Supporting Information

Dual-Functional Gel-Polymer Electrolyte for Lithium Ion Batteries with Superior Rate and Safety Performances

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Battery type	NCA/liquid electrolyte/graphite	NCA/liquid electrolyte/(graphite- Si/C)	NCA/gel-polymer electrolyte/graphite	NCA/gel-polymer electrolyte/(graphite- Si/C)	
Abbreviatio n	NLG	NLGS	NPG	NPGS	
Cathode	91 wt% LiNi _{0.85} Co _{0.15} Al _{0.05} O ₂ ; 1 wt% CNT; 4 wt% Super-P; 4 wt% PVDF				
Anode	93 wt % graphite; 1.6 wt % CMC; 3 wt % Super-P; 2.4 wt % SBR;	93 wt % graphite- Si/C (Si is around 4 wt %); 1.6 wt % CMC; 3 wt % Super-P; 2.4 wt % SBR;	93 wt % graphite; 1.6 wt % CMC; 3 wt % Super-P; 2.4 wt % SBR;	93 wt % graphite- Si/C (Si is around 4 wt %); 1.6 wt % CMC; 3 wt % Super-P; 2.4 wt % SBR;	
Electrolyte composition	Liquid electrolyte: 1M LiPF ₆ solution dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC) (volume ratio of EC:DEC:EMC = 1:1:1)		1.5 wt % gel-polymer precursors PETEA and 0.1 wt % AIBN in the liquid electrolyte		
Electrolyte amount (g)	7.60	7.63	7.77	7.87	

Table S1. Detailed parameters of the assembled full cells



Fig. S1. Linear sweep voltammetry of liquid electrolyte, liquid electrolyte+0.1% AIBN, liquid electrolyte+0.1% AIBN stored at 70 °C for 30min, and GPE at a scan rate of 0.2 mV s⁻¹ using stainless steel as the working electrode and Li as the counter and reference electrodes.



Fig. S2. Particle size distributions of (a) graphite powder and (b) graphite-Si/C composites. Their corresponding SEM images are shown as insets. (c) Comparison of electrochemical performance for graphite and graphite-Si/C anodes. (d) Electrochemical performance of NCA cathode.

The graphite particle has a size distribution of $10~30\mu$ m (**Fig. S2**a). The composites composed of graphite particles and Si nanoparticles possess a similar size distribution (i.e., $10~30\mu$ m) (**Fig. S2**b). Si nanoparticles were mainly distributed in the interspace between graphite particles (inset in **Fig. S2**b). This interspace plays an important role in not only buffering the large volume change of Si nanoparticles during cycling but also providing an electrical conduction pathway. The initial charge capacity of graphite-Si/C was 505 mAh g⁻¹ and the graphite anode delivered a capacity of 328 mAh g⁻¹ (**Fig. S2**c). Both graphite-Si/C and graphite exhibited a high initial columbic efficiency (ICE) of ~ 90%. The higher ICE of anode material is of importance in improving the energy density of batteries. On the other hand, the spherical NCA secondary particles were employed as active cathode material, delivering an

initial discharge capacity as high as 195 mAhg⁻¹ at 0.1 C-rate and a high ICE of 90% (**Fig. S2**d). The XRD pattern showed that the NCA has well-defined layerd structures (**Fig. S3**).



Fig. S3. Characterization of cathode materials. (a-c) SEM images of NCA cathode material at different magnification. (d) XRD pattern of NCA cathode.



Fig. S4. Digital images of gel electrolyte.



Fig. S5. The experimentally measured and fitted curves of the electrochemical impedance spectra of fresh batteries.

	NIDC	NH C	NDCC	NH GG
	NPG	NLG	NPGS	NLGS
$R_b(\mathrm{m}\Omega)$	23.2	21.5	22.9	21.6
R_{sei} (m Ω)	1.38	3.06	3.2	2.5
$R_{ct}(\mathrm{m}\Omega)$	23.44	19.8	18.1	18.2
R_{total} (m Ω)	48.02	44.36	44.2	42.3

Table S2. Simulated results from EIS curves in Fig. S5 by Z-view software



Fig. S6. Digital images of nail penetration tests. (a, b) The equipment. (c) Cell with GPE after penetration. (d) Cell with liquid electrolyte after penetration.



Fig. S7. Thermogravimetric analysis (TGA) of liquid electrolyte with commercial separator and gel polymer electrolyte with commercial separator under an air flow at a rate of 10 $^{\circ}$ C min⁻¹



Fig. S8. SEM images of cathode materials before and after cycling. (a, b) Fresh cathode before cycling. (c, d) Cycled cathode with PETEA-based GPE. (e, f) Cycled cathode with liquid electrolyte.



