

New recognitions about the cyclable capacity fading process of the pouch cell with Li-rich layered oxide cathodes

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Experimental

Pouch cells were manufactured at National Power Battery Innovation Center via the traditional pouch preparation procedure. Lithium-rich layered oxides (LLOs) with the formula of $\text{Li}_{1.15}\text{Mn}_{0.53}\text{Ni}_{0.265}\text{Co}_{0.055}\text{O}_2$ are used as the cathode material and its preparation method is reported in our previous report¹.

Artificial graphite (BTR, 360MB) is used as anode material. The cathode slurry was prepared by mixing 95% LLOs, 1.5% Super P (SP), 1% Carbon nanotube (CNT), and 2.5% poly(vinylidene fluoride) (PVDF) in N-methylpyrrolidone solvent via 1L mixer. Then the blended slurry was coated onto both sides of the 20 μm -thick Aluminum foil via a transfer type coater. The anode slurry was prepared by mixing 95% graphite, 1% SP, 1.5% Carboxymethyl cellulose Sodium (CMC) and 2.5% Polymerized Styrene Butadiene Rubber (SBR) in deionized water via 1L mixer. Then the blended slurry was coated to both sides of 8 μm -thick copper foil. The loading of the cathode and anode was 14 mg/cm^2 and 11 mg/cm^2 respectively. Then the electrodes were calendared into designed thicknesses that is 132 μm for the cathode and 156 μm for the anode. After the calendar and drying procedure, the electrode rolls were punched into small pieces with the required size. The jelly roll was assembled via a Z-type stacking procedure. Five pieces of cathodes, six pieces of anodes, and one belt of separator were stacked following the sequence of separator/anode/separator/cathode. After tab welding, the jelly roll was put into an aluminum plastic bag with three sides heat-sealed. Then, the pouch bag was transformed into a vacuum oven to be heated for about 8 h at 85 °C to remove residual water. After drying, the cells were placed in an argon-filled glove box without exposure to ambient air, where they were injected into 6 g electrolytes. The electrolyte contains 1 M LiPF_6 in a mixture solution of ethylene carbonate (EC), diethyl carbonate (DMC), and ethyl methyl carbonate with fluoroethylene carbonate (FEC) additives (FEC:EC:DEC:EMC=7:25:50:25,

by weight). Once cells were filled with electrolytes, they were sealed with a compact vacuum sealer with 5-second sealing time at 185 °C. After rest for about 12 h, the formation was started with a current density of 0.1C (C-rate is defined as the charge/discharge current divided by the nominally rated battery capacity) and voltage window of 2.0-4.6 V. After two cycles, the pouch was then de-gassed and resealed. The nominal capacity of the cells was then rated with the protocol of 0.33C within 2.0-4.6 V when aging time was reached 24 h. The final cell dimensions were 66 mm wide by 96 mm tall (without tab length). For cells used for gas testing, an extra gas bag with the size of 70 mm tall and 66 mm wide was designed. The cell exhibited a nominal capacity of about 1.2 Ah. Detailed information is listed in Table 1. The photos of the appearance of pouch cells are shown in Fig. 1 and 2. Coin cells were assembled via the electrode taken from cycled pouch cells. After being discharged to lower voltage, the pouch cell is transferred into a glove box and dismantled by a ceramic scissor. The electrode is washed with dimethyl carbonate (DMC) several times and then one side of the active material was erased before assembly.

Table 1 General information of the pouch cell

Parameter	Specification	Condition
Typical capacity / Ah	1.2	2.0-4.6V 0.33C/0.33C
Typical energy / Wh	4.2	
Average discharge voltage / V	3.54	
Cell weight / g	20	-
Inner resistance / mΩ	28	50%SOC Alternative impedance @5kHz



Fig.1 The photo of the pouch cell for cycling tests.

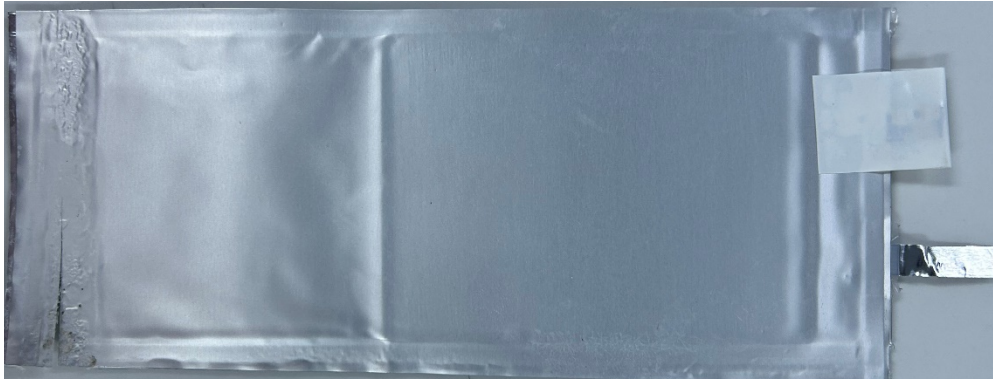


Fig. 2 The photo of the pouch cell for gas tests.

