Name of Journal: Energy Materials
Manuscript NO: 202333
Manuscript Type: Article

Supplementary Materials

Protective behavior of phosphonate-functionalized imidazolium ionic liquid and its impact on the Li-ion battery performance

Kaisi Liao[1,#], Jingbo Song[1,#], Jiawen Ge[1,#], Jia Si[1], Yinxiao Cai[1], Zijuan Luo[1], Mingjiong Zhou[1,*], Hongze Liang[1,*], Ya-Jun Cheng[2,*], Marija Milanovic[3], Atsushi Inoishi[4], Shigeto Okada[4]

[1]School of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, Zhejiang, China.
[2]Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, Zhejiang China.
[3]Department of Materials Engineering, Faculty of Technology Novi Sad, University of Novi Sad, Novi Sad 21000, Serbia.
[4]Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koen, Kasuga 816-8580, Japan.
[#]Authors contributed equally.

[*]**Correspondence to:** Prof./Dr. Mingjiong Zhou, School of Materials Science and Chemical Engineering, Ningbo University, 818 Fenghua Road, Jiangbei District, Ningbo 315211, Zhejiang, China. E-mail: zhoumingjiong@nbu.edu.cn; Prof./Dr. Hongze Liang, School of Materials Science and Chemical Engineering, Ningbo University, 818 Fenghua Road, Jiangbei District, Ningbo 315211, Zhejiang, China. E-mail: lianghongze@nbu.edu.cn; Prof./Dr. Ya-Jun Cheng, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 1219 Zhongguan West Road, Ningbo 315201, Zhejiang, China. E-mail: chengyj@nimte.ac.cn

Synthesis of PFIL

1-hexylimidazole (5.3 g, 35.1 mmol) and diethyl (3-bromopropyl) phosphonate (10.0 g, 38.6 mmol) were mixed in a 100 mL flask containing 20 mL toluene. The reaction solution was heated at 95 °C and stirred for 12 h. After addition 20 mL deionized water, aqueous phase was washed with toluene (10 × 10 mL) and ethyl acetate (3 × 30 mL). Lithium bis (trifluoro methane sulfonyl) imide (11.1 g, 38.6 mmol) in 20 mL water and dichloromethane (60 mL) was added to the above aqueous layer and stirred for 8 h. The aqueous layer was separated and washed with deionized water until complete removal of bromide checked by $AgNO_3$. Solvent was removed by evaporation and dried under vacuum for 4 h, yielding pale yellow viscous liquid (19.0 g, 78%).

NMR spectrogram analysis of PFIL

FTIR (cm^{-1}, KBr): 3150, 3115, 2962, 2861, 1565, 1467, 1353, 1197, 1138, 1057, 952, 761, 617, 570, 512. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.10. ^{1}H NMR (400 MHz, $CDCl_3$) δδ 0.84 (t, J = 6.4 Hz, 3H, N-C_5-CH_3), 1.29 (t, J = 6.4 Hz, 6H, P-O-CH_2-CH_3), 1.27-1.54 (m, 6H, N-C_2-CH_2-CH_2-CH_2), 1.73-1.77 (m, 2H, N-CH_2-CH_2-CH_2-CH_2-CH_2), 1.80-1.86 (m, 2H, P-CH_2-CH_2), 2.09-2.19 (m, 2H, P-CH_2), 4.05-4.09 (m, 4H, P-O-CH_2), 4.15 (t, J = 8.0 Hz, 2H, N-CH_2), 4.30 (t, J = 6.0 Hz, 2H, N-CH_2), 7.35 (s, 1H, Im-H), 7.47 (s, 1H, Im-H), 8.79 (s, 1H, Im-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.38, 122.67, 122.50, 119.70 (q, J = 321.0 Hz), 62.43 (d, J = 6.5 Hz), 50.17, 49.39 (d, J = 17.8 Hz), 30.87, 29.89, 25.67, 23.58 (d, J = 4.5 Hz), 22.22, 21.41 (d, J = 143.7 Hz), 16.10 (d, J = 6.0 Hz), 13.75.

