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NaN_3 addition, a strategy to overcome the problem of sodium deficiency in P2-$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ cathode for sodium-ion battery

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HIGHLIGHTS

- Na-ion battery full cell using P2-type layered oxide.
- Decrease of the 1st cycle capacity loss in the full cell by adding NaN_3.
- Reversible capacity of ~130 mAh g^{-1} in full cell configuration.

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ABSTRACT

Sodium-ion full cell with hard carbon as anode and a layered oxide cathode based on earth abundant elements i.e., $Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ is reported. The irreversible capacity of the negative electrode in the full cell configuration is compensated by the addition of a sacrificial salt such as NaN_3 to the P2-$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ cathode material. 60% increase in the reversible capacity is achieved with the addition of 10% of sodium azide in the composite cathode without compromise on the cycle life. Though, there is a limit in its use because of the capacity fade which can be observed with the further increase in NaN_3 content. The quantification of sodium ions at the end of discharge (at 1 V) after 40 cycles by *ex-situ* X-ray diffraction and solid state nuclear magnetic resonance supports the electrochemical data. Scanning electron microscopy shows the effect of NaN_3 on the electrode microstructure in terms of the porosity created by NaN_3 decomposition.

1. Introduction

Sodium-ion batteries possess large potential as an attractive choice for electrochemical energy storage. Some initial work on sodium based battery electrode materials was carried out in the 1980s [1,2]. However, the development of sodium-ion battery electrode materials for energy storage was overshadowed by lithium-ion battery development due to their high gravimetric as well as volumetric energy density. Recently, sodium-ion batteries have emerged as a low-cost alternative for aforementioned lithium-ion batteries and regained the interest of the scientific community. The reason behind it is the larger and more uniform presence and availability of sodium-containing components compared to lithium-containing ones in the Earth's crust, though a compromise on the energy density is there. Ceramic layered oxide cathodes, Na_xMO_2 (M = one or several transition metal/s), have gained the attention of the scientific community because of their ease of synthesis and their tap density [3]. The presence of inexpensive and earth abundant transition metals, as Fe and Mn, is another important factor in the selection of this type of materials as cathodes.

Sodium layered oxides can be categorized in the P2- and O3-type structures according to Delmas' notation [4], being P2-type structures usually sodium deficient ($x < 0.71$). This sodium deficiency gives a significant reduction in the delivered capacity when using non-sodium containing anode materials such as carbon and more specifically hard carbons (H.C.). Increasing the sodium content chemically from 0.71 to 1 has an impact on the crystal structure of the material, which changes from P2 to O3, showing inferior electrochemical performance in certain cases such as $Na[Fe_{0.5}Mn_{0.5}]O_2$ [5]. Increase in the sodium content electrochemically leads to the formation of the distorted orthorhombic P2

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structure, named as P2' [6].

Some researchers have performed the pre-sodiation of the carbon using half-cell configuration and then dismantled the cell and used the carbon anode against the sodiated cathode to overcome the irreversibility of the anode [7]. As an alternative, this study is focused on compensating the sodium utilized in the irreversible reaction of the anode in the full cell configuration. To increase the reversible capacity of the sodium deficient materials in a full cell which utilizes hard carbon as the anode is a significant challenge which has been addressed in few earlier reports [8,9]. NaN_3 was shown for the first time to have potentiality to overcome the sodium deficiency in the cathodes and it can be used as an extra reservoir of sodium, compensating the sodium consumption on the anode because of the SEI formation [6]. More recently some reports have been published on the similar line using Na_3P as the sacrificial salt to get higher reversible capacity and to compensate the sodium deficiency [8]. However Na_3P cannot be handled in air, even in a dry room and the fate of leftover P is unknown. Since NaN_3 decomposes during the electrochemical cycling, the concomitant N_2 can be withdrawn from the cell during the formation cycle and hence the compromise on the energy density is minimized. Cycling conditions and separate compartment dimensions in which the gases generated during formation will be stored will need to be carefully selected in order to avoid overpressure. Moreover, conversely to lithium, there is no formation of a nitride between sodium and nitrogen. In this study we analyzed the effect of using NaN_3 as sacrificial salt in the electrochemical performance of a sodium-ion full cell.

2. Experimental

P2-$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ has been synthesized by conventional solid-state synthesis route. Stoichiometric amounts of Na_2CO_3 (99.5%, Sigma Aldrich), Fe_2O_3 (99%, Alfa Aesar) and Mn_2O_3 (98%, Alfa Aesar) were mixed using wet ball milling in ethanol. Balls to powder mass ratio was fixed at 30:1 and other ball milling parameters such as speed and time were set at 300 rpm and 30 min, respectively. The powder mixture was compressed in the form of pellets using a uniaxial press under a load of 4 ton $in.^{-2}$. Then, the pellets were calcined in a box furnace, at a temperature of 900 °C for 12 h. After the calcination in air, the reaction product was quenched to room temperature and stored under dry conditions to avoid any moisture contamination.

