

Electronic Supplementary Information (ESI)

A Lithium ion/Oxygen Hybrid Battery with High-Energy and High-Power

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Experimental

Preparation of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

Precursor was synthesized by a hydrothermally-assisted co-precipitation method. Stoichiometric amounts of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in 3wt% ammonium-hydroxide solution. A certain amount of NaOH solution was added slowly into the above solution under magnetic stirring. After that, the mixed solution was solvothermally treated at 200 °C for 5 h in a sealed Teflon-lined autoclave. The as-obtained precursor was mixed with a stoichiometric amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ (5mol% excess), and further being calcined at 850 °C for 10 h in air to form the as-used $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM).

Preparation of Ru@graphene composite

150 mg commercial graphene (Changsha Qixi New Materials Technology Co., Ltd.) was dispersed into RuCl_3 (75 mg) / ethanol (100 ml) mixed solution with magnetic stirring for 48 h at room temperature. Then the mixture was dried at 60 °C overnight. Finally, the Ru-functionalized graphene was acquired by treating the dried sample at 350 °C for 3 h under 10% H_2/Ar atmosphere.

Physical characterization

Phase structure was characterized by X-ray diffraction (XRD) diffractometer (Dandong DX-2700B) with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Morphology was observed by field-emission scanning electron microscope (SEM) (FEI Inspect F50) and the energy-dispersive spectroscopy (EDS) mapping was obtained using Octane Super Det detector at 20 kV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were carried out using a FEI Titan G2 60-300 electron microscope. Surface chemistry was investigated using X-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250XI) with Al $K\alpha$ X-rays (1486.6 eV). Thermogravimetric analysis (TGA) was taken on a STA 449 F3 instrument with a heating rate of 10 °C min^{-1} in air. N_2 adsorption-desorption isotherms were carried out using a ASAP 2460 analyzer at a temperature of 77 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. Pore size distribution was derived from the adsorption branch using the Barrett-Joyner-Halenda (BJH) model.

Electrochemical characterization

NCM cathode was prepared by mixing active material, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 8:1:1 in N-methylpyrrolidone (NMP). The formed slurry was coated onto carbon-paper current collector with diameter of 14 mm. After that, the obtained electrode was dried in vacuum oven at 120 °C for 12 h. For the preparation of O_2 cathode, except using the nickel-foam current collector and the slurry comprising 90% Ru@G and 10% PVDF, other operations are the same as the preparation of NCM cathode. The loading weights of active materials are $\sim 2 \text{ mg cm}^{-2}$ for both NCM cathode and the O_2 cathode. Lithium foil was used as the anode. 1 M LiPF_6 / ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume), and 1 M lithiumtrifluoro-methane-sulfonimide (LiTFSI) / tetraethylene-glycol-dimethyl-ether (TEGDME) were used as the electrolytes for LIB and LOB respectively. Celgard 2500 film and glass micro-fibre membrane (Whatman) were used as separators for LIB and LOB respectively. All cells were assembled in an Ar-filled glove box (Shenzhen Kejing Star

Technology Co., Ltd.) with H₂O and O₂ level less than 0.1 ppm.

Galvanostatic discharge-charge tests were carried out using LAND testers (CT2001A, WuhanLAND Electronic Co., Ltd.) at room temperature. The used current density and the acquired electrochemical data were normalized by the mass of cathode active materials for both LIB and LOB. On the other hand, for the lithium ion/oxygen hybrid battery system, considering the reaction from NCM cathode takes place before that from O₂ cathode, the current and acquired electrochemical data were normalized by the mass of as-used NCM and the total mass of as-used NCM + Ru@G respectively. Cyclic voltammetry was performed using a MULTI AUTOLAB M204 potentiostat (Metrohm). All the measurements for LOBs were conducted under pure O₂ atmosphere. Besides, before the start of the test for hybrid battery system, the LIB and the LOB were firstly charged to a same voltage of 4.4 V vs. Li/Li⁺ separately and then the cathodes of the two batteries were connected together by the external circuits as the cathode of the system. For the continuous several 60 s-power tests of hybrid battery system, when the capacity of NCM cathode was exhausted, only the NCM cathode was replaced by a new “full-charged” one, and then subsequent tests were carried out based on this renewed system.

