Supporting Information

Ionic Liquid-Organic Carbonate Electrolyte Blends To Stabilize Silicon Electrodes for Extending Lithium Ion Battery Operability to 100 °C

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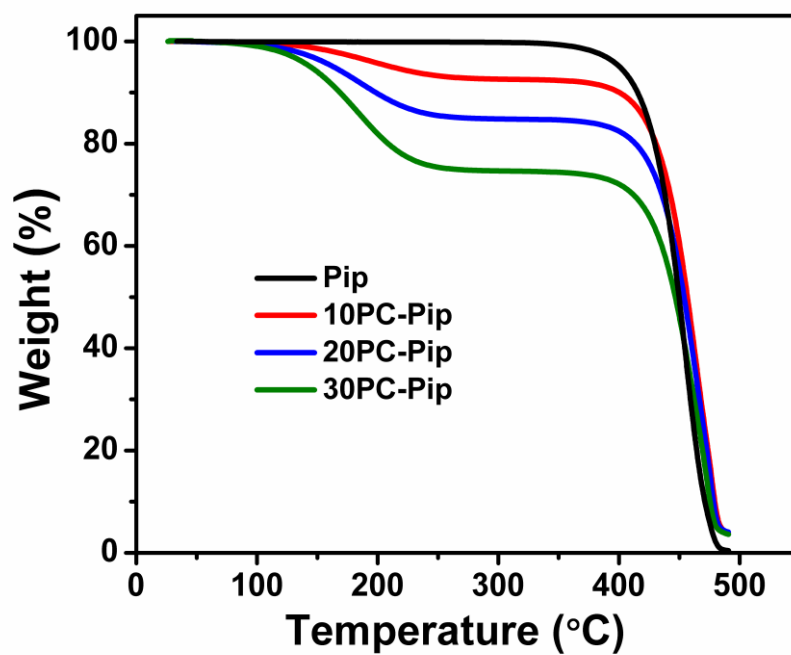
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Thermalgravimetric Analysis

Thermalgravimetric Analysis (TGA) measurements were performed with TGA Q50. All samples were heated from 20 to 500℃ at a heating rate of 20 ℃/min.

Figure S1. Thermal behavior of Pip electrolyte and propylene carbonate (PC) added Pip electrolytes

Conductivity Measurement

The conductivity measurements were performed using a Conductivity Meter (K912, Consort) that has a 4-electrode cell to prevent the polarization error and fouling of the electrode. The ionic liquid electrolytes were dried at $100^{\circ}C$ under high-vacuum overnight to remove any trace amount of moisture before testing. Samples were loaded in test tubes sealed with septum stopper in order to maintain N_2 environment. A heating block was used to control the temperature and stirring was maintained during the measurement to maintain homogeneity. A 30-minute equilibration time was used at each temperature.

General Procedure for Rheological Measurement

About 1 mL of each sample was placed on an AR 1000 Controlled Strain Rheometer from TA Instruments equipped with a peltier temperature control using a 20 mm diameter parallel aluminum plate. The gap was set to be 1.0-2.0 mm in all the runs. To minimize the effect of moisture in the air, the experiments were performed in a glove bag filled with nitrogen gas. Prior to each test, a pre-shear was done at shear rate 100 1/s for 10 s to eliminate the physical memory of the sample, followed by a 15 minutes equilibrium step in order for the sample to reach a steady state condition.

Strain amplitude from 0.1 to 10% was determined to lie within the linear viscoelastic region (LVR) via an oscillatory strain sweep at a fixed frequency (1 Hz). Dynamic shear measurements covering 0.628- 628 rad/s were conducted to obtain dynamic viscosity, storage modulus (G'), loss modulus (G") and phase angle. Measurements were typically performed at 25℃ unless temperature effect was investigated. Oscillatory temperature sweep was conducted from 10℃ to 95℃with increment of 5℃ and 1-minute equilibrium at each temperature. Strain and frequency were set to be 1.0% and 1 Hz, respectively.

Flammability Test

A torch flame was placed on the tested electrolytes for 10 seconds and then removed. The flammability was monitored.
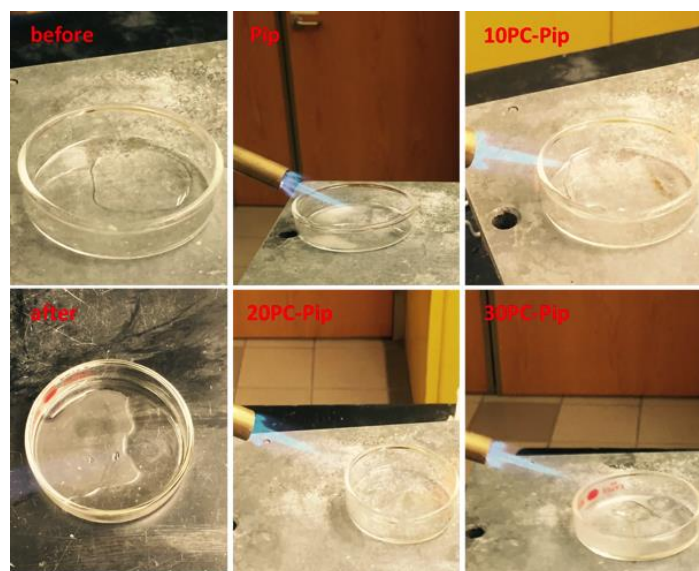
Figure S2. Flammability test to demonstrate the safety of Pip and Pip-PC electrolyte mixtures

