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New ether-functionalized pyrazolium ionic liquids electrolytes based on bis(fluorosulfonyl)imide anion for lithium-ion batteries

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Synthesis of Ether-Functionalized Pyrazolium ionic liquids

1-(2-Methoxyethyl)-2-methylpyrazolium bis(fluorosulfonyl)imide (PZ2o1-1-FSI)

1-(2-ethoxymethyl) pyrazole (7 g, 55.5 mmol), iodomethane (8.7 g, 61.1 mmol) and acetonitrile (10 mL) were mixed in a sealed 250 mL flask, and stirred for 48 h at ambient temperature. After washed with diethyl ether three times, the corresponding iodide was obtained. Then crude product and same molar amount lithium bis(fluorosulfonyl)imide (LiFSI) was dissolved in deionized water and stirred for 4h at ambient temperature. Dichloromethane was used to extract the IL from the mixture and then the solvent was washed with deionized water for 3 times until no halide residual could be detected by $AgNO_3$ solution. The product was dried under high vacuum more than 12 h at 100 ^oC. Colorless liquid; (acetone-d_6 as solvent) ^1H NMR: δ (ppm) 8.512-8.473 (m, 2 H), 6.993-6.895 (t, 1H), 4.948-4.857 (t, 2 H), 4.460-4.362 (s, 3 H), 3.996-3.855 (t, 2 H), 3.415-3.318(s, 3 H). ^{13}C NMR: δ (ppm) 138.344, 137.741, 107.501, 69.462, 58.162, 49.954, 37.070.

