Supplementary Information (SI) for ChemComm.

Electronic Supplementary Information

Enhancing Moisture Stability of Halide Solid Electrolytes via Graphitic Carbon Nitride Coating: A Case Study on Li_3YCl_6

Zuxin Long,[ab] Jichang Sun,[b] Yijie Zhang,[b] Kewei Hu,[b] Zhouwei Tan,[b] Liansheng Li *[b]
and Qinghua Liang *[b]

a. College of Rare Earths, Jiangxi University of Science & Technology, Ganzhou, 341000, China.

b. Key Laboratory of Rare Earths, Ganjiang Innovation Academy, Chinese Academy of Sciences, Ganzhou, 341100, China.

Email: lsli@gia.cas.cn; qhliang@gia.cas.cn

Experimental section

Material Synthesis

The halide solid electrolyte LYC was synthesized by a facile mechanochemical method. LiCl (99 %, Aladdin) and YCl_3 (99.99%, Aladdin) were mixed in a molar ratio of 3:1 and added to a 50 mL ZrO_2 ball mill jar. The mixture was then homogenized using ZrO_2 balls (Φ = 10 mm, 8 mm, and 5 mm) with a weight ratio of 2:3:5, operating at a planetary mill speed of 100 rpm (200 rpm for self-rotation) for 2 hours. Subsequently, the mixture was further milled at 550 rpm (1,100 rpm for self-rotation) for 12 h in a cyclic pattern: 2 min of milling, 1 min of rest, 2 min of reverse milling, and 1 min of rest. All operations, including weighing, ball milling, collection, and storage, were conducted within an argon-filled glove box.

g-C_3N_4 was prepared through the pyrolysis of urea. 10 g of urea (99%, Macklin) was placed in a 50 mL crucible, which was then placed in a muffle furnace and heated in air at a rate of 2°C/min to 520°C, maintained for 5 hours, and allowed to cool naturally to room temperature to yield g-C_3N_4.

The LYC@GCN samples were obtained by ball milling g-C_3N_4 powder and LYC powder in a specific mass ratio within an argon-filled glove box, mixed at 400 rpm (800 rpm for self-rotation) for 6 h in a cyclic pattern: 2 min of milling, 1 min of rest, 2 min of reverse milling, and 1 min of rest. resulting in LYC@GCN composites. The weighing and ball milling processes were also conducted within the glove box.

Exposure experiments

Exposure experiments under various atmospheres and humidity conditions were conducted using a homemade constant humidity test system. The target gas was introduced for 1 hour to stabilize the atmosphere before the sample chamber was connected. A specific mass of HSSEs was uniformly placed in a plastic bottle within the glove box, which was then sealed and removed from the glove box. The chamber was evacuated and connected to the end of the constant humidity testing system, and the exposure time was recorded. To create the target humidity atmosphere, dry Ar/Air/O_2/CO_2 was introduced into ultrapure water to generate high-humidity gas, which was subsequently mixed with dry Ar/Air/O_2/CO_2 to achieve the target humidity. The humidity was monitored by a hygrometer (Shandong Renke Control Technology Co., Ltd., accuracy ±2% relative humidity). After the specified exposure period, the gas was switched to high-purity argon to purge the sample chamber, which was then returned to the glove box for sample collection. Throughout the entire process, the samples were only exposed to high-purity argon and the target gas.

The mass time curves were obtained using a Mettler Toledo balance and associated software. A 50 mg portion of powder samples was placed on the balance, and their mass was automatically recorded at 2-minute intervals.

Material characterization

X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer with Cu Ka radiation (λ = 1.5418 Å), and the powder samples were sealed with a protective film under an Ar atmosphere to avoid air exposure (Fig. S1a). It should be noted that the protective film made of polyethylene (PE) exhibits a distinct peak at approximately 21.5°, which aligns with the XRD data reported in the literature.[1] The in situ XRD analysis was conducted without protective films, where the sample was compressed into a bulk under a pressure of 4 tons and directly subjected to continuous testing on the diffractometer. X-ray photoelectron spectroscopy (XPS) data was collected by operating an AXIS SUPRA+ spectrometer (Shimadzu Corporation). Sample preparation was carried out in a glove box and a vacuum transfer cassette was used for XPS sample loading. Scanning electron microscopy (SEM) images were collected using a JSM-IT800 (JEOL) equipped with energy dispersive X-ray spectroscopy (EDS; OXFORD instruments ULTIM MAX 100). The preparation of the samples and the gold sputtering process were both conducted within the glove box.

Electrochemical characterization

The ionic conductivity of the electrolyte was measured by the cold press method. A 150 mg aliquot of electrolyte powder was placed in a 10 mm diameter PEEK mold, and a pair of stainless-steel plungers applied a pressure of 4 tons (≈ 500 MPa). The Nyquist plot was recorded using an electrochemical workstation (VSP-300) over a frequency range of 7 MHz to 1 Hz. The ionic conductivity was calculated using the formula: $\sigma = d/AR$, where d is the pellet thickness, A is the pellet cross-sectional area, and R is the resistance. The activation energy was determined by measuring the ionic conductivity from 20 °C to 60 °C and calculated using the Arrhenius equation: $\sigma T = \sigma_0 \exp(-Ea/k_B T)$, where σ is the ionic conductivity, σ_0 is the pre-exponential factor, T is the absolute temperature, and k_B is the Boltzmann constant.

