

SUPPLEMENTARY INFORMATION

Investigation into the origin of pseudocapacitive behavior of Mn_3O_4 electrodes using *operando* Raman spectroscopy

5 Lufeng Yang^a, Shuang Cheng^{a, *}, Xu Ji^c, Yu Jiang^a, Meilin Liu^{a, b, **}

^aNew Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou, Guangdong 510006, China.

^bSchool of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332-0245, USA.

^cState 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 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.

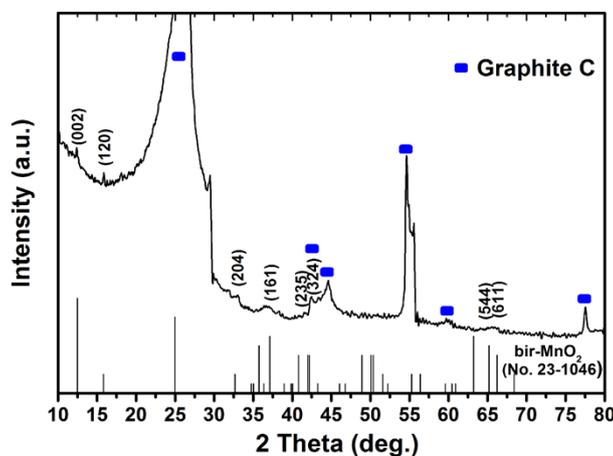


Fig. S1 XRD pattern of the active electrode materials after 5000 cycles test at a scan rate of 50 mV/s. Except the strong peaks marked with blue rectangles belong to graphite carbon substrate, all the other peaks are assigned to be birnessite MnO_2 .

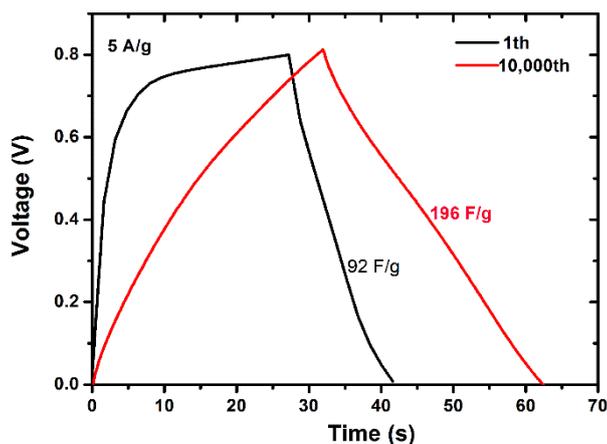


Fig. S2 Charge-discharge curves of the as-prepared and 10,000-cycled sample at 5 A/g.

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.² 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 area³ increased from 20 F g⁻¹ at the first cycle to 126 F g⁻¹ 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.

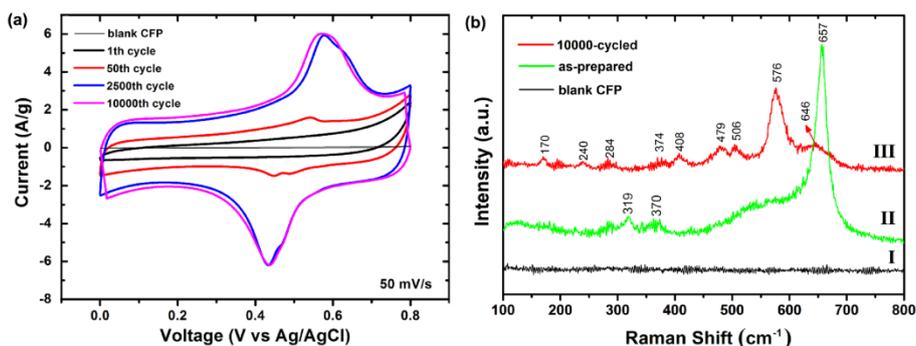


Fig. S3 (a) Cyclic voltammograms of the as prepared Mn_3O_4 electrode and blank carbon substrate in 1 M Na_2SO_4 electrolyte; (b) Raman spectra of I) the blank CFP, II) as-prepared and III) after 10,000 cycled sample.

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^+ .¹ 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.