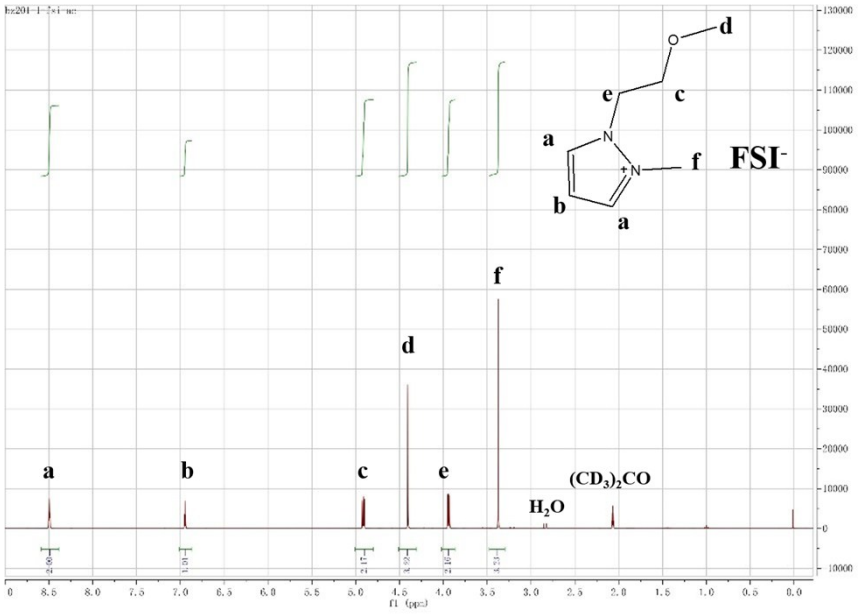

Fig. S1 ^1H NMR spectrum of PZ2o1-1-FSI

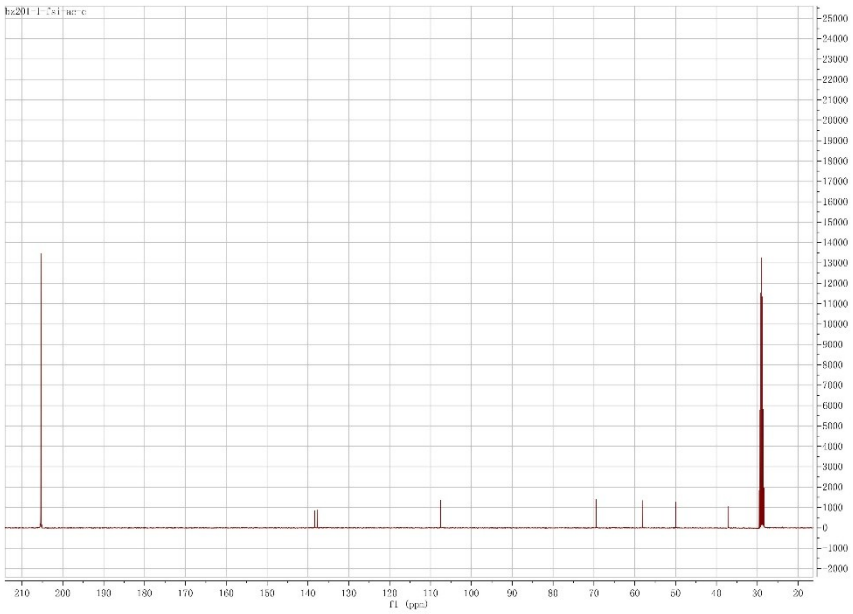

Fig. S2 ^{13}C NMR spectrum of PZ2o1-1-FSI

1-(2-Methoxyethyl)-2-ethylpyrazolium bis(fluorosulfonyl)imide (PZ2o1-2-FSI)

1-(2-ethoxymethyl) pyrazole (7 g, 55.5 mmol), iodoethane (9.5 g, 61.1 mmol) and acetonitrile (10 mL) were mixed in a sealed 250 mL flask, and stirred for 48 h at 60 ^{o}C. The following procedures were identical to PZ2o1-1-FSI. Colorless liquid; (acetone-d_6 as solvent) ^{1}H NMR: δ (ppm) 8.567-8.544 (d, 1H), 8.516-8.493 (d, 1H), 7.014-6.910 (t, 1H), 4.973- 4.834 (t, 2 H), 4.816-4.697 (q, 2 H), 3.992-3.862 (t, 2 H), 3.393-3.297 (s, 3H), 1.707-1.603 (t, 3H). ^{13}C NMR: δ (ppm) 138.021, 136.585, 107.757, 69.420, 58.170, 49.993, 45.793, 13.555.