Linear Sweep Voltammetry
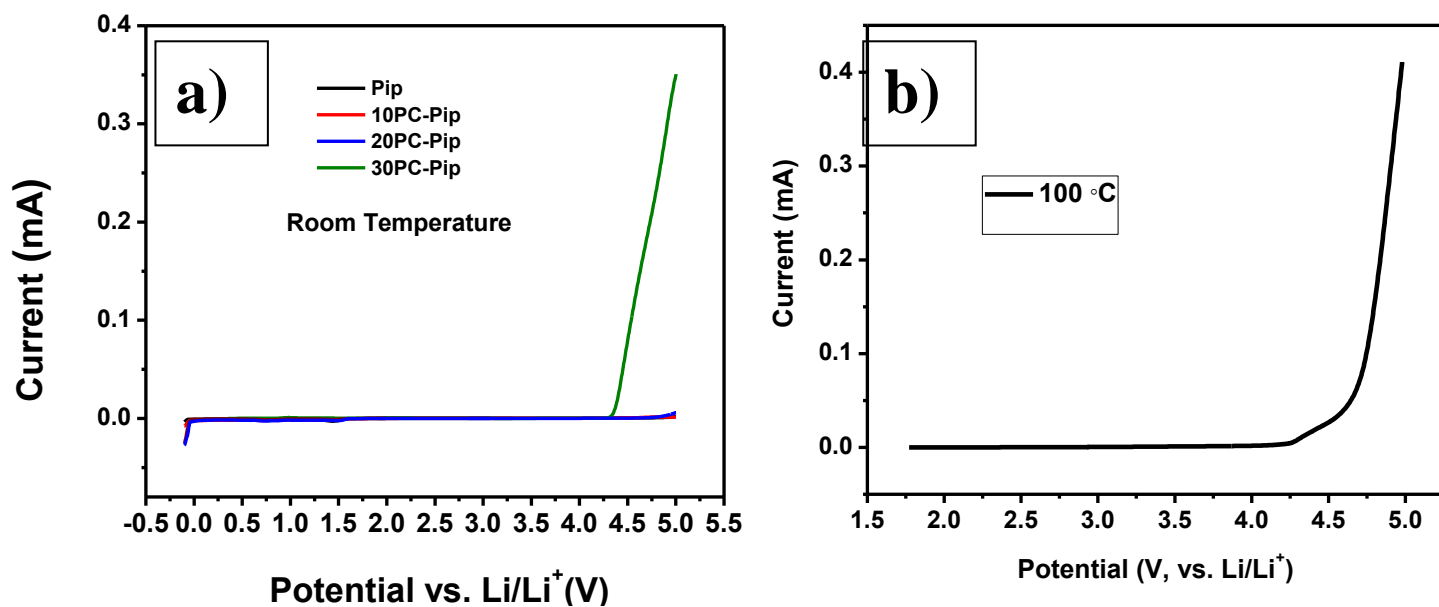
Figure S3. a) Electrochemical stability of Pip and Pip-PC electrolyte mixtures at room temperature from -0.1 to 5.0V and (b) Al current collector corrosion test using three electrode system with LiTSI salt containing electrolyte

Transport properties of electrolyte mixtures

The measured ionic conductivities were found to present a VTF behavior with temperature and were fitted using the Equation (S1),

$$\sigma = \frac{A}{\sqrt{T}} e^{-\frac{E_a}{R(T-T_o)}} \qquad (S1),$$

Where σ is the ionic conductivity, A is a pre-exponential factor, E_a is the pseudo activation energy, T_o is the ideal glass transition temperature, R is the gas constant and T is the absolute temperature.[1-3] The fitted parameters are presented in Table S1 and the VTF plot for the 4 samples is presented in Figure S4