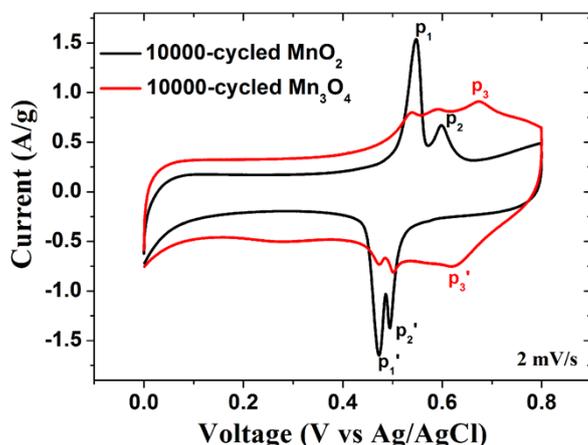


Fig. S4 The comparison of CV curves of MnO_2 (black) and Mn_3O_4 (red) after 10000 cycles test at a scan rate of 2 mV s⁻¹ in 1 M Na_2SO_4 .

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 cm^{-1} almost had no change along with the sweep, a new band at 655 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 cm^{-1} which corresponds to the weak bonding of intercalated Na^+ cations disappeared at higher potential, and the band at 586 cm^{-1} experienced a red shift to 574 cm^{-1} when the potential increased to 1 V from 0 V and then shift back when the potential dropped.

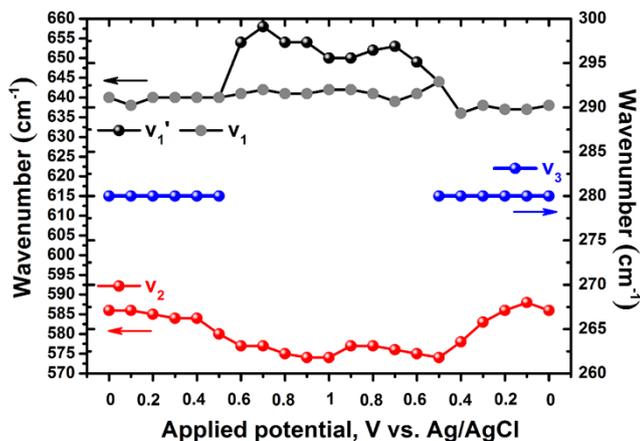


Fig. S5 Wavenumber change of four vibrational mode in birnessite MnO_2 against potential change. Black spheres correspond to the v_1' mode near 655 cm^{-1} , gray ones stand for the vibration near 640 cm^{-1} , the red correspond to the v_2 mode at $574\text{--}586\text{ cm}^{-1}$, and the blue correspond to the v_3 mode at 280 cm^{-1} .

10 To further verify the influence of Mn^{2+} , some additional Mn^{2+} was added into the electrolyte at open-circuit potential (OCP). The Raman signal change before and after the addition of Mn^{2+} is presented in Fig. S6. The Raman signal attributed to MnO_2 drastically changed into that of Mn_3O_4 (Fig. S6), which suggested an important role of Mn^{2+} in the energy storage process.

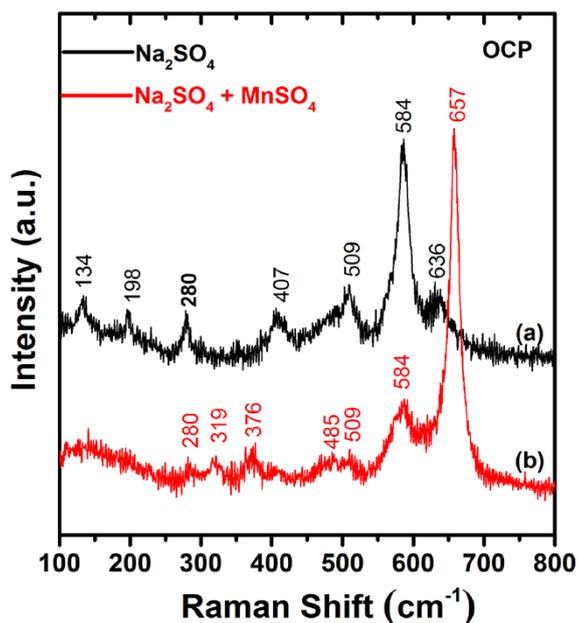


Fig. S6 Raman spectra of the 10,000 cycled electrode material in a three-electrode cell with (a) $1\text{ M Na}_2\text{SO}_4$ aqueous electrolyte, (b) $1\text{ M Na}_2\text{SO}_4$ + several drops of MnSO_4 aqueous electrolyte.

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.