Supporting Information

An aqueous rechargeable lithium ion battery with long cycle life and overcharge self-protection

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Experimental Section

Materials Synthesis

Aqueous electrolytes were prepared according to molarity (mol-salt in L-solvent) with Zn^{2+} addition, which are coded by abbreviated concentrations (1-1 (1 M Li_2SO_4 and 1 M Na_2SO_4), respectively. Li_2SO_4, Na_2SO_4, $ZnSO_4$, NaH_2PO_4, TiO_2, phosphoric acid (85 wt.%), glucose are analytically pure purchased from Sigma-Aldrich. Carbon coated $NaTi_2(PO_4)_3$ was prepared by a two-step reactions. First, $NaTi_2(PO_4)_3$ was synthesized by a hydrothermal reaction at 150 °C for 5 h using precursors NaH_2PO_4 (5 g), phosphoric acid (20 g) and TiO_2 (20 g) sealed in 100 mL hydrothermal reactor. Then, $NaTi_2(PO_4)_3$ and glucose (10 wt.%) were mixed by grinding using water media. Next, the suspension was spray-drying. The white powder was annealed at 750 °C for 2 h in high purity N_2.

The cathode material $LiMn_2O_4$ was prepared by solid-state reaction. Manganese dioxide and Li_2CO_3 were mixed in stoichiometric ratio. Appropriate amounts of starting materials were grounded. The resulting powder was heated at 900°C for 12 h and then at 650°C for 24 h in air. Then cool to room temperature. The $LiMn_2O_4$ powerder was obtained.

Materials Characterizations

X-ray diffraction patterns of products were carried out on a Philips X'pert X-ray diffractometer with Cu Ka radiation (λ = 1.54182 Å) at a scan rate of 0.008842 o s^{-1}. The microstructure of products was examined on a field-emitting scanning electron microscope (FESEM, JEOL-JSM-6700F). TEM, HR-TEM and EDS mapping were performed on a JEOL ARM200CF microscope at 200 kV. TG was conducted from room temperature to 800 °C at a ramping rate of 5 °C min^{-1} under an air flow. All the electrode samples were obtained from disassembled full cell after electrochemical cycling. The electrode samples were washed by water three times and then dried under vacuum for one day before TEM, XRD, and EDS measurement. *Electrochemical measurements*

The working cathode electrodes were prepared by mixing the active material, super P and polyvinylidene fluoride binder in a weight ratio of 93:4:3 to form a viscous slurry easy to be smeared onto Ti mesh (100 mesh). The anode electrodes were

prepared by mixing anode active material, super P and PVDF in a weight ratio of 92:4:4 and then pasted onto Ti mesh current collector. The as-prepared electrodes were dried in vacuum oven at 110 °C and then pressed at a pressure of 2 MPa. The active loading of $LiMn_2O_4$ cathode was about 20 mg cm^{-2} and the active loading of carbon coated $NaTi_2(PO_4)_3$ anode was about 18 mg cm^{-2}. The cycled galvanostatically on a Land cycler (Wuhan Kingnuo Electronic Co., China) at room-temperature. And all batteries as-assembled were treated with 10 hours standing before tested. The cyclic voltammetric and linear sweep voltammetry results of cathode and anode electrodes were measured using three-electrode system with a cathode or NTP working electrode, Pt counter electrode and Ag/AgCl reference electrode at a scan rate of 0.5 mV s^{-1} on CHI 600E electrochemical work station. The gas evolution during the charging process of full cell was quantitatively analyzed with differential electrochemical mass spectrometry (DEMS) and home-made gastight Swagelok cells, in which NTP anode, separator, LMO cathode, a Ti ring spacer (1.5 mm in height) and 100 μL of aqueous electrolytes were sequentially added. To ensure that only the gas generated from the electrochemical reaction be detected, the cells were purged with Ar (0.5 mL min^{-1}) for 30 mins, so that either dissolved O_2 in electrolytes or adsorbed air in separator, was completely removed. Because the evaporated liquids condenses in the cold trap and blocks the gas channel. Therefore, the cells in DEMS tests are charged or discharged at 1 C rate. Electrochemical impedance spectroscopy (EIS) was obtained from PGSTAT-30 electrochemical station (Metrohm, Netherlands) with a frequency range from 10^5 to 0.01 Hz at the potential amplitude of 5 mV.

Energy and power calculations:

The specific energy of a full cell (E) is calculated as the product of the cell voltage (V_{cell}) and cell specific capacity (C_{cell})

$$E = V_{cell} \times C_{cell}$$

The C_{cell} is typically calculated from the specific capacities of cathode and anode. In this work, the full cell capacity is calculated based on the mass of cathode. So, the C_{cell} should be:

C_{cell} = full cell capacity/(total mass of cathode and anode)

For example:

the energy density of as-prepared LMO/NTP full cell at 0.1 C:

$E = 1.76 \text{ V} \times 105 \text{ Ah}/(1+0.9) \text{ kg} = 100 \text{ Wh kg}^{-1}$

at 100 C rate:

$E = 1.55 \text{ V} \times 55 \text{ Ah}/(1+0.9) \text{ kg} = 45 \text{ Wh kg}^{-1}$