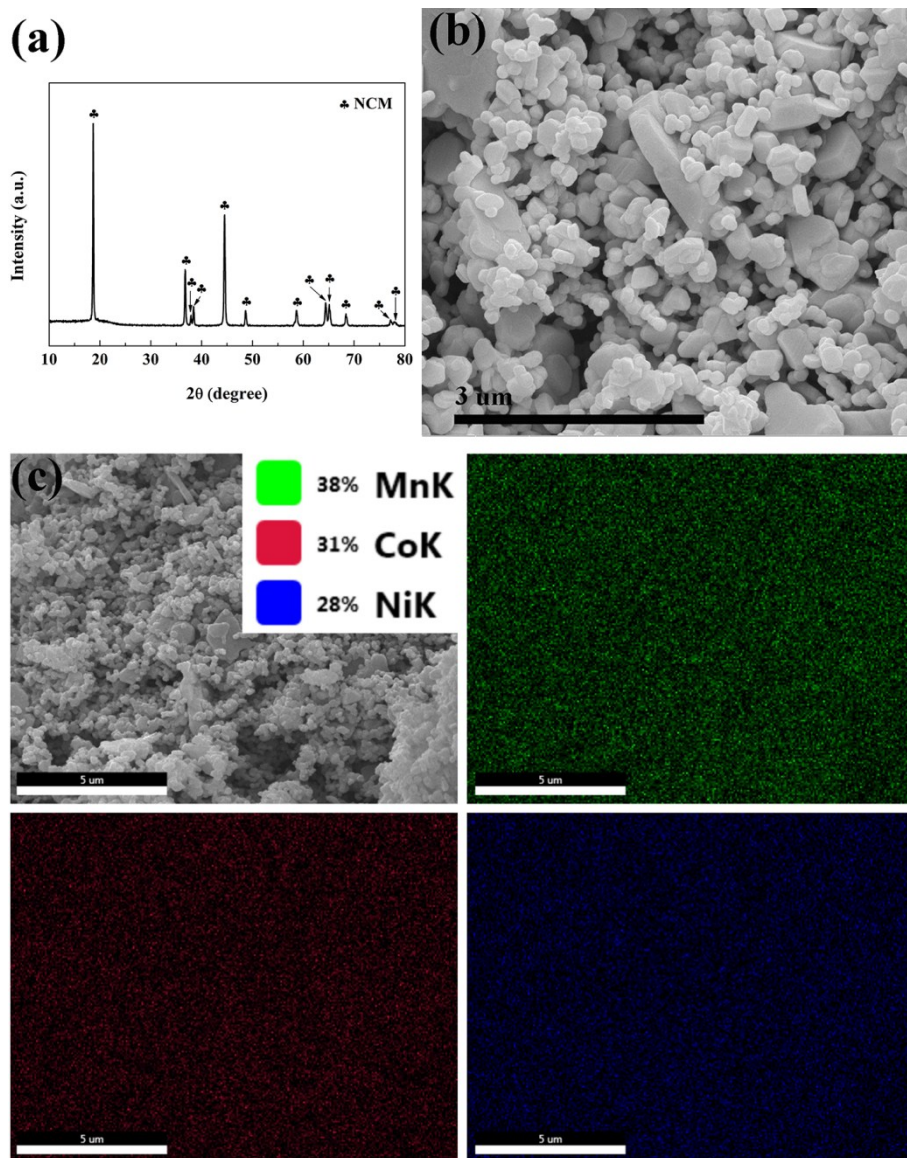


Fig. S1 (a) XRD pattern, (b) SEM image, (c) EDS mapping of as-prepared NCM. The sample is composed of mostly irregular spherical particles with the size distribution from 150 to 450 nm and some thin plates with the thickness of 200-300 nm and the width of 0.5-1.5 μm.