Fig. S9 Cross-sectional SEM images of (a) graphite-Si/C anode and (b) NCA cathode with three-dimensional network of the PETEA-based GPE.

The gas evolution is closely related to the SEI and by-products formation. Typically, the solvents of electrolyte decomposed on the electrode surface to form SEI film, which can be described by the following decomposition reactions:

EMC:

 $EMC + 2e^{-} + 2Li^{+} \rightarrow LiO(C=O)CH_{3} + CH_{3}CH_{2}OLi$

EC:

$$\begin{split} & \text{EC} + 2e^{-} + 2\text{Li}^{+} \rightarrow \text{Li}_{2}\text{CO}_{3}\downarrow + \text{C}_{2}\text{H}_{4}(g)\uparrow \\ & \text{EC} + 2e^{-} + 2\text{Li}^{+} \rightarrow \text{CH}_{3}\text{OLi}\downarrow + \text{CO}(g)\uparrow \\ & 2\text{EC} + 2e^{-} + 2\text{Li}^{+} \rightarrow \text{C}_{2}\text{H}_{4}(g)\uparrow + (\text{CH}_{2}\text{OCO}_{2}\text{Li})_{2}(s)\downarrow \\ & (\text{CH}_{2}\text{OCO}_{2}\text{Li})_{2} + \text{H}_{2}\text{O} \rightarrow \text{Li}_{2}\text{CO}_{3}\downarrow + (\text{CH}_{2}\text{OH})_{2}\downarrow + \text{CO}_{2}(g)\uparrow \end{split}$$

DEC:

DEC + e^{-} + 2Li⁺ \rightarrow C₂H₅OCO₂Li (s) \downarrow + CH₃• DEC + e^{-} + 2Li⁺ \rightarrow C₂H₅OLi (s) \downarrow + C₂H₅CO₂• C₂H₅CO₂• + CH₃• \rightarrow CH₃OCO₂CH₃ CH₃• + ¹/₂ H₂• \rightarrow CH₄ CH₃• + CH₃• \rightarrow C₂H₆ DEC + 2 e^{-} + 2Li⁺ \rightarrow CO (g) \uparrow + C₂H₅OLi (s) \downarrow It can be seen that Li_2CO_3 primarily forms from the solvents reacted with Li^+ . The main components of CH₄, CO₂ and CO and C₂H₄ come from the decomposition of DEC and EC. More detailed reaction process can be found in the reference listed below.¹⁻³



Fig. S10 XPS of O 1s of cycled graphite anode (a) and C 1s of cathode from NLGS and NPGS before and after cycling at 45 $^{\circ}$ C



Fig. S11 FTIR of NCA cathode from NLGS and NPGS before and after cycling at 45 $^{\circ}C$



Fig. S12 (a) Incremental capacity analysis (ICA) analysis (dQ/dV) of NLGS battery; and (b) ICA analysis (dQ/dV) of NPGS battery.

In order to uncover the evolution mechanism of electrochemical behavior and the change of cell chemistry for liquid electrolyte- and GPE-based batteries upon cycling, incremental capacity analysis (ICA) were conducted on the NLGS and NPGS batteries before and after cycling at 45 °C. **Fig. S12a-S12**b compare the ICA curves of NLGS and NPGS batteries. It is notable that the shape of the ICA curves correlated well with the previously reported results,⁴ suggesting that four reversible dQ/dV peaks can be identified during the charge/discharge process. The peak at 4.1 V (peak A) represents a single-phase solid solution and the two peaks followed (peaks B and C) come mainly from the first-order phase transformation either from anode or cathode. Peak D at 3.35V is from the NCA cathode material. After cycling, an obvious reduction in the peak intensities was observed for NLGS and NPGS batteries, implying the loss of active materials attributed to the loss of electrical contact of active materials in the local area ⁵ and crystal structure degradation of active materials. ⁶ It is noteworthy that some obvious differences were seen between NLGS and NPGS batteries. For the NLGS battery, the area of peak D and the corresponding oxidation peak shrink much heavily than that of NPGS battery. The decay of peak D reflects that the discharge was finished prematurely before a full Li insertion into the NCA cathode, ⁴ which may be resulted from the reversible lithium consumption and the increase of internal resistance. Typically, side-reactions occurred at the electrolyte/electrode interface can cause electrolyte decomposition and gassing, which in turn results in irreversible lithium consumption, electrode decay and SEI growth. ³ Thus, the much smaller depression of peak D observed in NPGS battery implies that GPE can effectively inhibit the interfacial side-reactions and preserve the electrode.

References

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