The specific power energy of a full cell (P) is calculated as the product of the cell voltage (V_{cell}) and cell specific discharge current (I_{cell})
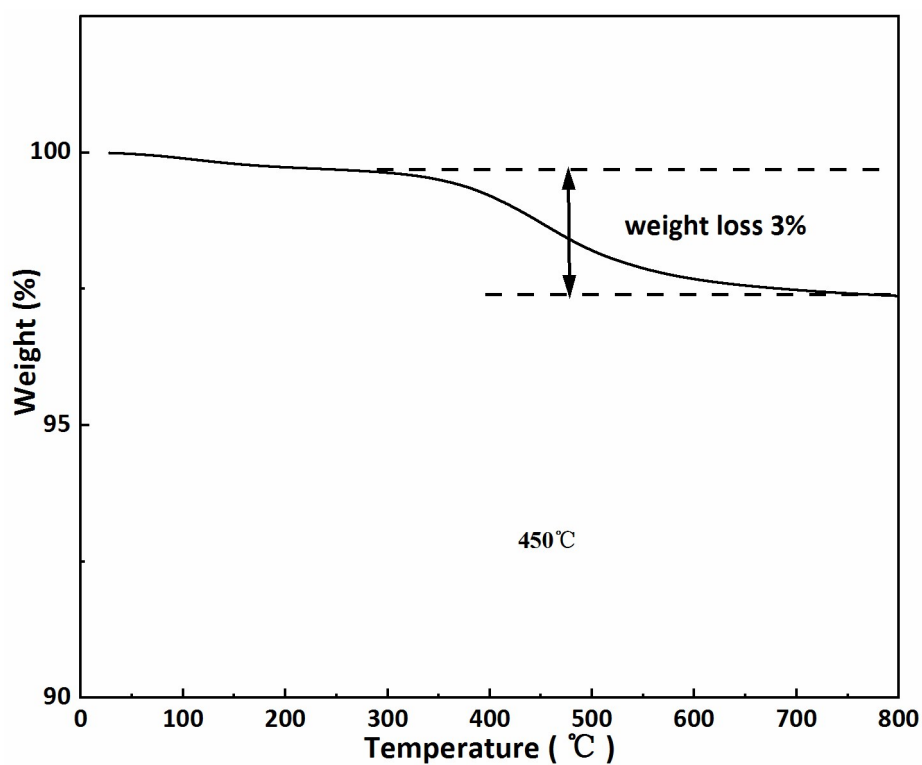
$P = V_{cell} \times I_{cell}$

For example:

the power density of as-prepared LMO/NTP full cell at 0.1 C rate:

$P = 1.76 \text{ V} \times 110*0.1 \text{ A}/(1+0.9) = 13 \text{ W kg}^{-1}$

at 100 C rate:

$P = 1.55 \text{ V} \times 110*100 \text{A}/(1+0.9) = 8973 \text{ W kg}^{-1}$

Figure S1. Thermogravimetric analysis of as-prepared NTP sample with a heating rate of 5 °C min^{-1} between 30 °C and 800 °C.
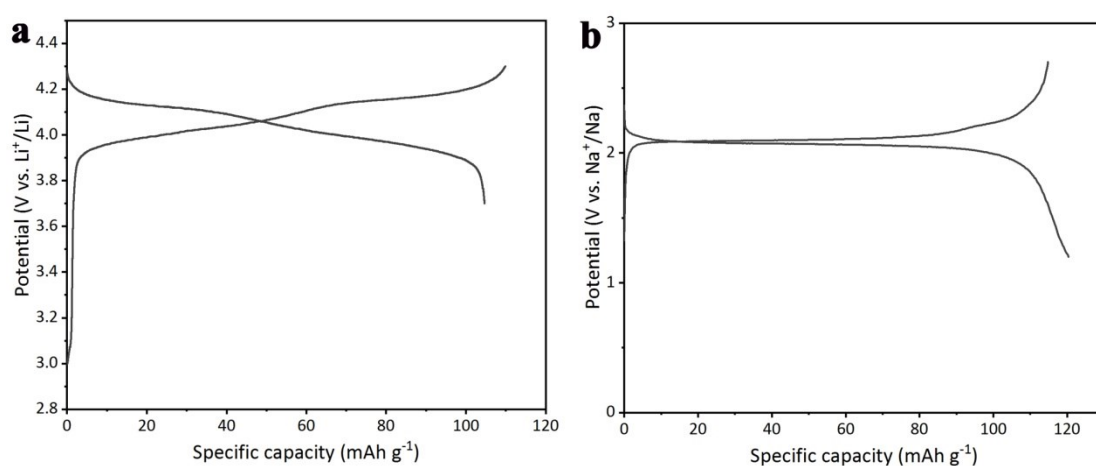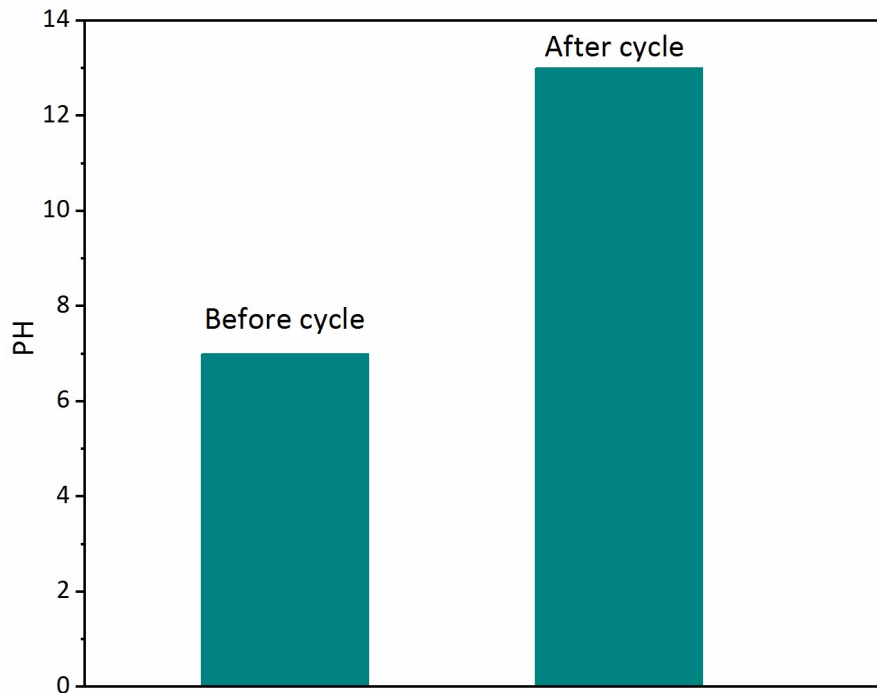