For RTIL-organic solvent mixtures, a decrease in T_o with solvent addition is a commonly reported result. However, the pseudo activation energy follows a trend that seems to be strongly dependent on the nature of the RTIL and the solvents being mixed, rendering i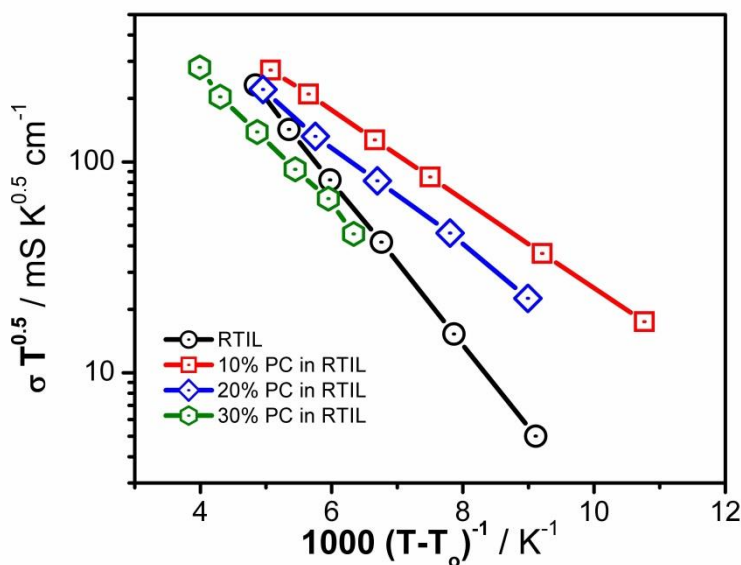ts behavior rather unpredictable. Since the VTF model assumes a free volume-mediated ionic motion,[3] the pseudo activation energies reflect the actual solvation state of the charge carriers in solution, which can be expected to change with salt concentration, RTIL structure, mutual solubility of the two liquids and content of organic solvent. Nevertheless, stoichiometries for the RTIL-organic solvent mixtures have been reported in wt%,[1,2] vol% and mol%,[3] extending the system to a broad range of composition and making comparisons difficult.

Figure S4. Vogel-Tammann-Fulcher ionic conductivity plot for the LiTFSI solutions in RTIL and solvent mixtures

Table S1. Parameters obtained by fitting the ionic conductivity data with the VTF equation

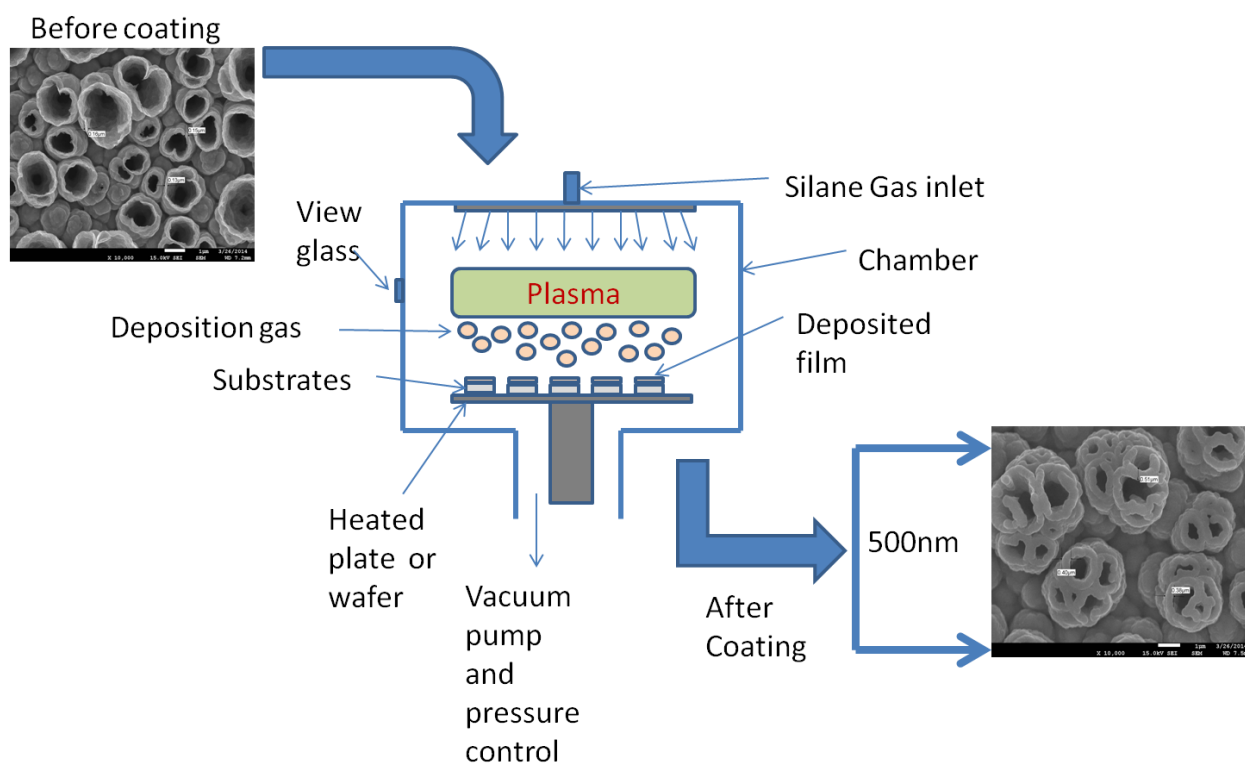| PC content / vol%	A / S K$^{0.5}$ cm^{-1}	Ea / kJ mol^{-1}	T_o / K	R^{2*}
0	17.4	7.4	185.9	0.99993
10	3.2	4.0	205.1	0.99996
20	3.3	4.6	185.0	0.99818
30	5.2	6.2	142.2	0.99501

*Correlation coefficient for the fitting.

