Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

In situ surface-enhanced Raman spectroelectrochemistry reveals the molecular conformation of electrolyte additives in Li-ion batteries

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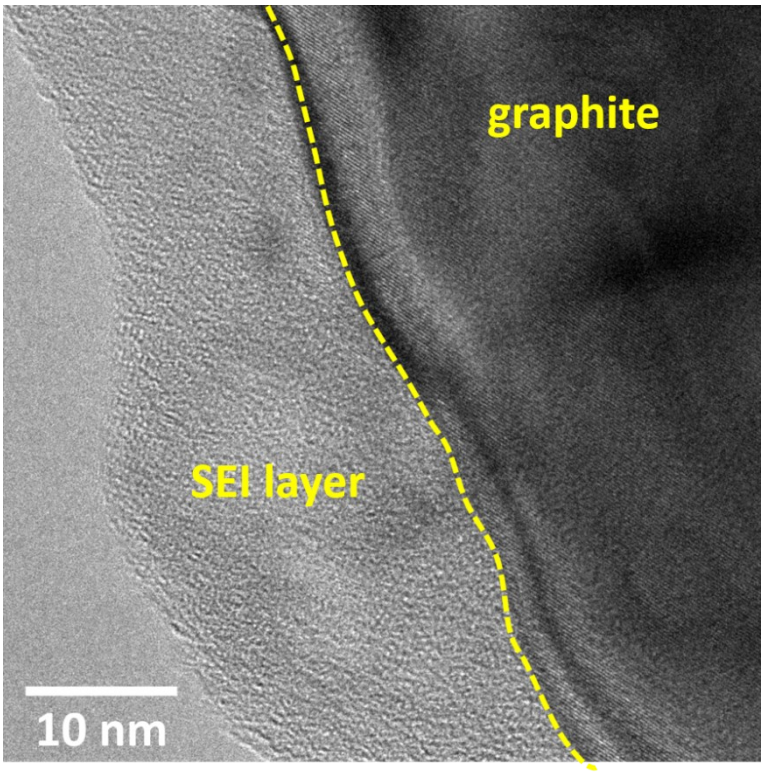

Figure S1. HRTEM image of graphite electrode without RhB after 3 cycles.

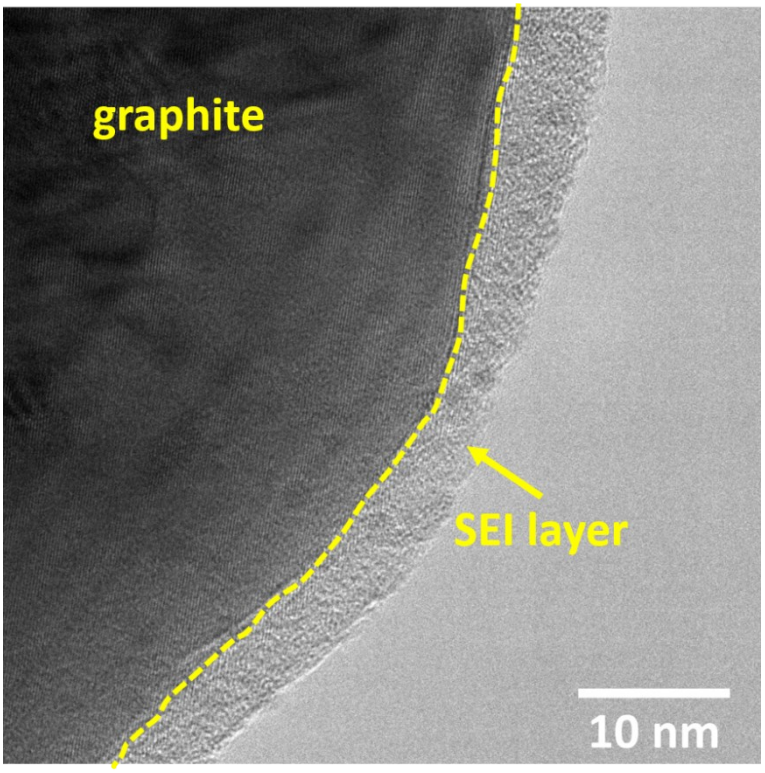

Figure S2. HRTEM image of graphite electrode with 0.2 wt% RhB after 3 cycles.

