Supporting Information

Sustainable release of $LiNO_3$ in carbonate electrolytes for stable lithium metal anodes

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1. Experimental Section

1.1 Fabrication of PAN/LNO/PP separator

PAN/LNO nanofibers were fabricated using electrospinning. Specifically, 0.41 g of PAN was dissolved in 5 mL of N,N-dimethylformamide to create the precursor solution. Separately, 0.5 g of LNO was combined with 5 mL of the above solution to produce a slurry, which was then electrospun to obtain PAN/LNO/PP. During electrospinning, a high voltage of 15 kV was applied between a needle and a PP separator situated on a rotating drum (rotation speed: 500 rpm; distance: 16 cm), with a solution injection rate of 1 mL h^{-1}. To mitigate the potential impact of H_2O on LNO stability, the ambient humidity was lowered to below 30% using a dehumidifier prior to spinning. Subsequently, the PAN/LNO/PP separator was dried at 60 ℃ for 12 h in a vacuum. It was then sectioned into 18 mm diameter pieces, ready for cell assembly. The areal mass loading of LNO inside a coin cell is ~1.44 mg.

1.2 Material characterizations

SEM images were collected using a scanning electron microscopy (Verios G4) at

an accelerating voltage of 3 kV. XRD patterns were measured on a Bruker D8 advance diffractometer with Cu Kα radiation. Contact angles were obtained using a drop shape analyzer system (DSA1005). XPS characterization was conducted on a Kratos AXIS Ultra DLD with Al (Kα) source and argon ion sputter gun. The binding energy values of all the data were referenced to the C 1s peak (284.6 eV). All the electrodes after cycling were rinsed in DMC several times to remove any residual salts and dried before characterizations.

1.3 Electrochemical measurements

All cells were assembled in an Ar-purified glovebox (H_2O < 0.1 ppm and O_2 < 0.1 ppm) and subsequently tested using a NEWARE battery testing system. Li|Cu cells utilized Cu and Li as the positive and negative electrodes, respectively. The electrolyte comprised 1 M $LiPF_6$ in EC:DEC with 5% FEC (1:1, v/v) and was added in a volume of 60 μL. The PAN/LNO/PP separator was integrated into a 2025 cell, resulting in the Li|Cu cell, hereafter referred to as PAN/LNO/PP. For comparison, Li|Cu cells were also assembled using PP. For Li|Li cell assembly, Li foil served as both the anode and cathode. For full-cell assembly, LFP with an areal loading of 3 mg cm^{-2}, was chosen as the cathode. The slurry was formulated by blending LFP, acetylene black, and polyvinylidene fluoride (in an 8:1:1 weight ratio) in N-methylpyrrolidone. This mixture was then spread onto carbon-coated aluminum foil and dried at 60 °C overnight in a vacuum. The cycling and rate tests for the full cells were conducted within a potential range of 2.5-4.0 V.

2. Supplementary Figures

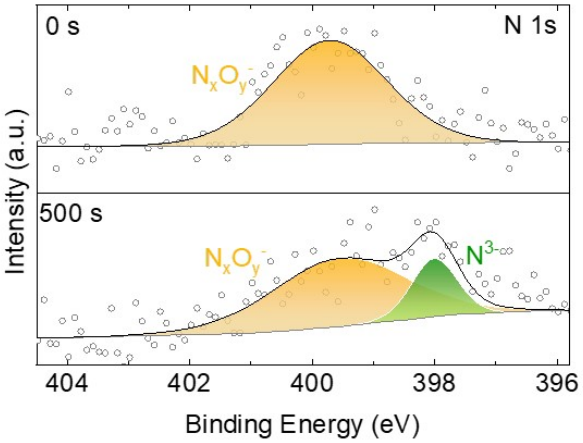

Figure S1. N 1s XPS spectra of the cycled Li metal anode with PAN/LNO/PP sputtering for 0 and 500 s.