Figure S2. (a) Charge and discharge curves of LMO cathode at 0.1 C in organic lithium ion battery electrolyte. (b) Charge/discharge profiles of NTP anode at 0.1 C in organic sodium ion battery electrolyte.
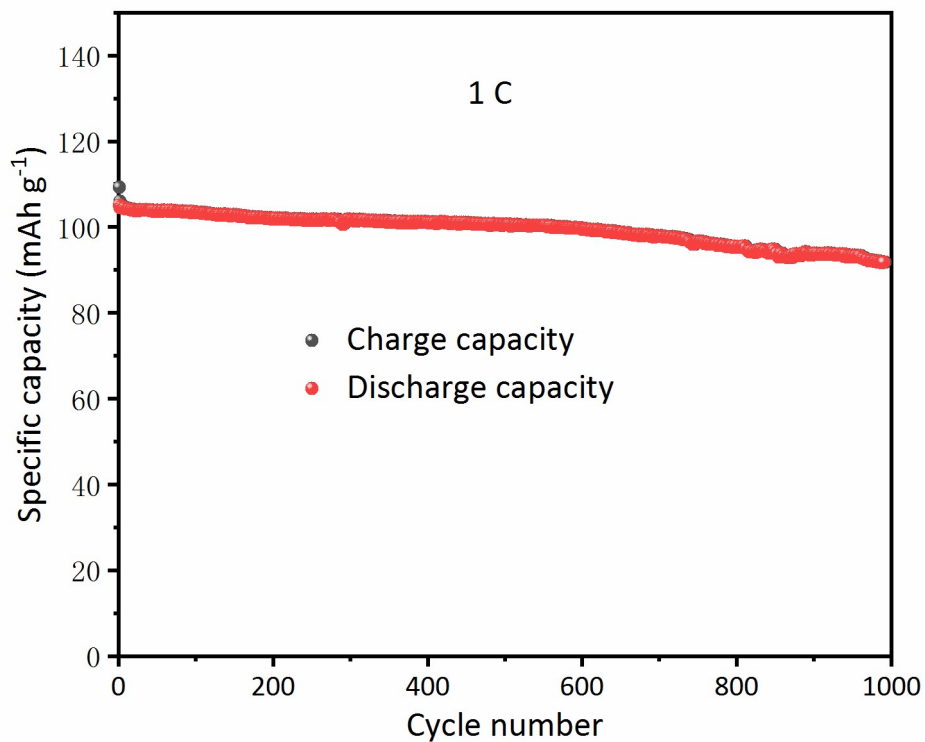
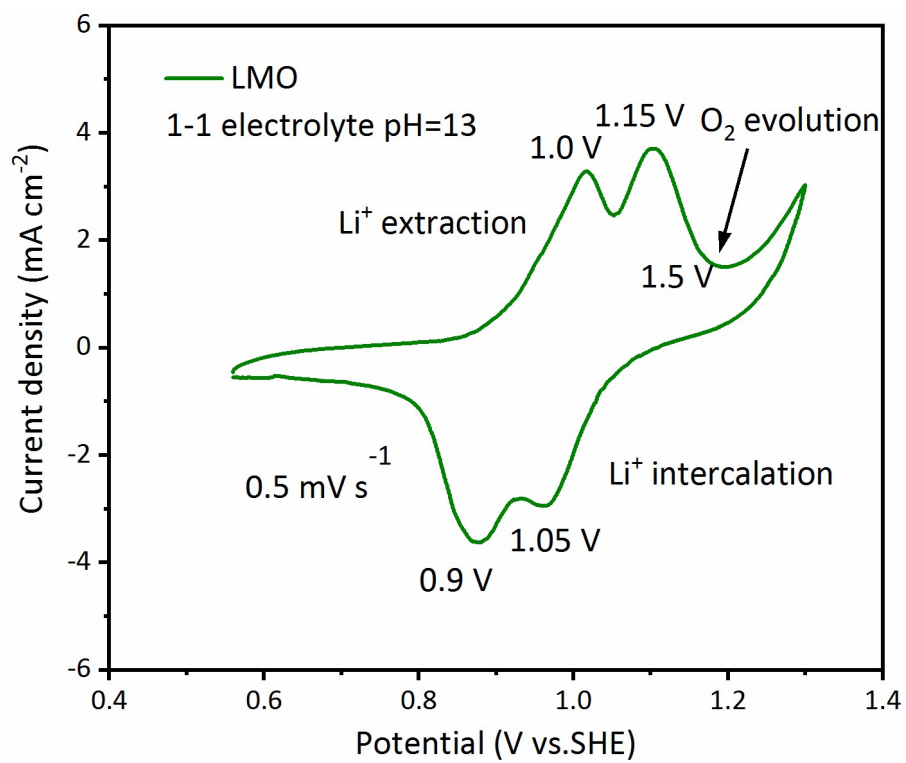**Figure S3.** Cycle stability of LMO cathode in 1-1 electrolyte at 1 C among 1.0 V and 1.3 V.
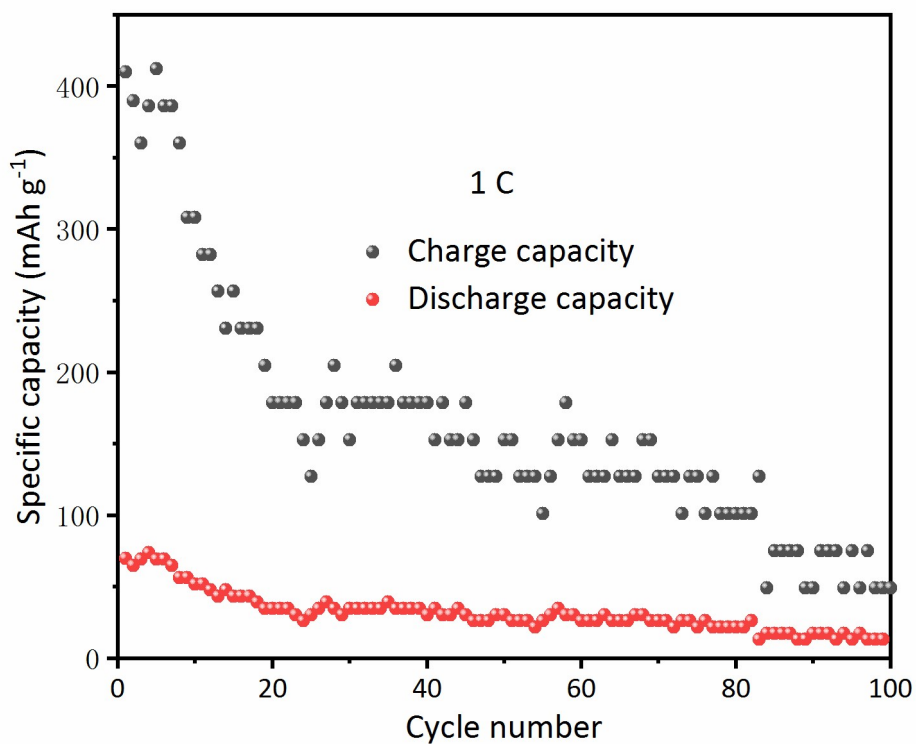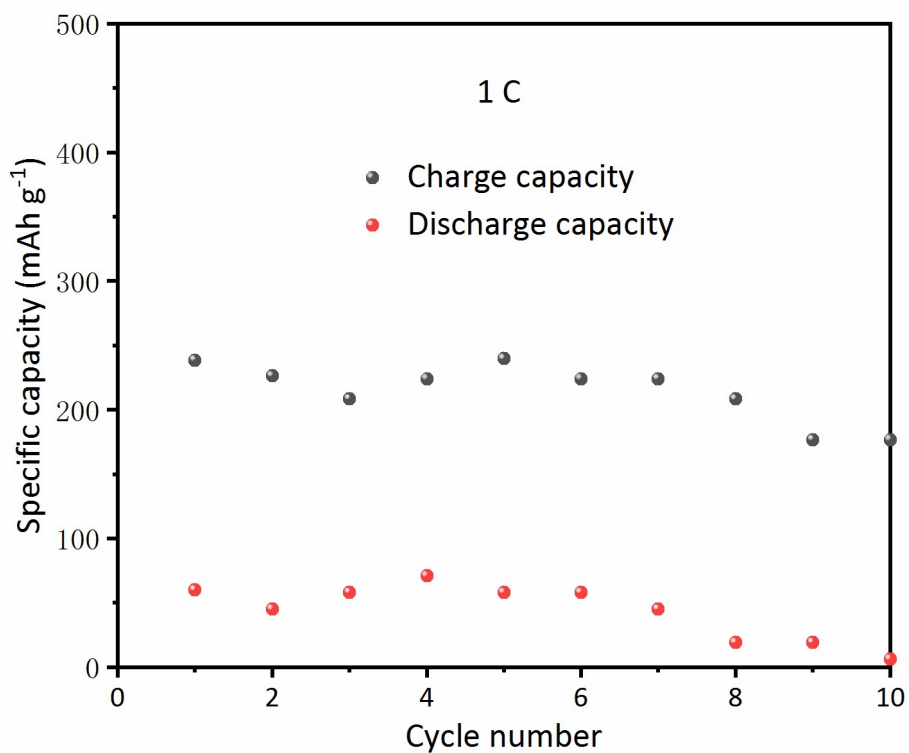

