

# SUPPORTING INFORMATION

## **Electrospun P2-type $\text{Na}_{2/3}(\text{Fe}_{1/2}\text{Mn}_{1/2})\text{O}_2$ hierarchical nanofibers as cathode material for sodium-ion batteries**

Sujith Kalluri,<sup>a</sup> Kuok Hau Seng,<sup>a</sup> Wei Kong Pang,<sup>a,c</sup> Zaiping Guo,<sup>\*a,b</sup> Zhixin Chen,<sup>b</sup> Hua Kun Liu,<sup>a</sup> and Shi Xue Dou<sup>a</sup>

<sup>a</sup>*Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2500, Australia.*

<sup>b</sup>*School of Mechanical, Materials and Mechatronics Engineering, University of Wollongong, NSW 2500, Australia.*

<sup>c</sup>*Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.*

<sup>\*</sup>*Corresponding Author:*      [zguo@uow.edu.au](mailto:zguo@uow.edu.au) (Prof. Zaiping Guo)

*Tel: +61-2-4221 5225, Fax: +61-2-4221 5731*

### **Experimental:**

#### **Preparation of $\text{Na}_{2/3}(\text{Fe}_{1/2}\text{Mn}_{1/2})\text{O}_2$ nanofibers and nanoparticles**

The precursor solution is prepared by dissolving stoichiometric amounts of sodium acetate, iron nitrate, and manganese acetate (all from Sigma-Aldrich with 99% purity) in a mixed solvent of ethanol and N,N-dimethylformamide (DMF). The selection of solvents (ethanol and DMF) is based on their compatibility with the electrospinning process. After stirring for an hour, 10 wt. % polyvinylpyrrolidone (PVP, 1,300,000 g/mol) is added to the resultant solution. After overnight stirring, electrospinning is carried out at room temperature by transferring the precursor solution into a syringe with a 21G stainless steel needle and feeding it into the electrospinning unit (NanoNC, South Korea) at constant parameters: applied voltage: 20 kV, tip to collector distance: 11 cm, feed rate: 0.8 ml h<sup>-1</sup> and relative humidity (RH): ~25%. After electrospinning, the as-spun nanofibrous mats are collected from the Al foil collector and calcined in a step-wise process as follows: 1° C/min, 350°C, 2h; 2° C/min, 500°C, 2h; and 3° C/min, 900°C, 2 h in compressed-air

atmosphere. Then, the resultant  $\text{Na}_{2/3}(\text{Fe}_{1/2}\text{Mn}_{1/2})\text{O}_2$  nanofibers (hereafter designated as NFMO NF) are quenched down to room temperature and stored in an Ar-filled glove box. The purpose of the step-wise calcination process in the case of the nanofibers is to protect their structure from collapse during the calcination process by employing slow heating rates in a step-wise fashion.

For the baseline reference sample, the same precursor solution is dried in a drying oven at  $100^\circ\text{C}$  overnight and further calcined at  $900^\circ\text{C}$  for 2 h in compressed-air atmosphere. The thus obtained  $\text{Na}_{2/3}(\text{Fe}_{1/2}\text{Mn}_{1/2})\text{O}_2$  nanopowder (hereafter designated as NFMO NP) is quenched down to room temperature.

