

## Supporting Information

### A High-Energy-Density Aqueous Zinc-Manganese Battery with a La-Ca Co-Doped $\epsilon$ -MnO<sub>2</sub> Cathode

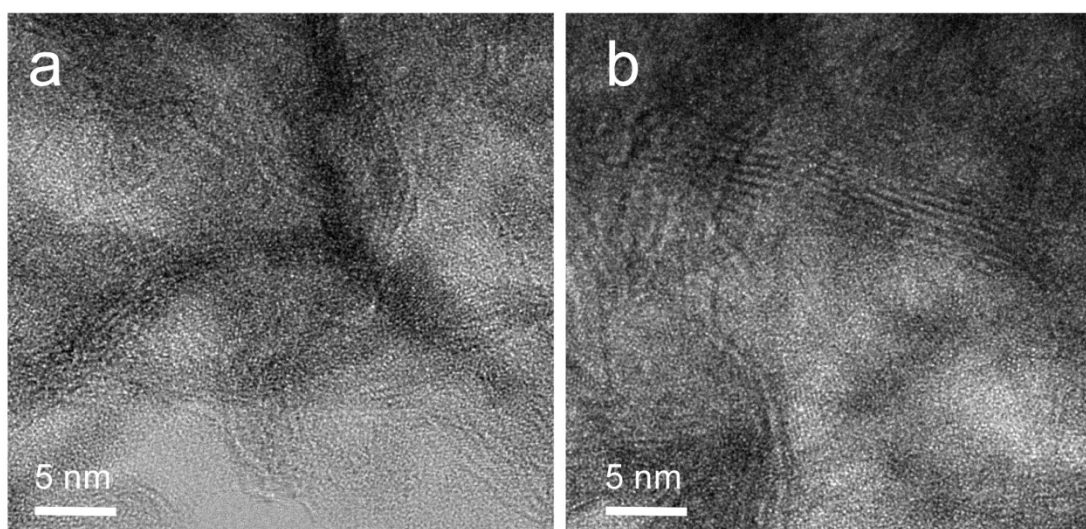
Manshu Zhang, ‡<sup>a</sup> Weixing Wu, ‡<sup>a</sup> Jiawei Luo, <sup>a</sup> Haozhe Zhang, <sup>a</sup> Jie Liu,<sup>c</sup> Xiaoqing Liu,<sup>\*a</sup> Yangyi Yang <sup>\*a</sup> and Xihong Lu <sup>\*a,b</sup>

<sup>a</sup> School of Materials Science and Engineering, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-carbon Chem & Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, PR China.

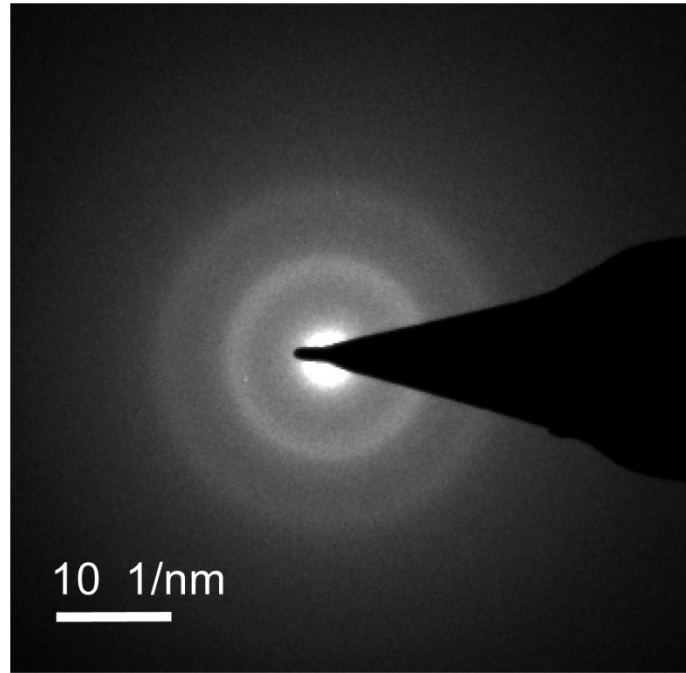
E-mail: [luxh6@mail.sysu.edu.cn](mailto:luxh6@mail.sysu.edu.cn); [cesyyy@mail.sysu.edu.cn](mailto:cesyyy@mail.sysu.edu.cn)., [liuxiaoq5@mail.sysu.edu.cn](mailto:liuxiaoq5@mail.sysu.edu.cn)

<sup>b</sup> School of Applied Physics and Materials, Wuyi University, Jiangmen, Guangdong, 529020, P. R. China.