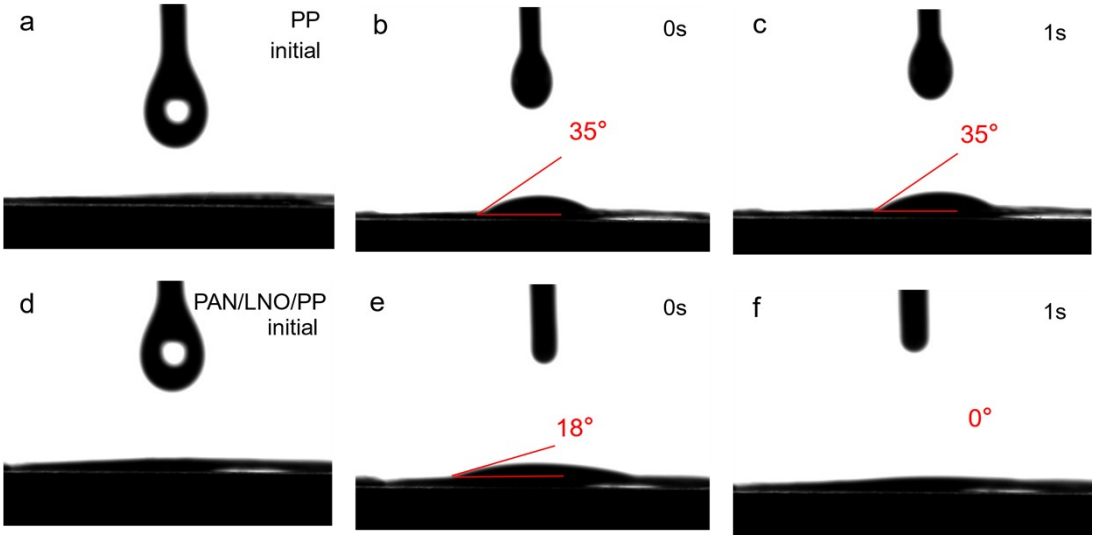

Figure S2. Contact angle tests of (a-c) PP and (d-f) PAN/LNO/PP.

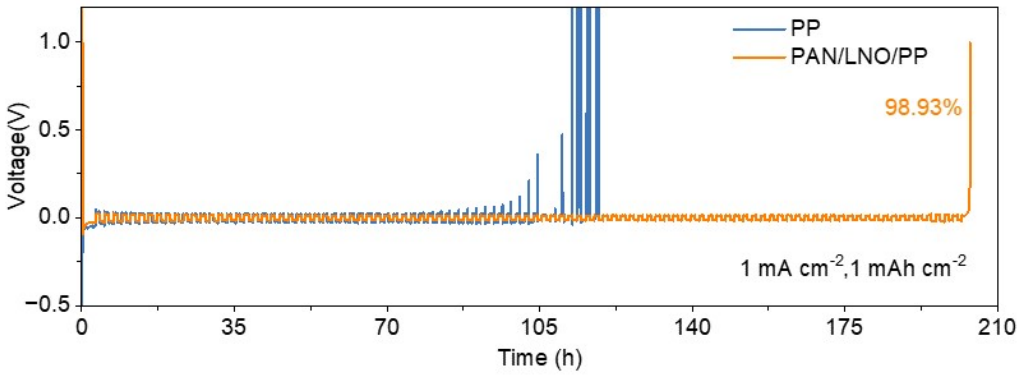

Figure S3. Aurbach CE test of Li|Cu cells assembled with PP and PAN/LNO/PP for 100 cycles.

