A comparative study on the thermal runaway process mechanism of a pouch cell based on Li-rich layered oxide cathodes with different activation degrees

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Experimental section

Preparation of the pouch cells

Pouch cells were manufactured at the National Power Battery Innovation Center using the traditional pouch preparation procedure. Lithium-rich layered oxides (LLOs) were used as the cathode material, with the preparation method detailed in a previous report[1].

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 an N-methylpyrrolidone solvent using a 1L mixer. The blended slurry was then coated onto both sides of a 20 μm-thick aluminum foil using a transfer-type coater. Artificial graphite (BTR, 360MB) was used as the anode material. 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 using a 1L mixer. This slurry was coated onto both sides of an 8 μm-thick copper foil. The cathode electrode with mass loadings of 14 mg/cm² are used for all the three types of pouch cells, while anode electrodes with different mass loadings are used to match the cathode. Relative information is also listed in Table S1. The electrodes were then calendared to the designed thicknesses, achieving a volume density of 2.8 g/cm³ for the cathode and 1.5 g/cm³ for the anode. After calendaring and drying, the electrode rolls were punched into pieces of the required size. The jelly roll was assembled using a Z-type stacking procedure, stacking 16 pieces of cathodes, 17 pieces of anodes, and one separator belt in the sequence of separator/anode/separator/cathode. After tab welding, the jelly roll was placed into an aluminum plastic bag with three sides heat-

sealed. The pouch bag was then heated in a vacuum oven at 85°C for about 8 hours to remove residual water. Following drying, the cells were placed in an argon-filled glove box without exposure to ambient air and injected with 6g of electrolyte containing 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DMC), and ethyl methyl carbonate (EMC) with fluoroethylene carbonate (FEC) additives (FEC:EC:DMC=7:25:50:25 by weight). Once filled with electrolytes, the cells were sealed using a compact vacuum sealer with a 5-second sealing time at 185°C. After resting for about 12 hours, formation began with a current density of 0.1C (C-rate is defined as the charge/discharge current divided by the nominally rated battery capacity). To achieve different activation degrees, the voltage window was set to 2.0-4.2 V, 2.0-4.4 V, and 2.0-4.6 V respectively. After two cycles, the pouch was de-gassed and resealed. These three cells were named as C2, C4, and C6, respectively. The nominal capacity of the cells was rated using the 0.1C protocol after 24 hours of aging. The final cell dimensions were 66 mm wide by 96 mm tall (excluding tab length) with the photo presented below.

The cationic capacity is mainly originating from the electrochemical reactions of the transition metals, corresponding the values between 2.5 and 4.2 V for the first discharge capacity curves. The anionic capacity is originating from the electrochemical reactions of oxygen anions, when Li_2MnO_3 phase is activated. The values refer to the capacity between 4.2 and 4.4 V for the discharge capacity curves. Relative values are also listed in Table. S1.