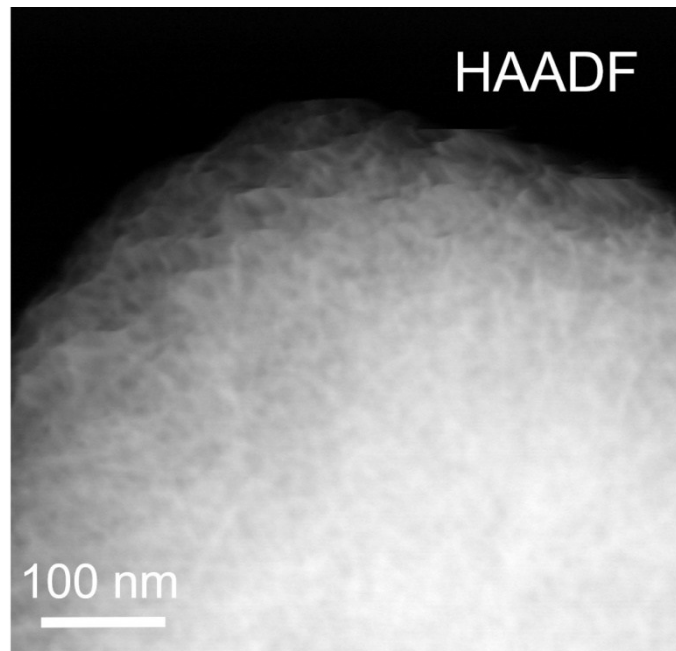
<sup>c</sup> College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, PR China.



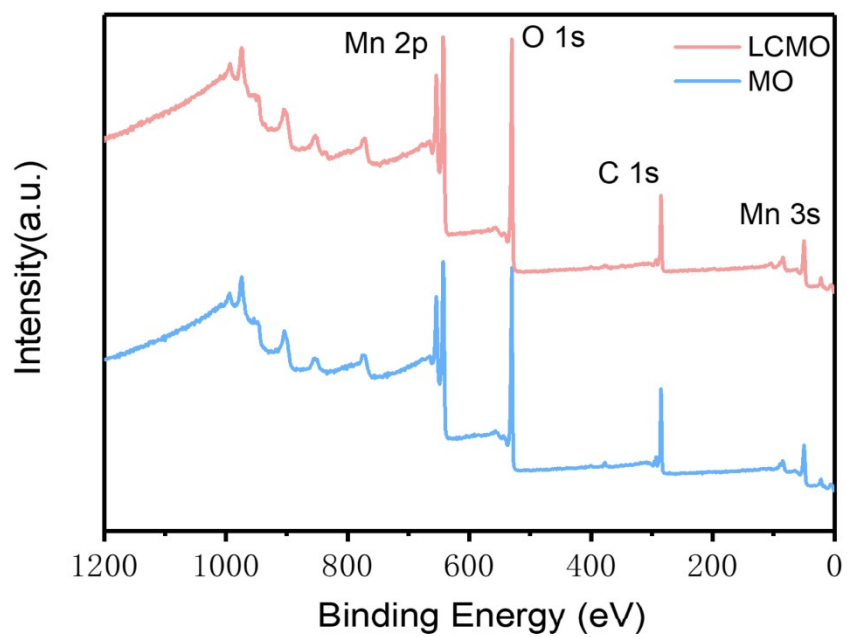
**Fig. S1** HRTEM images of (a) MO and (b) LCMO.



