# Romanechite-structural Na<sub>0.31</sub>MnO<sub>1.9</sub> nanofibers as highperformance cathode material for sodium ion battery

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# **Experimental Details**

# Synthesis of tunneled Na<sub>0.31</sub>MnO<sub>1.9</sub>:

The Na<sub>0.31</sub>MnO<sub>1.9</sub> nanofibers with Romanechite structure was synthesis by a simple liquid phase process using 2.66 mmol NaOH, 9.97mmol EDTA and 8.72mmol Mn(CH<sub>3</sub>COO)<sub>2</sub> as the initial materials. The stoichiometric ratio of sodium and manganese was 0.31. After adjusting the pH to 7, mixing stoichiometric amounts of the reactants. The precursor obtained after filtrating and dried at 80 °C in the drying oven for 24 hours. The product was precalcined at 350 °C for 3 hours and calcination at 650 °C for 8 hours.

### Electrode preparation and battery assemble:

The cathode electrode was prepared by mixing active material, acetylene black and Polyvinylidene Fluoride (PVDF) in a weight ratio of 70:20:10. The cathode material was coated onto the aluminium sheet and dried at 120 °C for 10 hours. The electrolyte was 1 mol/L NaClO<sub>4</sub> in ethylene carbonate-propylene carbonate (EC/PC, 1:1 in weight ratio). The CR2032 coin cells were assembled in argon-filled glove box.

### **Electrochemical characterization:**

The galvanostatic charge-discharge tests were performed on a LAND CT2001A between 2 V to 4.5 V with sodium metal as the counter electrodes. The cyclic voltammetry (CV) test were taken by a VersaSTAT 3 (Princeton Applied Research) with potential ranges 2 V to 4.5 V at a scan rate of 0.1 mV s<sup>-1</sup>. And the electrochemical impedance spectroscopy technique(EIS) were

implemented by a VersaSTAT 3 (Princeton Applied Research) with the frequency ranging from 1 MHz to 100 mHz with an amplitude voltage of 5 mV. **Physicochemical characterization:** 

Power X-ray diffraction (XRD) patterns were tested on the Rigaku, D/max200PC and the scan rate is 0.15°/min. The ex-situ XRD patterns of the electrodes were collected at the scan rate of 3°/min.The morphology was recorded by scanning electron microscopy (Philips XL 30) and transmission electron microscopy (JEOL JSM-6700F). The inductively coupled plasma– atomic emission spectroscopy (ICP-AES) was used Shimadzu, ICPS-8100). Further, the Na1s, Mn2p, Mn3s and O1s peak were carried out by X-ray photoelectron spectroscopy (VG (ESCALABMKLL)).The N<sub>2</sub> adsorptiondesorption test was measured at 77.4 K with Quantachrome Instruments version 3.01.

<b>Table 1.</b> The ICP test results for the prapared NMO material.						
	Concentration tested (µg mL <sup>-1</sup> )			Molar ratio calculated		
Elements	Na	Mn	Na	Mn	0	
Data	0.7551	5.9079	0.31	1	1.9	



Figure S1. the corresponding EDX pattern of the Na<sub>0.31</sub>MnO<sub>1.9</sub> nanofibers



**Figure S2.** High-resolution XPS spectra of the prepared NMO material: (a) O1s and (b) Na1s.



Figure S3.the corresponding discharge curves of the NMO-650 sample.



**Figure S4.** (a) One single-titration curve of the NMO electrode charged to 2.7 V (vs.  $Na^{+}/Na$ ). (b) The linear fitting for the titration curve shown in (a).



**Figure S5.** The ex-situ XRD analysis of the  $Na_{0.31}MnO_{1.9}$  electrodes at various charge voltage stages upon its first charge process. The main diffraction peak of (201) shifts gradually to the lower diffraction angle along with the increase of charge voltage, which is resulted from gradual extraction of large sodium ions and the shrinkage of the  $Na_{0.31}MnO_{1.9}$  crystal lattice. The appearance of new shoulder peaks indicated by the arrows demonstrate the formation of new crystalline phase during cycling.