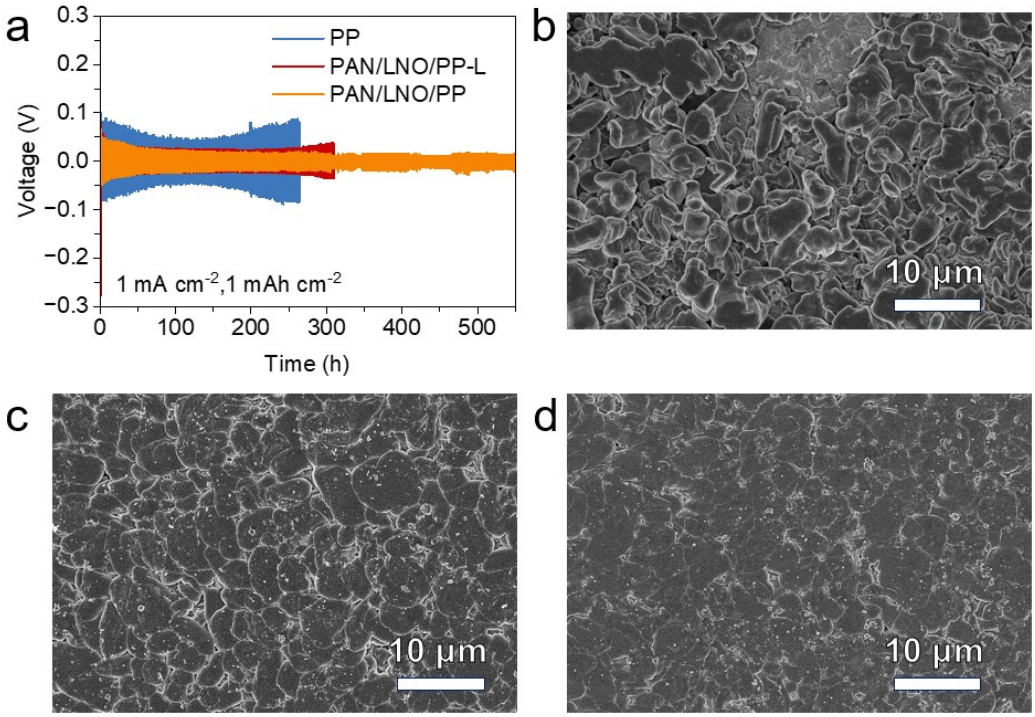

Figure S4. (a) Cycling performance of Li|Li symmetrical cells assembled with PP and PAN/LNO/PP-L and PAN/LNO/PP. Morphologies of electrodeposited Li on copper foil (b) without and (c) with PAN/LNO/PP interlayer, and (d) with PAN/LNO/PP-L at 1 mA cm^{-2}, 3 mAh cm^{-2}.

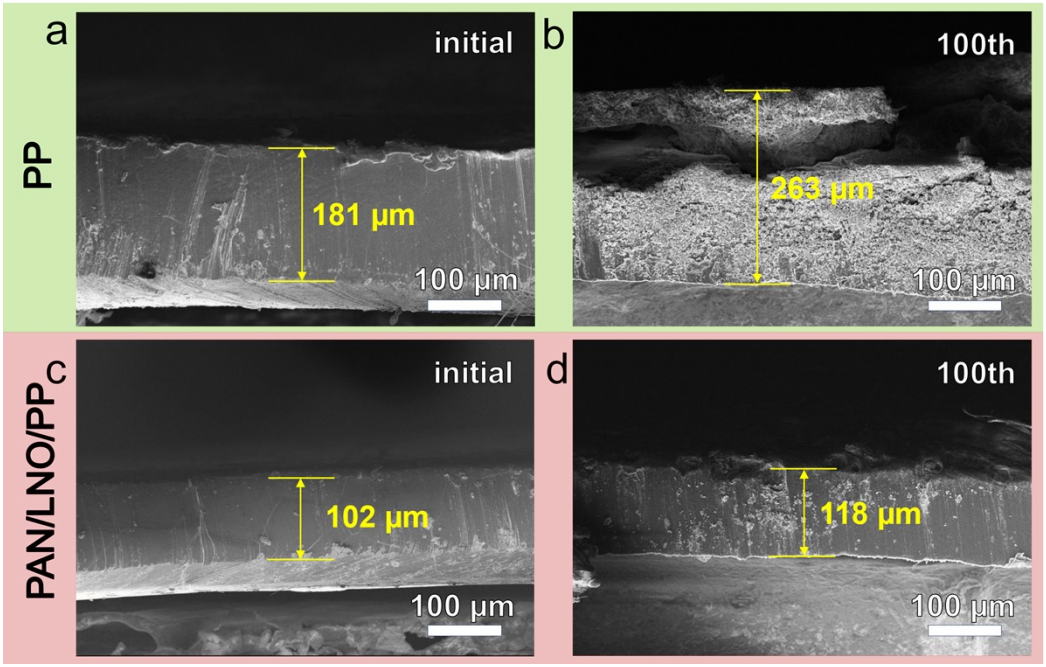

Figure S5. Cross-section SEM images of initial (a) PP and (c) PAN/LNO/PP. Cross-section SEM images (b) PP and (d) PAN/LNO/PP after 100 cycles.

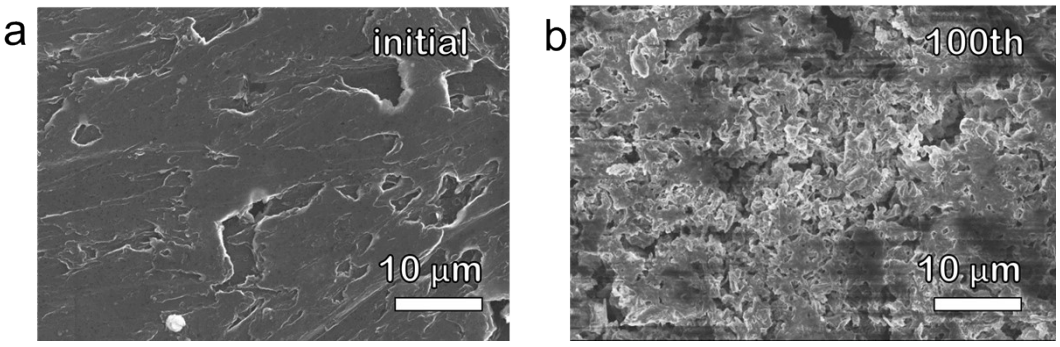

Figure S6. SEM of (a) initial Li foil and (b) after 100th cycles assembled with LNO in the electrolyte.