Pre-lithiation strategy to design high-performance zinc oxide anode for lithium-ion batteries

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S1. Experiment and characterization methods

$ZnSO_4 \cdot 7H_2O$ and $LiNO_3$ were dissolved in 50 mL of distilled water with different stoichiometric ratio. The solution was kept on a magnetic stirrer and rotated homogeneously to form mixture. After that, ammonia was added to precipitate the dissolved mental ions. The obtained suspension was migrated into a Teflon-lined stainless-steel autoclave and heated up to 180 ℃ for 8 h. After the hydrothermal reaction, the autoclave was cooled to room temperature. Finally, the sediment was acquired and washed with distilled water and ethanol for 5 times, and then dried at 60 ℃ overnight in vacuum oven. All the synthesized Li_x-ZnO (x = 0.00, 0.01, 0.05 and 0.10) were indexed as ZnO, ZnO-Li-1, ZnO-Li-5 and ZnO-Li-10.

The structure and morphology of the ZnO and ZnO-Li-5 were characterized by scanning electron microscopy (SEM, Hitachi S-4800). Energy-dispersive spectroscopy (EDS) elemental scans were performed on the same instrument equip with detector (7593-H, Horiba). The particle X-ray diffraction (XRD) measurements were performed on a Rigaku D/MAXRB diffractometer (Philips, X'pert Pro MPD, Netherlands), and the excitation wavelength is Cu Kα radiation (λ =0.15443 nm). Transmission electron microscopy (TEM) and corresponding high-resolution images were obtained using a Philips Tecnai 20U-Twin microscope at an acceleration voltage of 200 kV. As for TEM sample preparation, ZnO and ZnO-Li-5 were dispersed in ethanol and then dropped on a copper micro-grid covered by a carbon film. The specimen for TEM was set statically and dried naturally in the air before its characterization. The room-temperature Raman spectra were measured with 532 nm photons from an Ar^+ laser. The laser power used

was < 1.5 mW. The binding energies of ZnO and ZnO-Li-5 particles were acquired by X-ray photoelectron spectroscopy (XPS) on the Thermo ESCALAB 250 with Al Kα radiation (1486.8 eV) as the excitation source. Raman spectra were performed on a Raman spectrometer with 532 nm laser radiation. The electron spin states of the samples were observed via electron paramagnetic resonance (EPR) spectroscopy (Bruker EMXplus). The chemical composition of Li_x-ZnO were identified by Inductively coupled Plasma Emission Spectrometer Avio 200 (Perkinelmer, USA).

S2. Electrochemical characterization methods

Electrochemical performance was evaluated via assembling and testing CR2032 coin cell. ZnO active materials, carbon black and polyvinylidene fluoride (PVDF) were uniformly dissolved in N-methly-2pyrrolidone (NMP) with a ratio of 8:1:1, then the slurry was pasted on copper foil and dried in oven under 80 ℃ to obtain working electrode. Lithium foil, polypropylene film (Celgard 2400) as well as a solution containing $LiPF_6$ (1M) in vinyl carbonate/dimethyl carbonate/diethyl carbonate (1:1:1 vol%) were used as counter electrode, separator and electrolyte, respectively. The active material had an average loading density of about 1.0 mg and a diameter of 12 mm. Lithium metal has been used as counter and reference electrode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on CHI660D electrochemical workstation. The galvanostatic charge/discharge curves are recorded on Neware CT-3008 W battery system.