The electrochemical stability was evaluated by cyclic voltammetry using an electrochemical workstation (VSP-300) with a $LiIn|Li_3YCl_6|Li_3YCl_6$-SP cell in a scanning range of 0 to 5 V (vs. Li^+/Li) at 0.1 mV s^{-1}. To evaluate cycling performance, ASSLBs with a configuration of cathode||halide electrolyte||LiIn were fabricated. The assembly of the ASSLBs is performed in an Ar glove box using mold battery. The composite cathode, composed of 70:30 (w/w) LCO and LYC, was prepared by manual grinding for 1 hour. Firstly, 100 mg of solid electrolyte was weighed, loaded into the ceramic liner of the mold, and pressurized at 1 ton. Subsequently, 10 mg of the composite cathode was evenly spread on the electrolyte layer and pressurized at 4 tons. Finally, indium foil (50 µm thick, 9 mm diameter) and lithium foil (50 µm thick, 6 mm diameter) were sequentially placed on opposite sides of the electrolyte layer, and the assembly was compressed at 1.5 tons and maintained under pressure. The ASSLBs were tested in

2.38–3.58 V (vs Li^+/LiIn) and at 25°C using a LAND CT3002A battery test system.

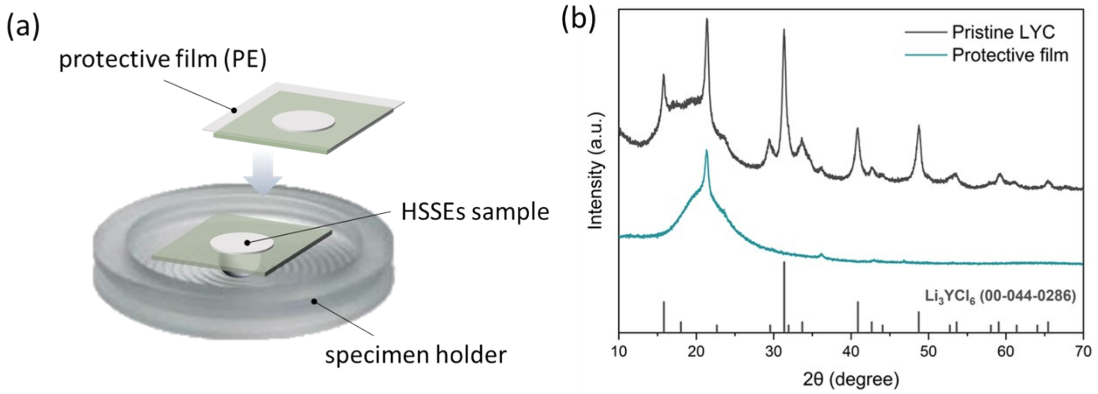

Fig. S1 (a) Schematic illustration of ex situ XRD sample holder. (b) The XRD pattern of synthesized LYC.

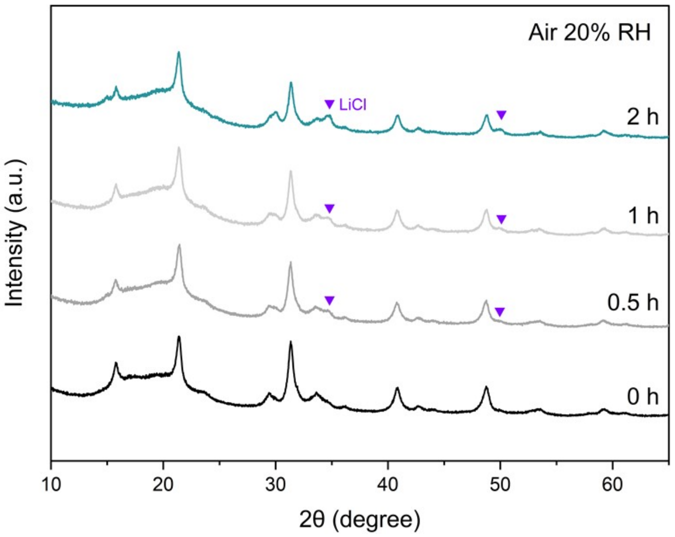

Fig. S2 The XRD patterns of 200 mg LYC exposed in humid air (20 °C, 20% RH) for different times.