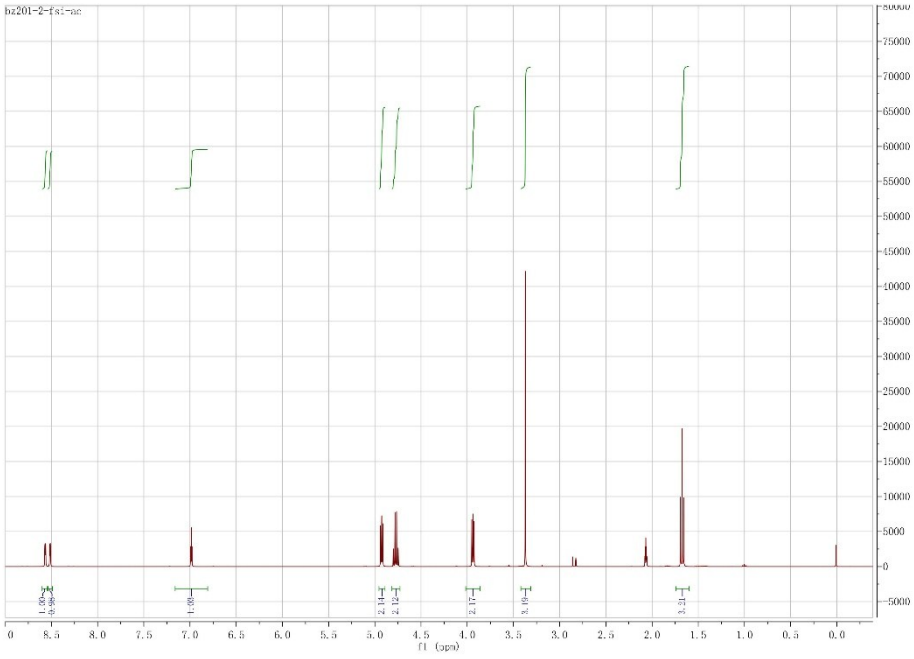

Fig. S3 ^{1}H NMR spectrum of PZ2o1-2-FSI

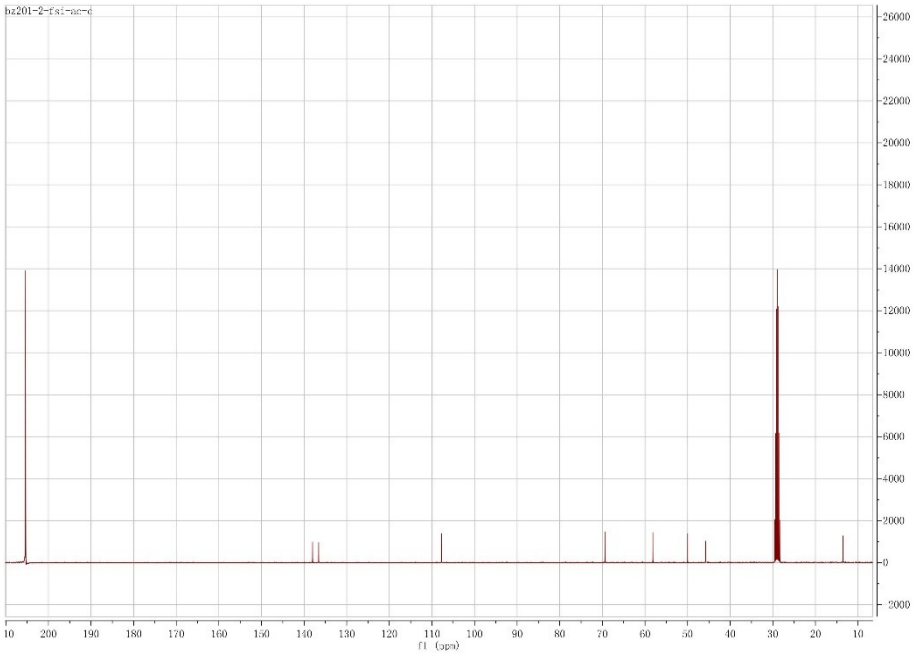

Fig. S4 ^{13}C NMR spectrum of PZ2o1-2-FSI

1-(2-Ethoxyethyl)-2-methylpyrazolium bis(fluorosulfonyl)imide (PZ2o2-1-FSI)

1-(2-ethoxyethyl) pyrazole (7.8 g, 55.5 mmol), iodomethane (8.7 g, 61.1 mmol) and acetonitrile (10 mL) were mixed in a sealed 250 mL flask, and stirred for 48 h at ambient temperature. The

following procedures were also identical to PZ2o1-1-FSI. Colorless liquid; (chloroform-d as solvent) ^{1}H NMR: δ (ppm) 8.138-8.082(d, 1H), 8.039-7.978 (d, 1H), 6.770-6.687 (t, 1H), 4.700-4.550 (t, 2 H), 4.234-4.123 (s, 3 H), 3.879-3.759 (t, 2 H), 3.570-3.420 (q, 2 H), 1.215-1.057 (t, 3 H). ^{13}C NMR: δ (ppm) 137.951, 137.444, 107. 951, 67.668, 67.034, 50.554, 37.719, 14.849.

