

## SUPPLEMENTARY INFORMATION

# Investigation into the origin of pseudocapacitive behavior of $\text{Mn}_3\text{O}_4$ electrodes using *operando* Raman spectroscopy

5 Lufeng Yang<sup>a</sup>, Shuang Cheng<sup>a, \*</sup>, Xu Ji<sup>c</sup>, Yu Jiang<sup>a</sup>, Meilin Liu<sup>a, b, \*\*</sup>

<sup>a</sup>New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong 510006, China.

<sup>b</sup>School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332-0245, USA.

<sup>c</sup>State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, China

\* escheng@scut.edu.cn

\*\*meilin.liu@mse.gatech.edu

The XRD pattern of the long-cycled sample is presented here. Because the active layer was very thin and the material was not well crystallized, the peaks are very weak, as seen in Fig. S1. Except the strong peaks marked with blue rectangles belong to graphite carbon substrate, all the other peaks are assigned to be birnessite  $\text{MnO}_2$  (card No. 23-1046). For comparison, the charge/discharge curves at a constant current of 5 A/g before and after long time cycling are also exhibited here as Fig. S2.

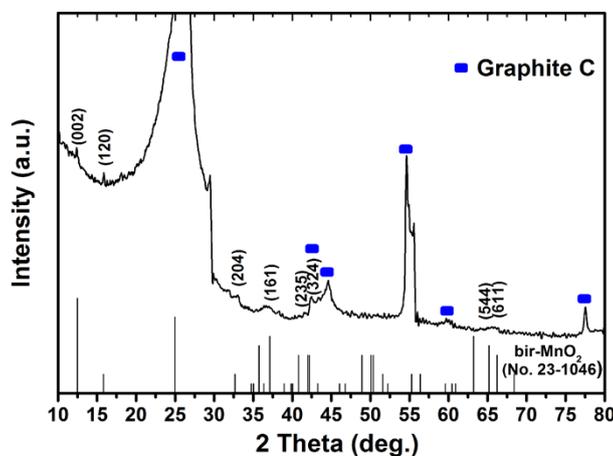


Fig. S1 XRD pattern of the active electrode materials after 5000 cycles test at a scan rate of 50 mV/s. Except the strong peaks marked with blue rectangles belong to graphite carbon substrate, all the other peaks are assigned to be birnessite  $\text{MnO}_2$ .

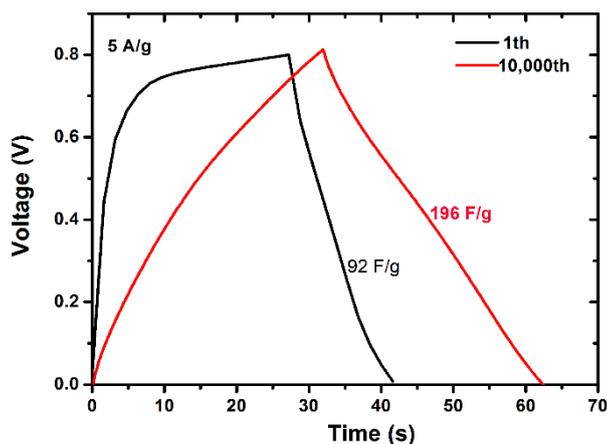
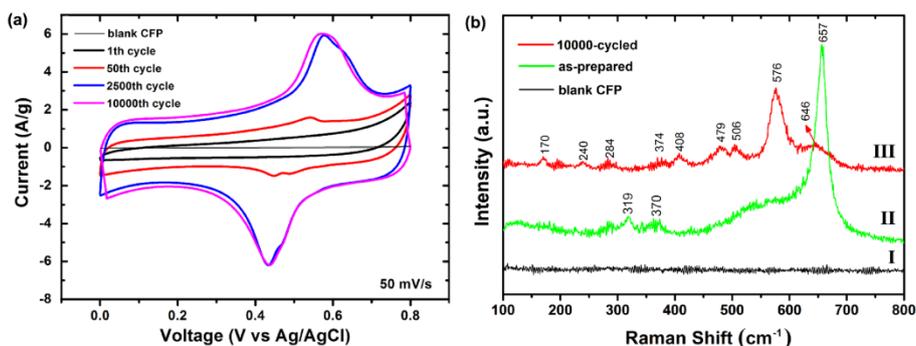