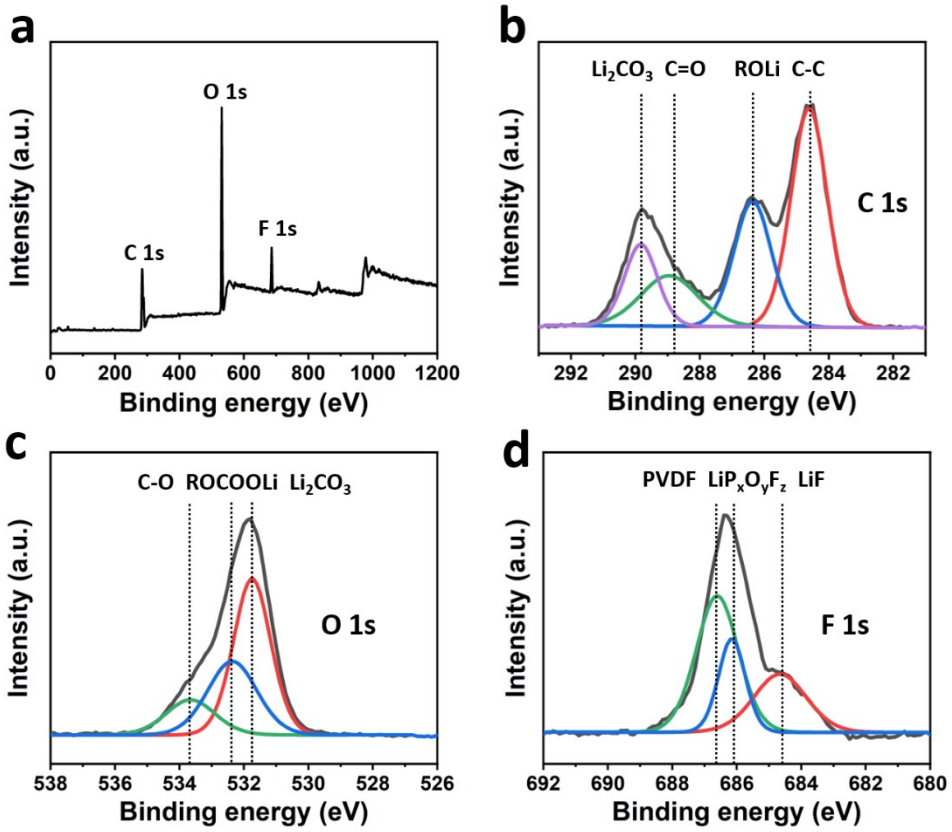

Figure S3. XPS spectra of the graphite electrode after 10 cycles in the electrolyte (1 M $LiPF_6$ in EC/DEC) without RhB.

