading of Na<sub>0.7</sub>MnO<sub>2</sub> can be suppressed by substitution of inert cations such as Li, Mg or active transition metals such as Fe and Co into its structure to inhibit phase transformation, orthorhombic distortion and Na<sup>+</sup>/vacancy ordering [11–20]. However, the overall capacity is reduced through these methods. Surface coating of P2-type materials with inert oxides such as Al<sub>2</sub>O<sub>3</sub> and MgO with atomic layered deposition or wet chemistry processes were also reported [10,21–23]. Even though cycle stability is generally improved, the inert oxides are typically electrically insulating and inactive. Herein, we propose a one-step method to surface-coat Na<sub>0.7</sub>MnO<sub>2</sub> with a stable P2-Na<sub>0.7</sub>Ni<sub>0.33</sub>Mn<sub>0.67</sub>O<sub>2</sub> layer and co-

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dope the bulk with Ni at the same time to enhance its cycle stability without sacrificing the initial capacity.

P2- $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  is selected and applied as a coating layer based on four structural and chemical advantages. First of all, P2- $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  has the same structure as the underlying P2- $\text{Na}_{0.7}\text{MnO}_2$  with a lattice mismatch of only 0.57% in the *c* axis (PDF#27–0751 and PDF#54–0894). This reduces the strain energy between the surface coating and the bulk material and improves material stability during battery cycling. To further reduce the interface effect, the coating process is carried out at a high temperature of 900 °C to allow part of the Ni atoms to diffuse into  $\text{Na}_{0.7}\text{MnO}_2$ . Secondly,  $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  is an air-stable material, as opposed to  $\text{Na}_{0.7}\text{MnO}_2$  which reacts in the atmosphere with moisture and carbon dioxide [24]. So, the surface coating improves the processibility of the active material powder in air. Thirdly,  $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  possesses superior surface chemical stability in electrolyte as it only utilizes the redox reaction of  $\text{Ni}^{2+}/\text{Ni}^{4+}$ , while the oxidation state of Mn ion remains 4+ [25]. Therefore,  $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  is able to act as a protective surface layer to prevent dissolution of Mn ions from  $\text{Na}_{0.7}\text{MnO}_2$ . Lastly,  $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  is electrochemically active with a capacity of 86 mAh  $\text{g}^{-1}$  between 2.0 V and 4.0 V with transport channels for Na ions and electrons, so the overall capacity will not be significantly compromised with the coating [26].

In this work,  $\text{Na}_{0.7}\text{MnO}_2$  (NMO) is first synthesized and then coated with different amounts of  $\text{Na}_{0.7}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  (NNMO) via a wet-chemistry method followed by annealing to stabilize the material. The resulting materials show better stability against air-exposure, indicating the effectiveness of the surface layer. The process suppresses the orthorhombic distortion of the  $\text{Na}_{0.7}\text{MnO}_2$  bulk material, suggesting that some of the Ni ions are doped into  $\text{Na}_{0.7}\text{MnO}_2$ . These lead to improved cycle stability of the material when tested in a NIB.

## 2. Experimental

### 2.1. Material synthesis and characterizations

Preparation of the bare  $\text{Na}_{0.7}\text{MnO}_2$  (NMO) sample: Raw materials of  $\text{Na}_2\text{CO}_3$  and  $\text{Mn}_2\text{O}_3$  (Sigma Aldrich) with a molar ratio of 0.7:1 were first mixed uniformly with ball milling (Fritsch pulverisette 7) at 200 rpm for 6 h with acetone as dispersant. The obtained mixture was then calcined at 900 °C for 20 h in air followed by quenching. The synthesized sample was transferred to a glove box filled with argon immediately after the synthesis process.

Coating process: A solution with acetate precursors of  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ ,  $(\text{CH}_3\text{COO})_2\text{Ni}\cdot 4\text{H}_2\text{O}$  and  $(\text{CH}_3\text{COO})_2\text{Mn}\cdot 4\text{H}_2\text{O}$  was first prepared in absolute ethanol with a molar ratio of 2:1:2 in the glove box. Different amounts of  $\text{Na}_{0.7}\text{MnO}_2$  were added to the solution, stirred for 30 min and then dried at 140 °C to remove the ethanol. The obtained powder was then annealed at 900 °C for 20 h in air followed by quenching. The samples are denoted as NMO/*x* wt% NNMO, wherein *x* wt% refers to the mass ratio of NNMO relative to the total mass of NMO and NNMO. All the samples were also stored in a glove box after synthesis.