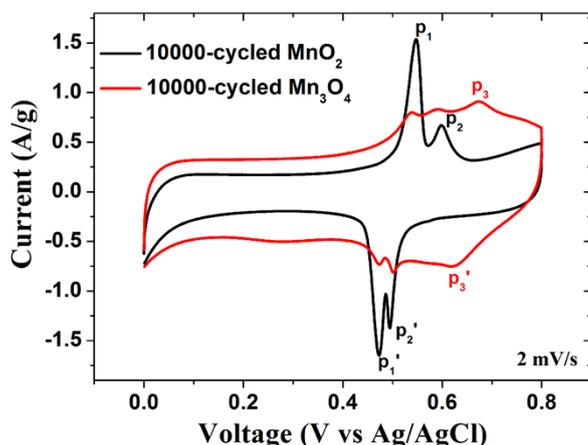
Fig. S2 Charge-discharge curves of the as-prepared and 10,000-cycled sample at 5 A/g.

In order to figure out whether other  $Mn_3O_4$  sample prepared via different method will exhibit performance enhancement during endurance test, a new hausmannite  $Mn_3O_4$  sample was synthesized by a hydrothermal method.<sup>2</sup> Cyclic voltammetry (CV) was used to characterize the capacitive behavior of the  $Mn_3O_4$  thin film electrode in a same three-electrode system. A similar result with our previous  $Mn_3O_4$  electrode was found, the specific capacitance calculated from the CV area<sup>3</sup> increased from 20 F g<sup>-1</sup> at the first cycle to 126 F g<sup>-1</sup> at the 10,000th cycle (Fig. S3a). In addition, Raman spectra presented in Fig. S3b indicate that the spinel  $Mn_3O_4$  also transformed into layered birnessite-type  $MnO_2$  after electrochemical cycling in the  $Na_2SO_4$  electrolyte. While, both the electrochemical performance and Raman signal of the carbon substrate are ignorable in this research according to the relevant results shown in Fig. S3.



**Fig. S3** (a) Cyclic voltammograms of the as prepared  $Mn_3O_4$  electrode and blank carbon substrate in 1 M  $Na_2SO_4$  electrolyte; (b) Raman spectra of I) the blank CFP, II) as-prepared and III) after 10,000 cycled sample.

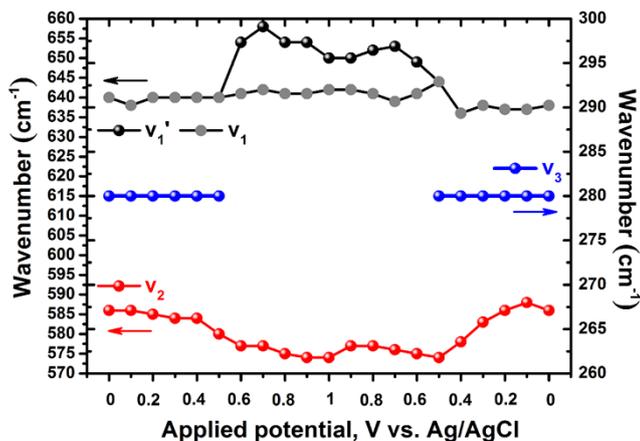
The electrochemical performance of a  $MnO_2$  thin film sample synthesized by the same electrochemical deposition procedure but a different heat treatment of 150 °C for 3 h in air was also characterized for comparison. The  $MnO_2$  thin film was operated in a same potential cycling test as the  $Mn_3O_4$  sample first. Then its CV curve of after 10,000 cycles test sample as well as after 10,000 cycles test  $Mn_3O_4$  at 2 mV/s is shown in Fig. S4. It was found that only two anodic peak centered at (0.549 and 0.601) V vs Ag/AgCl and two corresponding reverse cathodic peaks centered at (0.473 and 0.496) V appeared in the CV curve of the cycled  $MnO_2$  sample, closing to the  $P_1$  and  $P_{II}$  redox pairs of the cycled  $Mn_3O_4$  sample. This result suggests that the  $P_1$  and  $P_2$  peaks can be attributed to the  $Na^+$  intercalation/deintercalation proceeded in two steps, respectively, which agrees with the two sites of sodium birnessite-type manganese oxide for  $Li^+$ .<sup>1</sup> While the  $P_3$  and  $P_3'$  redox peaks are supposed to be  $Mn^{2+}$  involved redox reaction as a result of  $Mn^{2+}$  filling in the defect sites or between the laminates of the cycled  $Mn_3O_4$  sample.