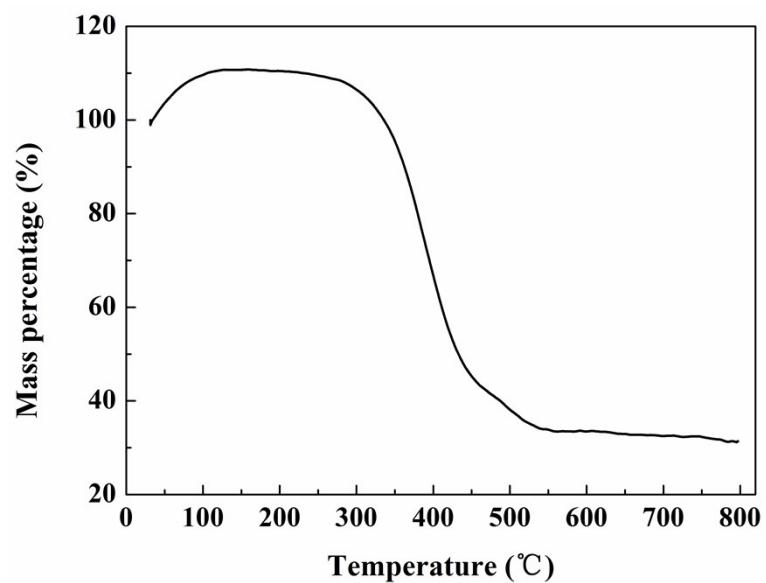


Fig. S2 TGA curve of Ru@G composite. The residual weight at 800 °C is 31.37%. So, the Ru content is 23.82% according to the oxidation of Ru to RuO₂.