Figure S4. Cycle stability of NTP anode in 1-1 electrolyte at 1 C among -1.0 V and -0.4 V.
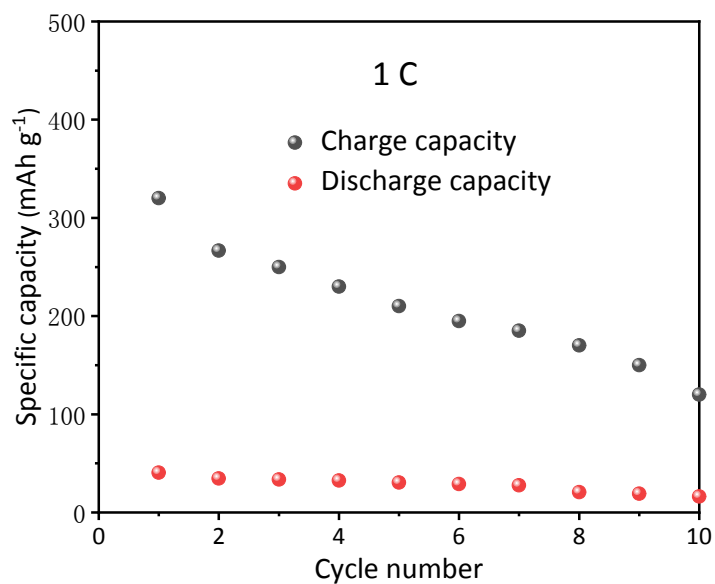
Figure S5. PH of electrolytes before and after cycle.