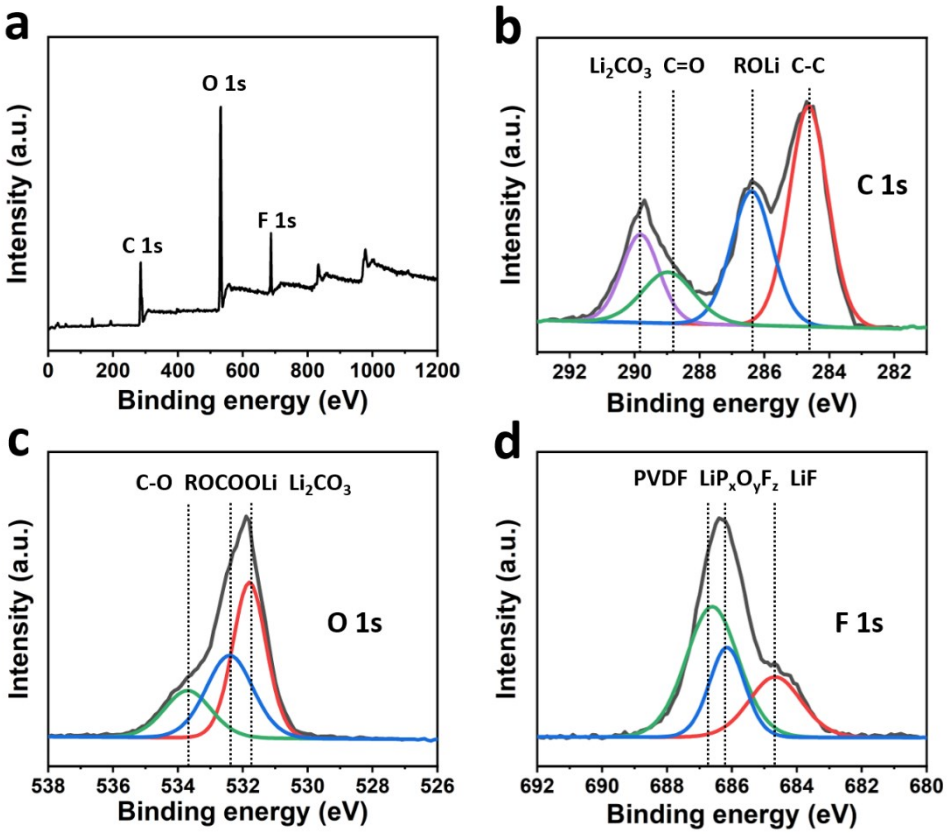

Figure S4. XPS spectra of the graphite electrode after 10 cycles in the electrolyte (1 M $LiPF_6$ in EC/DEC) with RhB.

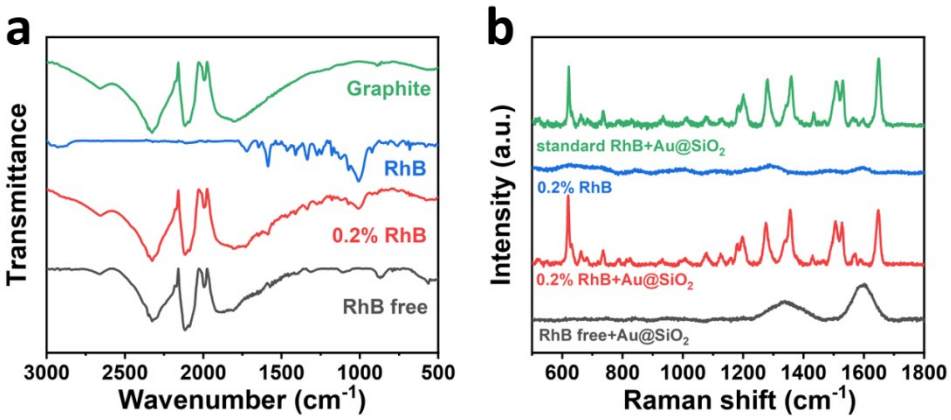

Figure S5. *Ex-situ* (a) IR and (b) SERS spectra of the graphite electrode with and without 0.2 wt% RhB after 10 cycles.

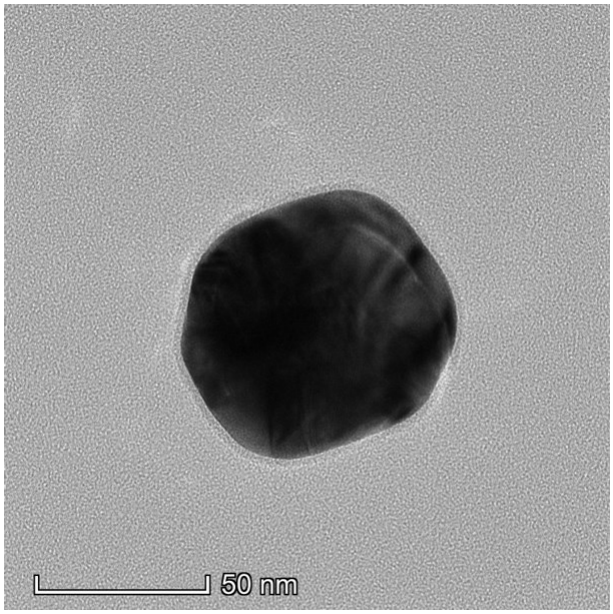

Figure S6. TEM image of the SiO_2-coated Au nanoparticle.

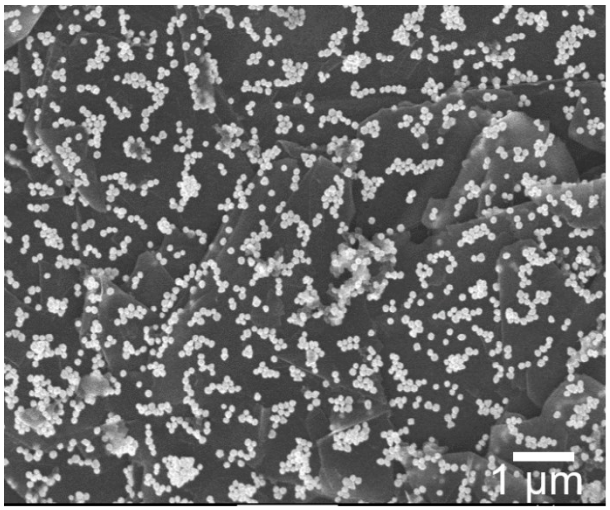

Figure S7. SEM image of the graphite electrode with deposited Au@SiO_2 nanoparticles.