S3. Results and discussion

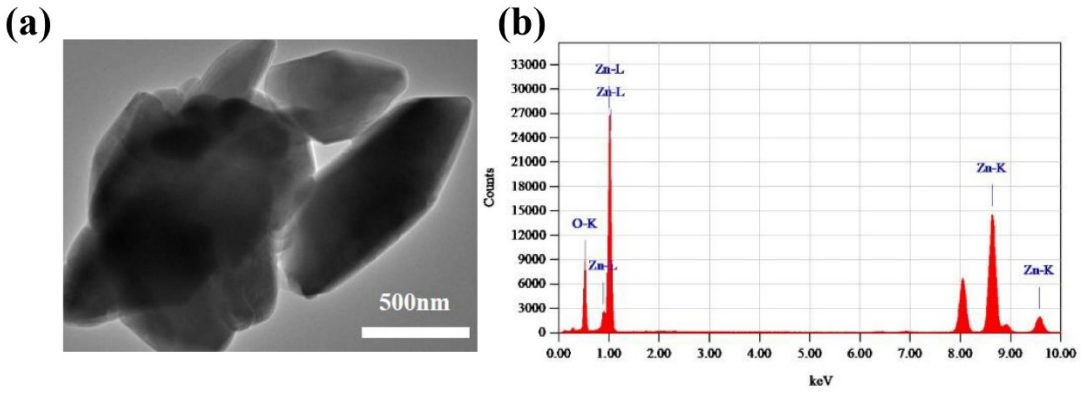

Fig. S1 (a) TEM image and (b) elemental analysis of ZnO nanorod.

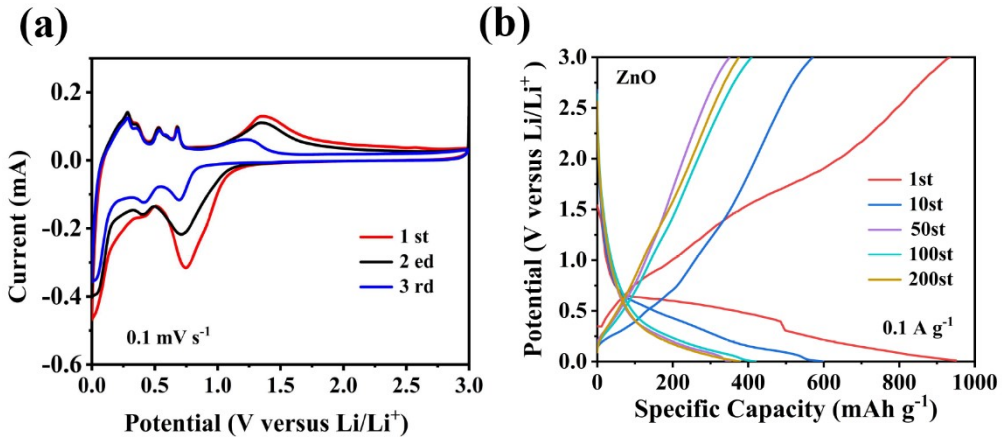

Fig. S2 (a) CV plots at 0.1mV s^{-1} (b) charge/discharge profile of ZnO anode at 0.1 A g^{-1}.

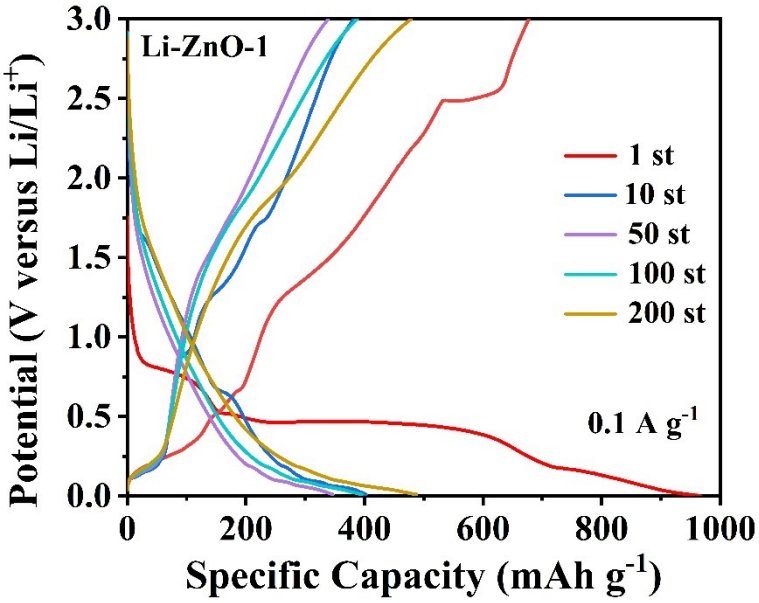

Fig. S3 Charge/discharge profile of Li-ZnO-1 anode at 0.1 A g^{-1}.