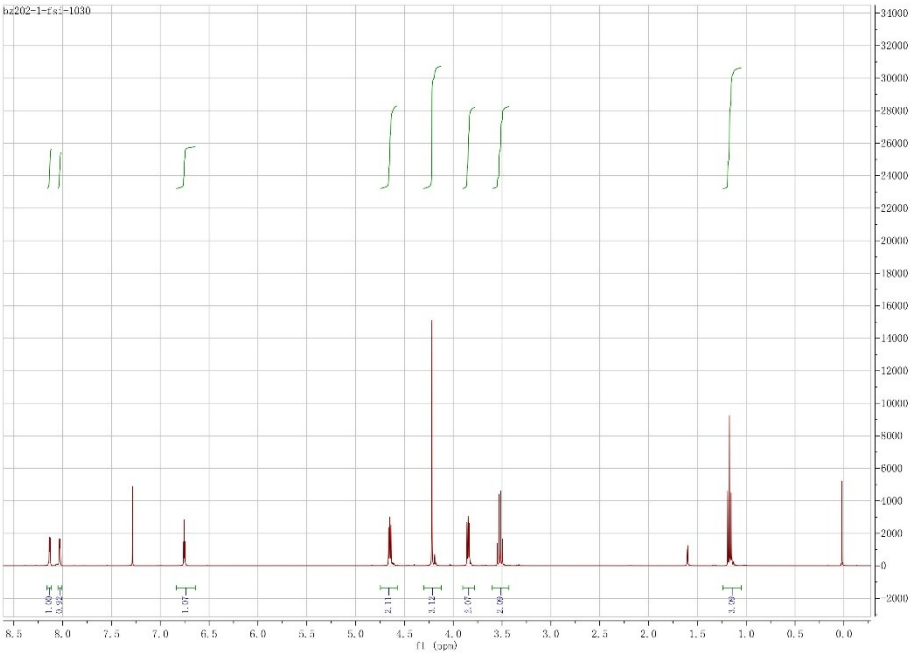

Fig. S5 ^{1}H NMR spectrum of PZ2o2-1-FSI

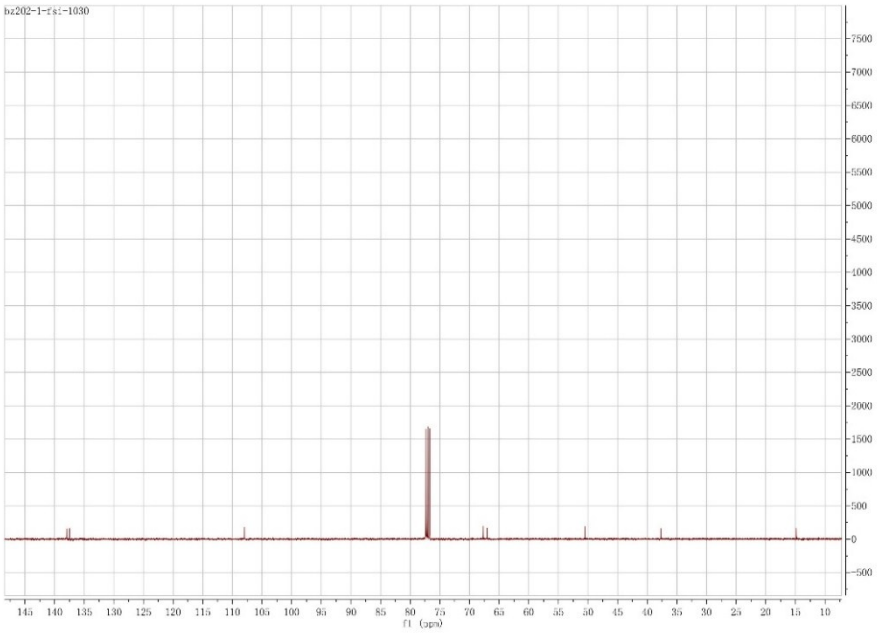

Fig. S6 ^{13}C NMR spectrum of PZ2o2-1-FSI

1-(2-Ethoxyethyl)-2-ethylpyrazolium bis(fluorosulfonyl)imide (PZ2o2-2-FSI)

1-(2-ethoxyethyl) pyrazole (7.8 g, 55.5 mmol), iodoethane (9.5 g, 61.1 mmol) and acetonitrile (10 mL) were sealed in a 50 mL autoclave for 24 h at 80 °C. The following procedures were identical to PZ2o1-1-FSI.Colorless liquid; (chloroform-d as solvent) ^{1}H NMR: δ (ppm) 8.208-8.147 (d, 1H), 8.082-8.030 (d, 1H), 6.824-6.769 (t, 1 H), 4.717-4.632 (t, 2 H), 4.620-4.520 (q, 2 H), 3.914-3.796 (t, 2H), 3.594-3.453 (q, 2 H), 1.730-1.606 (t, 3H), 1.235-1.117 (t, 3 H). ^{13}C NMR: δ (ppm) 137.653, 135.555, 108.150, 67.547, 67.055, 50.545, 46.093, 14.867, 13.859.