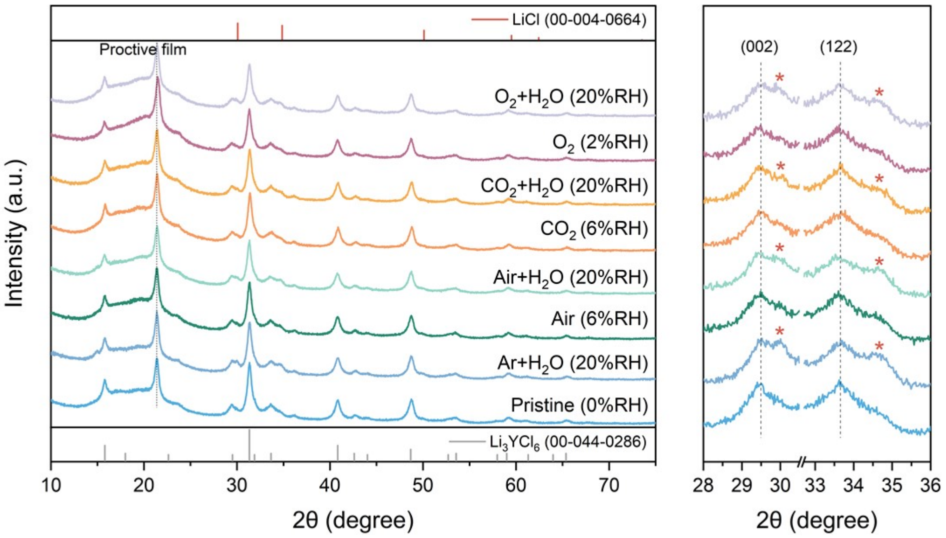

Fig. S3 XRD patterns of 200 mg LYC after exposure to different atmospheres without or with water vapor (20% RH), the purchased dry air, O_2 and CO_2 contain trace moisture, the actual humidity is indicated within parentheses.

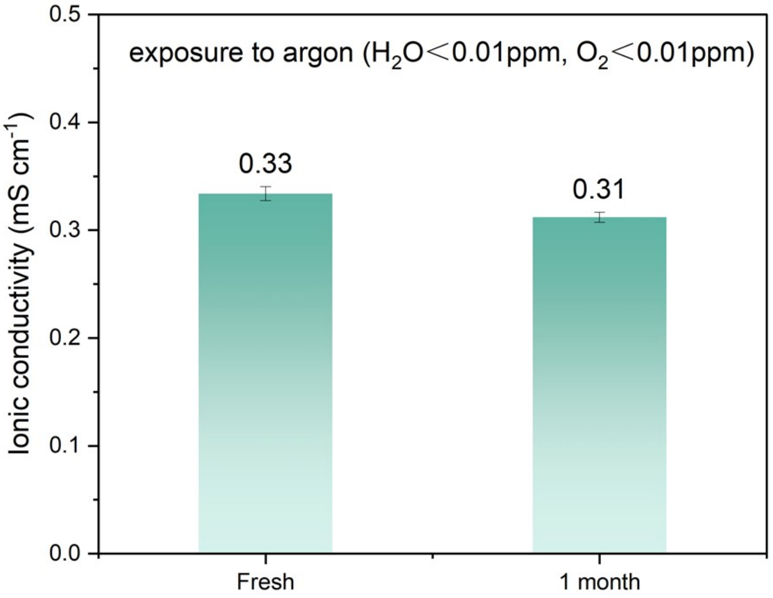

Fig. S4 The ionic conductivities of LYC before and after prolonged exposure to Ar for 1 month.

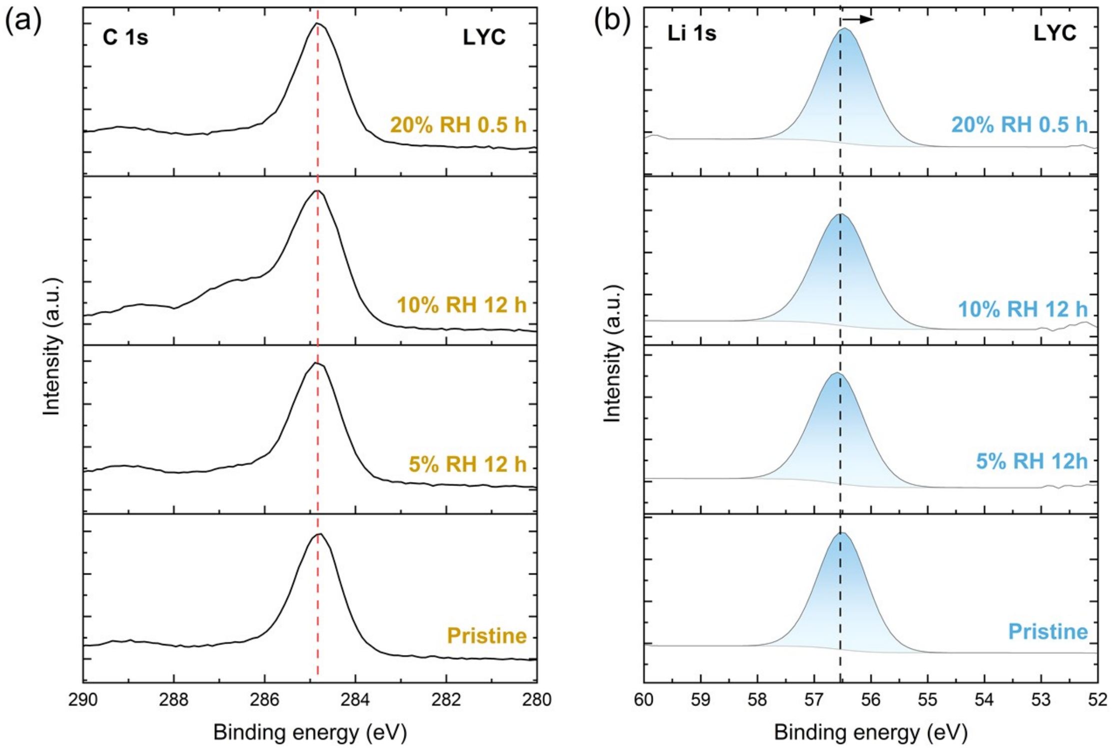

Fig. S5 (a) XPS C 1s spectra and (b) Li 1s spectra of LYC after exposure to Ar with different water vapor content and exposure times.