Long-term cycling. Cells were cycled using a LANHE BTS3000 series charger (5V/10A, Wuhan, China) at room temperature (approx. 25°C). Cells were cycled at a charging rate of 0.33C and discharging rate of 1C, between 2.0-4.6 V, in a constant current-constant voltage (CCCV) mode. Cells were held at the upper voltage until the current reached C/20.

Polarization analysis. Electrochemical impedance spectra (EIS) of the cells with different cycling times were collected using a Chenhua V6 with ten points per decade from 100 kHz to 10 MHz and a 10 mV input signal amplitude. Galvanostatic intermittent titration technique (GITT) measurements were conducted using a LAND battery testing system (CT-2001A) with two different settings: (1) with a titration current of 1C and a titration time of 30 s, followed by 15 h relaxation, or (2) a titration current of 0.1C and a titration time of 1 h, followed by 15 h relaxation. GITT1 was used for polarization analysis, while GITT2 was used for the calculation of diffusion coefficient.

The detailed calculation method for instant loss, non-instant loss and whole voltage loss via GITT1 is provide in the Fig. 3. When titration ends, the relaxion can be divided into two parts. First, the OCV (open-circuit voltage) will recover to a higher value instantly (the time increment of sampling points is about 0.5s) as soon as titration stopped. This volage range recovered is called instant loss. Specifically, the instant loss comprises three components: The first is the overpotential due to electronic conductive resistance between the current collector and active particles, with a response time of about 0.1 milliseconds. The second is the overpotential due to ion transfer resistance through the SEI, with a response time of about 1 millisecond. The third is the overpotential due to charge transfer resistance at the electrode-electrolyte interface, with a response time of approximately 100 to several hundred milliseconds. Consequently, a 500-millisecond interval is chosen to approximate the calculation of instant voltage loss². Subsequently, after a rest period of more than 15 hours, the cell is expected to reach an equilibrium state, and any further voltage recovery is termed non-instant loss. For non-instant loss, the overall overpotential generally

includes two components. One is the overpotential due to concentration polarization in the electrolyte, with a response time of about 5 to 10 seconds. The other is caused by the relaxation of diffusion polarization in the solid particles, which can last for several hours². A 15-hour period is selected in our work to ensure that the relaxation time is significantly greater than the titration time and that the cell reaches an equilibrium state. This approach is also utilized in another report on our research³.

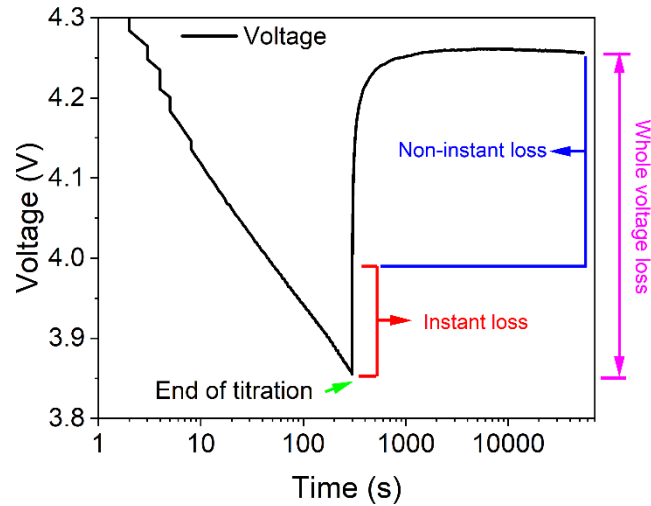


Fig. 3 Calculation method about different types of polarization

The diffusion coefficient of Li^+ was calculated according to the formula next with parameters obtained by GITT⁴.

$$D_{\text{Li}} = \frac{4}{\pi} \left(\frac{V_M}{AFZ} \right)^2 \left[I_0 \frac{dE/d\delta}{dE/d\sqrt{t}} \right]^2, \quad t \ll \frac{L^2}{D_{\text{Li}}}$$

where V_M was the molar volume of active material (for simplification, here we used cm^3/mol for LLOs), A was the contact area between electrolyte and electrodes, F was the Faraday constant, I_0 was the applied titration current, Z was 1 (valence of Li^+), E was electrode voltage, δ was the deviation from the initial stoichiometry, L was the thickness of the electrode, and t was the duration of the titration step.

Gas volume was tested via a self-constructed device using Archimedes principle with a gas bag immersed in the silicon oil, as was shown in the next pictures, which is shown in Fig. 4. Gas chromatography-mass spectra (GC-MS, Aglient7890A) were employed to determine the components of gas.