### 2.2. Material characterizations

The crystal structures of the as-prepared samples were carefully examined with X-ray diffraction (XRD, SmartLab, Rigaku) using a  $\text{Cu-K}\alpha$  radiation source ( $\lambda = 0.1541$  nm) in the  $2\theta$  range of 10–70°. Morphologies of samples were observed with a scanning electron microscope (SEM, Quanta 200, FEI). The detailed structure of the samples was also studied with high resolution transmission electron microscopy (HRTEM, FEI TECNAIG2F30) at 300 kV.

### 2.3. Electrochemical tests

Active material was mixed with acetylene black (AB) and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 in 1-methyl-2-pyrrolidone (NMP) to form homogeneous slurry. The slurry was then coated with a doctor blade onto aluminum current collectors and dried at 80 °C. Electrodes with a diameter of 16 mm were cut out and pressed by a calender to a packing density between 1.9 and 2.2  $\text{g cm}^{-3}$ . These electrodes were assembled with Na metal as counter electrode and a layer of glass fiber as separator in an argon-filled glove box into 2032-type coin cells. 1 M  $\text{NaClO}_4$  in propylene carbonate (PC) with 5 wt% fluoroethylene carbonate (FEC) was used as electrolyte.

The coin cells were galvanostatically charged and discharged over a potential range of 2.0 V–4.0 V versus  $\text{Na}/\text{Na}^+$  using a multichannel battery tester (Neware, Shenzhen). Galvanostatic intermittent titration technique (GITT) experiments were carried out with a succession of current pulses (1 h at 15  $\text{mA g}^{-1}$ ) and relaxation steps (4 h). Cyclic voltammetry (CV) was performed on a potentiostat (VMP3, Bio-logic) at a slow scan rate of 0.1  $\text{mV s}^{-1}$ . VMP3 was also used in the electrochemical impedance spectroscopy (EIS) tests over a frequency range from 10 mHz to 100 kHz by applying an AC signal of 10 mV. All experiments were carried out at room temperature of 22 °C unless otherwise specified.

## 3. Results and discussions

Fig. 1 shows the XRD patterns of the as-prepared samples with or without NNMO coating. Bare NMO shows a hexagonal structure with orthorhombic distortion (marked by “X”) due to the presence of Jahn-Teller active  $\text{Mn}^{3+}$ , consistent with previous reports [7,13]. The orthorhombic distortion in the bulk material disappears with the introduction of NNMO. The XRD peaks of the coated samples are shifted gradually to the left with increasing NNMO amount, rather than a convolution of two distinct types of peaks from NNMO and NMO. These results suggest that part of the Ni ions are doped into the NMO material, as ionic radius of Ni ion ( $\text{Ni}^{2+} = 0.69$  Å) is larger than that of Mn ion (0.58 Å and 0.53 Å for  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ , respectively). Lattice parameters and unit cell volumes of NMO/NNMO samples are obtained with least-square refinement of the XRD profiles with a P2 structure (Table S1), showing a smaller increase in lattice constants with NNMO modification. In particular, the difference in lattice constant *c* between NMO and NMO/20 wt% NNMO is only 0.57%. Peak intensities are also higher for the NNMO-coated samples, indicating better crystallization, due to the additional annealing process during coating.

Morphologies of the as-prepared samples are presented with SEM images in Fig. 2. All the samples consist of polyhedral plate-like

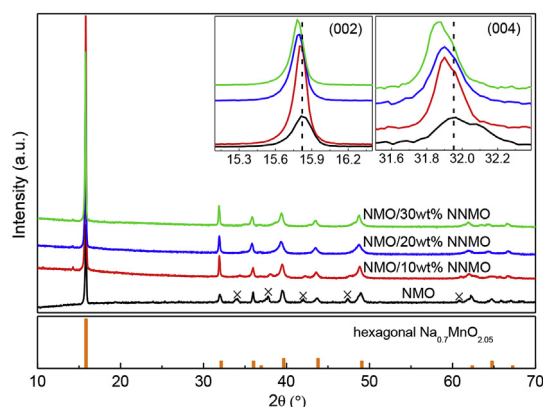


Fig. 1. XRD patterns of as-prepared samples. Orthorhombic distortion of the bare sample is marked by “X” in the figure, and more detailed information of the (002) and (004) peaks are shown in the insets. Standard are also presented for comparison.

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