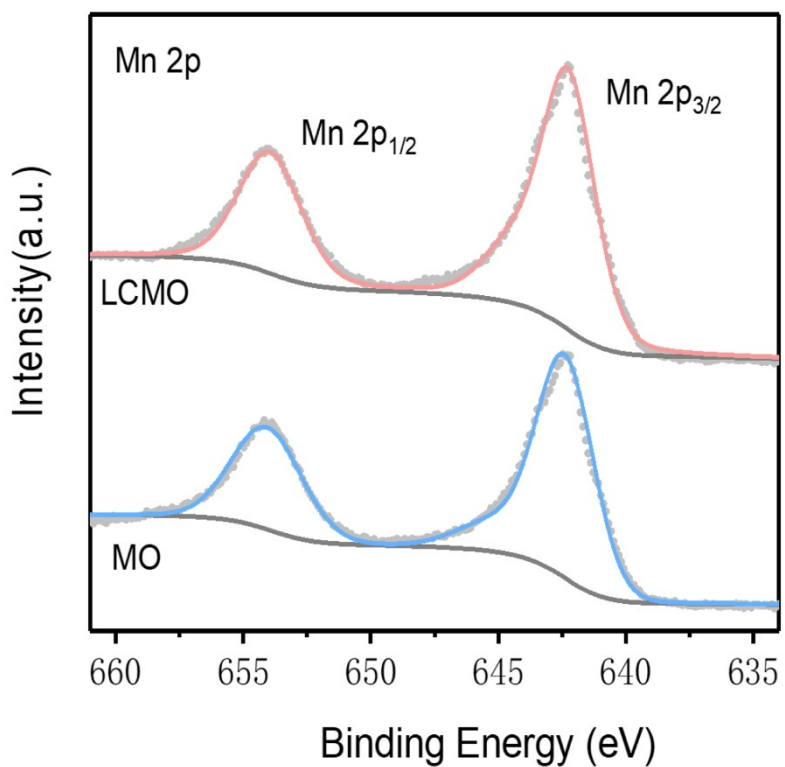
**Fig. S2** SAED pattern of MO sample.



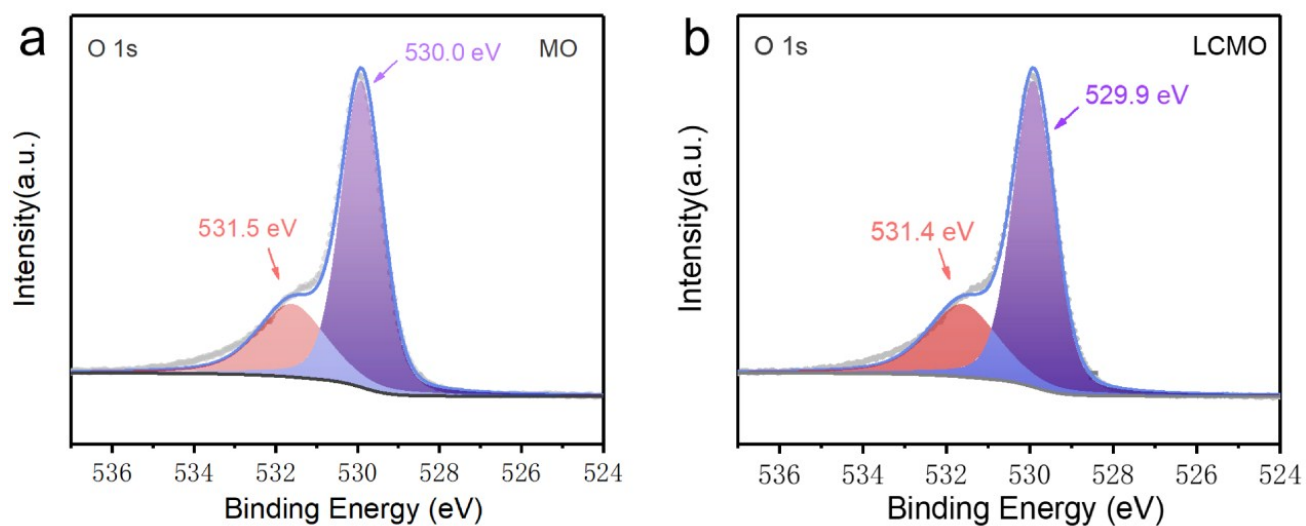
**Fig. S3** High-angle annular dark field (HAADF) image of the LCMO sample.