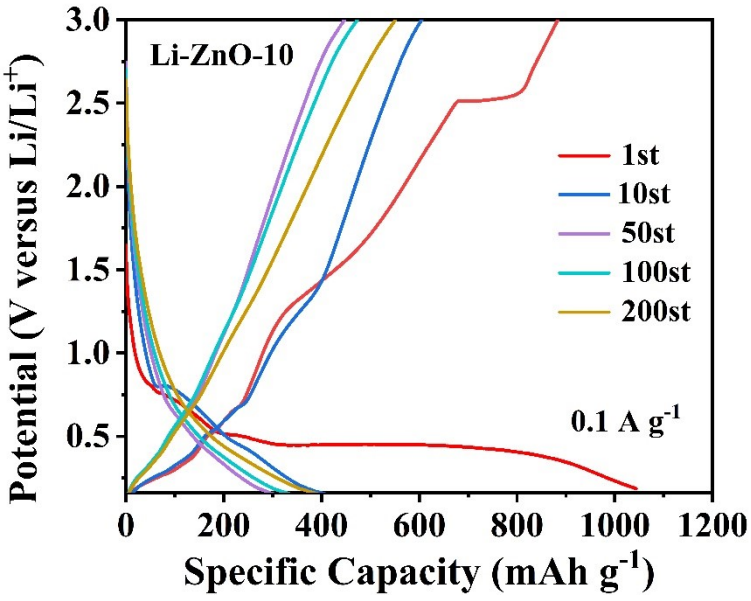

Fig. S4 Charge/discharge profile of Li-ZnO-10 anode at 0.1 A g^{-1}.

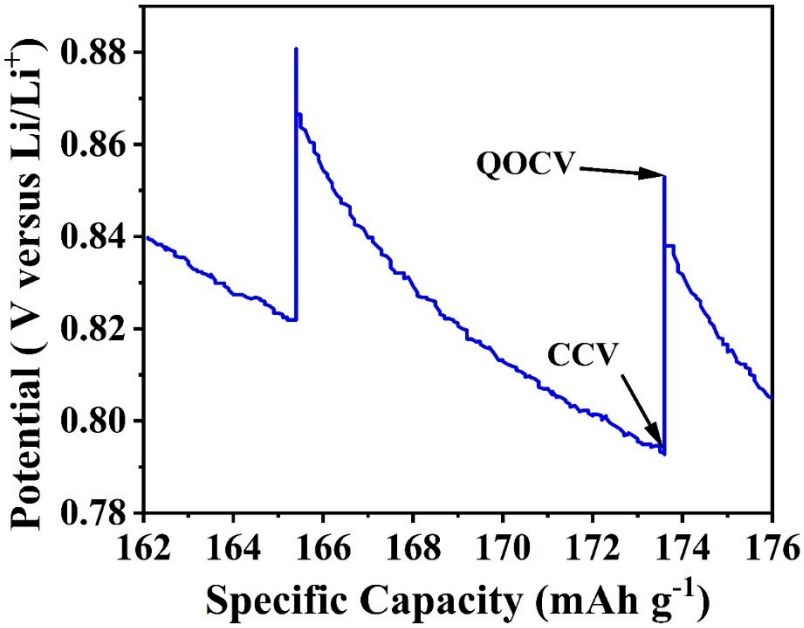

Fig. S5 In-situ reaction resistances during charge and discharge processes.

Galvanostatic intermittent titration technique (GITT) was performed to investigate the charge transfer properties and the equilibrium potentials of the ZnO nanorod and Li-ZnO-5 anodes upon cycling. During the GITT measurements, a constant current density of 0.1 A g^{-1} for 5 mins was adopted to obtain the closed-circuit voltage (CCV), coupled with duration of 10 mins to collect the quasi-open-circuit voltage (QOCV).

