

Fig. S1 EDS element maps of a) the RuO<sub>2</sub>-modified LNMO prepared with the NaOH solution, b) the Al<sub>2</sub>O<sub>3</sub>-modified LNMO.

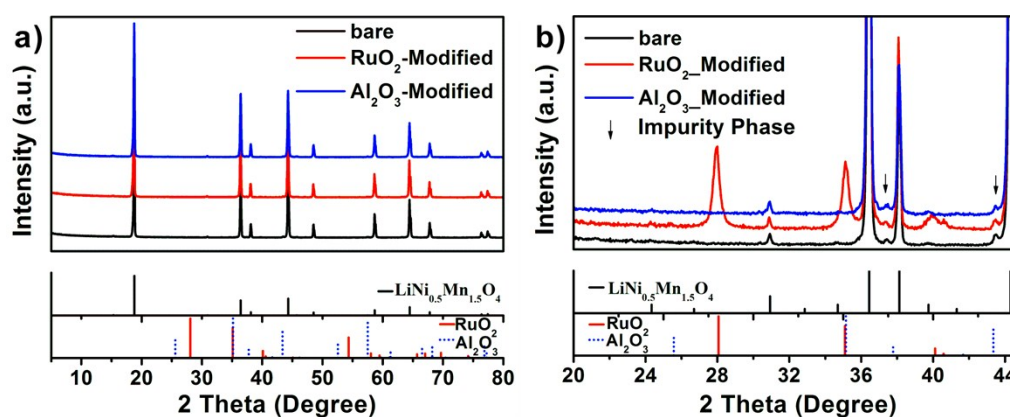


Fig. S2 XRD patterns of a) the bare LNMO, RuO<sub>2</sub> modified and Al<sub>2</sub>O<sub>3</sub> modified LNMOs. b) magnification of region between 20 and 45 °.

The LNMO used here is a mixture of ordered and disordered phase. Disordered LNMO usually comes out after high-temperature calcinations in air with release of oxygen around Mn ion. As a result, some Mn<sup>4+</sup> ions have to be reduced to Mn<sup>3+</sup> to keep the electric neutrality, and a nonstoichiometric disordered phase (Fd32 space group) is formed.<sup>1-3</sup>

Fig. S2b is a magnification of Fig 2a ranging from 20 ° to 45 °. In addition to typical peaks of LNMO, peaks at 28.1 ° and 35.1 ° from the crystallized RuO<sub>2</sub> are present,<sup>4</sup> while peaks at 37.3 ° and 43.4 ° are belonged to Li<sub>x</sub>Ni<sub>y</sub>O impurity phase.<sup>5</sup> No Al<sub>2</sub>O<sub>3</sub> diffraction peak is detected indicating that the Al<sub>2</sub>O<sub>3</sub> deposited is amorphous or very poorly crystallized.

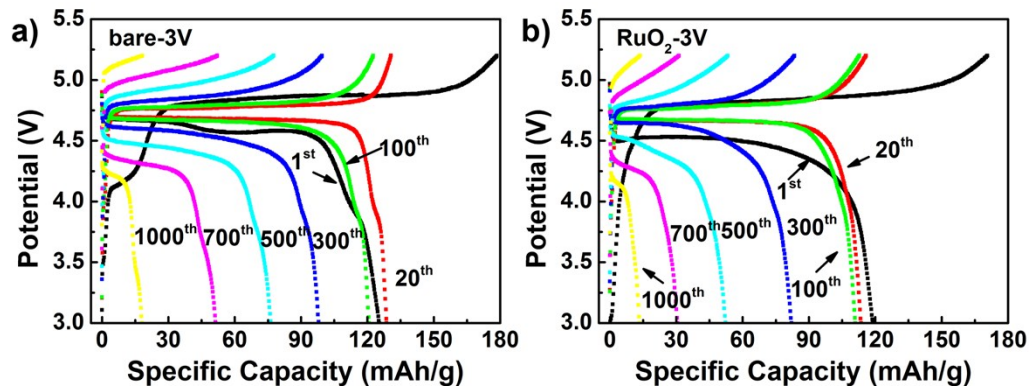


Fig. S3 Charge and discharge curves of a) the bare-3V and b) the  $\text{RuO}_2$ -3V during cycle performance test.