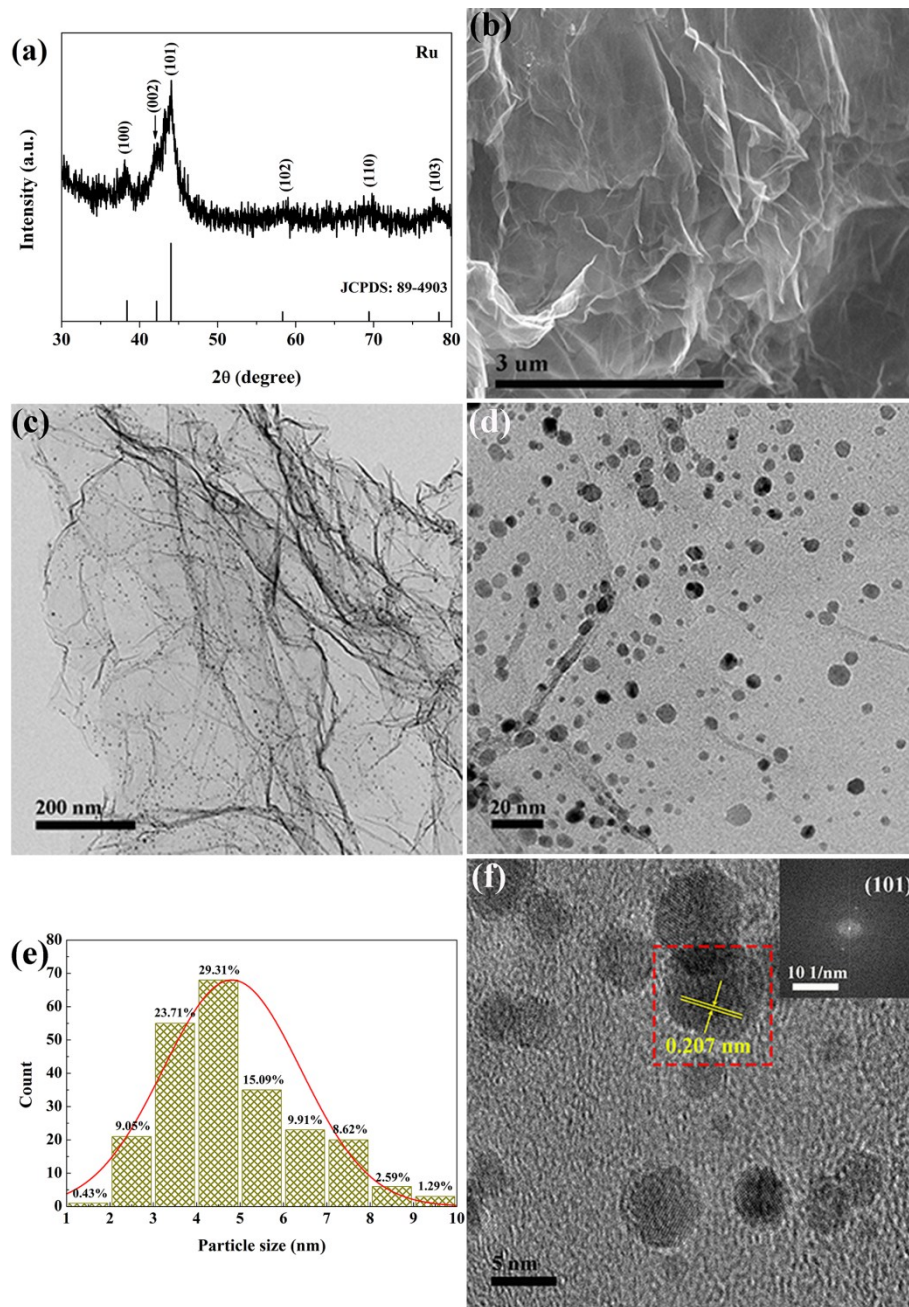


Fig. S3 (a) XRD pattern, (b) SEM image and (c, d) TEM images of as-prepared Ru@G composite. (e) Size distribution plot of Ru nanoparticles. (f) HRTEM image of Ru@G composite. The insets is the fast Fourier transform (FFT) of electron diffraction pattern of Ru particle in the composite marked with a red box.

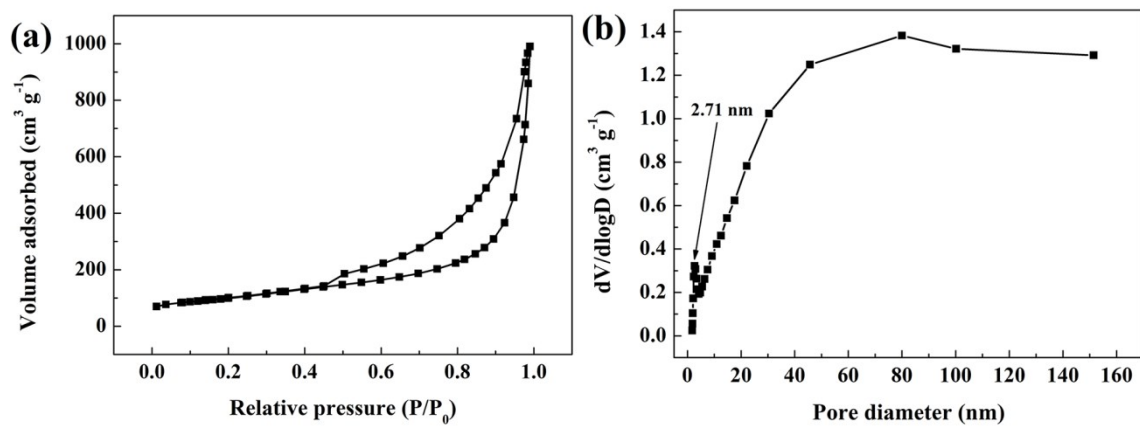


Fig. S4 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution of as-prepared Ru@G composite.