Fig. The photo of the pouch cell prepared for research

Table S1 The first discharging capacity information of the three pouch cells

Sample	The loadings of the cathode/mg/cm^2	The loadings of the anode/mg/cm^2	Initial discharging capacity/Ah	The specific capacity of the cathode materials	Cationic capacity contributions/Ah	Anionic capacity contributions/Ah	Ratio of anionic contributions / %
C2	14	5.5	2.35	123	2.35	0	0
C4	14	7.2	3.11	162	2.35	0.76	24.4
C6	14	10.2	4.43	231	2.35	2.08	46.9
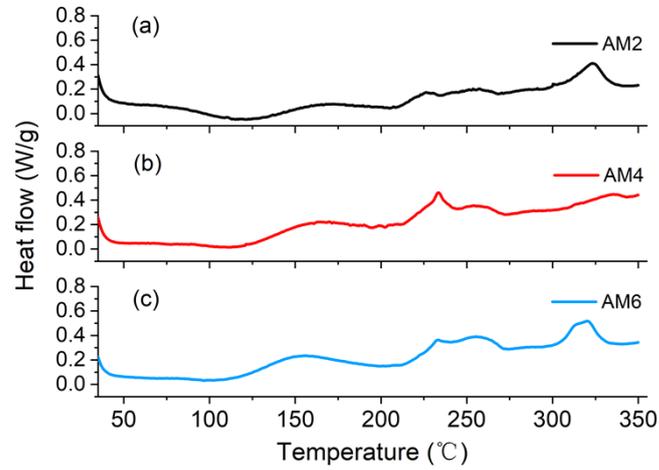
Fig. S1 DSC curves of the anodes with 100%SOC retrieved from the pouch cells with different activation degrees
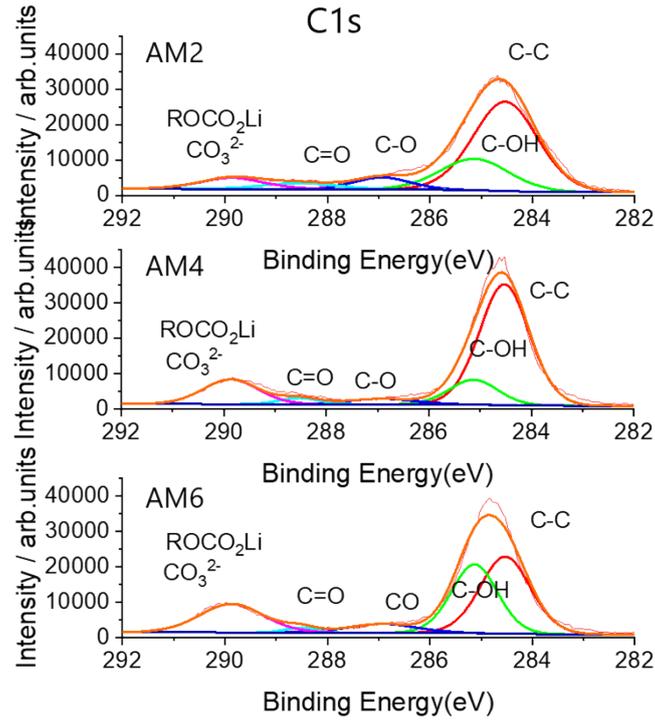
Fig. S2 XPS spectra of C1s for the graphite materials retrieved from the pouch cells with different activation degrees
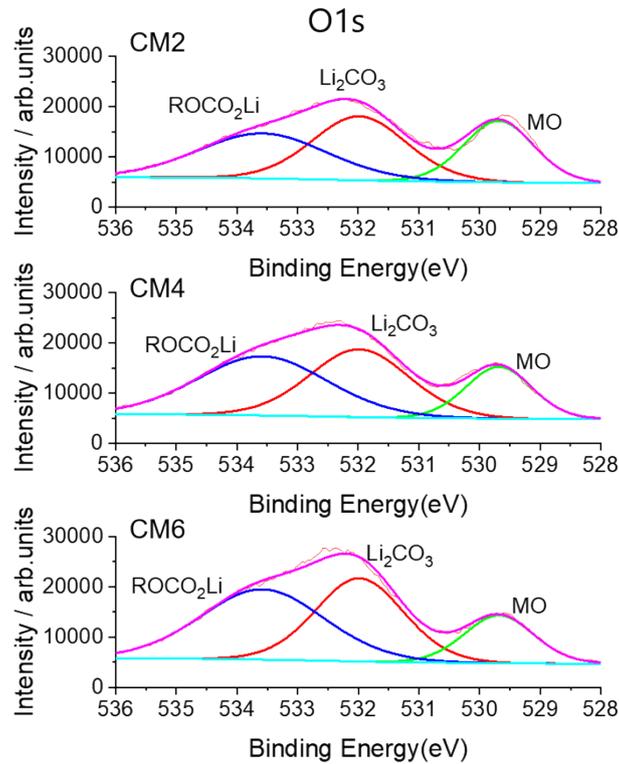
Fig. S3 XPS spectra of O1s for the graphite materials retrieved from the pouch cells with different activation degrees

References

1. G. Li, Z. Ren, A. Li, R. Yu, W. Quan, C. Wang, T. Lin, D. Yi, Y. Liu, Q. Zhang, J. Wang, H. Yu and X. Sun, Nano Energy, 2022, 98, 107169.