X-ray diffraction (XRD) patterns of $Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ powder and $Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2 + NaN_3$ electrodes were obtained by using CuK_α radiation of $\lambda = 1.5418$ Å within 2θ range of 15–80° in a Brüker D8 Advance X-ray diffractometer equipped with a LYNXEYE detector mounted with Ni filter to attenuate the diffraction of K_β radiation.

Cathode and anode laminates were prepared for electrochemical characterization of half and full cells. Synthesized cathode material (AM) was coated on an aluminum foil (Hohsen, 20 μm thick) after mixing it with C65 carbon black (CB, Timcal) as a conductive agent and polyvinylidene fluoride (PVDF, Solvay) as a binder, in the weight ratio AM:CB:PVDF = 75:15:10. *N*-methyl-2-pyrrolidone (NMP, Sigma Aldrich) was used as a solvent for the preparation of the slurry. Two more composites were coated by adding 10% and 20% of NaN_3 in weight to the final slurry of the positive electrode. In case of the anode, hard carbon (Kuraray):PVDF ratio was maintained at 95:5 by wt% and NMP was used as the solvent. Anode material was also coated on top of the same characteristic aluminum foil used for positive electrode fabrication. Cathode active material average loading was 6.19 mg cm^{-2} with a deviation between electrodes of less than 0.62 mg cm^{-2}. In the case of the anode active material, average loading was 7.69 mg cm^{-2} with a deviation between electrodes of less than 0.44 mg cm^{-2}. All the coated foils were dried in a vacuum oven at 120 °C for 2 h.

Anode and cathode electrodes were punched out of the coated foil with a diameter of 12 mm and before assembling the cells, they were pressed by applying 4 ton $in.^{-2}$ of uniaxial pressure. Metallic sodium was used as counter electrode in the half cell electrochemical studies and the electrolyte used for all the electrochemical cell testing was 1 M $NaPF_6$ in ethylene carbonate:diethyl carbonate (EC:DEC) (50:50 by wt%). Cells were assembled in the CR2032 coin cell format to analyze the performance of the materials. Coin cells were tested using multichannel Maccor battery tester Series 4000 at room temperature at 15 mA g^{-1}. The voltage range for the anode half cells was 0.01–2 V, while for the cathode it was 1.5–4.3 V. For the full cell configuration, high and low cut-off voltages were 4.1 V and 1.0 V, respectively. Mass ratio between the positive and the negative electrode was maintained at 1.8. Capacity of the full cells is based on the cathode mass loadings.

Ex-situ XRD analysis of P2-$Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ electrodes after 40 cycles in the full cell configuration (fully discharged at 1 V and washed in dimethyl carbonate) was performed in the cells without NaN_3, and with 10% wt and 20% wt of NaN_3. To analyze the morphology of the cycled electrodes, Scanning Electron Microscopy (SEM) was used. SEM images were obtained using a FEI Quanta 200 Field Emission Gun-SEM.

^{23}Na Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) experiments were performed at 52.9 MHz, on a Bruker-300 spectrometer charged to a field of 4.7 T using a 1.3 mm MAS probe. The rotor spinning speeds were set to 50 kHz for the sample without NaN_3, 58 kHz for the sample with 10% wt NaN_3 and 60 kHz for the sample with 20% wt NaN_3. The spinning rates were selected in order to avoid the superposition of the signals with MAS sidebands. A rotor synchronized spin–echo pulse sequence ($90°-\tau-180°-\tau1-$acquisition) was used with a 90° pulse of 1.2 μs, and a recycle delay of 1 s. The spectra were referenced to a 0.2 M solution of $^{23}NaCl$.

3. Results and discussion

3.1. Structural characterization of $Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$

XRD pattern of $Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ shows the formation of single phase P2 layered structure (Fig. 1). Most of the peaks can be indexed to α-$NaFeO_2$ type crystal structure with space group *P*6

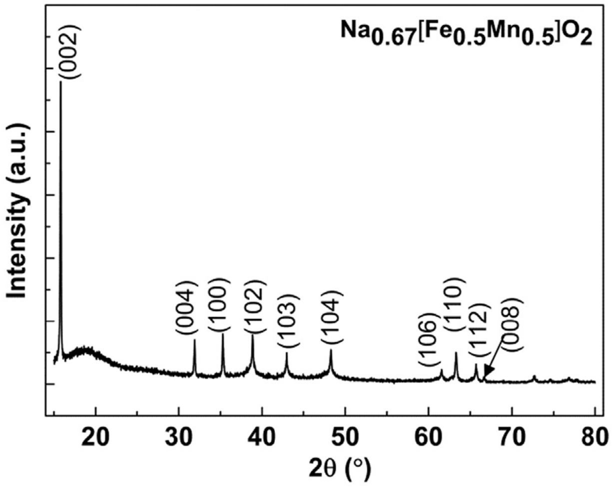

Fig. 1. XRD pattern of $Na_{0.67}[Fe_{0.5}Mn_{0.5}]O_2$ powder.

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