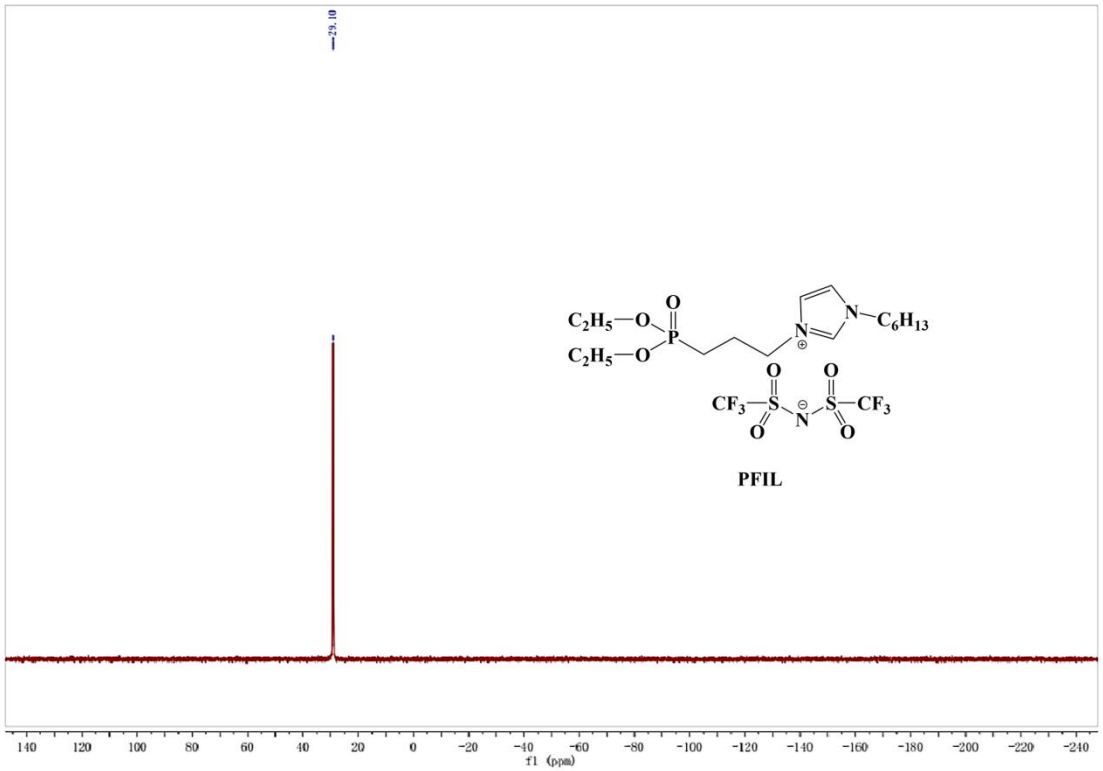

Figure S1. ^{31}P NMR of PFIL.