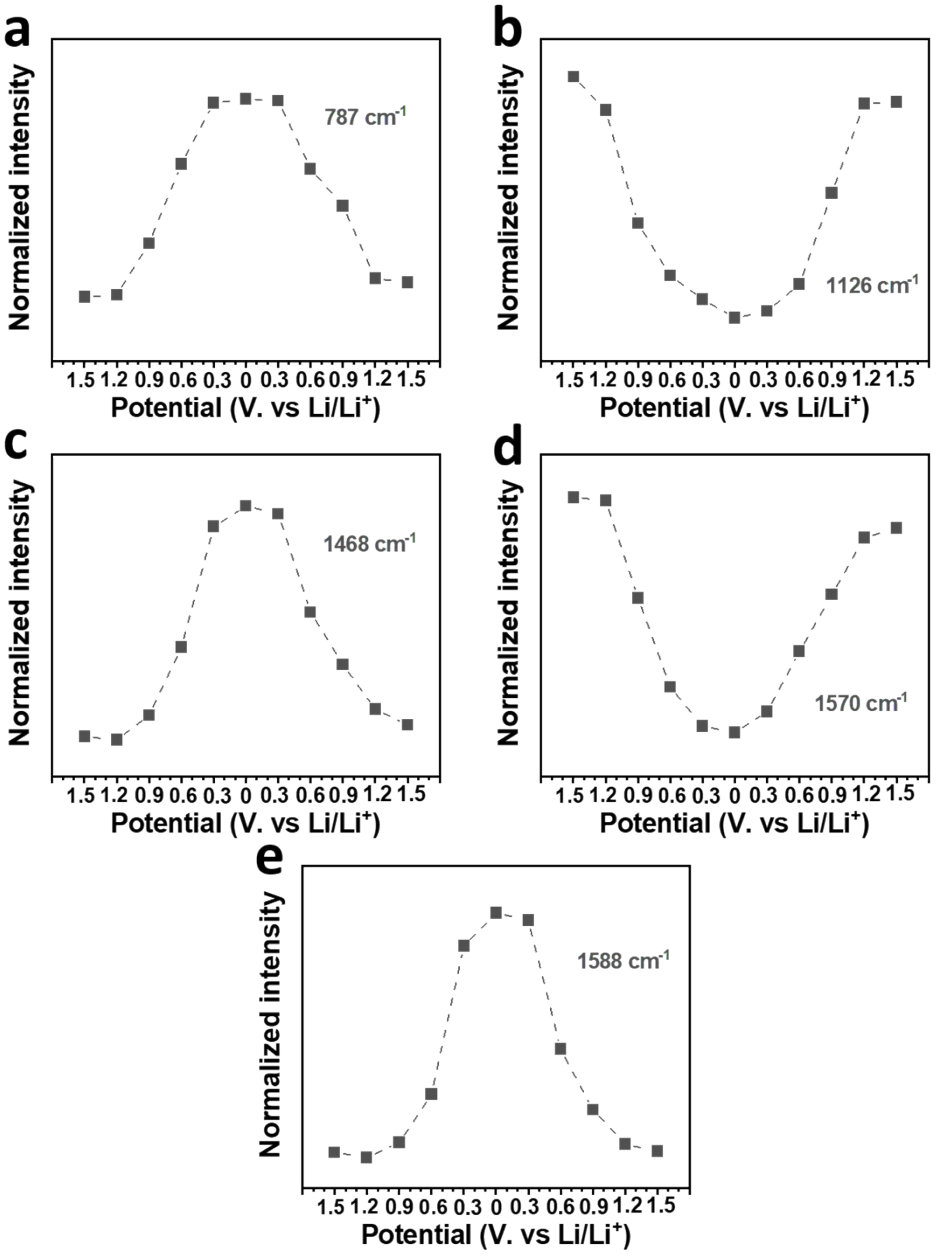

Figure S8. Intensity variation of the RhB Raman peaks at (a) 787 cm^{-1}, (b) 1126 cm^{-1}, (c) 1468 cm^{-1}, (d) 1570 cm^{-1} and (e) 1588 cm^{-1} with the applied potential, respectively.