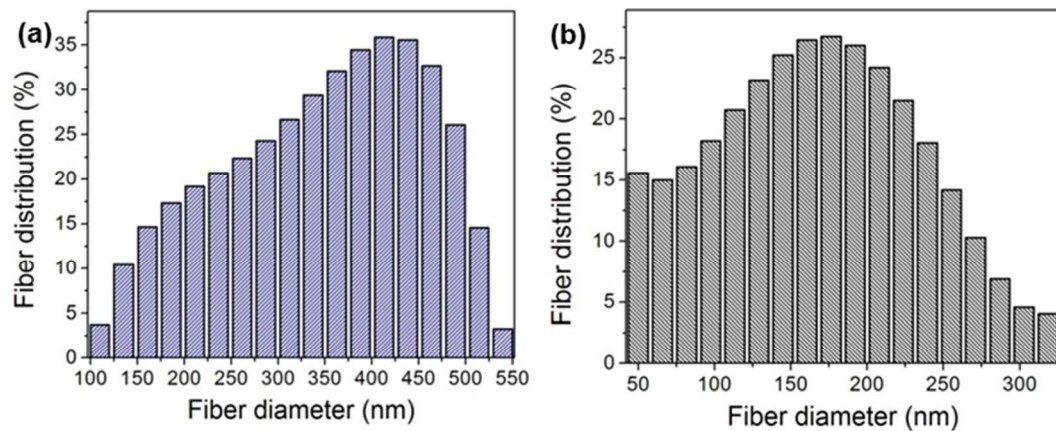
### **Sample characterization**

Structural and crystallographic properties for both NFMO NF and NFMO NP were obtained by X-ray powder diffraction (XRD, GBC MMA) with  $\text{Cu-K}\alpha$  radiation. Morphological studies were performed using scanning electron microscopy (SEM, JEOL JSM-7500, Japan) and high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2010, Japan). Fast Fourier transform (FFT) analysis on the HR-TEM images was performed using digital micrograph software. The fiber diameter and particle size distributions were calculated using ImageJ software. For *ex-situ* SEM characterization after 40 cycles, the coin-cells of NFMO NF and NP were disassembled in a glove box, washed three times with diethyl carbonate (DEC), and dried in the glove box. The thus obtained samples were characterized with SEM, and the corresponding images are shown in Figure S5(a-b).

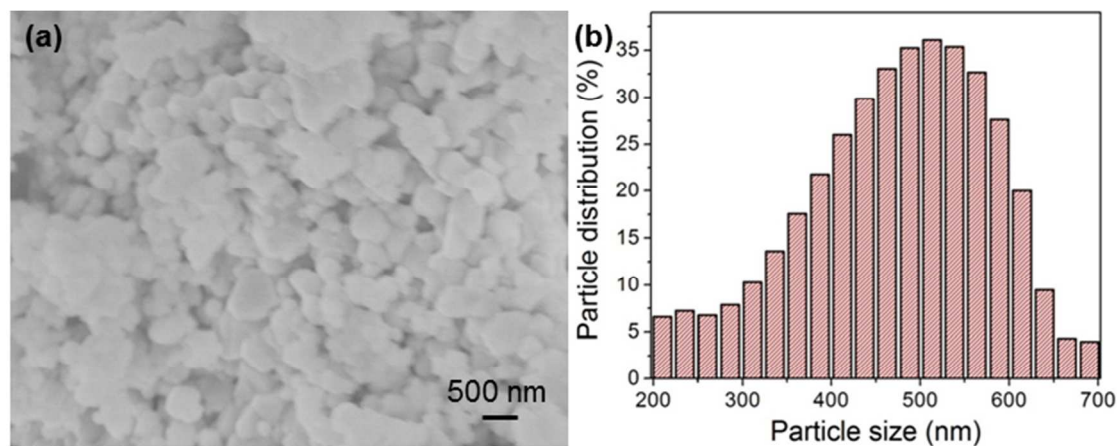
### **Electrochemical characterization**

The electrochemical properties of the as-prepared samples were evaluated in CR2032 coin-cells assembled in an Ar-filled glove box (MBraun, Germany) in the half-cell configuration. Both the