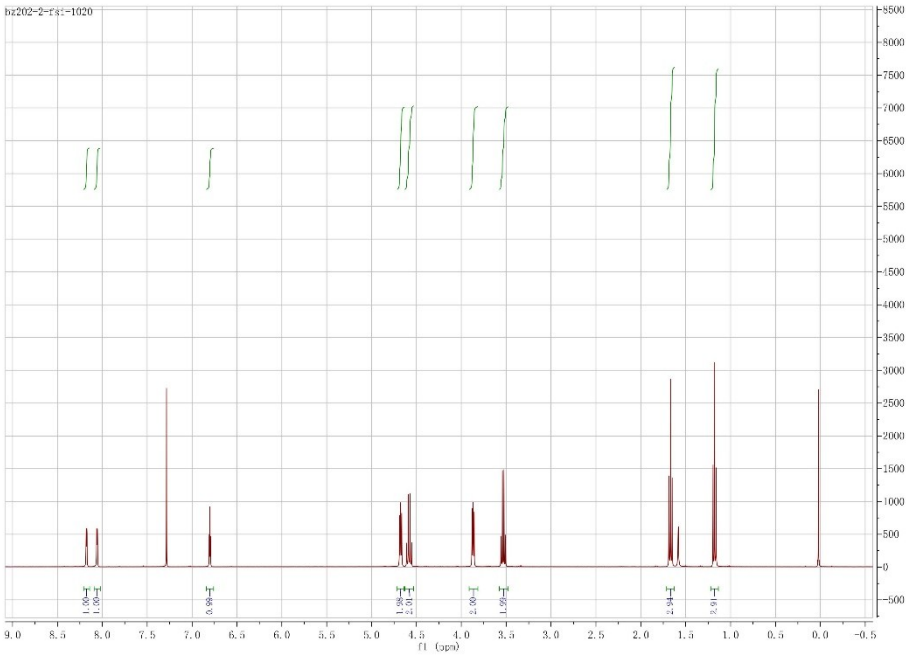

Fig. S7 ^{1}H NMR spectrum of PZ2o2-2-FSI

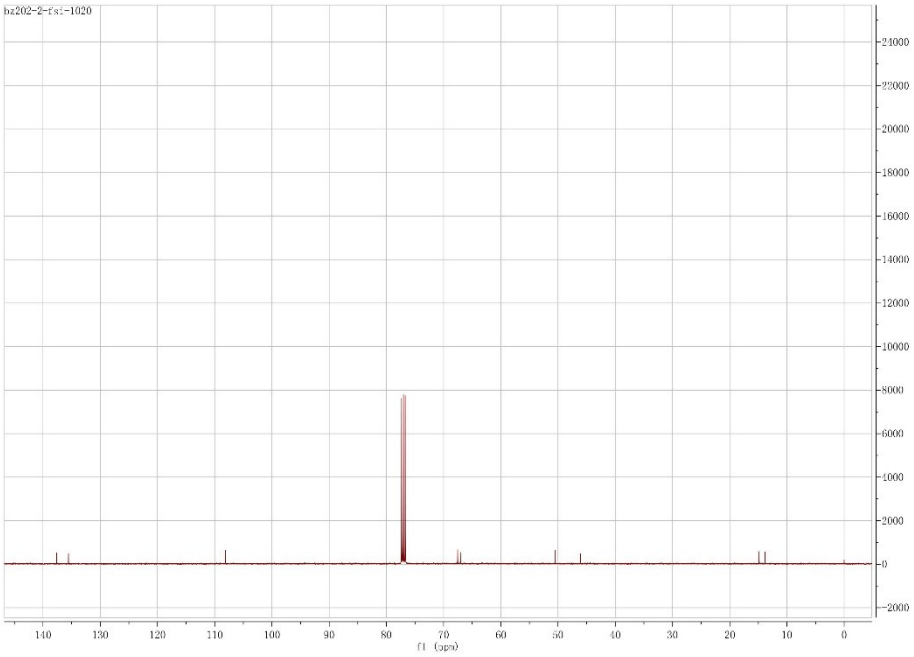

Fig. S8 ^{13}C NMR spectrum of PZ2o2-2-FSI

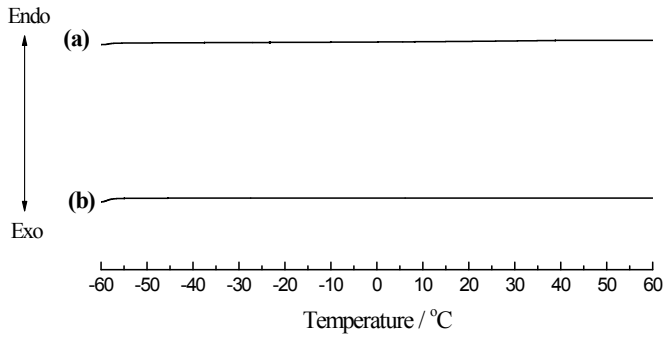