Fabrication of 3D Ni current collector and conformal deposition of silicon to form 3D Si

In order to understand the stability and electrochemical performance of chosen RTIL and RTIL mixtures as an electrolyte for Li-ion batteries at elevated temperatures, high capacity 3D Si electrodes have been used as a working electrode vs. Li/Li$^+$. To develop 3D Si structure, porous 3D Ni current collectors are prepared by customization of electrodeposition procedure. Electro deposition has been performed to prepare Ni-Cu alloy on the stainless steel substrate galvanostatically at -10mA/cm^2 for 2h. The selective etching of Cu component from Ni-Cu alloy film resulted in 3D porous Ni current collector. Then, conformal coating of silicon on the 3D Ni current collector is done using plasma-enhanced chemical vapor deposition (PECVD) technique. The PECVD was tailored by optimizing deposition time, flow rate and power etc. so that deposition of 500 nm of silicon is equivalent to planar thicknesses on 3D Ni under vacuum. The surface morphology of the electrodeposited 3D porous Ni before and after the Si deposition is shown in Figure S4 along with the schematic representation of PECVD technique used for Si deposition. FESEM images confirm the porous structure with the uniform size of 1~2 μm and the same could be tuned by changing deposition parameters. The thickness of deposited silicon (>400 nm) on 3D Ni structure has been understood from the difference in 3D Ni wall thickness before and after coating (Figure S5).

Prior to testing ionic liquid based electrolytes, electrochemical performance of 3D Si has been verified by fabricating cells with 1 M of LiPF$_6$ in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as an electrolyte with celgard separator and the results are displayed in Figure S5 and Figure S6. It is seen from study that 3D silicon anode delivered a capacity as high as 2400 mAh/g (0.45 mAh/cm^2) with an appreciable capacity retention and a negligible capacity fade of 7% corresponding to 50 cycles. Also, rate capability test is performed to understand the feasibility of 3D Si for high rate applications, it has been observed that stable reversible discharge capacities of 2400, 2000, 1450 and 970 mAh/g were observed at C/10, C/5, C/2 and C-rates, respectively. Based on these intriguing results, extended rate capability behaviour of silicon anode has been studied and an appreciable capacity of > 1000 mAh g^{-1} has been observed with 500 nm of Si on 3D Ni for 50 cycles with ~99% capacity retention. Thus, 3D Si is qualified as a potential anode with commercial organic electrolytes for room temperature lithium battery applications.