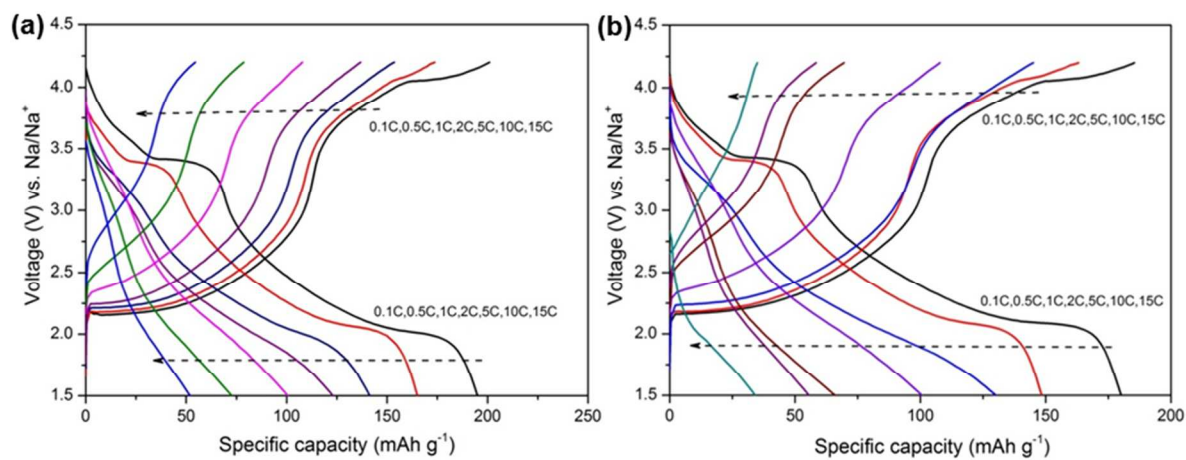
NFMO NF and the NFMO NP cathodes were prepared by milling the active material with carbon black (Super P, TIMCAL, Switzerland) and polyvinylidene fluoride (PVDF) (80:10:10) with N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) in planetary mixer (Kurabo Mazerustar, Japan). The resultant slurries were coated on Al current collectors by traditional doctor blading and dried in a vacuum oven at 120°C overnight. The coin-cells were assembled using Na disks (Sigma-Aldrich, USA) as counter electrode, porous glass fiber (Milli pore, Australia) as the separator, and 1M NaClO<sub>4</sub> in propylene carbonate (PC) as the electrolyte, with 2 wt.% fluoroethylene carbonate (FEC) as an additive. The FEC electrolyte additive acts as a stabilizing agent for the solid electrolyte interphase (SEI) film and helps in improving the Na-ion intercalation/de-intercalation kinetics and thus the cycle life as shown in Figure S7.<sup>1,2</sup> Galvanostatic charge-discharge behaviour was investigated using an automatic battery analyzer (Land, China). A Biologic VMP3 electrochemical workstation was used to collect cyclic voltammograms (CVs) and Nyquist plots. The CV curves were collected with the scan rate of 1 mV s<sup>-1</sup> and Na-foil as the counter electrode, while the impedance Nyquist plots were collected in the frequency range of 100 kHz to 100 mHz at open circuit voltage. Since this NFMO material is highly sensitive to moisture/air, all the post-synthesis characterizations of both samples were conducted under highly controlled inert conditions. In order to understand the stability of this material in air/moisture, XRD patterns were collected for three successive weeks after exposing the material to air/moisture, as shown in Figure S6. This reveals the structural degradation with time and possibly the formation of some by-products due to the high reactivity of Na with air/moisture.



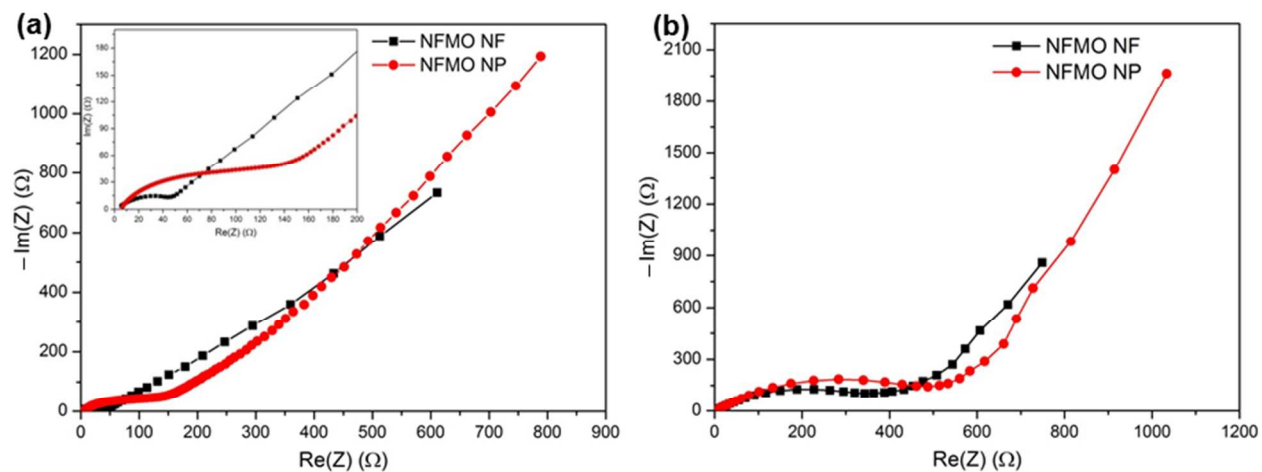
**Fig. S1:** Fiber diameter size distribution of NFMO NF (a) as-spun and (b) heat-treated.