Fig. S9 DSC curves of (a) PZ2o1-1-FSI and (b) PZ2o2-2-FSI

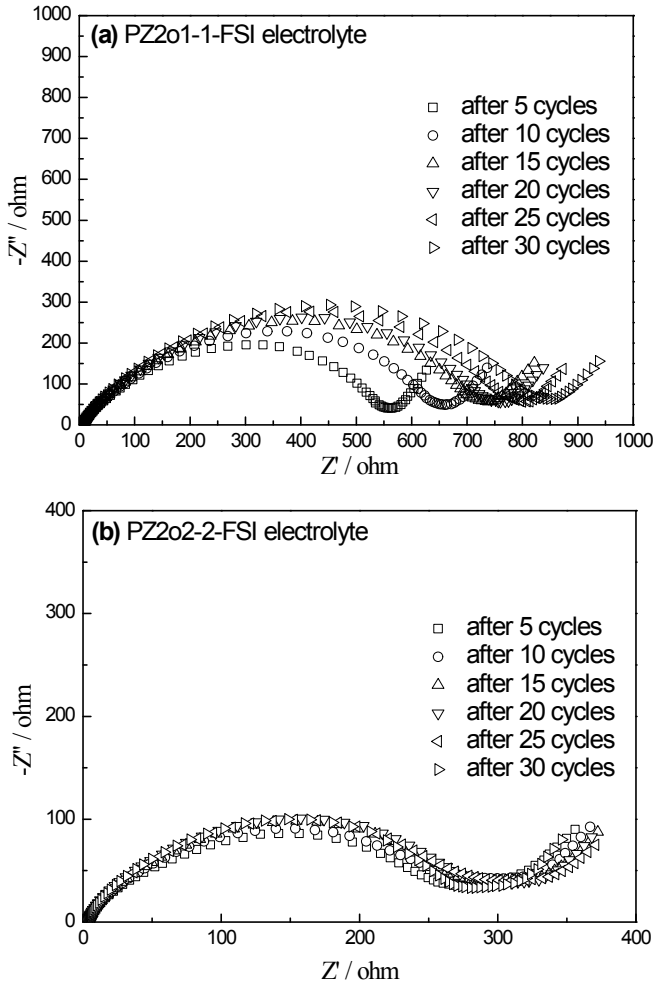

Fig. S10 EIS plots of Li/$LiFePO_4$ cells at 0.1 C after 5, 10, 15, 20, 25, 30 cycles using (a) PZ2o1-1-FSI electrolyte, (b) PZ2o2-2-FSI eletrolyte