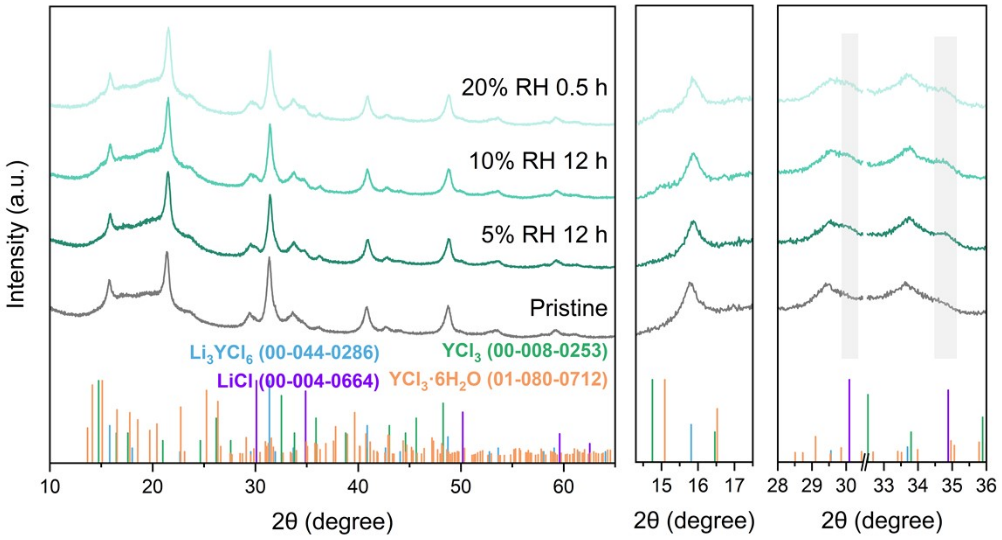

Fig. S6 XRD patterns of 200 mg LYC after exposure to Ar with different water vapor content and exposure times.

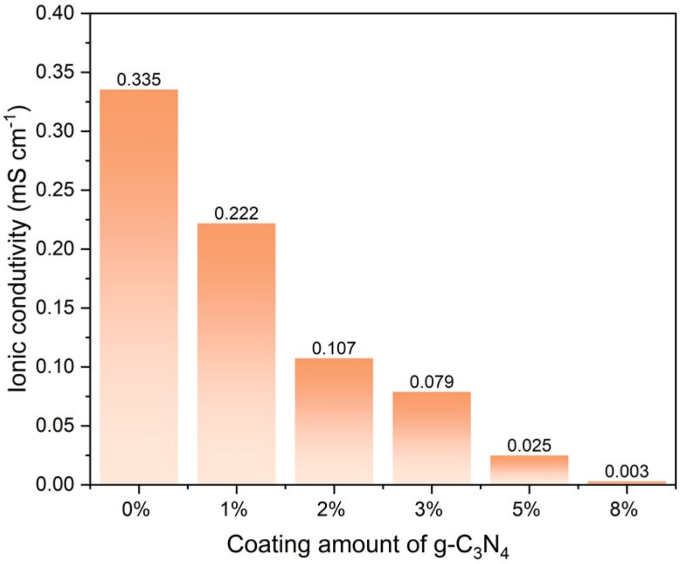

Fig. S7 The RT ionic conductivities of LYC with different coating contents.

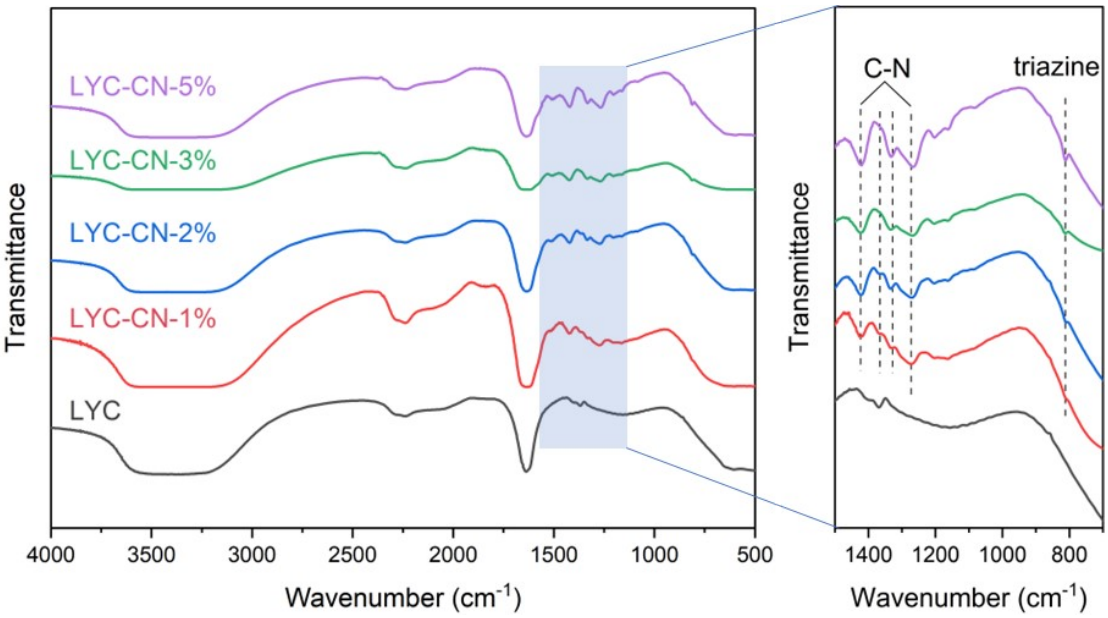

Fig. S8 FTIR spectra of LYC with different g-C_3N_4 coating amount.

