Support Information

Enhancing High-Voltage Cycling Stability of $LiCoO_2$ via a Cyclized Polyacrylonitrile Coating

Xiangnan Dai[ab], Guojun Zha[ab*], Kexin Chen[ab], Xiaofei Zhang[ab], Mufei Xue[ab], Yunming Li[ab], Hongzhi Luo[ab], Fenning Zhao[ab]

[a]*Schoolof new energy science and engineering, Xinyu University, Xinyu, China.*

[b]*Jiangxi Provincial Key Laboratory of Power Batteries & Energy Storage Materials, Xinyu University, Xinyu, China.*

**e-mail: zhaguojun@xyc.edu.cn*

Experimental Section

Preparation of cPAN-LCO.

Pristine $LiCoO_2$ (LCO) was synthesized using a citric acid-assisted solid-phase method. Li_2CO_3 and Co_3O_4 were combined in a molar ratio of 3:2.1, citric acid was used as the chelating agent, and the addition amount of citric acid was controlled at a molar ratio of 1:1 with the Co element (that is, the molar number of citric acid was equal to the total molar number of Co in the system), to ensure the uniform chelation of metal ions and the uniformity of the precursor during the subsequent calcination process. Following ball milling and mixing, the mixture was pre-calcined at 500°C for 5 hours and subsequently calcined at 800°C for 12 hours, yielding well-crystallized LCO powder. The LCO produced through this method exhibits a degree of irregularity and high surface activity, making it particularly suitable for investigating the effects of polyacrylonitrile (PAN) coating. The coating is achieved via a straightforward liquid-phase impregnation method combined with heat treatment.Firstly, PAN was dissolved in N, N-dimethylformamide (DMF) to prepare a uniform PAN/DMF solution. The liquid-phase impregnation treatment was carried out using LCO with a solid-liquid ratio of 1 g:10 mL for the PAN/DMF solution.Next, LCO powder was dispersed in this solution and subjected to continuous magnetic stirring at 50°C for 6 hours to ensure complete wetting. The slurry was then stirred and evaporated at 80°C to eliminate the DMF solvent, resulting in the PAN pre-coated LCO precursor (LCO@PAN). Finally, the precursor was heated at a rate of 2°C min^{-1} to 300°C and maintained at that temperature for 3 hours to cyclize PAN into conductive cPAN, thereby producing the final LCO@cPAN composite material[37].The concentrations of coated PAN were 1 wt%, 3 wt%, and 6 wt%, designated as cPAN-LCO-1, cPAN-LCO-3, and cPAN-LCO-6, respectively.

Preparation of Sample and Characterization.

When preparing the cathode on aluminum foil, the active material, conductive carbon black and the binder polyvinylidene fluoride (PVDF) are mixed in a mass ratio of 80 wt%, 10 wt% and 10 wt% respectively, and thoroughly stirred in NMP solvent to form a uniform slurry, which is then evenly coated on the clean aluminum foil. Subsequently, the coated electrode sheet was

vacuum and constant-temperature dried at 110 ℃ for 10 hours to ensure that the NMP solvent was completely evaporated. Punch the prepared anode into disc shapes. A polyvinylidene fluoride (PVDF) membrane separates the positive and negative electrodes. Both electrodes are immersion-dipped in an electrolyte solution prepared by dissolution of 1 mol LiPF6 in a mixed solvent (1L) of DMC, EMC, and EC (volume ratio 1:1:1). Finally, these cells were assembled in glove boxes filled with high-purity argon gas and cycled on the CT2001A Land, undergoing constant current charge-discharge (GCD) tests at different rates (1C=150mAg^{-1}), with a voltage range of 3-4.6V.To further explore the lithium-ion diffusion kinetics of the material, the constant current intermittent titration technique (GITT) was used for testing on the CT2001A system. To evaluate the application potential of the material in actual pouch cells, pouch full cells (with graphite as the anode) were assembled.The crystal structures of the original lithium cobalt oxide and cPAN-LCO-3 samples were characterized by X-ray diffraction (XRD). The morphology and elemental distribution of the pristine LCO and cPAN-LCO-3 samples were observed by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The cPAN-LCO-3 samples were observed in detail using a transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition, chemical valence state and surface electronic structure changes on the surface of the original LCO and cPAN-LCO-3 samples.The delocalized $sp^2\pi$ bond of cPAN was determined by Raman spectroscopy measurement. Electrochemical polarization and impedance characteristics during cycling were analyzed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements performed with a CHI660A electrochemical workstation.The electrochemical properties of the measured samples were determined by constructing an assembly using CR2032 battery cells.