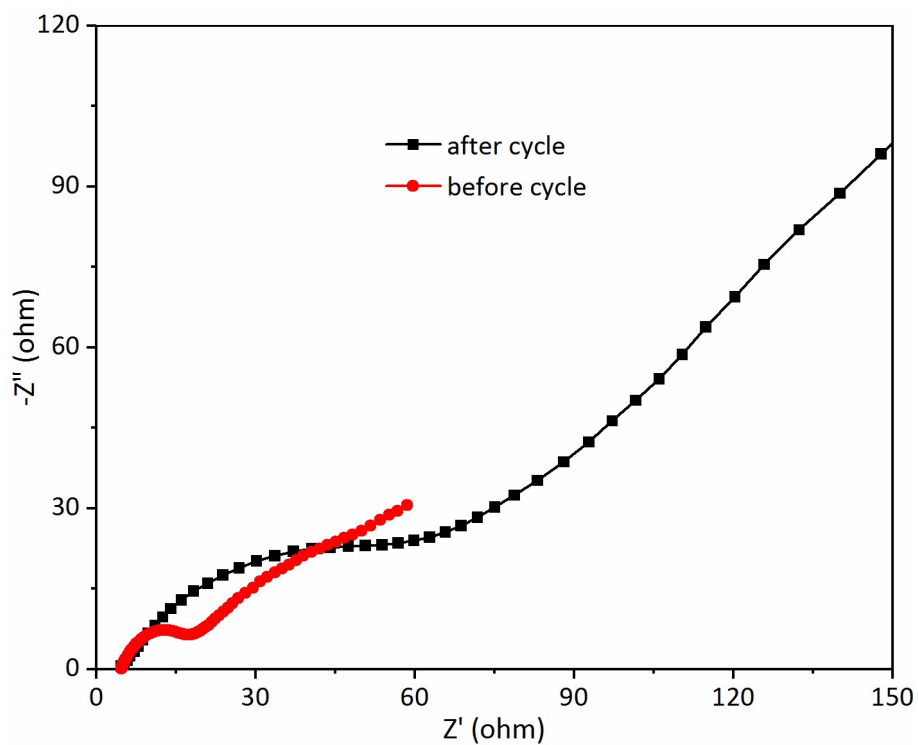**Figure S6.** CV results of LMO cathode in 1-1 electrolyte at pH of 13.

Figure S7. Cycle stability of LMO/NTP full cell in 1-1 electrolyte at 1 C among 1.0 V and 2.0 V.
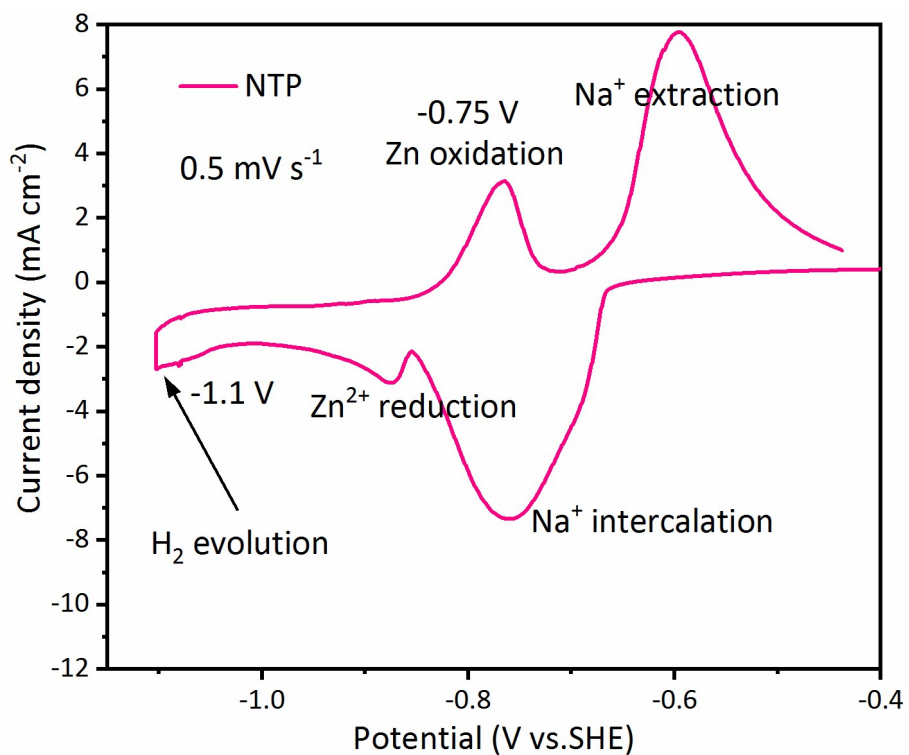