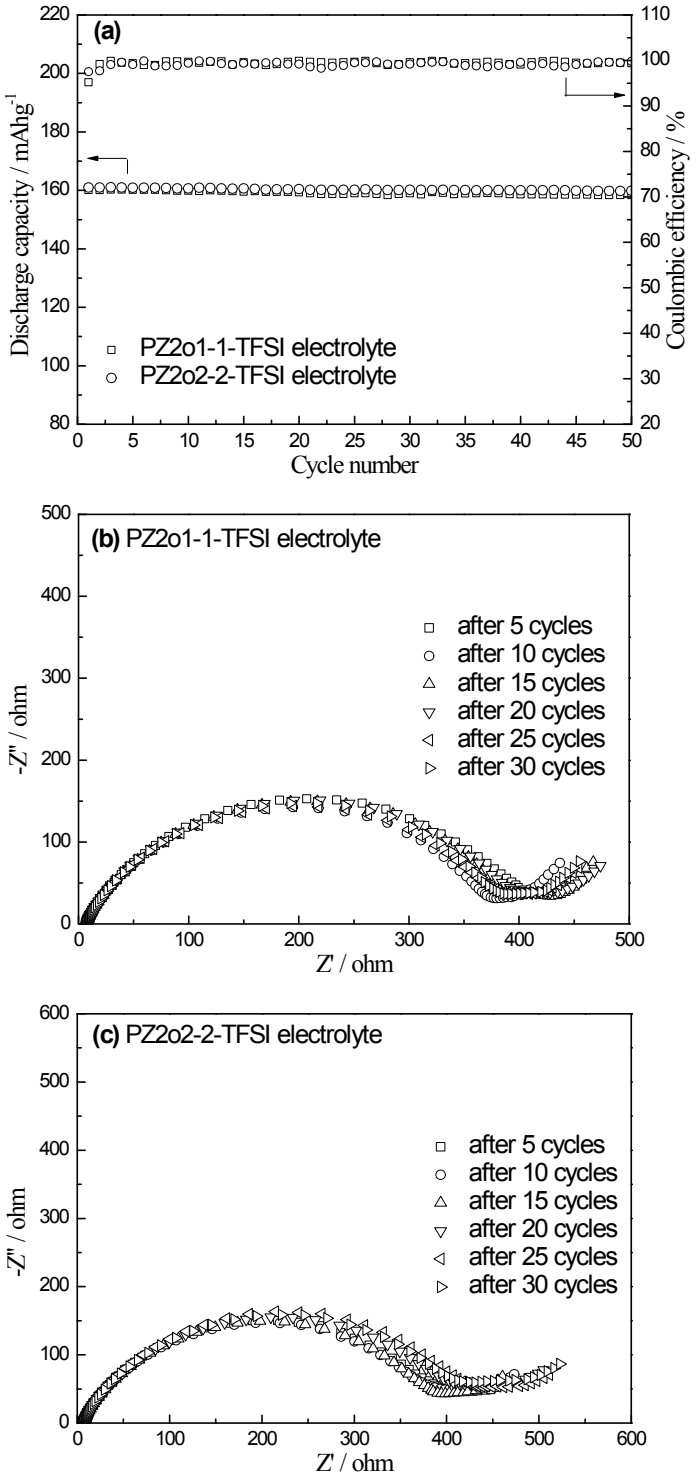

Fig. S11 (a) discharge capacity and coulombic efficiency during cycling of Li/$LiFePO_4$ cells, and EIS plots of Li/$LiFePO_4$ cells at 0.1 C after 5, 10, 15, 20, 25, 30 cycles using (b) PZ2o1-1-TFSI electrolyte, (c) PZ2o2-2-TFSI eletrolyte

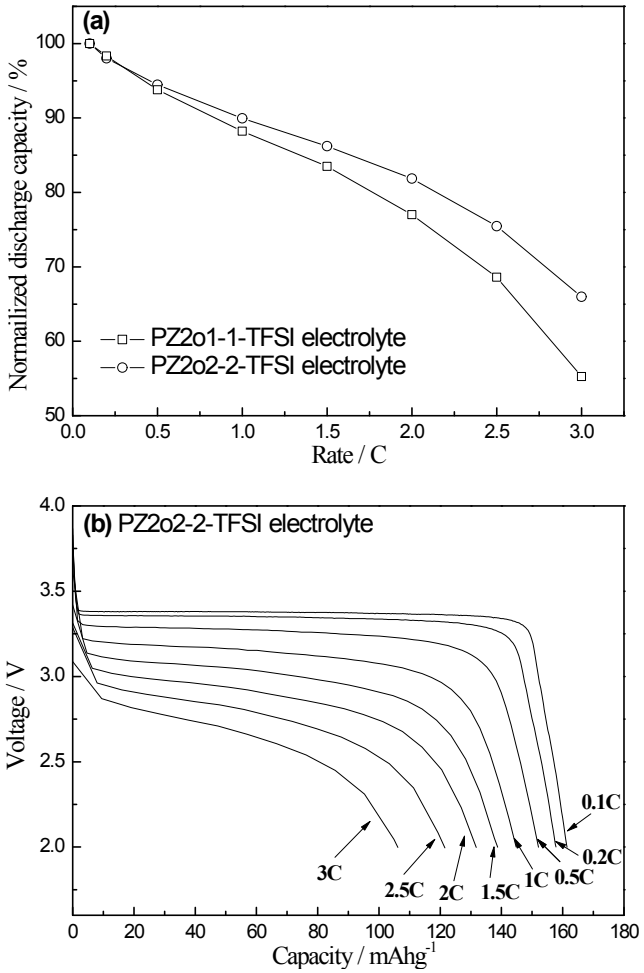

Fig. S12 (a) Variation of normalized discharge capacity with rate for Li/$LiFePO_4$ cells and (b) the corresponding discharge curves of Li/$LiFePO_4$ cell using PZ2o2-2-TFSI electrolyte at room temperature. Charge rate was 0.1 C and discharge rates were 0.1, 0.2, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 C.