Theoretical simulation

This work was performed using first-principles calculations based on density functional theory (DFT). The optimization of the LCO crystal structure and high-precision solution of its electronic structure were both carried out within the Vienna Ab initio Simulation Package (VASP). The exchange-correlation effects between electrons were described using the Perdew-Burke-Ernzerhof (PBE) functional under the framework of the Generalized Gradient Approximation (GGA), while the electron-ion interactions were modeled via the plane-wave ultra-soft pseudopotential approach. Notably, the GGA-PBE functional exhibits inherent deviations in band gap predictions.

The diffusion behavior of Li^+ on the surfaces of $LiCoO_2$ and cPAN-LCO-3 was investigated using the Climbing Image Nudged Elastic Band (CI-NEB) method. Specifically, four intermediate diffusion sites were inserted between the initial and final states of the diffusion pathway through linear interpolation. All inserted configurations were optimized to identify the minimum-energy saddle point and diffusion path, with the relaxation process continuing until the maximum ionic force along the path was reduced to less than 0.05 eV/Å.

For both systems, the energy cutoff for the plane-wave basis set was fixed at 450 eV. The k-point grid was generated using the Monkhorst-Pack scheme and centered at the Γ point, with a grid density of 3×3×1 employed for all calculations.

The Li-ion diffusion coefficient of the pristine LCO and cPAN-LCO-3 is calculated from Warburg impedance by the formula (1):

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4C^2F^4\sigma^2} \qquad (1)$$

$$Z_{R_S} = K + \sigma\omega^{-\frac{1}{2}} \qquad (2)$$

R and T represents the gas constant and absolute temperature, respectively. A and n represents the electrode area and the number of electrons,respectively. C represents the concentration of Li^+. F is the Faraday constant. σ is calculated by the slope of Re(Z) and $\omega^{-1/2}$, the relationship is shown as formula (2).

$$D_{Li^+} = \frac{4}{\pi\tau}(\frac{m_B V_M}{M_B S})^2(\frac{\Delta E_S}{\Delta E_\tau})^2 \qquad (3)$$

In the formula (3),V_M ($cm^3\ mol^{-1}$) represents the molar volume of the sample. M_B ($g\ mol^{-1}$) and m_s (g) represent the molar mass and mass of the cathode material of the battery, respectively. S(cm^2) represents the area of the electrode; ΔE_s and ΔE_τ are respectively the average values of the charge and discharge differences. Among them, GITT conforms to the linear relationship between the square root of time ($\tau^{1/2}$) and potential energy (E).

Based on the transition state theory, the diffusion coefficient (D) of Li^+ on the surfaces of LCO and cPAN-LCO-3 is calculated using the Arrhenius-like formula. Without considering the variation of vibrational free energy, the calculation formula for the diffusion coefficient is:

$$D = \frac{d_0^2 w}{e^{\frac{E_a}{TK_B}}} \qquad (4)$$

In the formula (4), d_0 represents the diffusion distance of Li^+, w is the vibration frequency (w=1013Hz),E_a is the activation energy,K_B is the Boltzmann constant (1.38×10^{-23} J/K), and T is the absolute temperature.