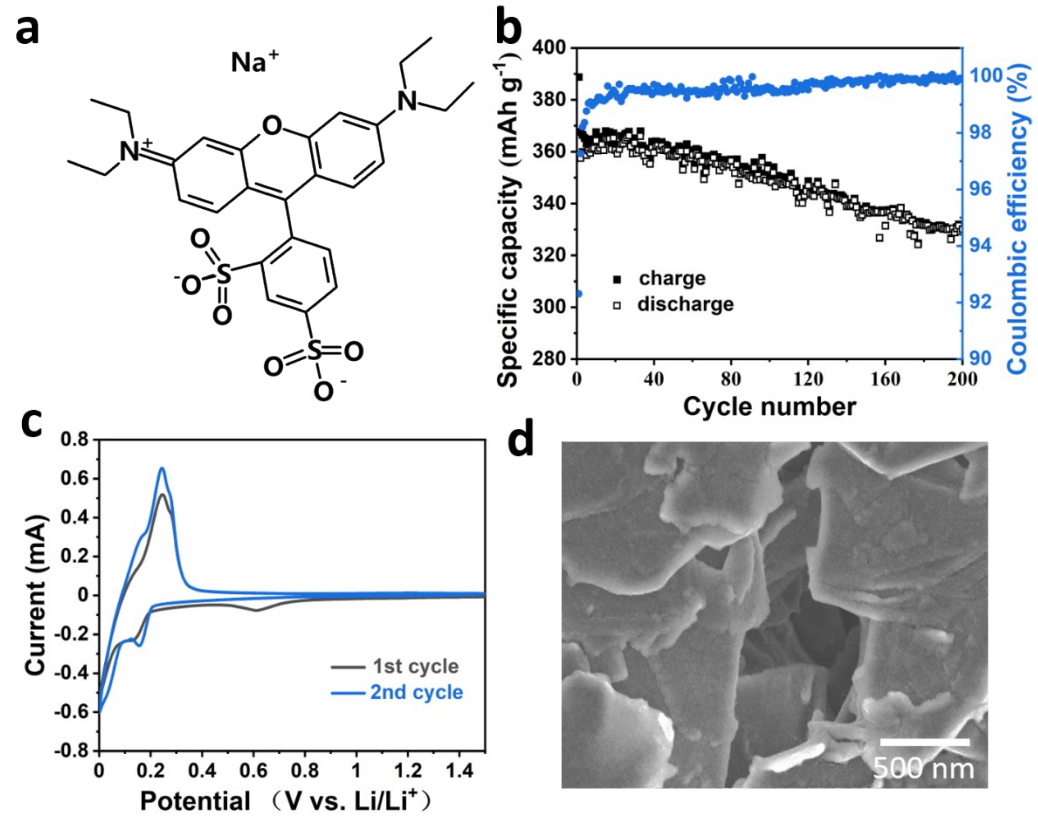

Figure S9. (a) The molecular structure of sulforhodamine B (S-RhB). (b) Cycle performance and coulombic efficiency of Li/graphite cells with 0.2 wt% S-RhB at 0.2 C between 1.5 V and 0.005 V. (c) Cyclic voltammetry curves of Li/graphite cells with 0.2 wt% S-RhB at the sweep rate of 0.2 mV s^{-1}. (d) SEM image of the graphite electrode with 0.2 wt% S-RhB after 100 cycles.