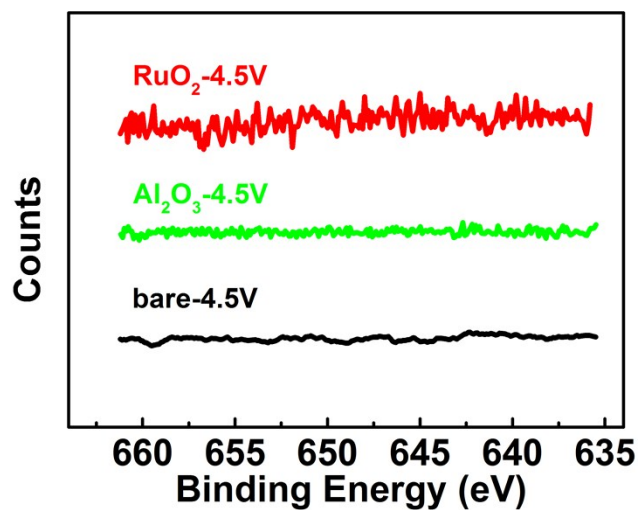


Fig. S4 Mn 2p X-ray photoelectron spectra of the lithium metal anodes used in bare-4.5V,  $\text{RuO}_2$ -4.5V and  $\text{Al}_2\text{O}_3$ -4.5V coin cells.

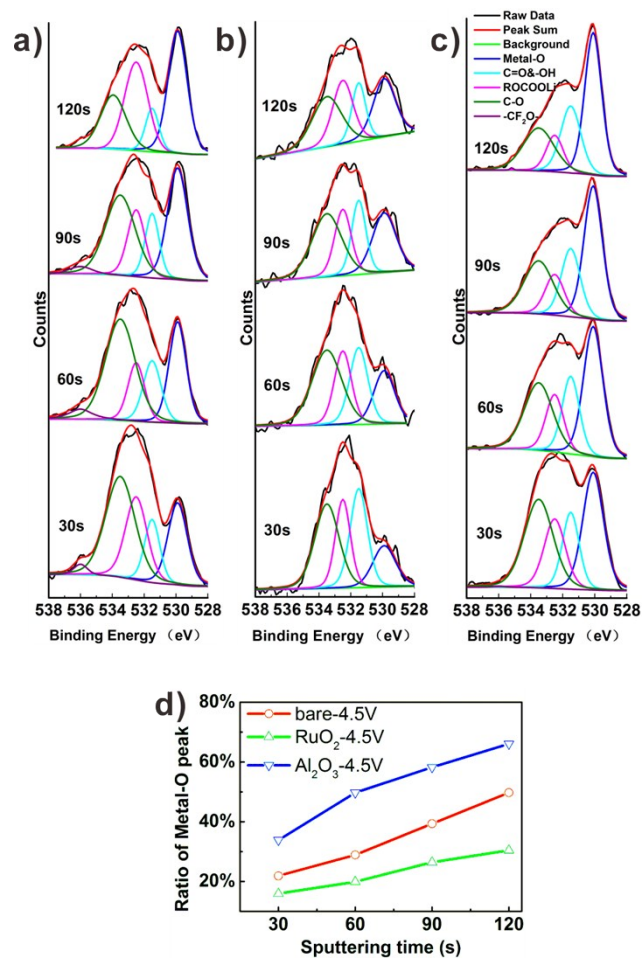


Fig. S5 O1s XPS of a) bare-4.5V, b) RuO<sub>2</sub>-4.5V, c) Al<sub>2</sub>O<sub>3</sub>-4.5V after 500 cycles and Ar ion sputtering for 30, 60, 90 and 120 s. d) Variation of the ratio between the metal-oxygen (M-O) O1s peak around 530 eV and the sum of other O1s peaks with the sputtering time.