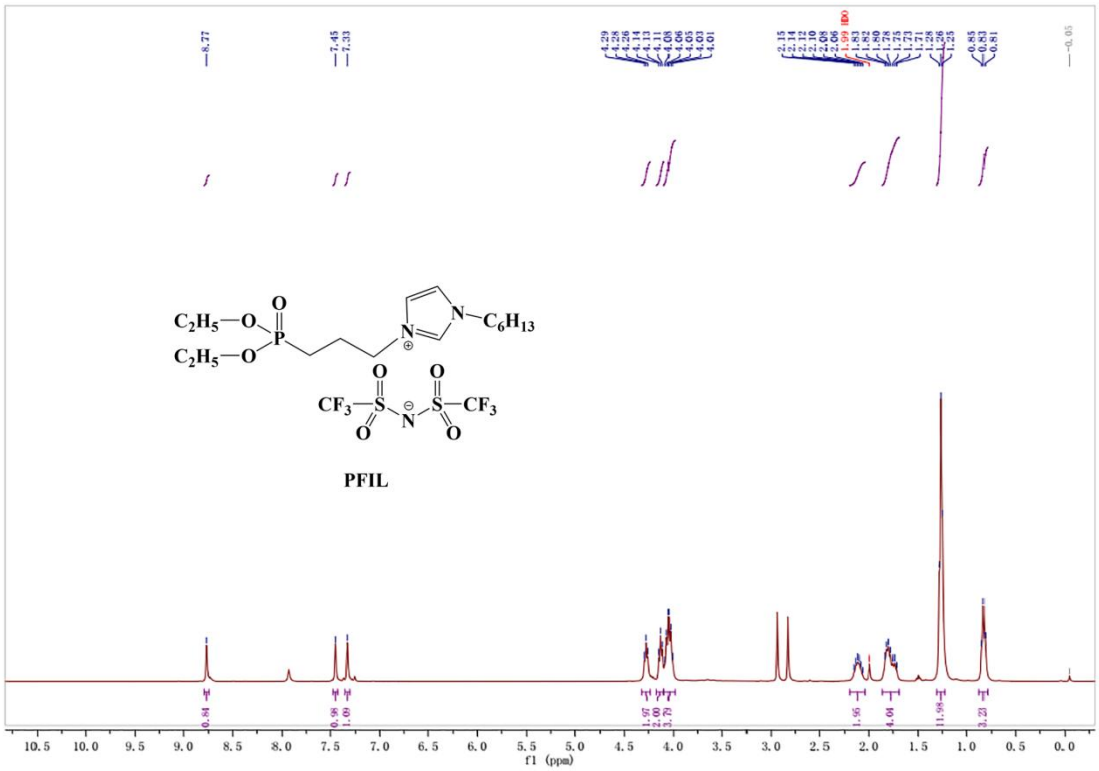

Figure S2. ^{1}H NMR of PFIL.

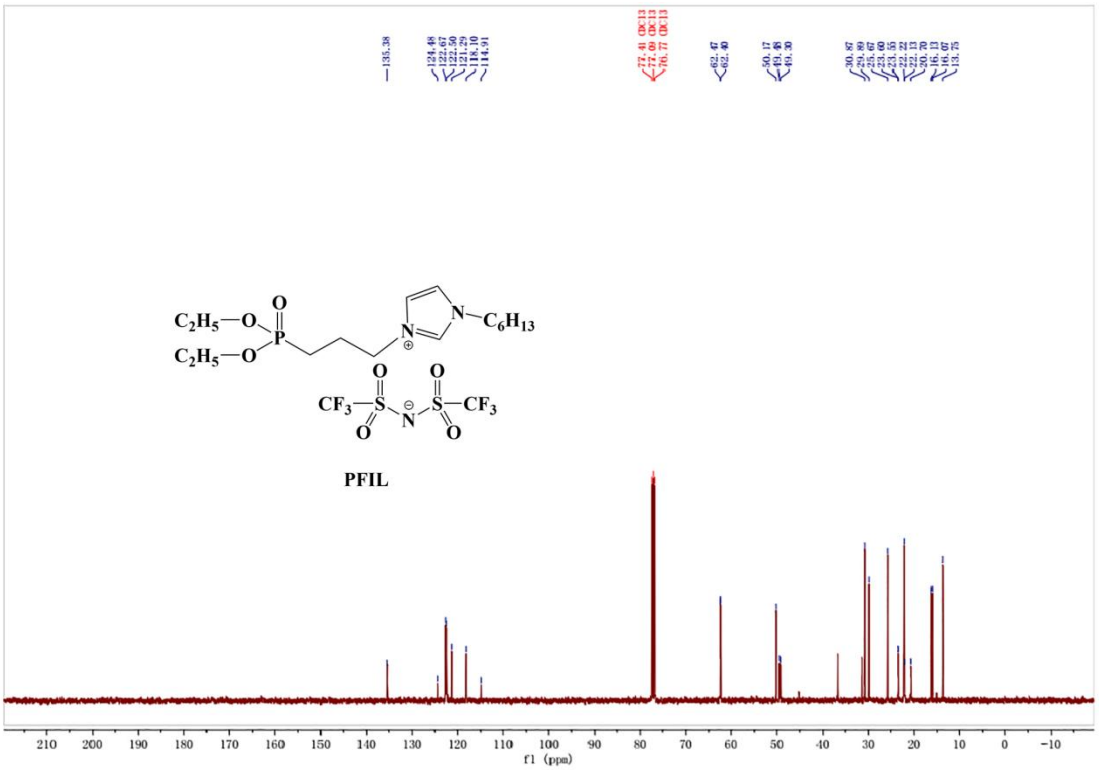

Figure S3. ^{13}C NMR of PFIL.