Figure S8. Cycle stability of LMO/NTP full cell in 1 M Li_2SO_4 electrolyte at 1 C among 1.0 V and 2.0 V.
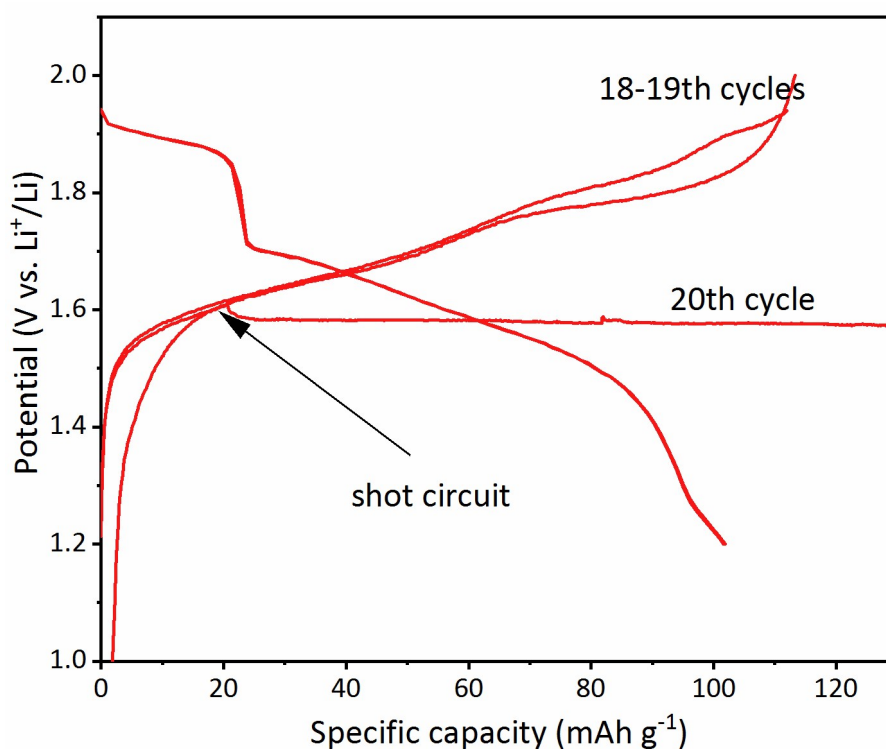
Figure S9. EIS results of LMO/NTP full cell in 1-1 electrolyte before and after cycle.
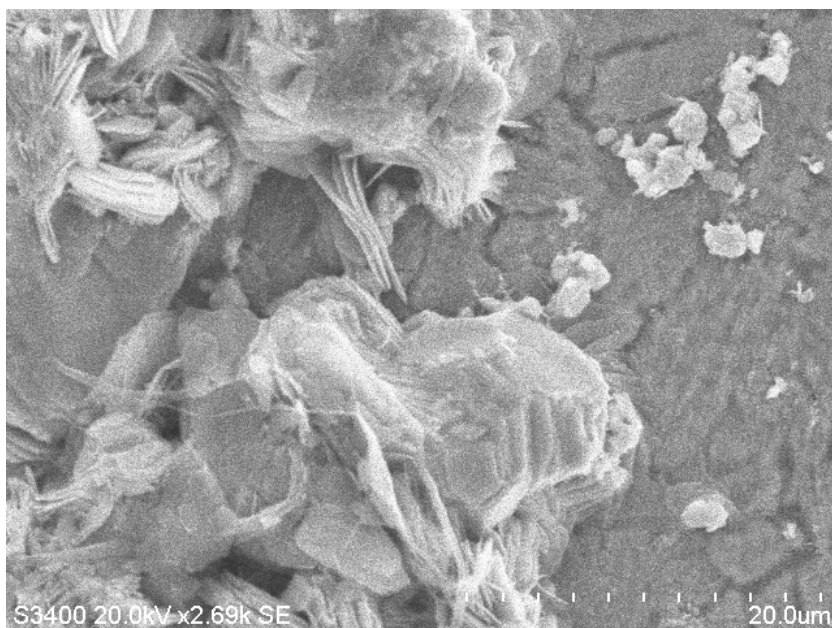

Figure S10. CV results of NTP anode in 1-1 electrolyte with 0.1 M Zn^{2+} addition.