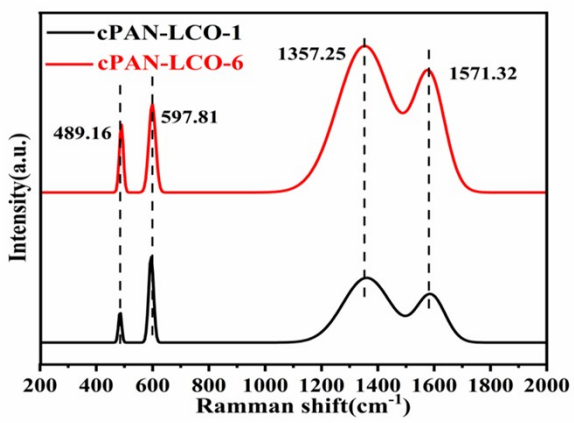

Fig.S1. Raman spectra of cPAN-LCO-1 and cPAN-LCO-6.

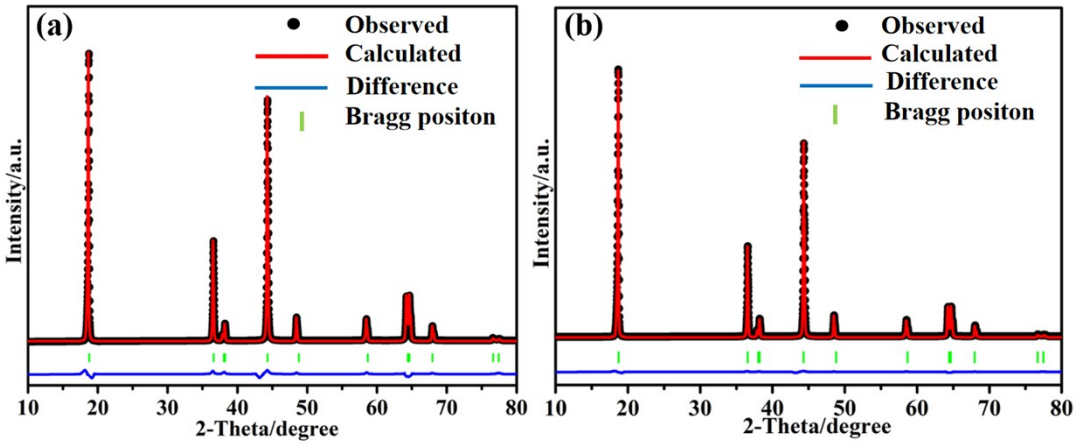

Fig.S2. (a) Rietveld refinement of pristine LCO. (b) Rietveld refinement of cPAN-LCO-3.

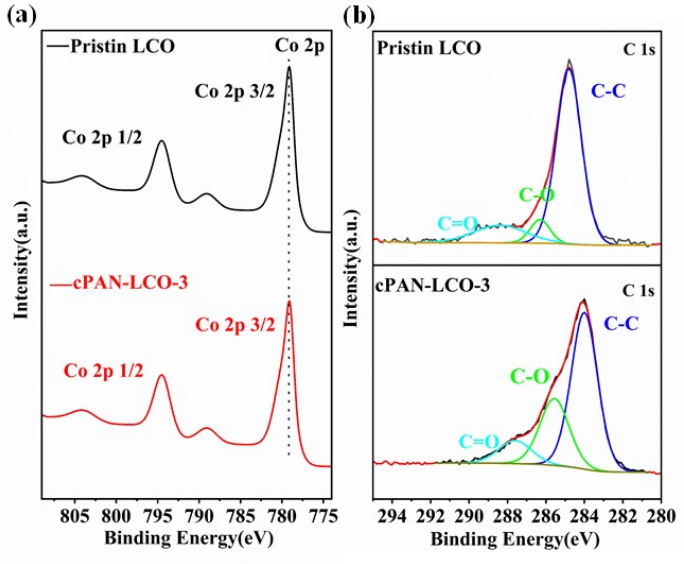

Fig.S3. (a) High-resolution Co 2p spectra of pristine LCO and cPAN-LCO-3. (b) High-resolution C 1s spectra of pristine LCO and cPAN-LCO-3.