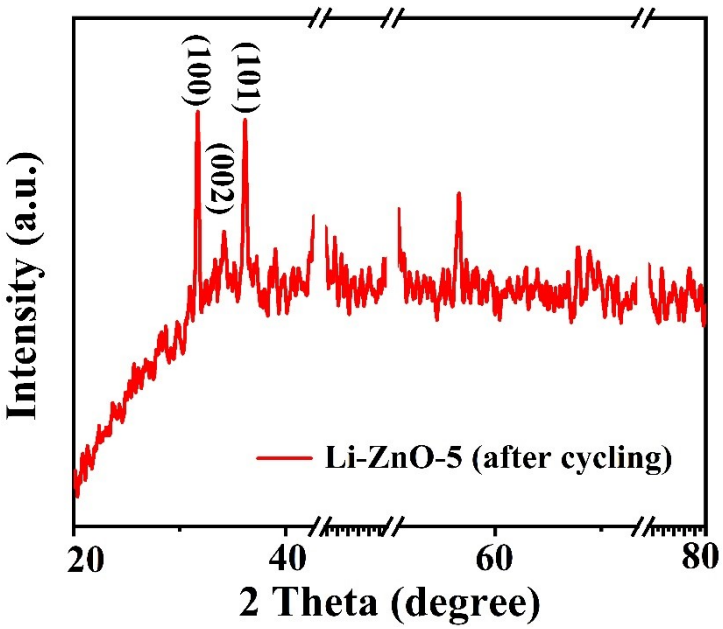

Fig. S6 XRD pattern of Li-ZnO-5 after 200 cycles.

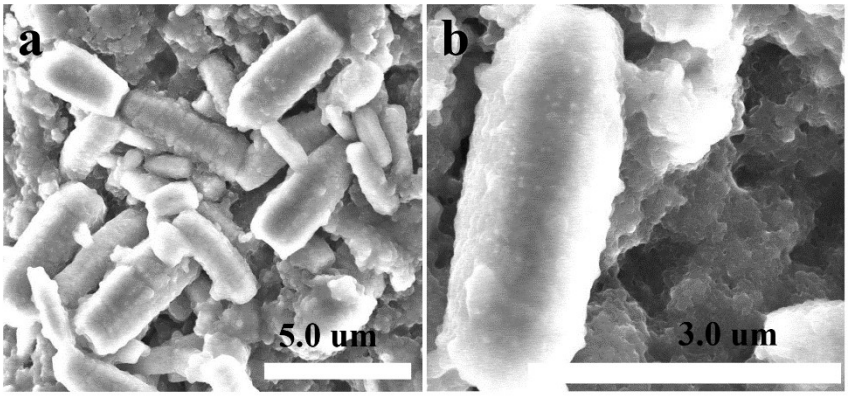

Fig. S7 SEM images of Li-ZnO-5 after 200 cycles.

Table S1. Comparisons of the electrochemical performance between Li-ZnO-5 nanorod anode and other previously reported ZnO-based LIBs anodes.

Material	Method	Current density ($mA\ g^{-1}$)	Cycle number	Capacity ($mAh\ g^{-1}$)
Li-ZnO-5 (this work)	one-step hydrothermal	100 1000	200 1440	639 380
ZnO/C [1]	sol-gel and calcination	100	100	495
ZnO/Cu_2MgO_3 [2]	one-step ultrasonic spray py-rolysis	500	400	441
ZnO spheres [3]	one-step hydrothermal	100	100	109
SnO_2-ZnO [4]	Electro-spinning	100	20	430.6
ZnO/C [5]	microwave-assisted hydrothermal	50	100	800
ZnO@ZnS [6]	solvothermal	200	100	513
ZnO/C [7]	electrospinning and water bath	200	150	535
$ZnFe_2O_4$/ZnO [8]	metal-organic-framework	1000	500	383

S4. REFERENCES

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