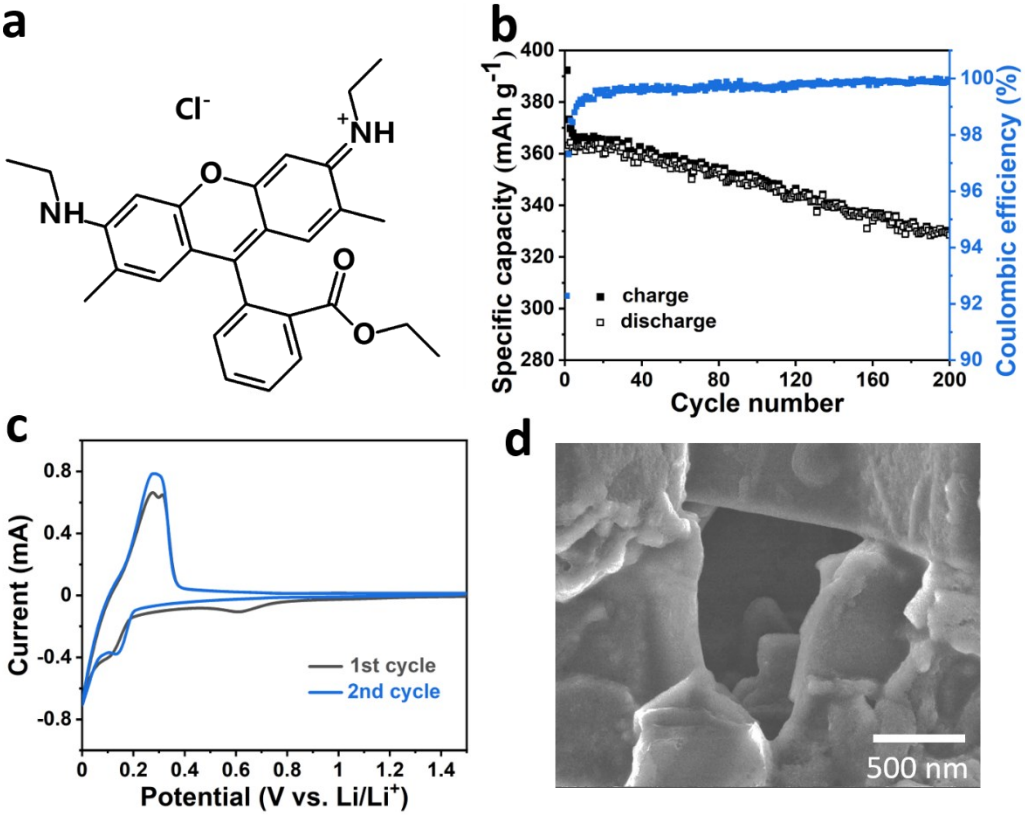

Figure S10. (a) The molecular structure of rhodamine 6G (Rh6G). (b) Cycle performance and coulombic efficiency of Li/graphite cells with 0.2 wt% Rh6G at 0.2 C between 1.5 V and 0.005 V. (c) Cyclic voltammetry curves of Li/graphite cells without 0.2 wt% Rh6G at the sweep rate of 0.2 mV s^{-1}. (d) SEM image of the graphite electrode with 0.2 wt% Rh6G after 100 cycles.