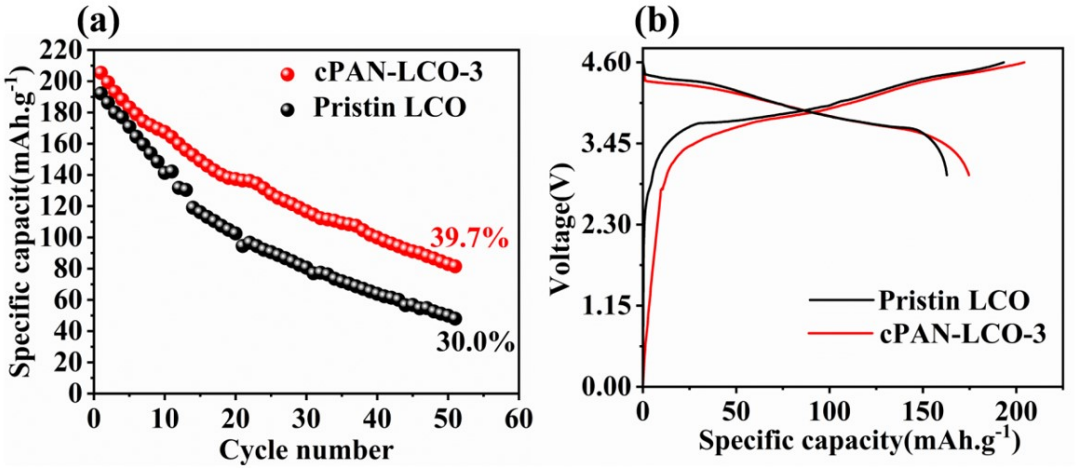

Fig.S4.(a)Specific capacity evolution of pouch cells during 50 cycles. (b) Initial charge-discharge voltage profiles of pouch cells.

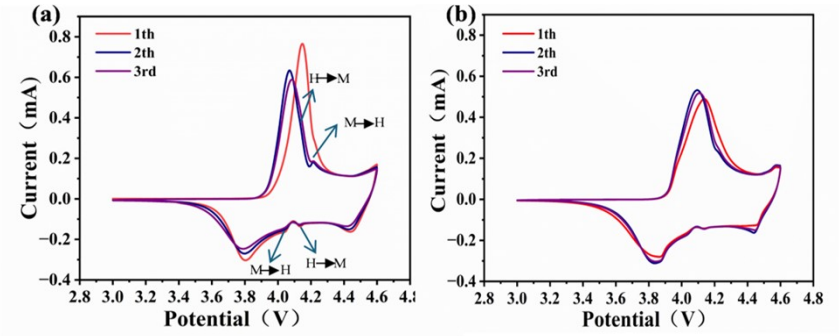

Fig.S5.(a)Cyclic voltammetry curves of (a) pristine LCO. (b)cPAN-LCO-3between 3 and 4.6 V at a scan rate of 0.1 mV/s.

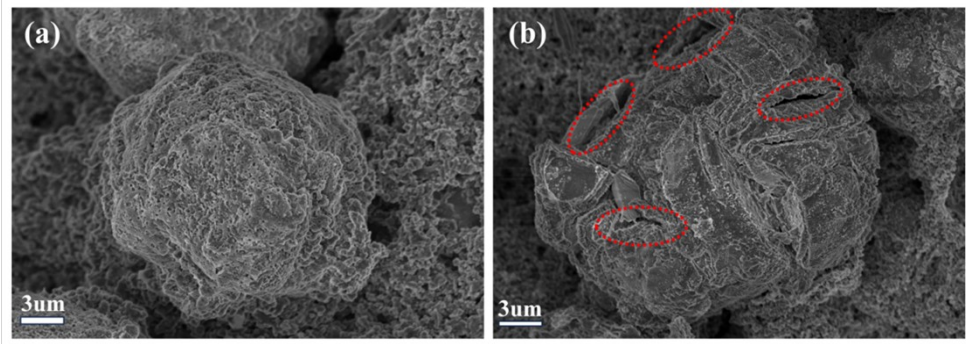

Fig.S6. SEM images of (a) cPAN-LCO-3 and (b) pristine LCO after 100 cycle.