Table S1. The water content of PFIL

PFIL					
Sample	Weight (Sample 1; g)	Moisture value (%)	Weight (Sample 2; g)	Moisture value (%)	Average value of moisture (%)
PFIL	0.6802	0.28	0.2976	0.23	0.26

Note: The PFIL samples have been stored in a glove box, and there is a possibility of water absorption during transportation for testing and during the sample preparation process. Therefore, the test results may indicate a higher water content.

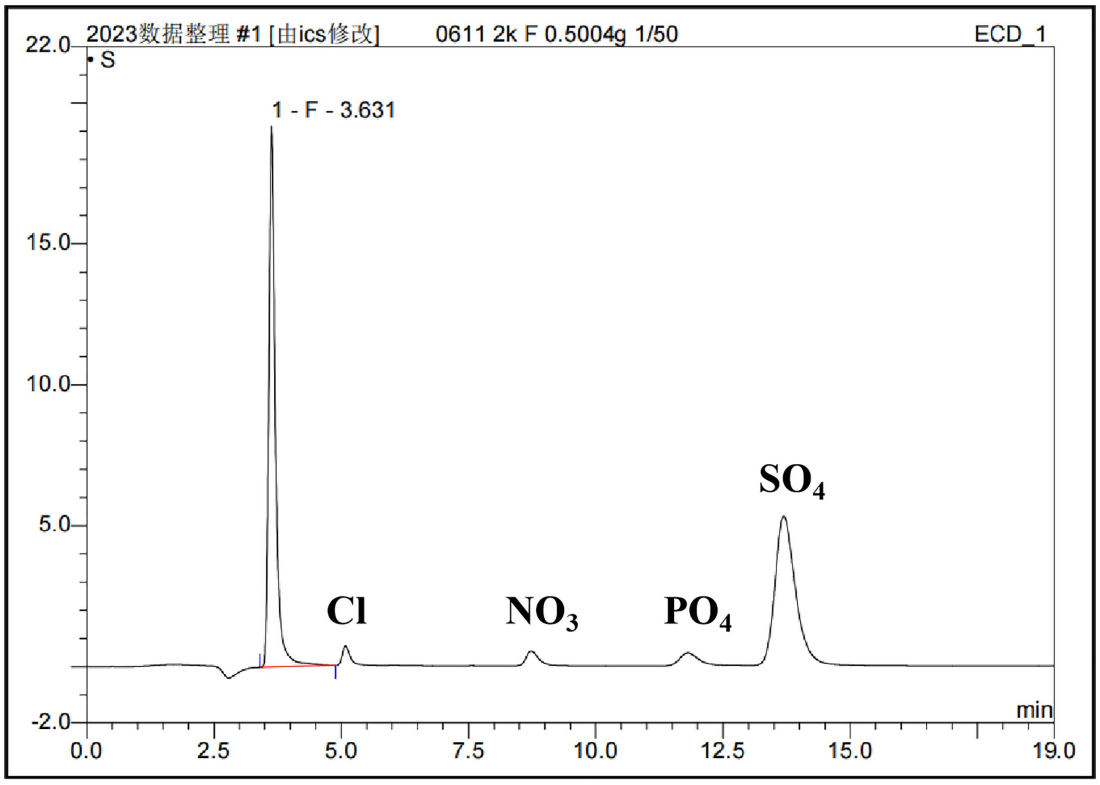

Figure S4. The halide content of PFIL was determined using ion chromatography. Note: Other four anions were supposed to be due to drying process by unhydrous $MgSO_4$ (CP grade).