Before coating

View glass

Silane Gas inlet

Chamber

Plasma

Deposition gas

Deposited film

Substrates

Heated plate or wafer

Vacuum pump and pressure control

After Coating

500nm

Figure S5. FE-SEM images of bare porous 3D Ni current collector and the same deposited with 500 nm of silicon to form 3D Si electrode
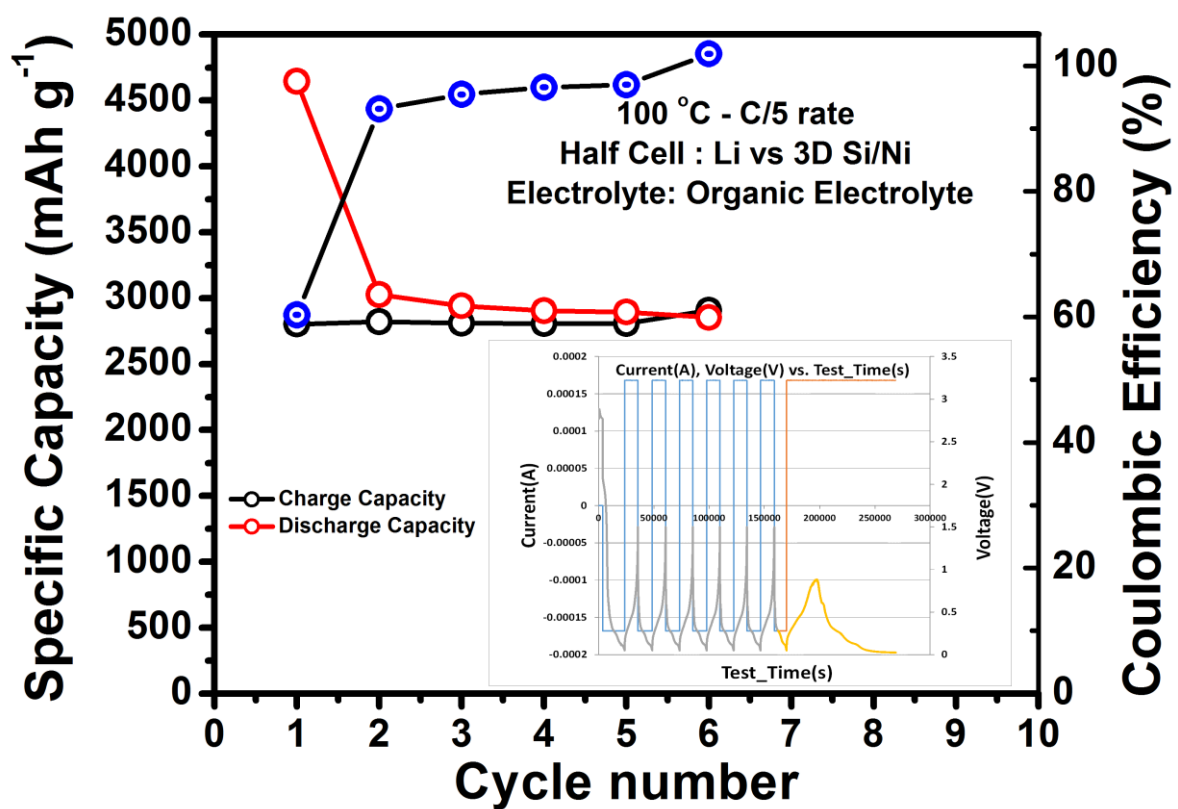