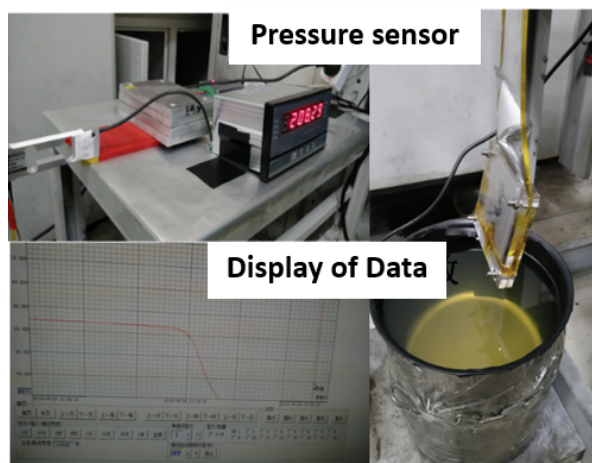


Fig. 4 Self-constructed device for gas volume testing

Morphology and interface characterization. Scanning electron microscopy (SEM, Hitachi-S-4800) is operated to present the surface morphology of LLO particles, while an X-ray photoelectron spectrometer (XPS, Thermo ESCA250) is used to characterize the surface chemistry of cathode electrolyte interface (CEI).

Results discussions

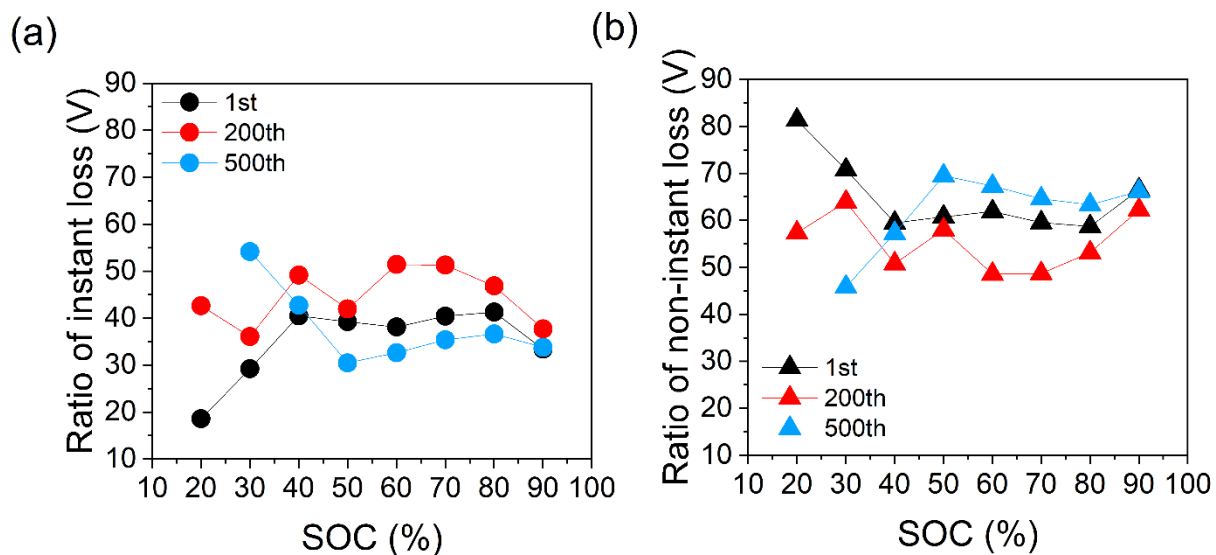


Fig. S1 Ratios of (a) Instant voltage loss and (b) non-instant voltage in whole voltage loss during different cycle period.

Table S1 Parameters for fitting EIS spectra of all samples

Cycle number	R_s (m Ω)	R_{SEI} (m Ω)	R_{ct} (m Ω)	R_{total} (m Ω)
1st	11.3	16.8	23.1	53.2
200th	14.0	24.1	94.2	132.2
500th	16.8	32.9	159.9	209.7