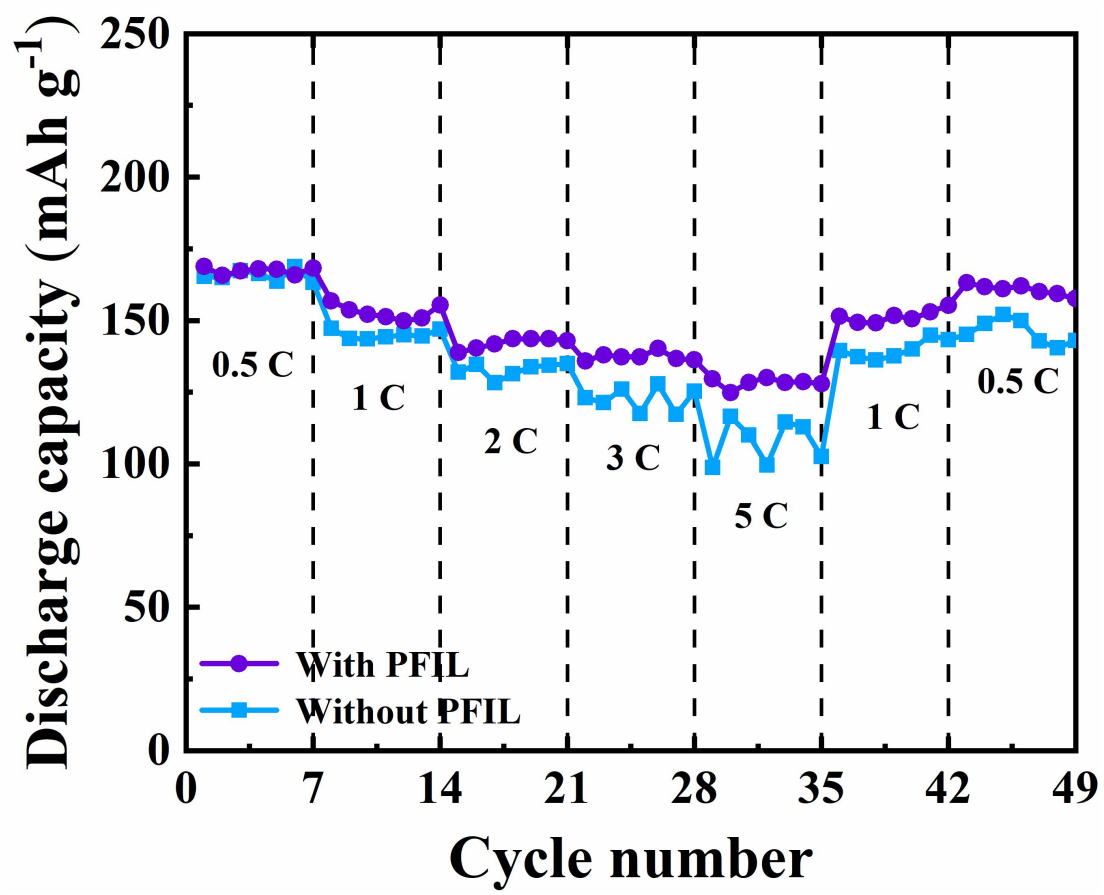

Figure S5. Rate performance of the Li||NCM811 cell cycled with the base electrolyte and the hybrid electrolyte.