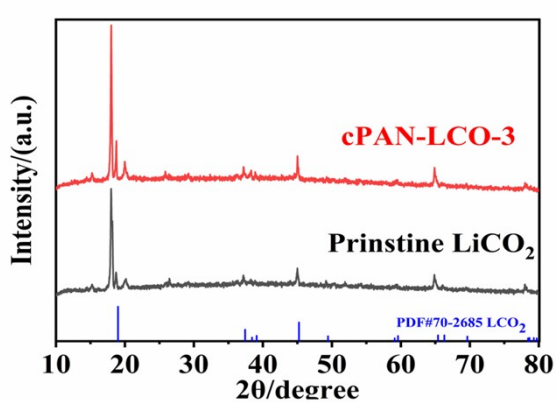

Fig.S7. XRD patterns of pristine LCO and cPAN-LCO-3 after 100 cycles.

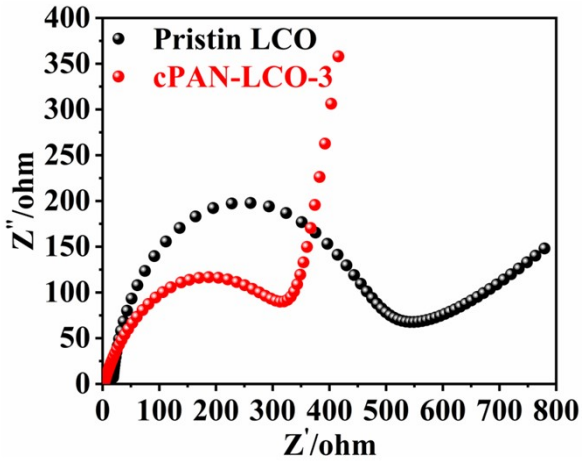

Fig.S8. EIS spectra of pristine LCO and cPAN-LCO-3 after 100 cycles.

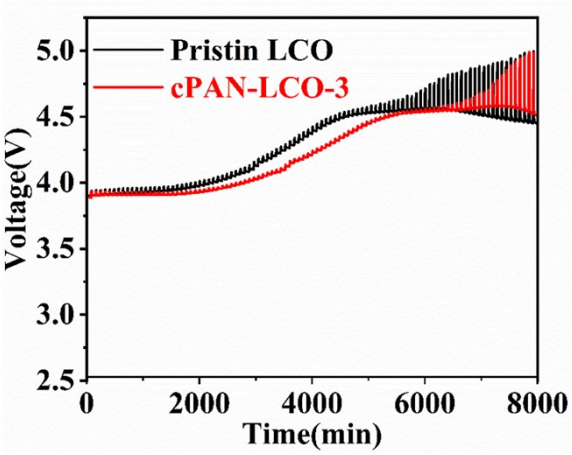

Fig.S9.Galvanostatic intermittent titration technique of Pristin LCO and cPAN-LCO-3.

Tab.S1.Comparison of recent studies about cPAN and LCO.

Literature/Research Objects	Voltage Range	Cycle number	Specific capacity retention	Specific discharge capacity(mAh.g^{-1})	References
cPAN Coated LCO	3.0-4.6V	100(0.5C)	80.1%	219.0 (0.1C)	This work
Al2O3-TiO2 coated LCO	3.0-4.5V	100(1C)	87%	192(0.1C)	[1]
LiF/PAN coated LCO	3.0-4.5V	100(0.5C)	90%	181(0.1C)	[2]
Carbon coated coated LCO	3.0-4.6V	800(1000 mAg^{-1})	84.83%	245(0.1C)	[3]

Reference

[1]Kim, J. S. *Lim, S. Ingole, R.S. Munakata, H. Kim,S.-S. Kanamura,K.* Improving the high-rate performa nce of LCO cathode by metal oxide coating: Evaluation using single particle measurement. *Journal of El ectroanalytical Chemistry* **2023,** 933:117190.

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[3]Jia,R. Yu,L. Zeng,H. Wang,C. Li, H. Xu. B.Metal-organic framework cobalt gallate derived high-voltage carbon coated lithium cobalt oxide cathode and porous carbon supported cobalt oxide anode materials for superior lithium-ion storage.*Sustain. Mater. Techno.* 2024,40 :e00978.