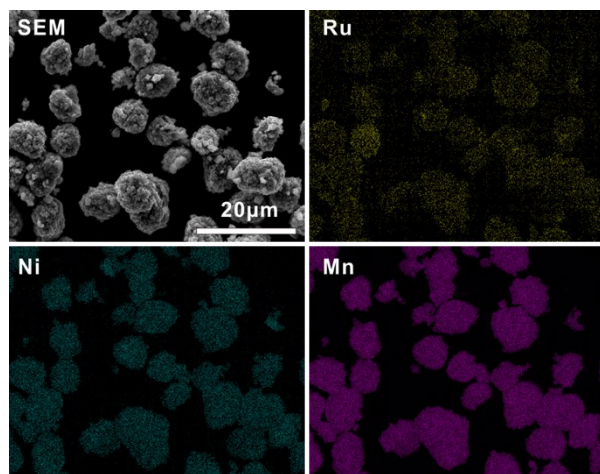


Fig S6. EDS element maps of the LiOH-RuO<sub>2</sub>-LNMO

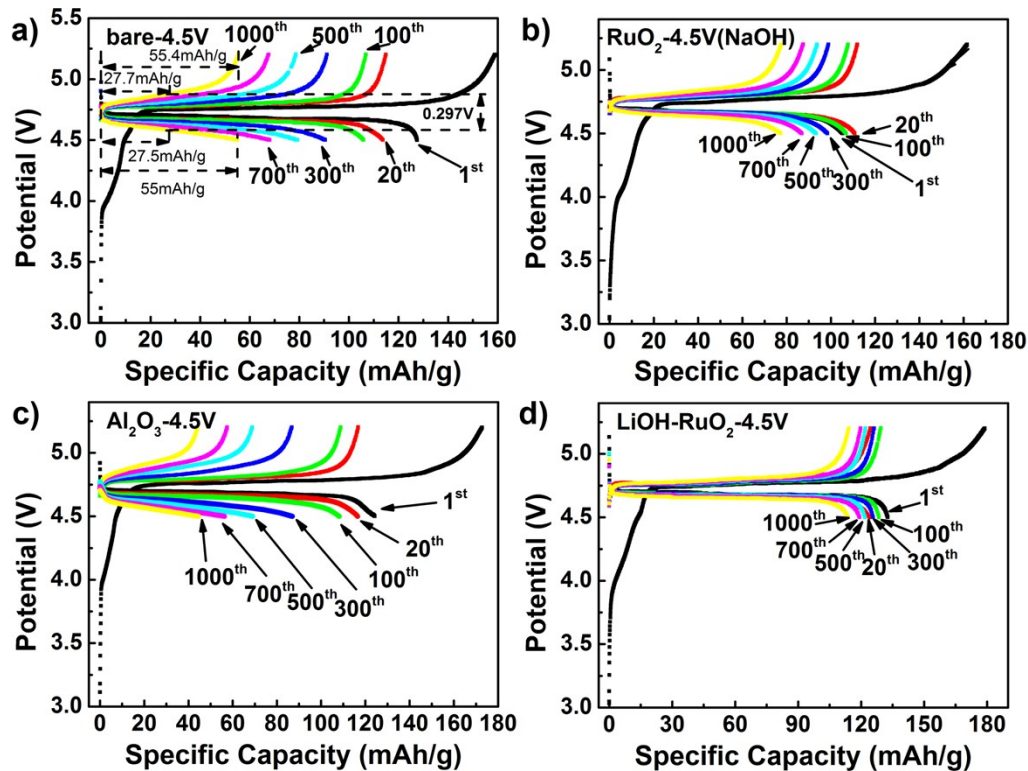


Fig. S7 Charge and discharge curves of a) bare-4.5V, b) RuO<sub>2</sub>-4.5V (NaOH), c) Al<sub>2</sub>O<sub>3</sub>-4.5V and d) LiOH-RuO<sub>2</sub>-LNMO electrode discharged to 4.5 V (LiOH-RuO<sub>2</sub>-4.5V). An example for measuring differences between charge and discharge medium potentials is shown in a).