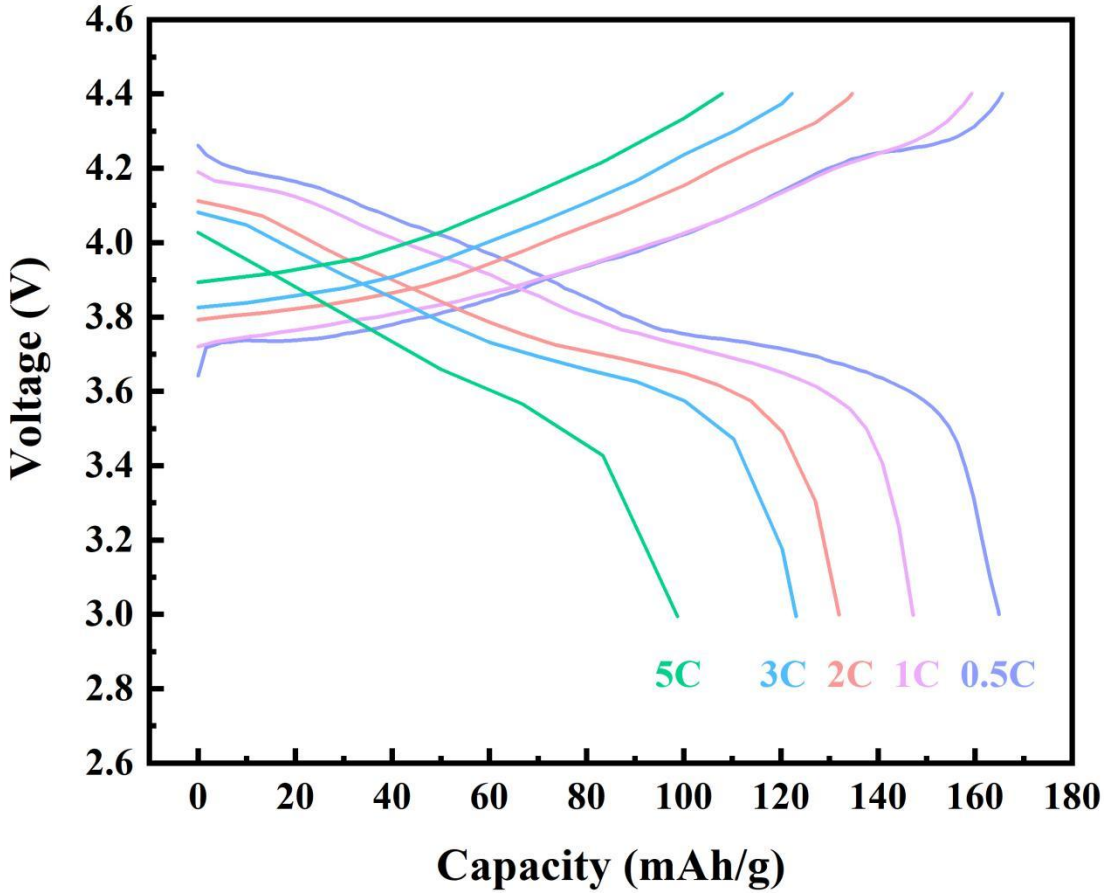

Figure S6. Galvanostatic charge-discharge (GCD) curves at different C-rates of the Li||NCM811 cell cycled with the base electrolyte.