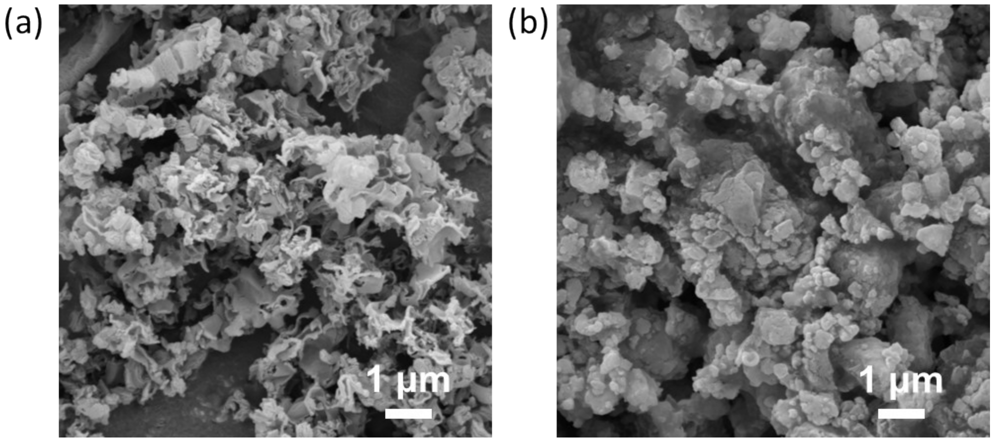

Fig. S9 SEM images of synthesized (a) g-C_3N_4 and (b) LYC samples.

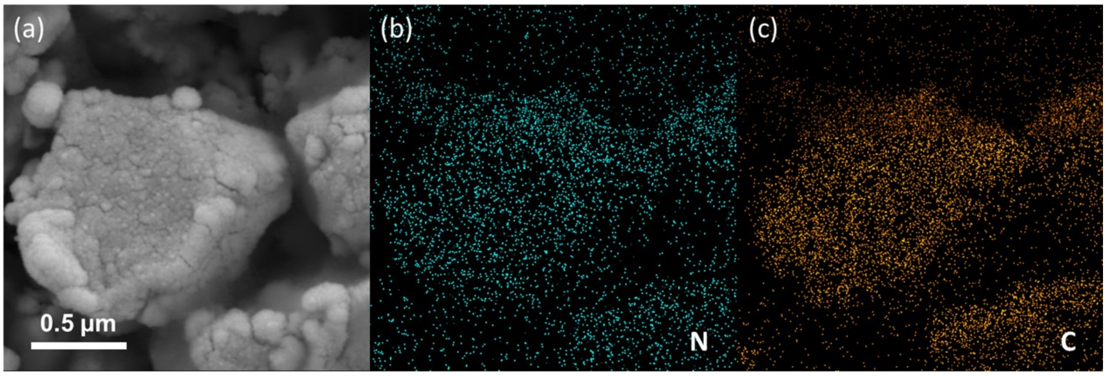

Fig. S10 (a) SEM image at high magnification, and EDS mapping of (b) N and (c) C of LYC@GCN

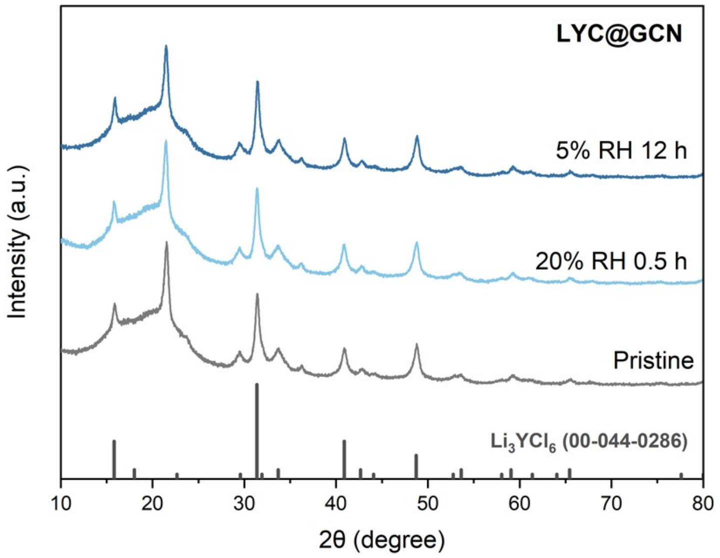

Fig. S11 XRD patterns of 200 mg LYC@GCN after exposure to Ar with 20% RH for half an hour and 5% RH for 12 hours.