| Element	Concentration ($\mu g \, L^{-1}$)
Zn	0.075
Ti	1.95

Table S1. The ICP-AES results of full discharged NTP anode. The fully discharged NTP anode in 1-1 electrolyte with 0.1 M Zn^{2+} addition was washed by three times with distilled water and treated by ultrasound in 10 mL water to exfoliation of active materials from current collector. Then, 10 mL 5 M HNO_3 solution was added under magnetic stirring for one day to dissolve NTP and Zn. The obtained solution was transferred to a 50-mL volumetric flask, dilute with water to volume. At last, the above solution was diluted 100 times to be tested.
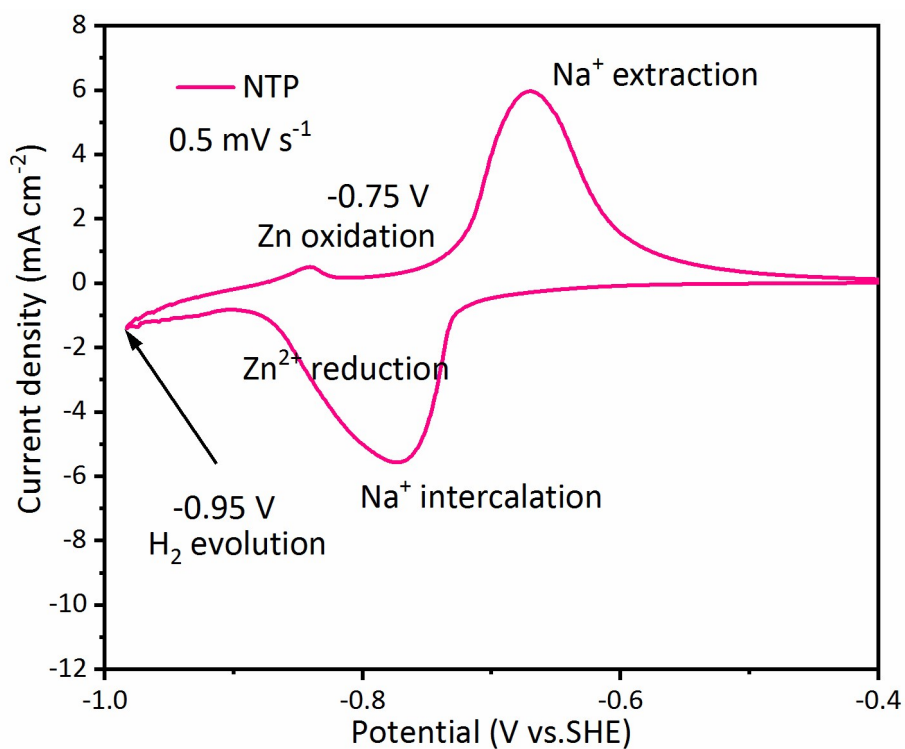

Figure S11. Charge/discharge curvels of LMO/NTP full cell in 1-1 electrolyte with 0.2 M Zn^{2+} addition.

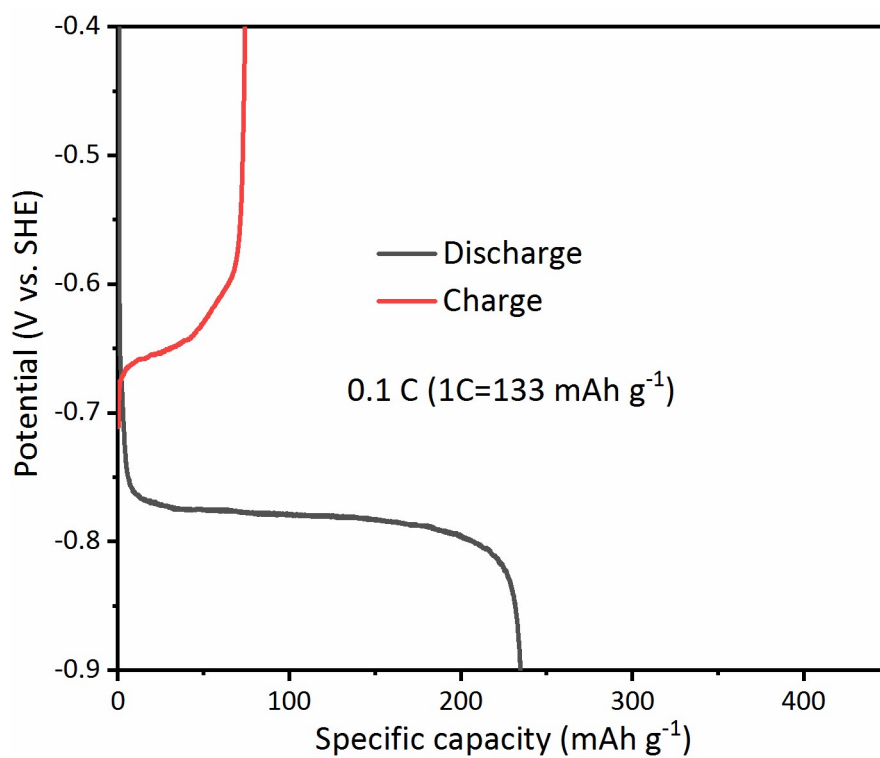**Figure S12.** SEM image of NTP anode after 20 cycles in 1-1 electrolyte with 0.2 M Zn^{2+} addition.
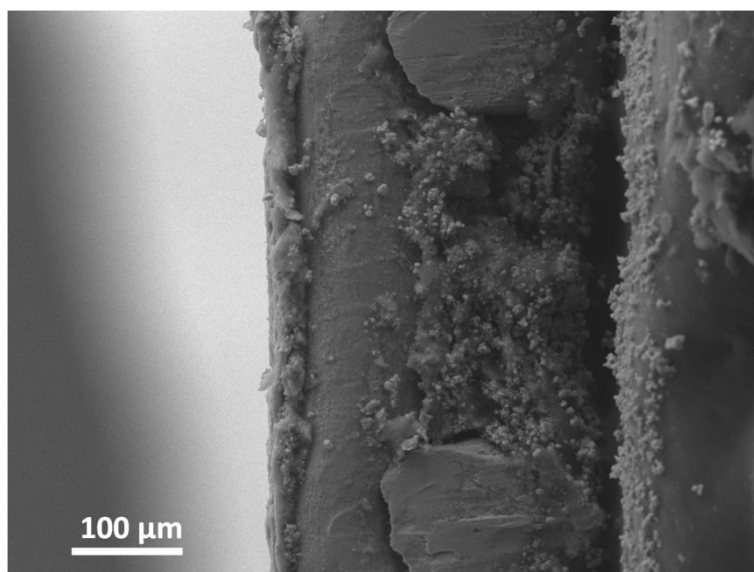
Figure S13. SEM image of NTP anode from side view after 100 cycles at 1 C in 1-1 electrolyte with 0.1 M Zn^{2+} addition.