**Additional Battery Testing Results**
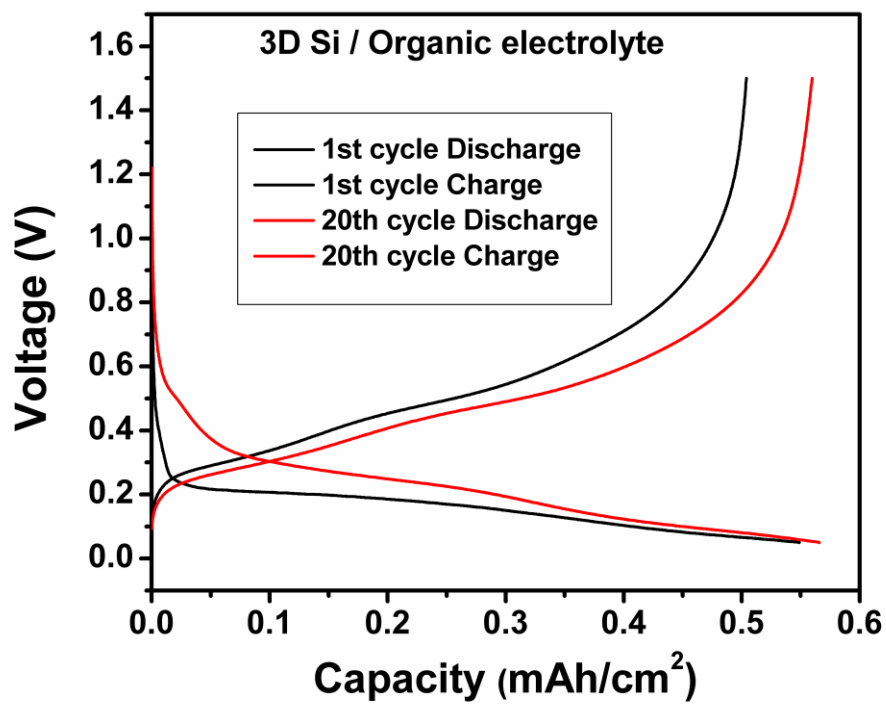
Figure S6. Typical charge-discharge profiles of 3D Si electrode with organic electrolyte
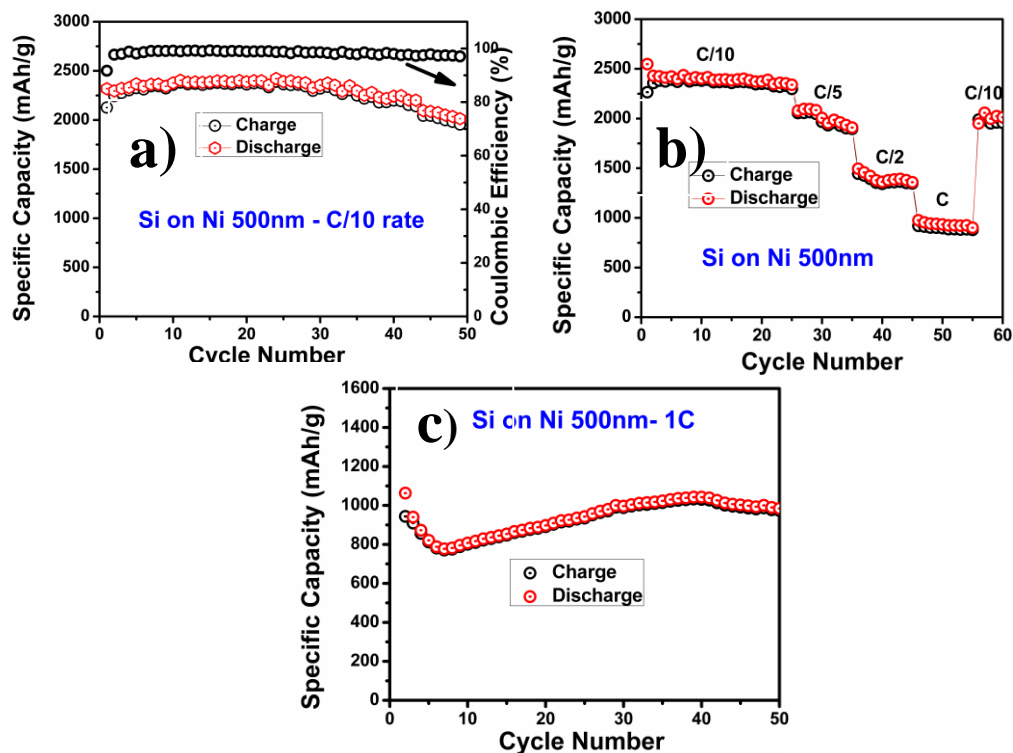
Figure S7. Electrochemical properties of 3D Si electrode with organic electrolyte a) specific capacity vs. cycle number, b) rate capability and c) cycling behavior at 1C