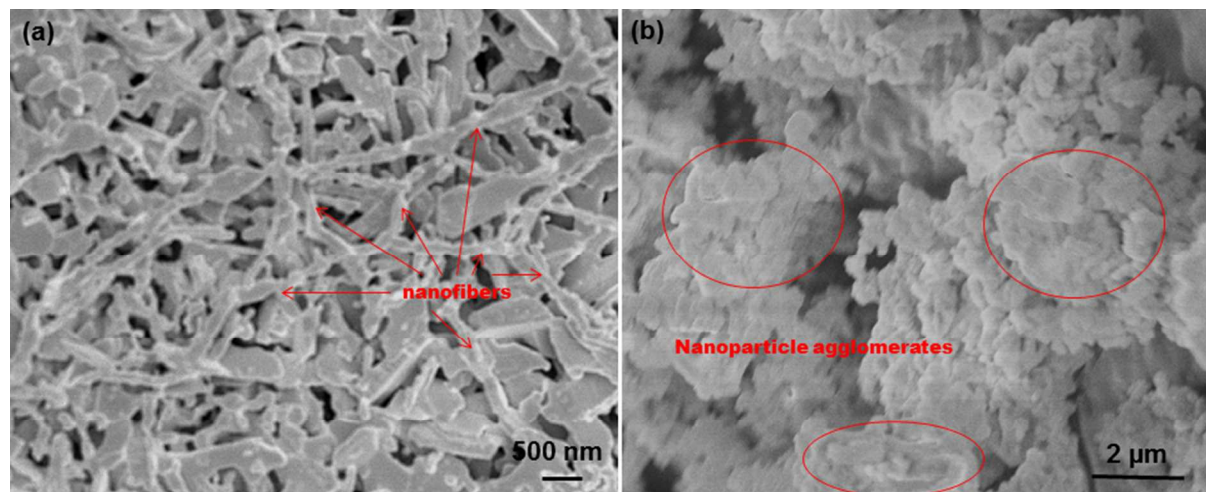
**Fig. S2:** (a) SEM image of NFMO NP and (b) particle size distribution



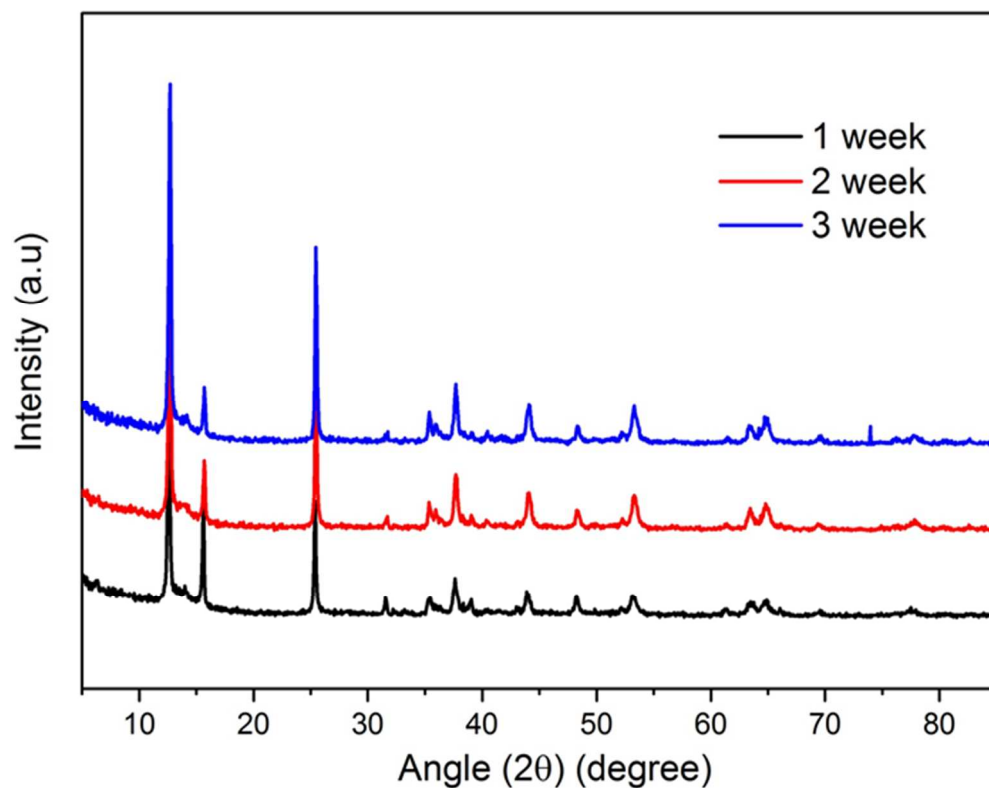
**Fig. S3:** Charge-discharge curves at various current rates measured in the voltage range of 1.5 - 4.2 V for (a) NFMO NF and (b) NFMO NP.