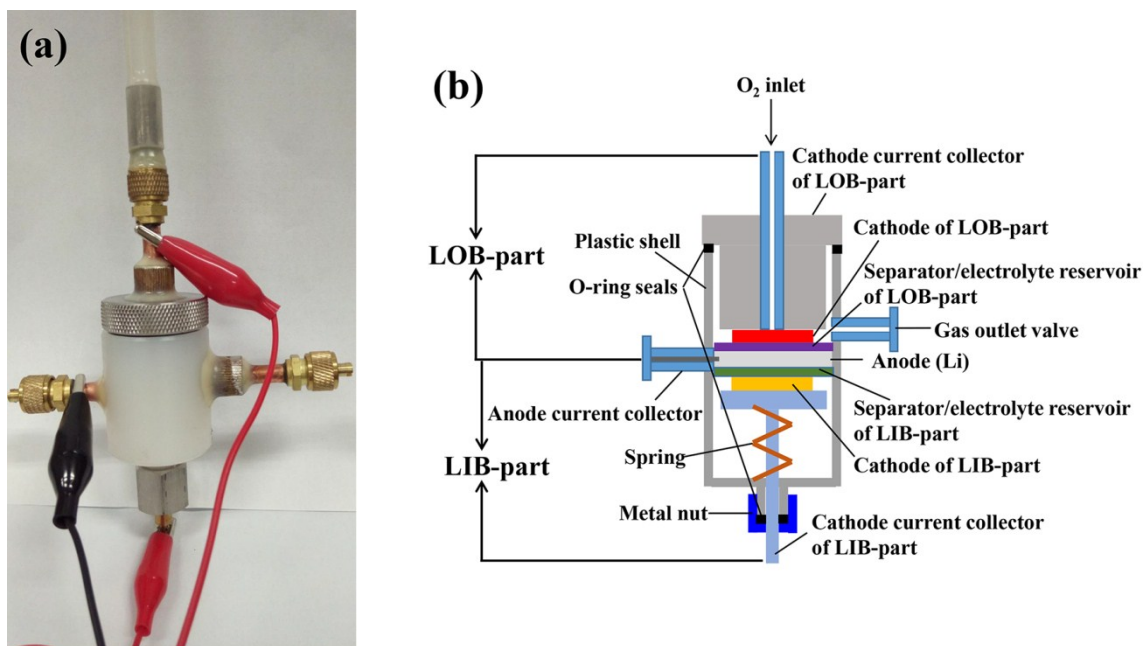


Fig. S5 (a) Photograph of lithium ion/oxygen hybrid battery system and (b) correspondingly its schematic diagram. During the tests, the cathodes of the LIB-part and the LOB-part were connected together by the external circuits as the cathode of the system.

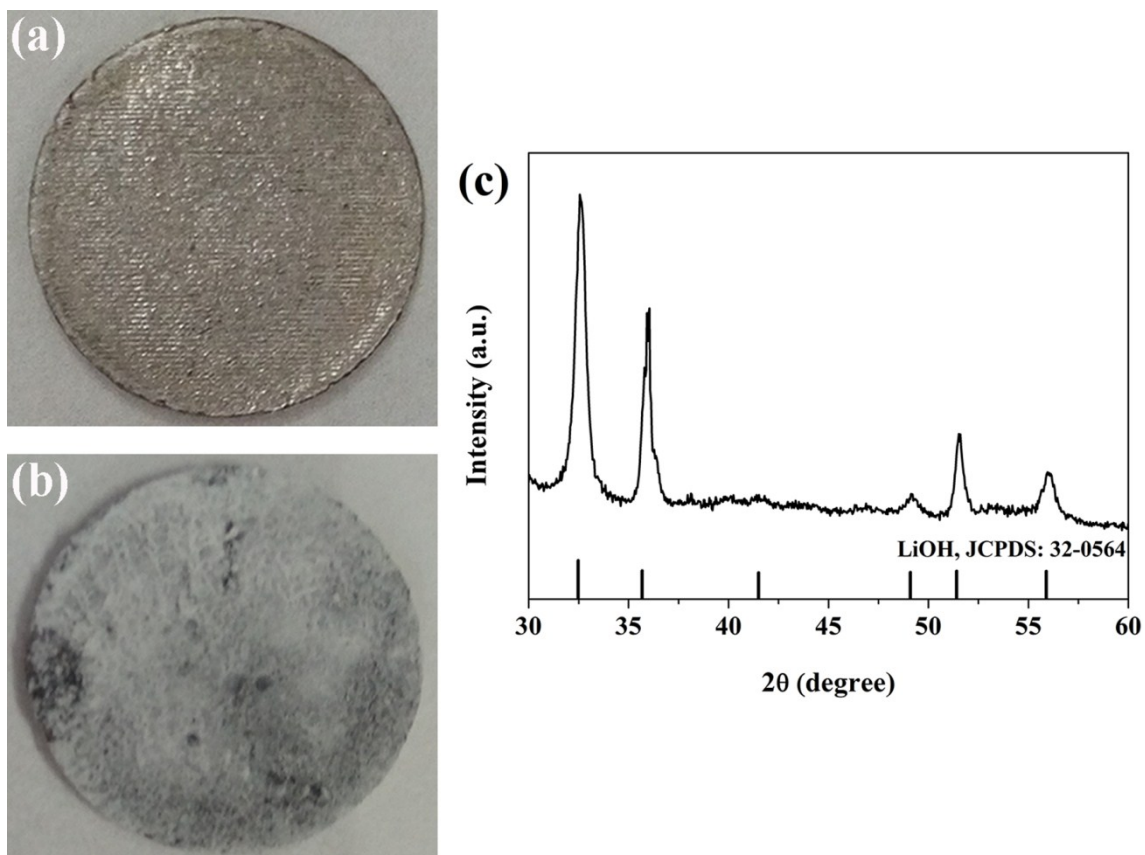


Fig. S6 Photographs of anode lithium before (a) and after (b) 17 discharge-charge cycles with a limited capacity of $500 \text{ mAh g}_{\text{NCM+Ru@G}}^{-1}$ at $100 \text{ mA g}_{\text{NCM}}^{-1}$ in the voltage range of 2.3-4.5 V for LOB-part in the lithium ion/oxygen hybrid battery system. (c) Correspondingly, the XRD pattern of anode lithium after cycle.