Figure S14. CV results of NTP anode in 1-1 electrolyte with 0.05 M Zn^{2+} addition.

Figure S15. Galvanostatic discharge-charge curvels of NTP anode using three electrode system at 0.1 C in 1-1 electrolyte with 0.05 M Zn^{2+} addition.

Cathode/Anode	Max. gravimetric energy density at power density Wh kg^{-1} (W kg^{-1})	Gravimetric Energy density at max. power density Wh kg^{-1} (W kg^{-1})[a]	Cycling stability[b]	Ref.
$LiMn_2O_4$ /VO_2	75 (7.5)	75 (7.5)	5	S1
$LiMn_2O_4$/$LiTi_2(PO_4)_3$	60 (60)	40 (800)	80%/200	S2
$LiMn_2O_4$ /MoO_3	45 (350)	38 (6000)	90%/150	S3
$LiFePO_4$/$LiTi_2(PO_4)_3$	50 (50)	40 (440)	90%/1000	S4
$LiMn_2O_4$ /Mo_6S_8	80 (16)	80 (16)	68%/1000	S5
$LiCoO_2$ /Mo_6S_8	120 (50)	60 (255)	87%/1000	S6
$LiMn_2O_4$ /TiO_2	100 (78)	100 (78)	80%/100	S7
$LiNi_{0.5}Mn_{1.5}O_4$/Mo_6S_8	126 (63)	58 (529)	72%/400	S8
$LiMn_2O_4$/$NaTi_2(PO_4)_3$	100	45 (8973)	90%/10,000	**This work**

Table S2. Comparison of the electrochemical performances of reported ARLIBs. The energy and power densities have been normalized to the total mass from both anode and cathode active materials. [a] The results are based on the reported data or calculated based on the given data (some works didn't give out the rate capability). [b] The cycling stability is calculated with *m* cycles at the *n*% of capacity retention for the battery.
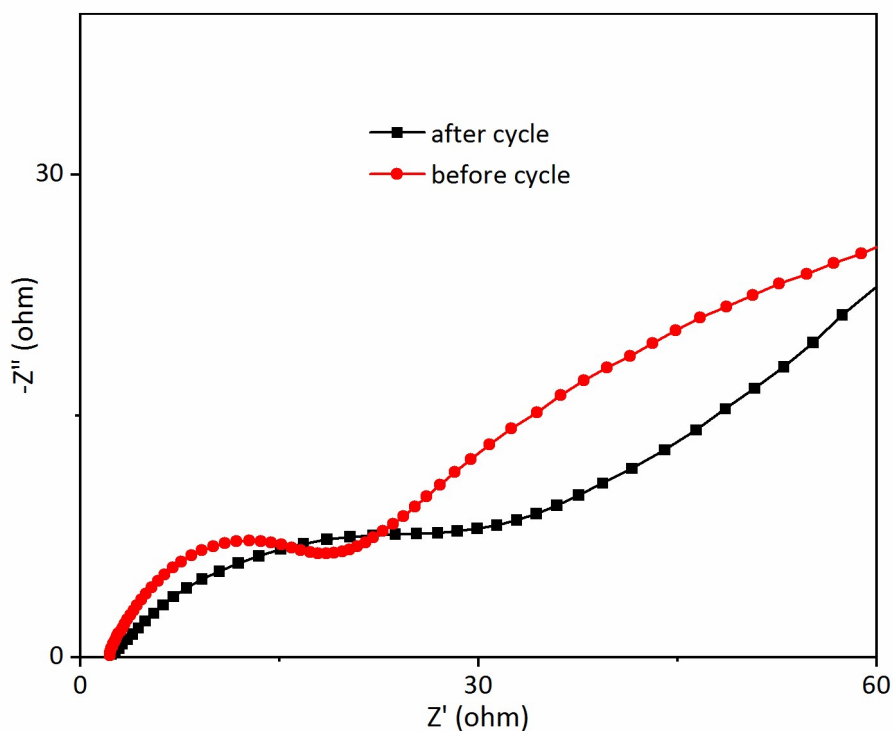
Figure S16. EIS results of LMO/NTP full cell in 1-1 electrolyte with 0.1 M Zn^{2+} addition before and after cycle.

Reference

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