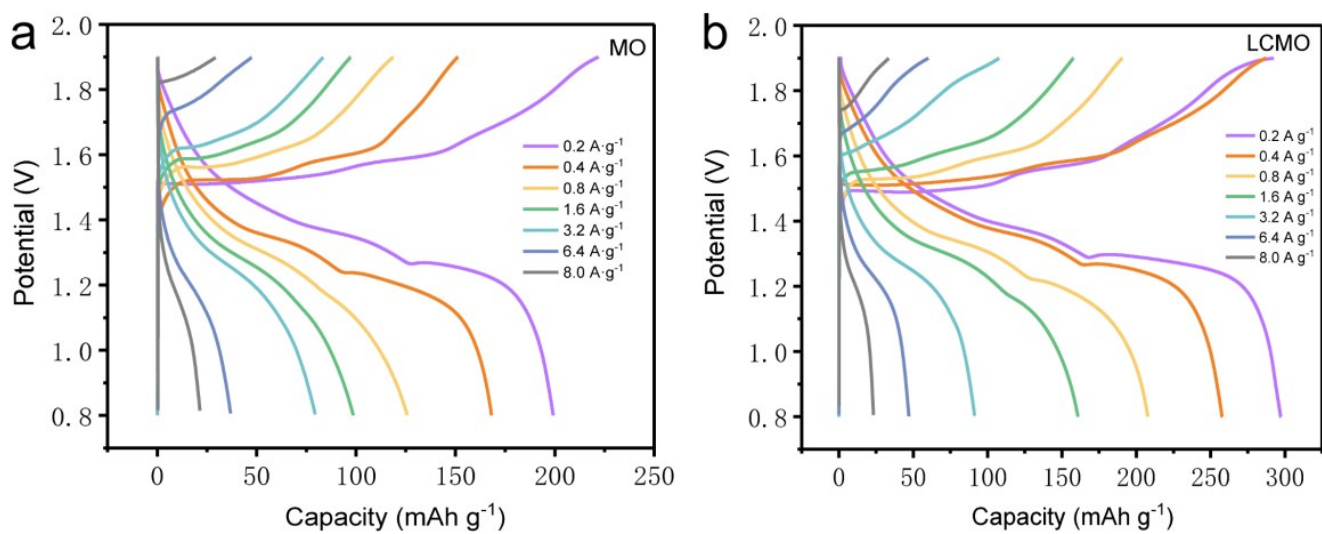
**Fig. S4** XPS survey spectra of MO and LCMO.



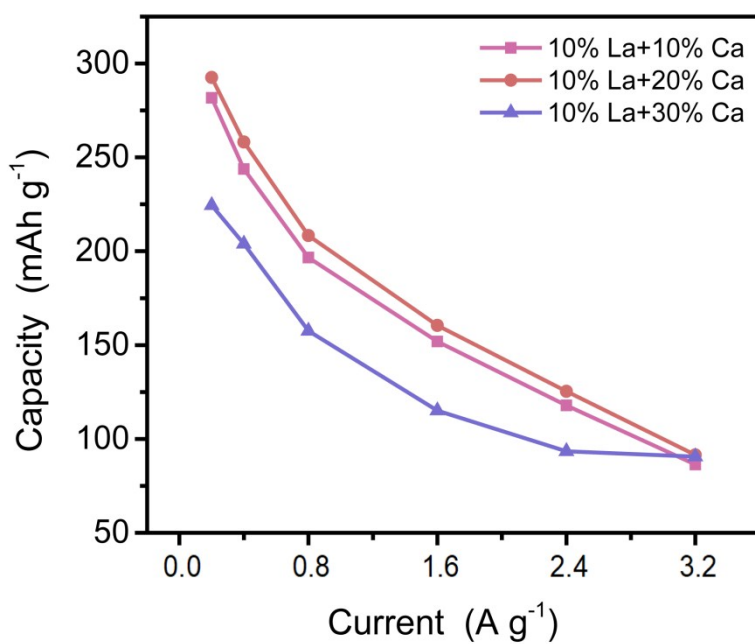
**Fig. S5** XPS Mn 2p spectra of MO and LCMO.