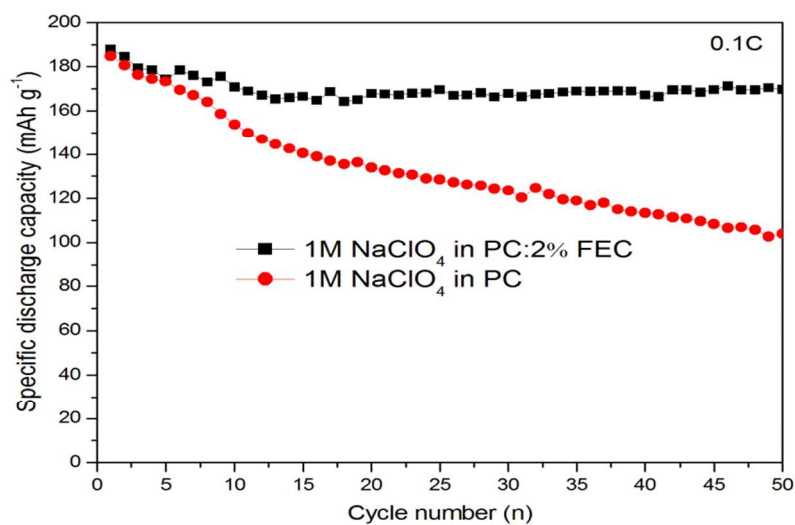
**Fig. S4:** Electrochemical impedance spectroscopy Nyquist plots of NFMO NF and NFMO NP (a) before cycling (inset: highly magnified region of plot) and (b) after cycling, with all plots collected at open circuit voltage (OCV) in the frequency range of 100 kHz to 100 mHz.



**Fig. S5:** *Ex-situ* SEM images of (a) NFMO NF and (b) NFMO NP after electrochemical cycling.



**Fig. S6:** XRD patterns of NFMO after exposure to moisture /air for three successive weeks.



**Fig. S7:** Cycling stability of NFMO NF with and without FEC electrolyte additive at 0.1 C rate.

## REFERENCES

- (1) Darwiche, A.; Marino, C; Sougrati, M. T.; Fraise, B.; Stievano, L.; Monconduit, L. Better Cycling Performances of Bulk Sb in Na-Ion Batteries Compared to Li-Ion Systems: An Unexpected Electrochemical Mechanism. *J. Am. Chem. Soc.* **2012**, *134*, 20805-20811.
- (2) Etacheri, V.; Haik, O.; Goffer, Y.; Roberts, G. A.; Stefan, L. C.; Fasching, R.; Aurbach, D. Effect of Fluoroethylene Carbonate (FEC) on the Performance and Surface Chemistry of Si-Nanowire Li-Ion Battery Anodes. *Langmuir* **2012**, *28*, 965-976.