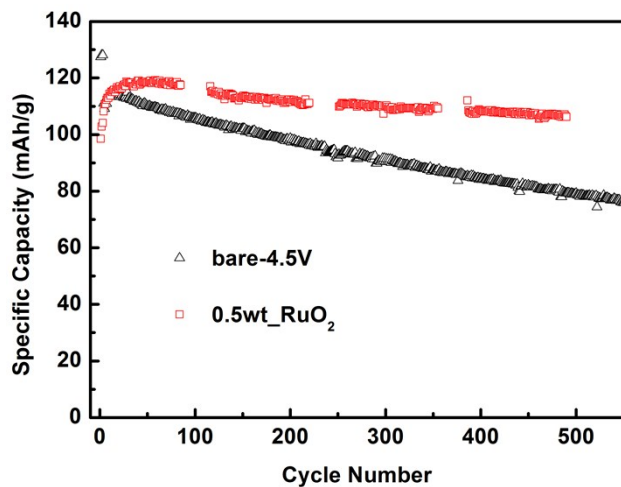


Fig. S8 Comparison of cycle performance between the bare-4.5V and LNMO modified by RuO<sub>2</sub> with content as low as 0.5 wt% (denoted as 0.5wt\_RuO<sub>2</sub>). The 0.5wt\_RuO<sub>2</sub> was synthesized by using LiOH solution and also heat treated at 400°C for 19 h. The 0.5wt\_RuO<sub>2</sub> electrode was cycled at 1C rate for first 10 cycles between 4.1-5.2V, subsequently cycled between 4.5-5.2 V. It is worth noting that gaps between

cycle performance tests are rate capability tests, and we get rid of the rate-capability data to clearly compare the cycle performance.

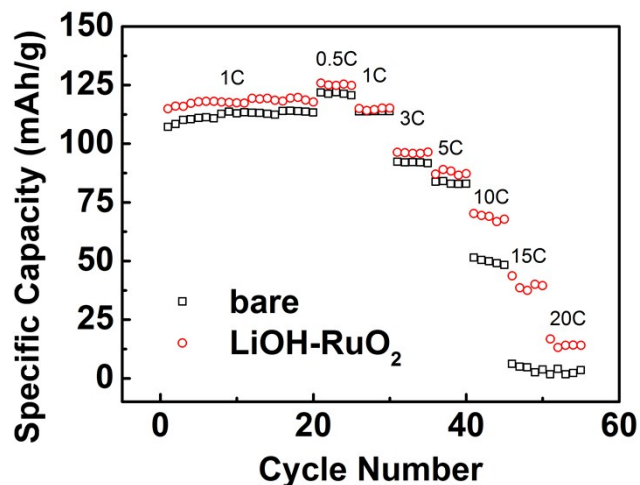


Fig. S9 Comparison of rate capability between the bare LNMO and LiOH-RuO<sub>2</sub>-LNMO electrodes. Both electrodes were cycled between 3 and 5.2 V at 1C rate for 20 cycles and then charge and discharge at various C rates for 5 cycles. The wide potential range of 3~5.2 V but not 4.5~5.2 V is used for rate tests because the decrease of the discharge potential plateau below 4.5 V at high rates complicates the comparison. The capacity difference is more obviously at high rates, about 40mAh/g at 15 C for the LiOH-RuO<sub>2</sub>-LNMO, while no capacity for the bare LNMO.

1. M. Kunduraci and G. G. Amatucci, *Journal of the Electrochemical Society*, 2006, **153**, A1345-A1352.
2. Q. M. Zhong, A. Bonakdarpour, M. J. Zhang, Y. Gao and J. R. Dahn, *Journal of the Electrochemical Society*, 1997, **144**, 205-213.
3. K. M. Shaju and P. G. Bruce, *Dalton Transactions*, 2008, 5471-5475.
4. Y. G. Guo, Y. S. Hu, W. Sigle and J. Maier, *Advanced Materials*, 2007, **19**, 2087-+.
5. J. Song, D. W. Shin, Y. H. Lu, C. D. Amos, A. Manthiram and J. B. Goodenough, *Chemistry of Materials*, 2012, **24**, 3101-3109.