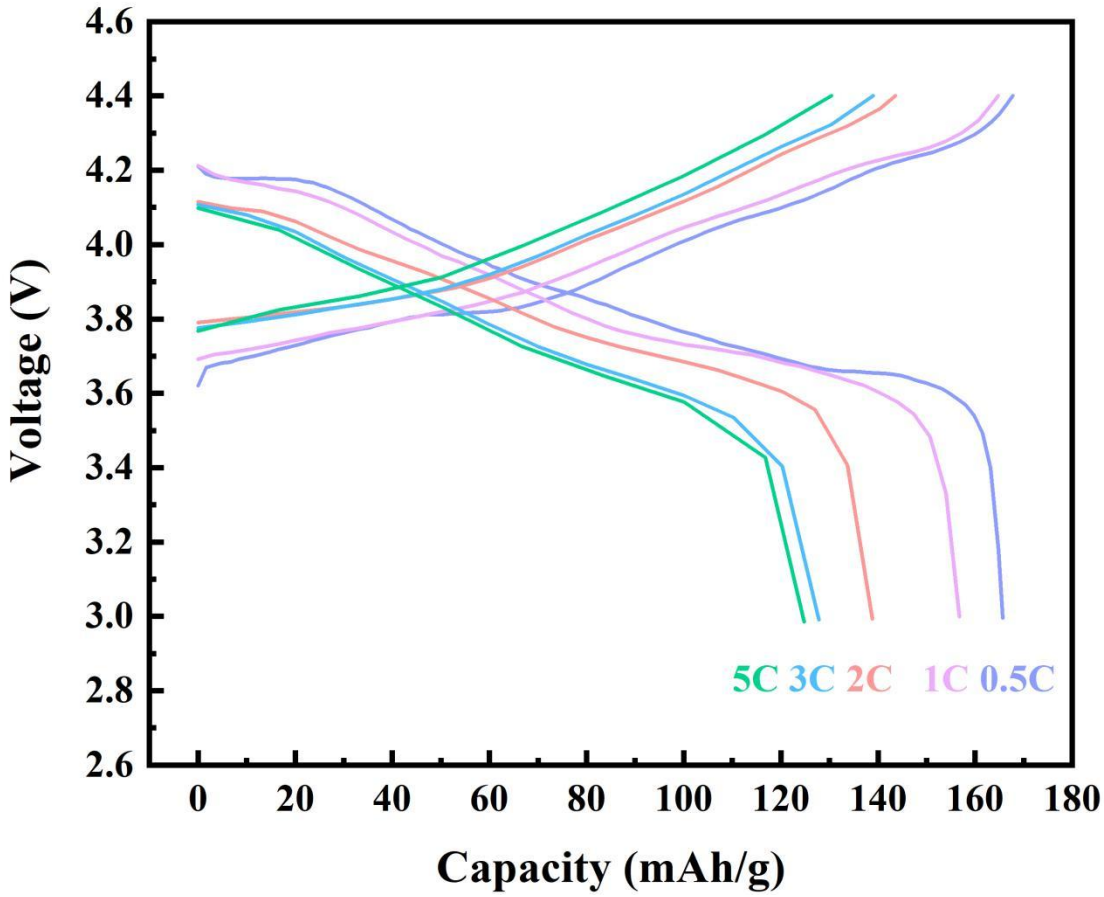

Figure S7. Galvanostatic charge-discharge (GCD) curves at different C-rates of the Li||NCM811 cell cycled with the hybrid electrolyte.

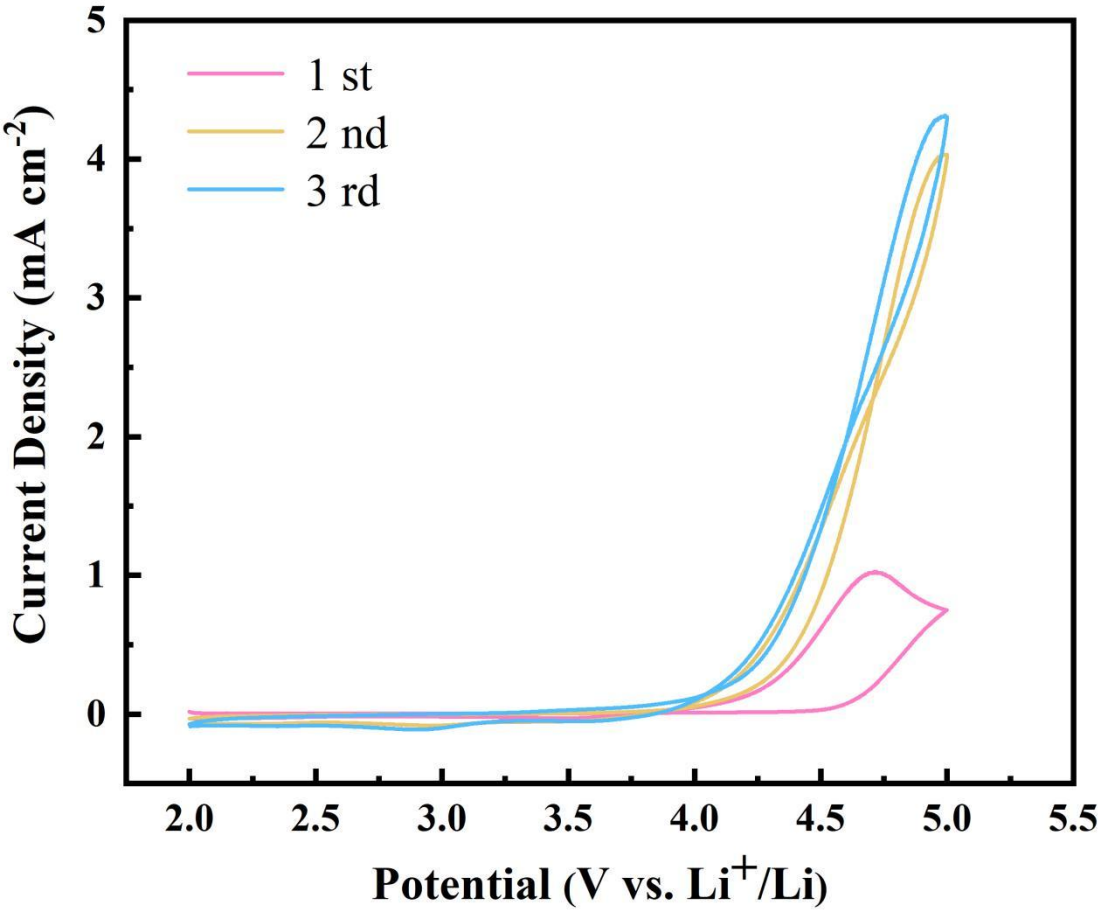

Figure S8. Cyclic voltammetry of the Al electrodes in the electrolyte containing 20 wt% non-functionalized imidazole ionic liquid [1-hexyl-3-propylimidazole bis (trifluoromethyl sulfonyl) imide].