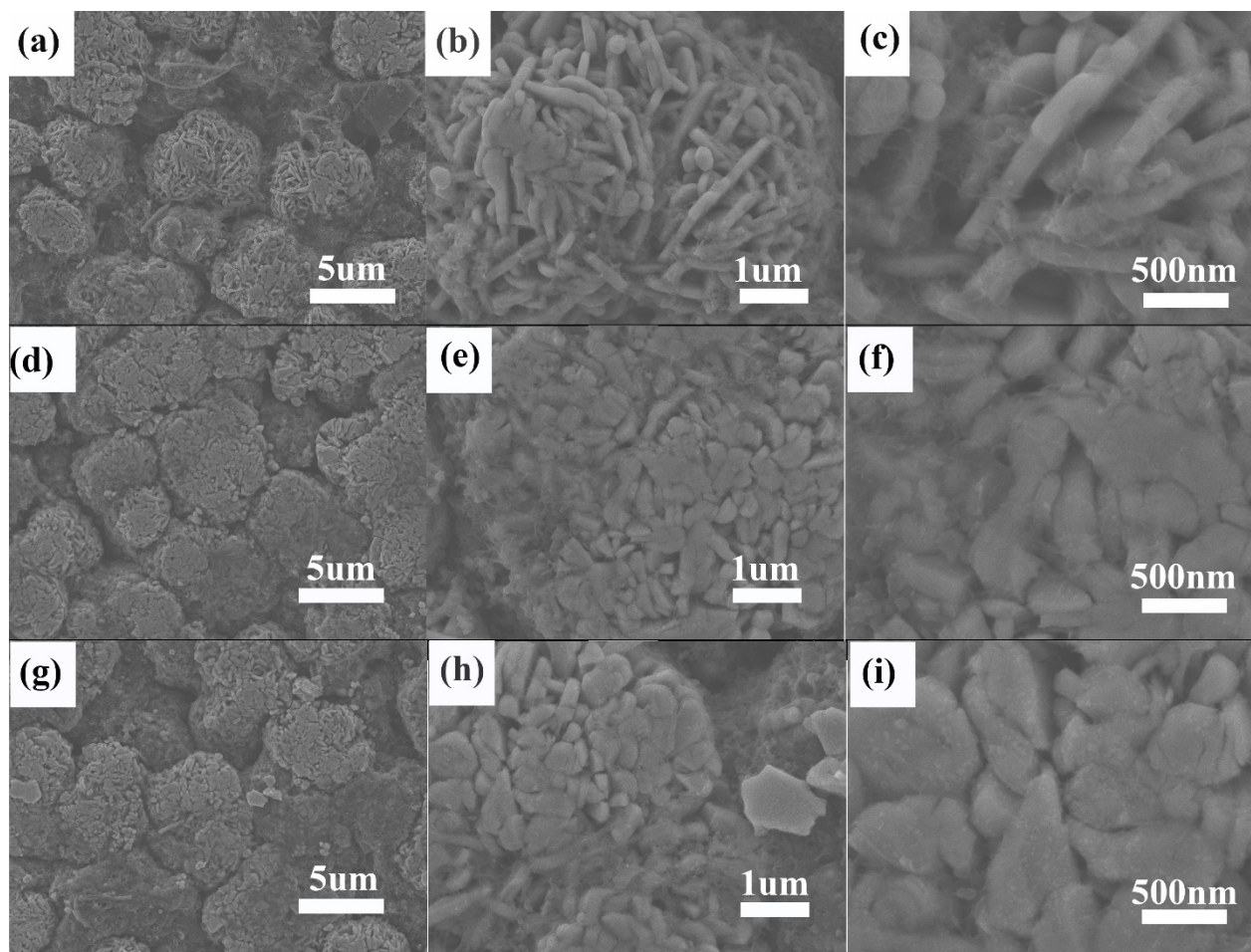


Fig. S2 SEM images of the cathode electrodes with different cycle numbers of (a, b, c) 1st, (d, e, f) 200th and (g, h, i) 500th.

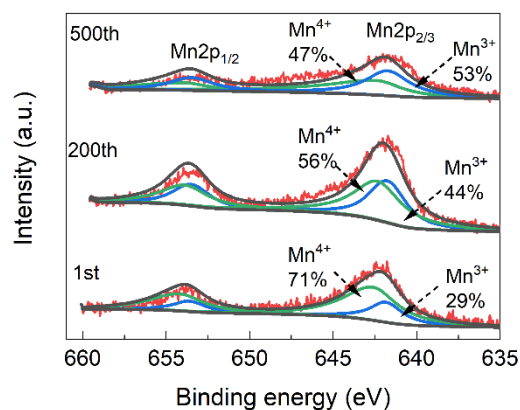


Fig. S3 XPS spectra of Mn 2p

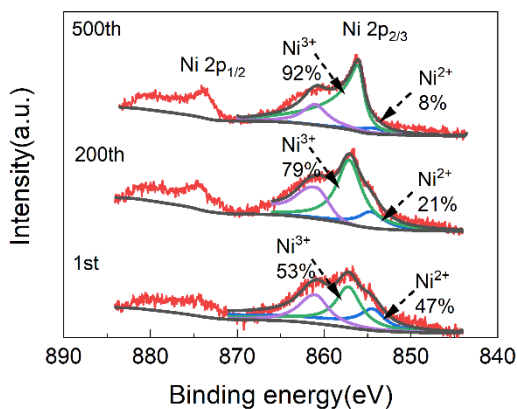


Fig. S4 XPS spectra of Ni 2p

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