**Fig. S4** The comparison of CV curves of  $MnO_2$  (black) and  $Mn_3O_4$  (red) after 10000 cycles test at a scan rate of 2 mV s<sup>-1</sup> in 1 M  $Na_2SO_4$ .

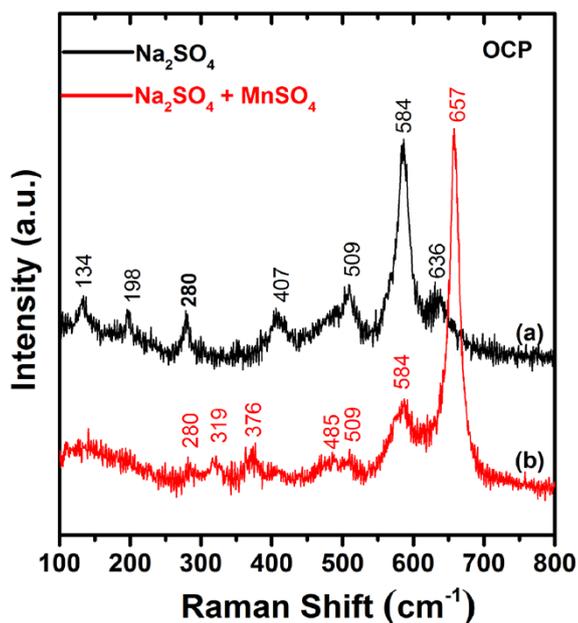
More detailed Raman data of the *in situ* Raman spectra of the birnessite-type  $MnO_2$  collected at different potentials separated by 0.1 V

are illustrated in Fig. S5, which presents four different vibrational mode evolution against potential change during the sweep. The band near  $640\text{ cm}^{-1}$  almost had no change along with the sweep, a new band at  $655\text{ cm}^{-1}$  appeared and only existed during the potential of  $0.7\text{V}\sim 1\text{V}\sim 0.6\text{V}$ , the band at  $280\text{ cm}^{-1}$  which corresponds to the weak bonding of intercalated  $\text{Na}^+$  cations disappeared at higher potential, and the band at  $586\text{ cm}^{-1}$  experienced a red shift to  $574\text{ cm}^{-1}$  when the potential increased to  $1\text{ V}$  from  $0\text{ V}$  and then shift back when the potential dropped.



**Fig. S5** Wavenumber change of four vibrational mode in birnessite  $\text{MnO}_2$  against potential change. Black spheres correspond to the  $v_1'$  mode near  $655\text{ cm}^{-1}$ , gray ones stand for the vibration near  $640\text{ cm}^{-1}$ , the red correspond to the  $v_2$  mode at  $574\text{--}586\text{ cm}^{-1}$ , and the blue correspond to the  $v_3$  mode at  $280\text{ cm}^{-1}$ .

10 To further verify the influence of  $\text{Mn}^{2+}$ , some additional  $\text{Mn}^{2+}$  was added into the electrolyte at open-circuit potential (OCP). The Raman signal change before and after the addition of  $\text{Mn}^{2+}$  is presented in Fig. S6. The Raman signal attributed to  $\text{MnO}_2$  drastically changed into that of  $\text{Mn}_3\text{O}_4$  (Fig. S6), which suggested an important role of  $\text{Mn}^{2+}$  in the energy storage process.



**Fig. S6** Raman spectra of the 10,000 cycled electrode material in a three-electrode cell with (a)  $1\text{ M Na}_2\text{SO}_4$  aqueous electrolyte, (b)  $1\text{ M Na}_2\text{SO}_4$  + several drops of  $\text{MnSO}_4$  aqueous electrolyte.

## Reference

1. Q. Feng, H. Kanoh, Y. Miyai and K. Ooi, *Chem. Mater.*, 7 (1995) 1226-1232.
- 5 2. R. Song, S. Feng, H. Wang and C. Hou, *J. Solid State Chem.*, 2013, 202, 57-60.
3. C. Xu, H. Du, B. Li, F. Kang and Y. Zeng, *J. Electrochem. Soc.*, 2009, 156, A435-A441.