Figure S8. Electrochemical performance of silicon electrode with organic electrolyte at 100 °C
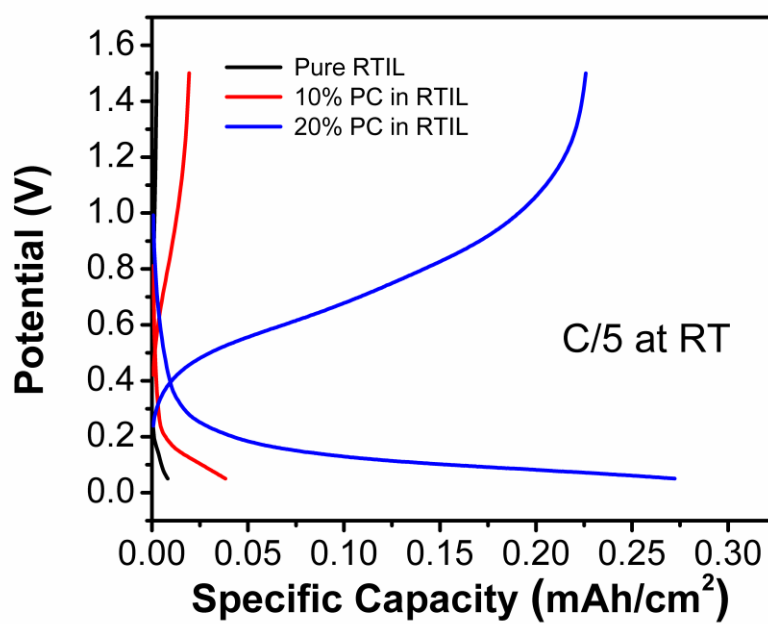
Figure S9. Comparative charge-discharge profiles with different PC concentration in RTIL electrolyte at RT
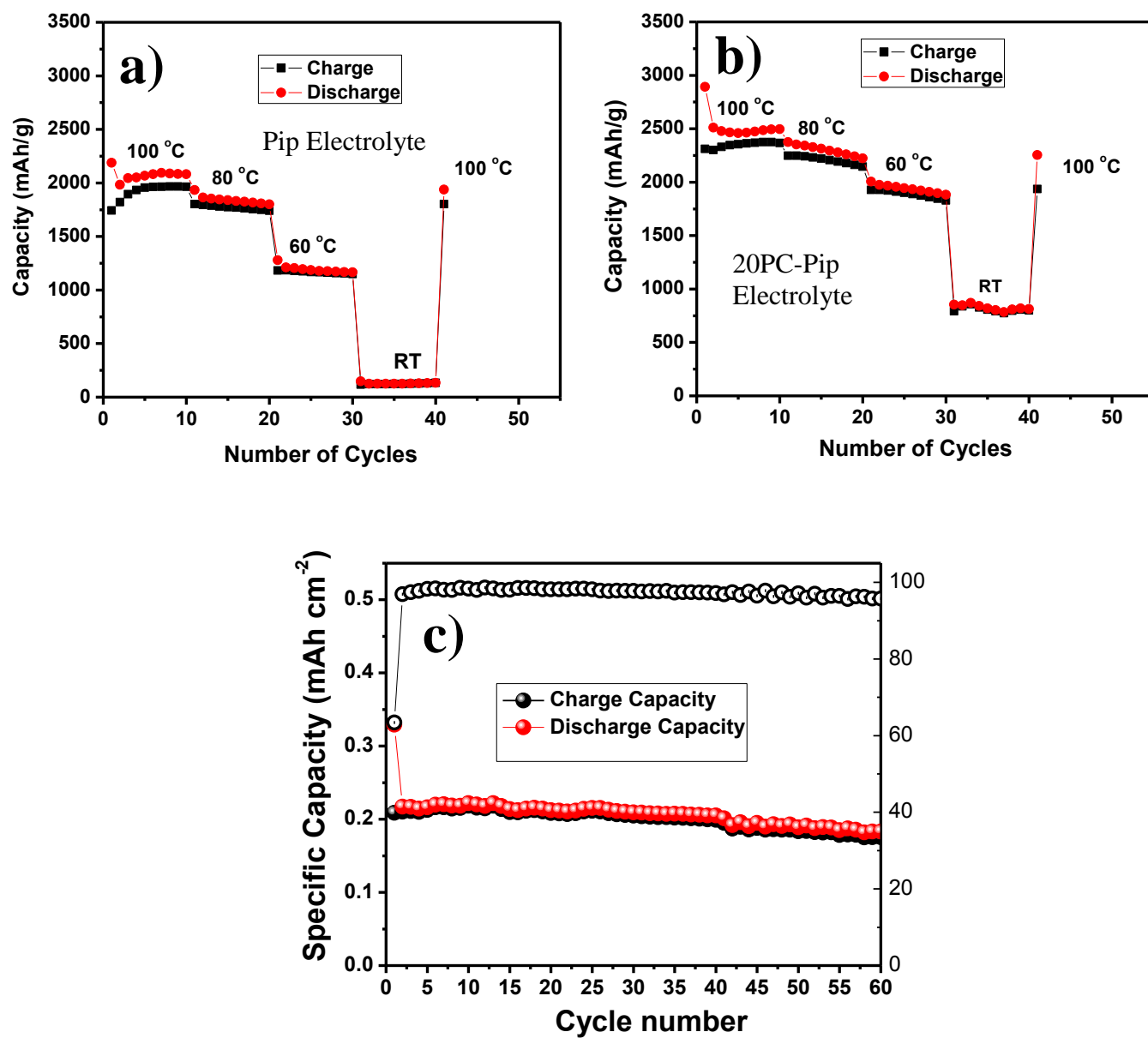
Figure S10. Gravimetric electrochemical performance of silicon electrode with (a) Pip, (b) 20PC- Pip electrolyte mixture and (c) high rate (2C) cycling performance of silicon electrode at 100 °C with 20PC-Pip electrolyte.
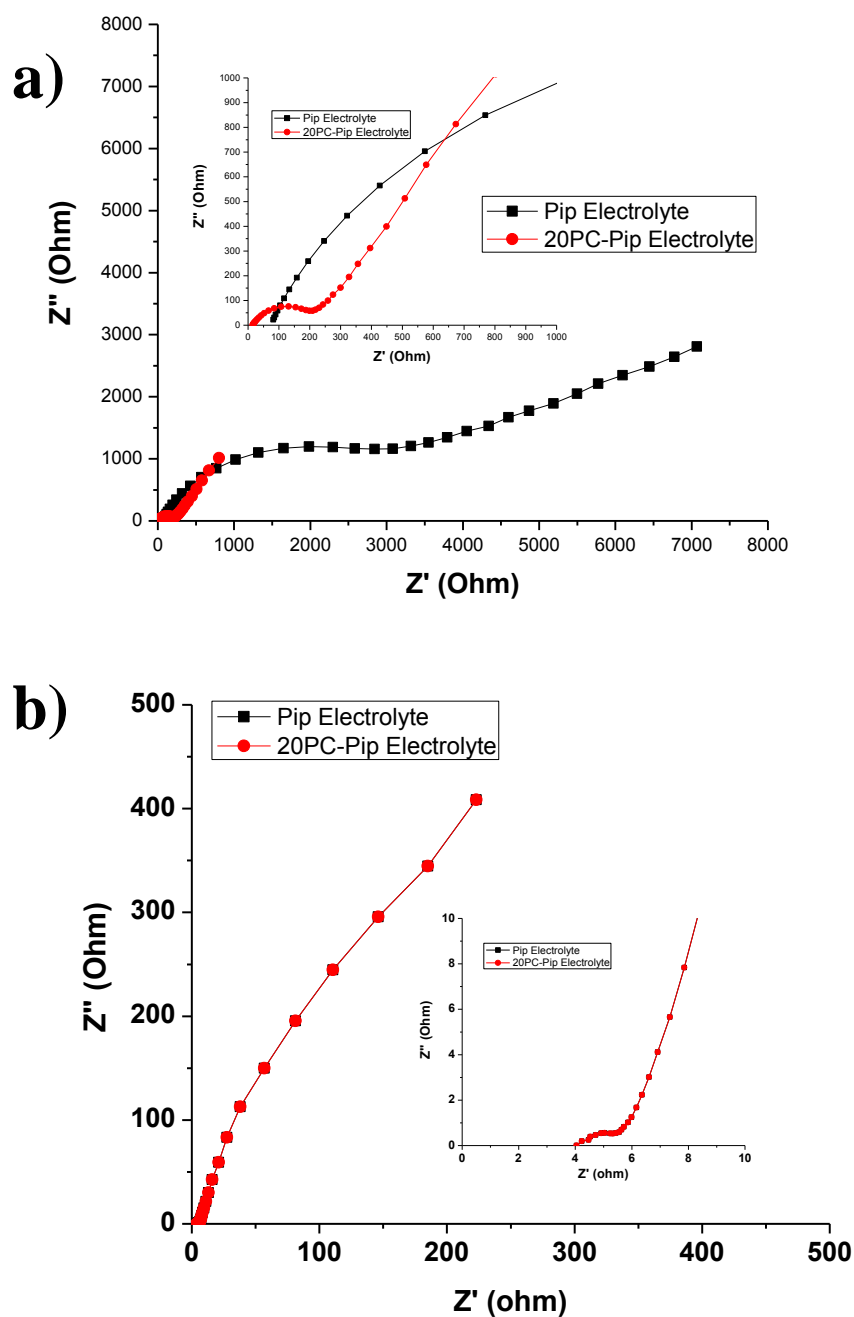
Figure S11. Electrochemical impedance spectroscopy studies of silcion electrodes with Pip and 20PC-Pip electyrolytes at (a) RT and (b) 100 °C