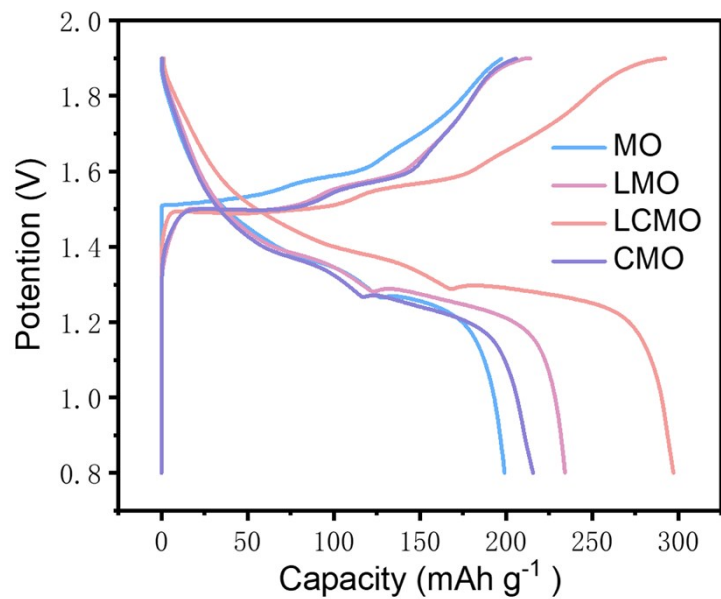
**Fig. S6** XPS O1s spectra of (a) MO and (b) LCMO.



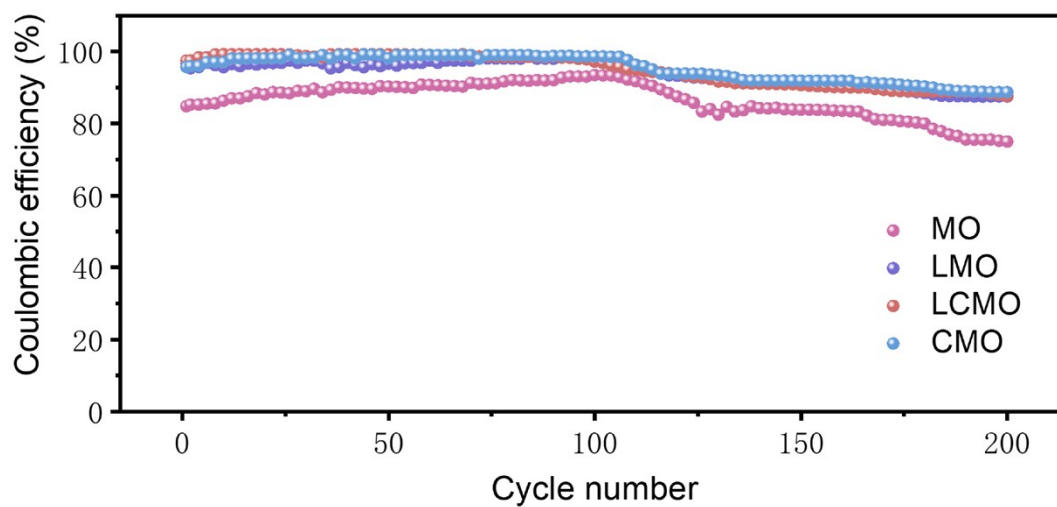
**Fig. S7** GCD curves of (a) MO and (b) LCMO at different current densities.