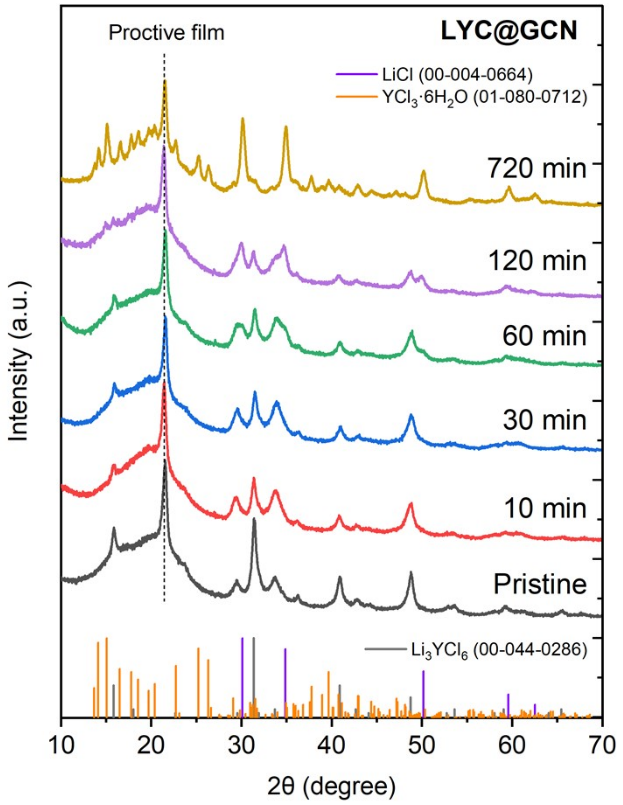

Fig. S12 Ex-situ XRD patterns of 30 mg LYC@GCN powder exposed in humid air (20 °C, 20% RH) after different times.

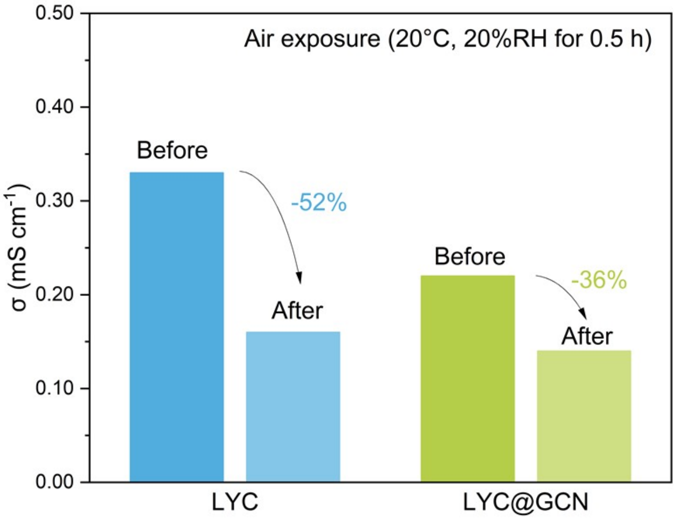

Fig. S13 Changes in ionic conductivities of LYC and LYC@GCN before and after air exposure for 0.5 h.

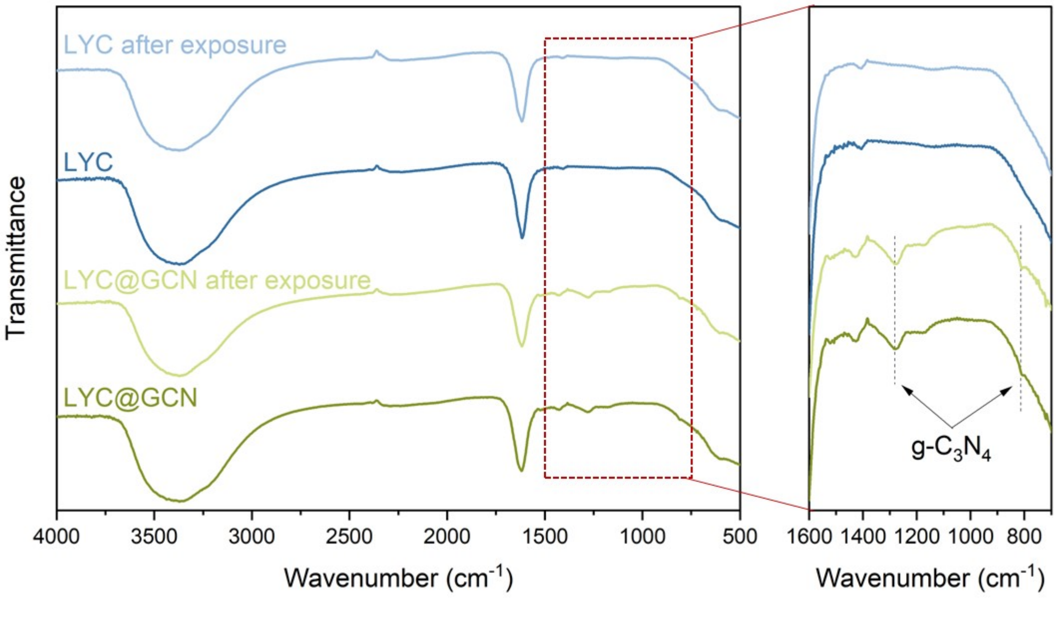

Fig. S14 FTIR spectra of LYC and g-C_3N_4 coated LYC before and after air exposure upon 20% RH for 30 min