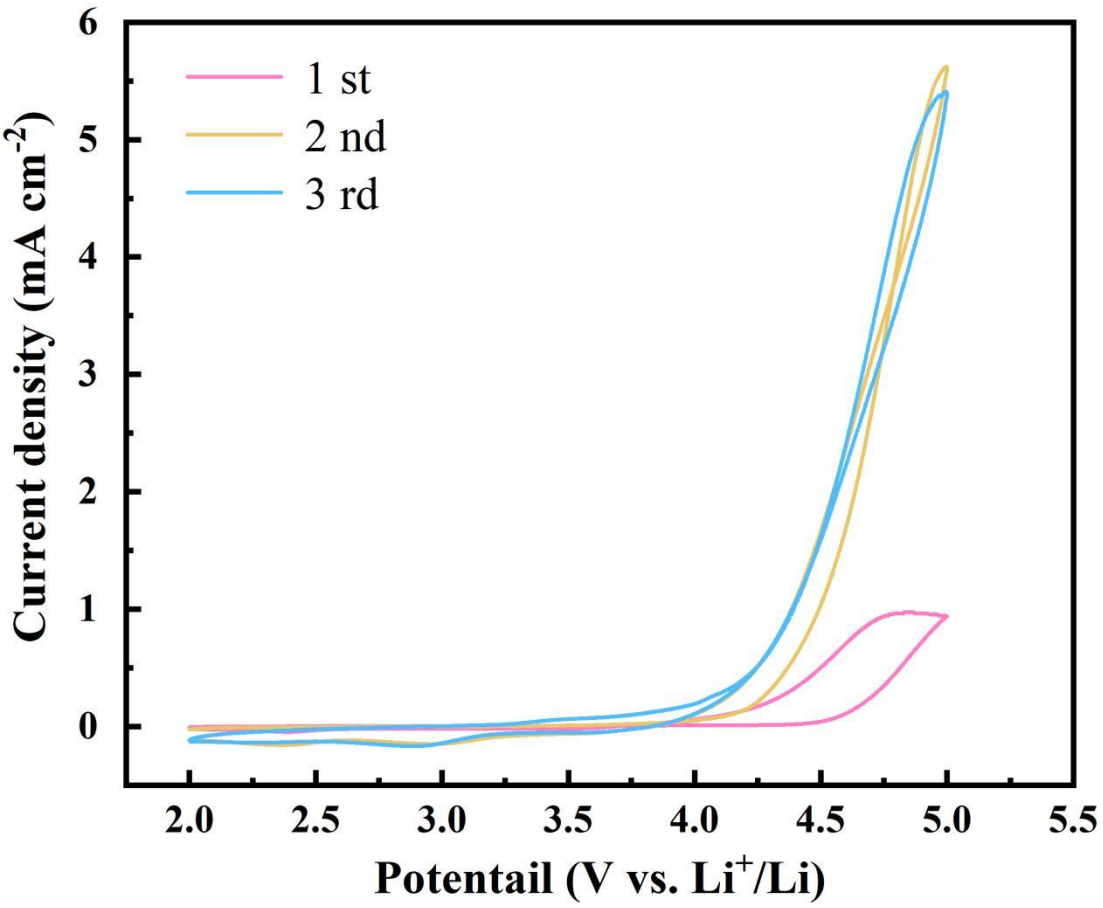

Figure S9. Cyclic voltammetry of the Al electrodes in the electrolyte containing 20 wt% BMPyrr TFSI [1-butyl-1-methylpyrrolidonium bis (trifluoromethyl sulfonyl) imide].

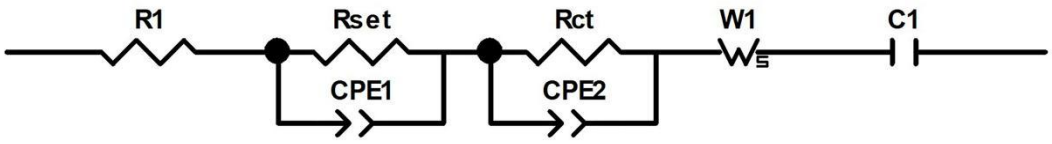

Figure S10. Equivalent circuit model used for the EIS fitting.