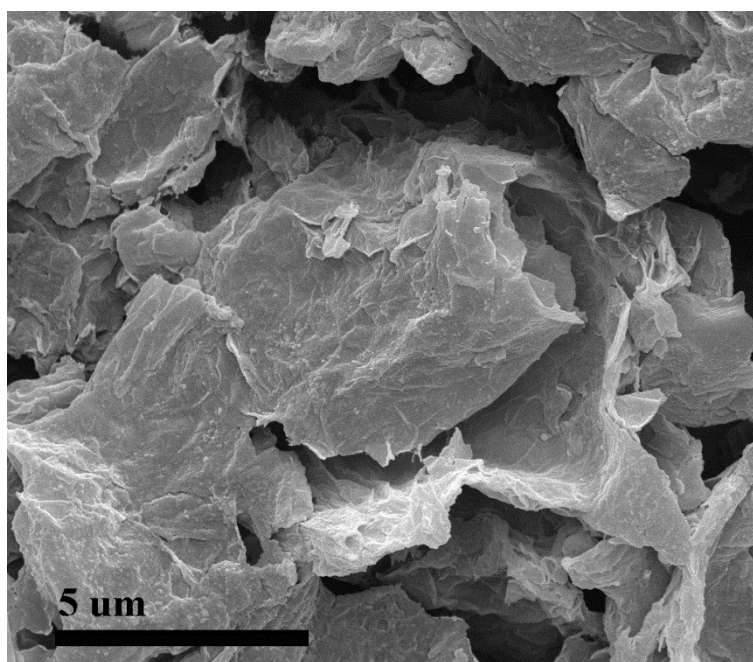


Fig. S7 SEM image of Ru@G cathode of lithium ion/oxygen hybrid battery system after 17 discharge-charge cycles with a limited capacity of $500 \text{ mAh g}_{\text{NCM+Ru@G}}^{-1}$ at $100 \text{ mA g}_{\text{NCM}}^{-1}$ in the voltage range of 2.3-4.5 V.

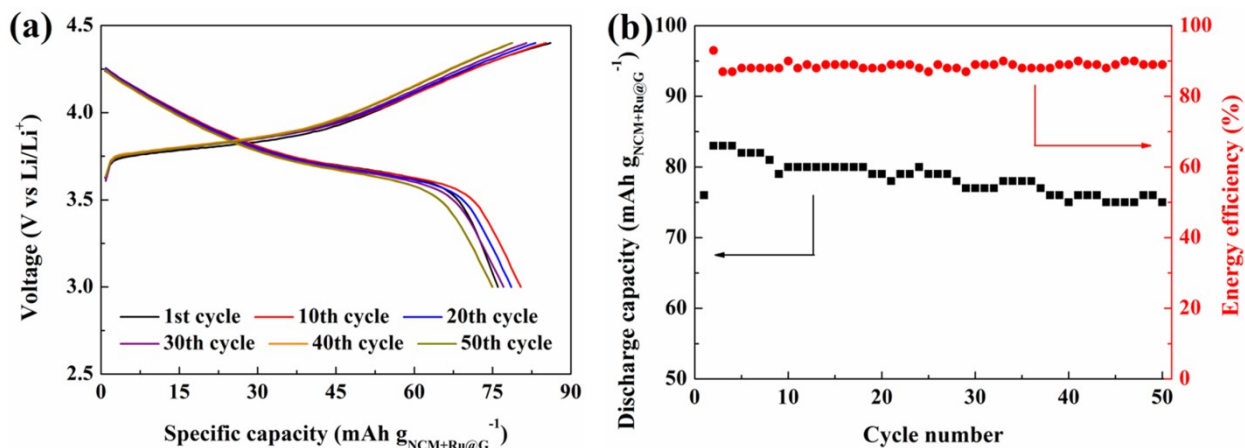


Fig. S8 (a) Discharge-charge curves of the lithium ion/oxygen hybrid battery system for selected cycles within the voltage range of 3.0-4.4 V at 100 mA g_{NCM}⁻¹. (b) Correspondingly, the cycle discharge-capacity and energy-efficiency vs. cycle number.