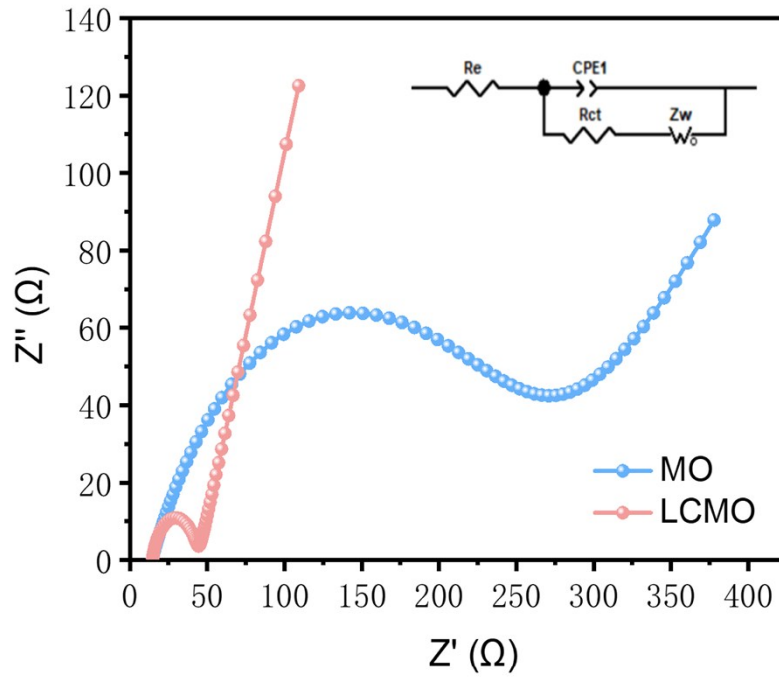
**Fig. S8** Capacities of  $\epsilon$ -MnO<sub>2</sub> cathodes with different La and Ca proportion colloccated at 0.2 A g<sup>-1</sup>. All the samples are synthesized by simply adjusting the addition ratio in the precursor solution. The mole percentages of La and Ca additions are calculated based on the theoretical mole yield of MnO<sub>2</sub>, which means the number of moles of MnO<sub>2</sub> is set to be 100%. For example, 5 mmol MnSO<sub>4</sub>·H<sub>2</sub>O, 1.67 mmol CaCl<sub>2</sub> and 0.83 mmol La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were dissolved into 150 mL H<sub>2</sub>O to obtain precursor solution of the 10% La + 20% Ca sample.



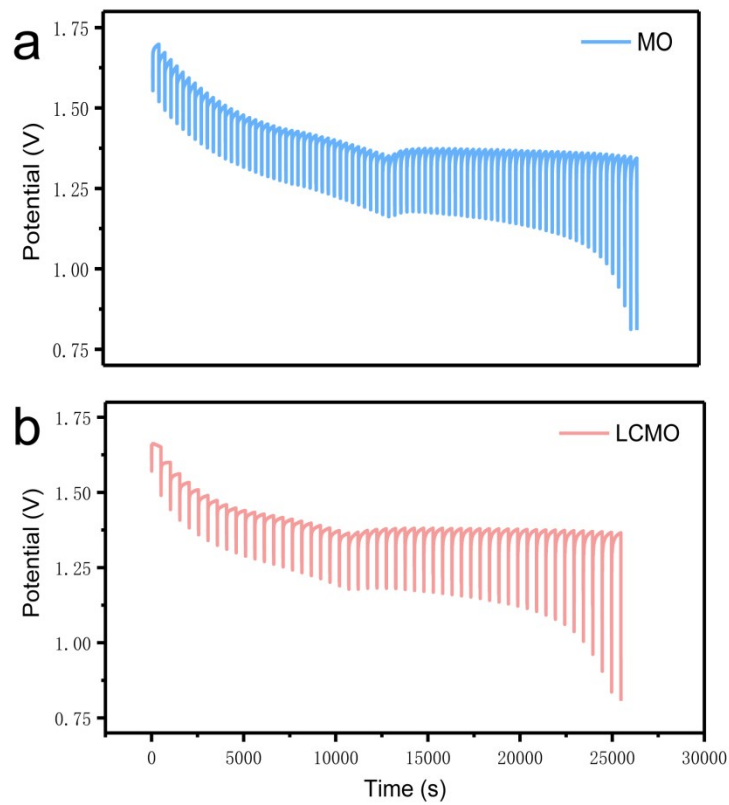
**Fig. S9** GCD curves of MO, CMO, LMO and LCMO at 0.2 A g<sup>-1</sup>.