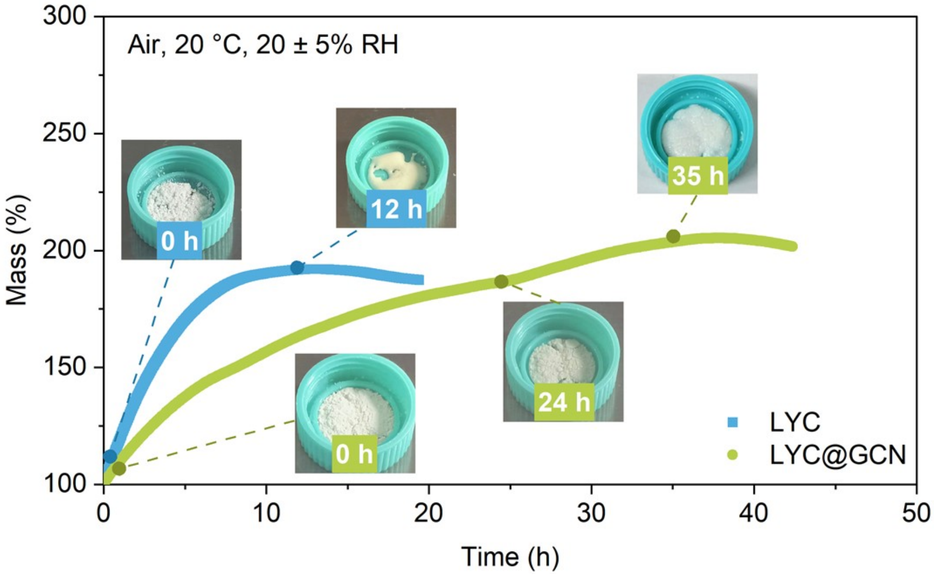

Fig. S15 Mass-time curves and corresponding optical photographs of LYC powders before and after coating, operate in ambient air (20 °C, 20 ± 5% RH).

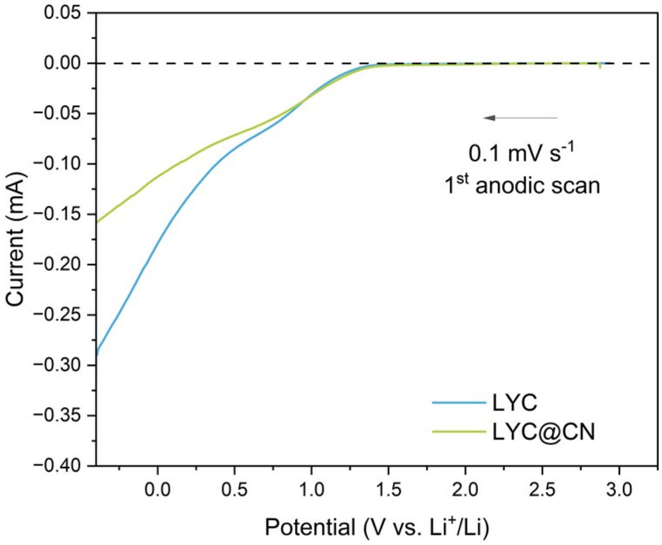

Fig. S16 Linear sweep voltammetry of LYC and LYC@GCN in first anodic scan.

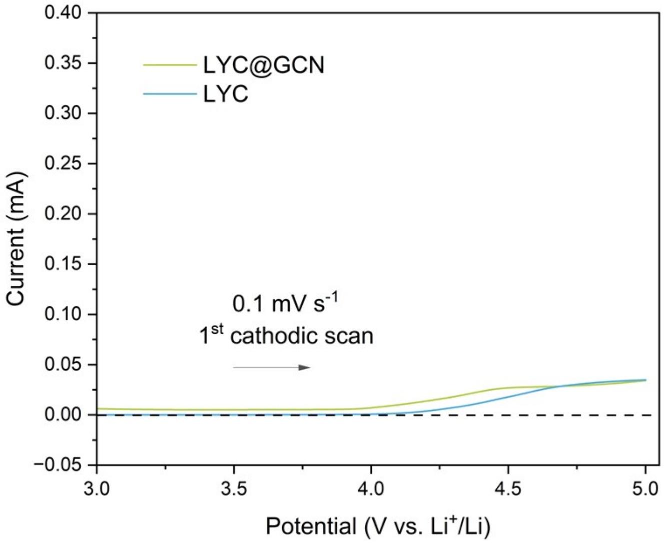

Fig. S17 Linear sweep voltammetry of LYC and LYC@GCN in first cathodic scan.

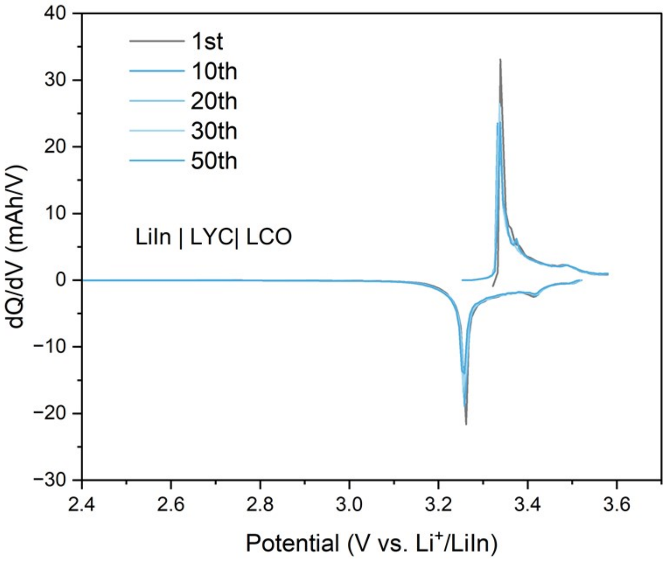

Fig. S18 The dQ/dV curves for LCO cathode with LYC electrolytes during cycling.