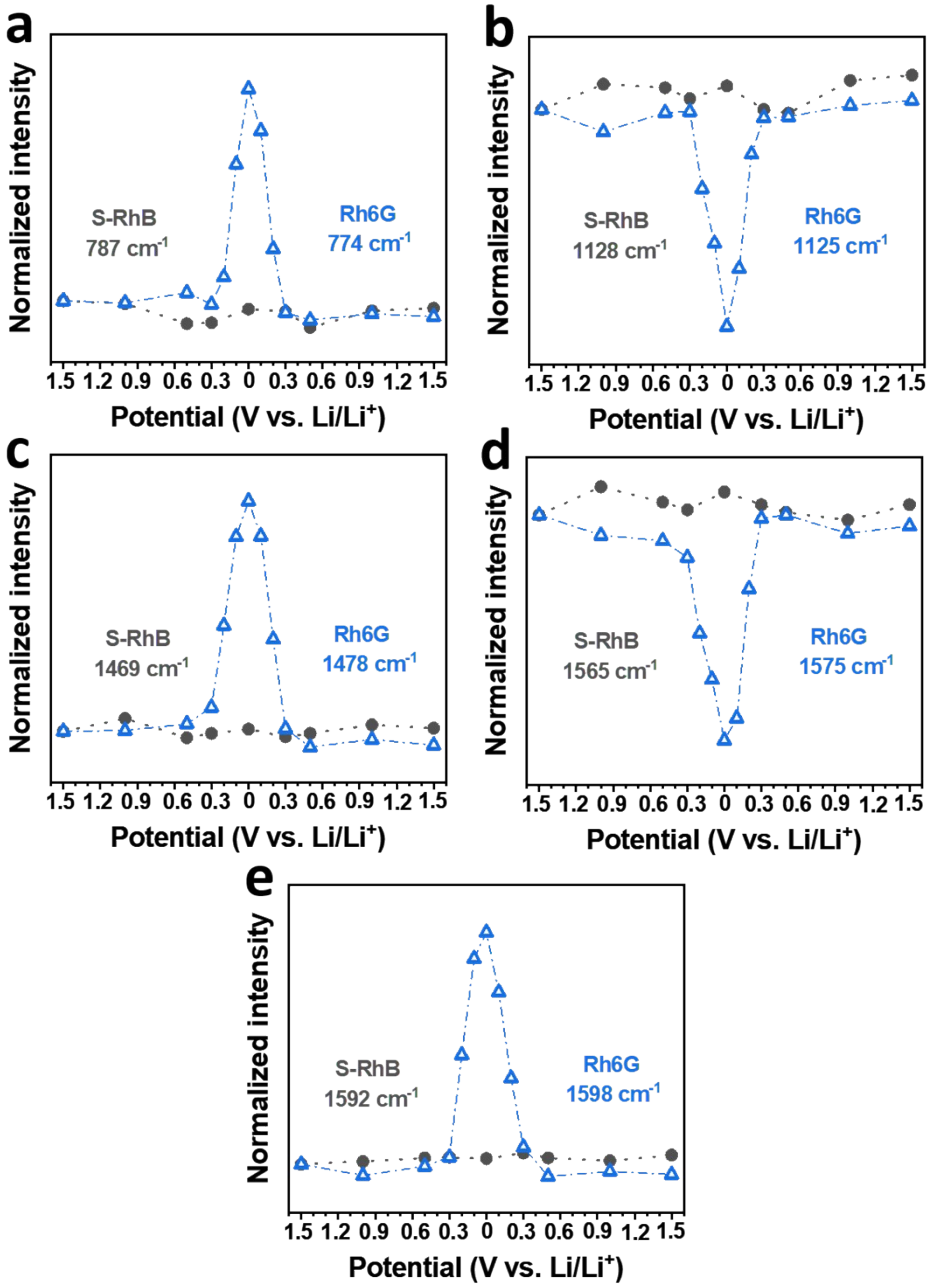

Figure S11. Intensity variation of the S-RhB and Rh6G Raman peaks at around (a) 774-787 cm^{-1}, (b) 1125-1128 cm^{-1}, (c) 1469-1478 cm^{-1}, (d) 1565-1575 cm^{-1} and (e) 1592-1598 cm^{-1} with the applied potential, respectively.

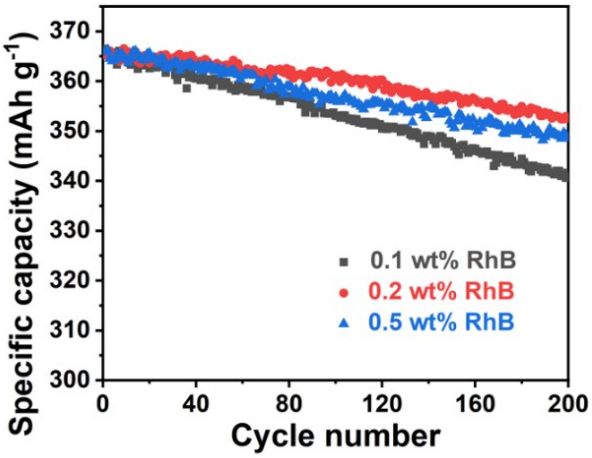

Figure S12. Cycle performance of the Li/graphite cells containing the different concentrations of RhB cycled at 0.2 C between 1.5 V and 0.005 V.

Table S1. The positions and assignments of partial SERS bands of RhB, S-RhB and Rh6G.

RhB (cm^{-1})	S-RhB (cm^{-1})	Rh6G (cm^{-1})	Assignment
787	787	774	C_x-H out-of-band bend
1126	1128	1125	C_x-H in-plane bend
1444	1436	1446	C_e-H bend
1468	1469	1478	C_e-H bend
1506	1512	1509	Xanthene ring in-plane stretch
1570	1565	1575	Xanthene ring in-plane-stretch
1588	1592	1598	Xanthene ring out-of-plane bend

[a] Assignment is based on [1-5].

[b] Subscript x and e denote xanthene ring and ethylamine, respectively.

Table S2. The DFT computational adsorption energy of EC, DEC and RhB on graphite (100) and (001) surface.

	Ead (eV)	
	100	**001**
EC	-0.17	-0.42
DEC	-1.32	-0.58
RhB	-3.56	-5.33

References:

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