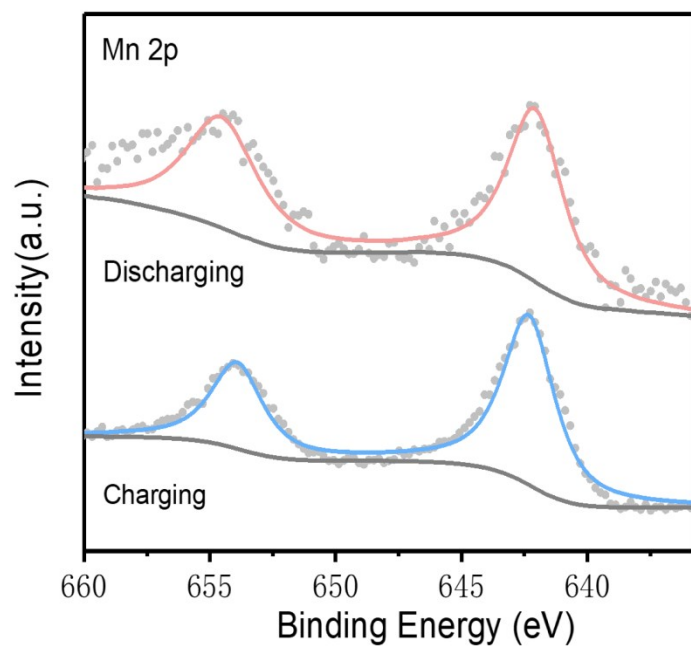
**Fig. S10.** Coulombic efficiency of the MO, LMO, CMO and LCMO electrodes calculated from cycling performance.



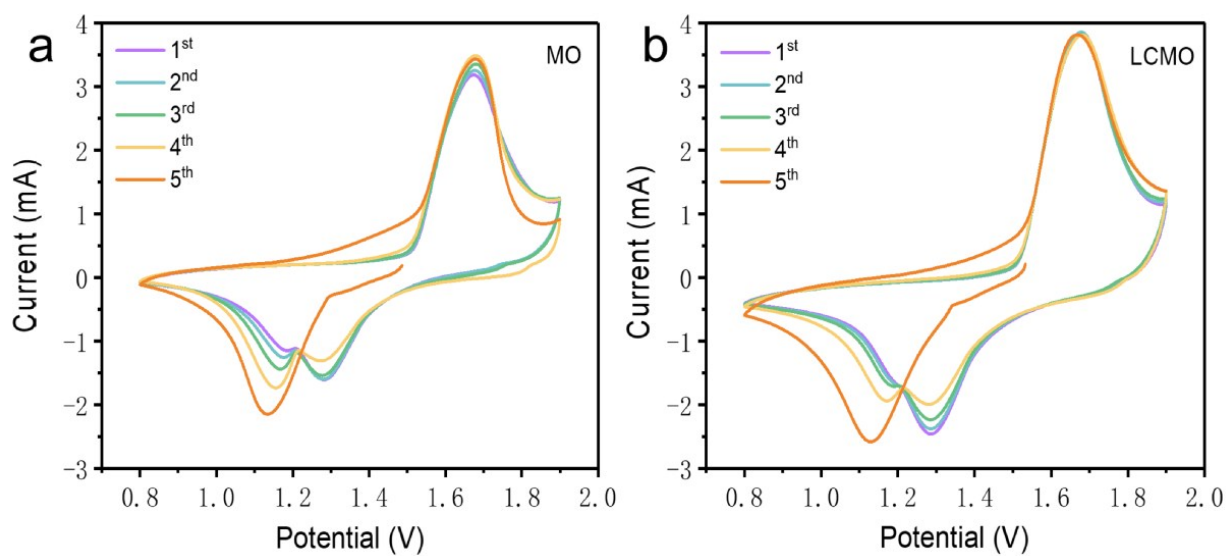
**Fig. S11.** Fitting curves of Nyquist plots of MO and LCMO cathodes.



**Fig. S12** GITT tests of (a) MO and (b) LCMO.



**Fig. S13** XPS Mn 2p spectra of LCMO in charging and discharging state.



**Fig. S14** First five CV curves of the MO and LCMO electrode at the scan rate of  $1 \text{ mV s}^{-1}$ .