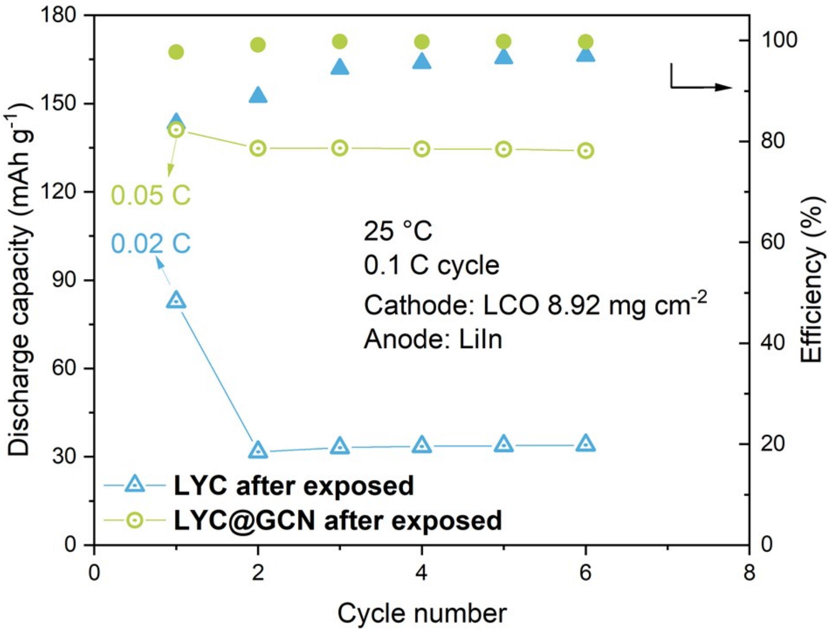

Fig. S19 Cycling stability of the LCO-cells employing humidity exposed (20% RH for 0.5 h) LYC and LYC@GCN electrolytes at 25 °C and 0.1 C.

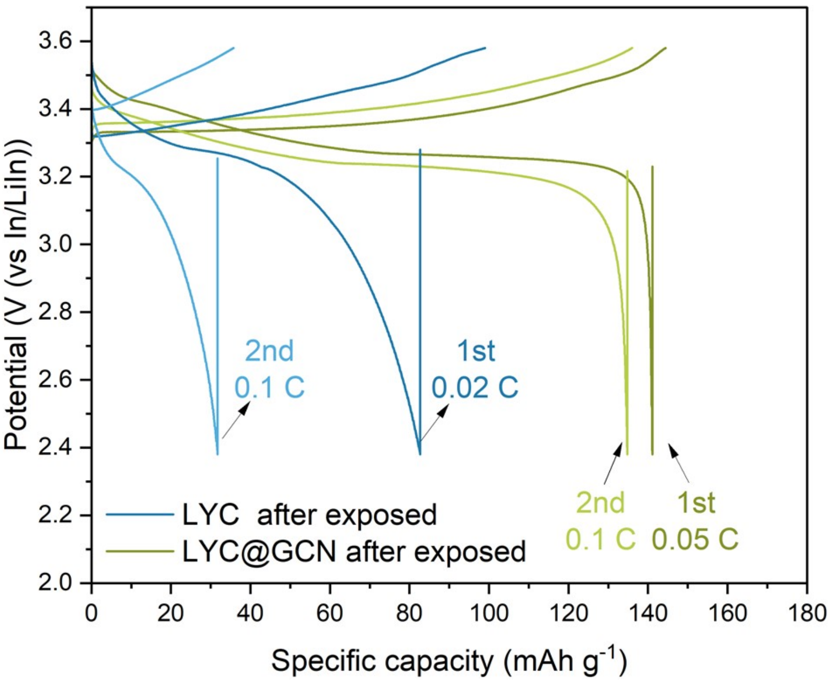

Fig. S20 The first two voltage–capacity curves of the LCO-cells employing humidity-exposed (20% RH for 0.5 h) LYC and LYC@GCN electrolytes.

Table S1. Fitting parameters for XPS spectra of LYC after exposure to Ar with different water vapor content and exposure times shown in Fig. 2b-c.

		Y 3d	**Cl 2p**
Pristine	Position / eV	159.0	198.8
	FWHM / eV	1.16	1.17
5% RH 12 h	Position / eV	159.0	198.9
	FWHM / eV	1.14	1.12
10 % RH 12 h	Position / eV	159.1	199.0
	FWHM / eV	1.22	1.19
20 % RH 0.5 h	Position / eV	158.9	198.7
	FWHM / eV	1.16	1.14

References

1. Y. Yang, Z. Wang, C. Du, B. Wang, X. Li, S. Wu, X. Li, X. Zhang, X. Wang, Y. Niu, F. Ding, X. Rong, Y. Lu, N. Zhang, J. Xu, R. Xiao, Q. Zhang, X. Wang, W. Yin, J. Zhao, L. Chen, J. Huang and Y.-S. Hu, *Science*, 2024, **385**, 744-752.