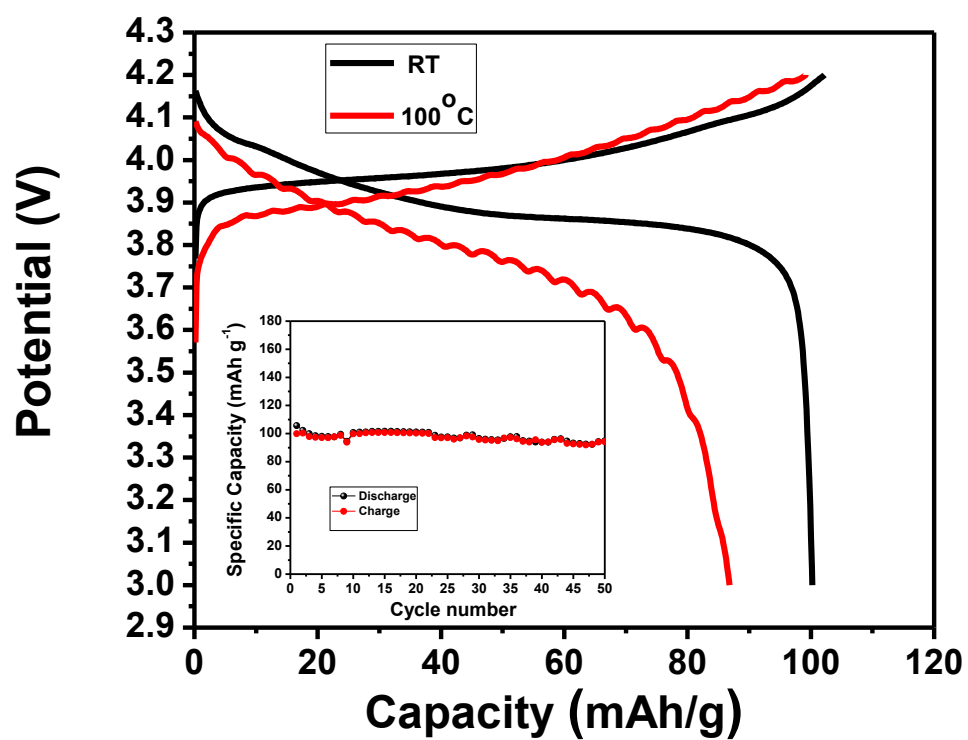
**Figure S12**. Feasibility tests of 20PC- Pip electrolyte mixture for LiCoO$_2$ cathodes

XPS Chacterization

The disassembled silicon electrodes (on discharged state) are carefully transferred from glove box to XPS fast entry lock using transferable vacuum chamber without exposing them to atmospheric air. XPS measurements were carried out with a Thermo Scientific K-Alpha XPS (ESCA) using focused mono- chromatized Al Ka radiation (hn 1⁄4 1486.6 eV). The pass energy was set to 20 eV allowing an energy resolution of approximately 400 meV. No charge neutralization was used. The binding energy scale was calibrated from the hydrocarbon C 1s peak at 284.8 eV.
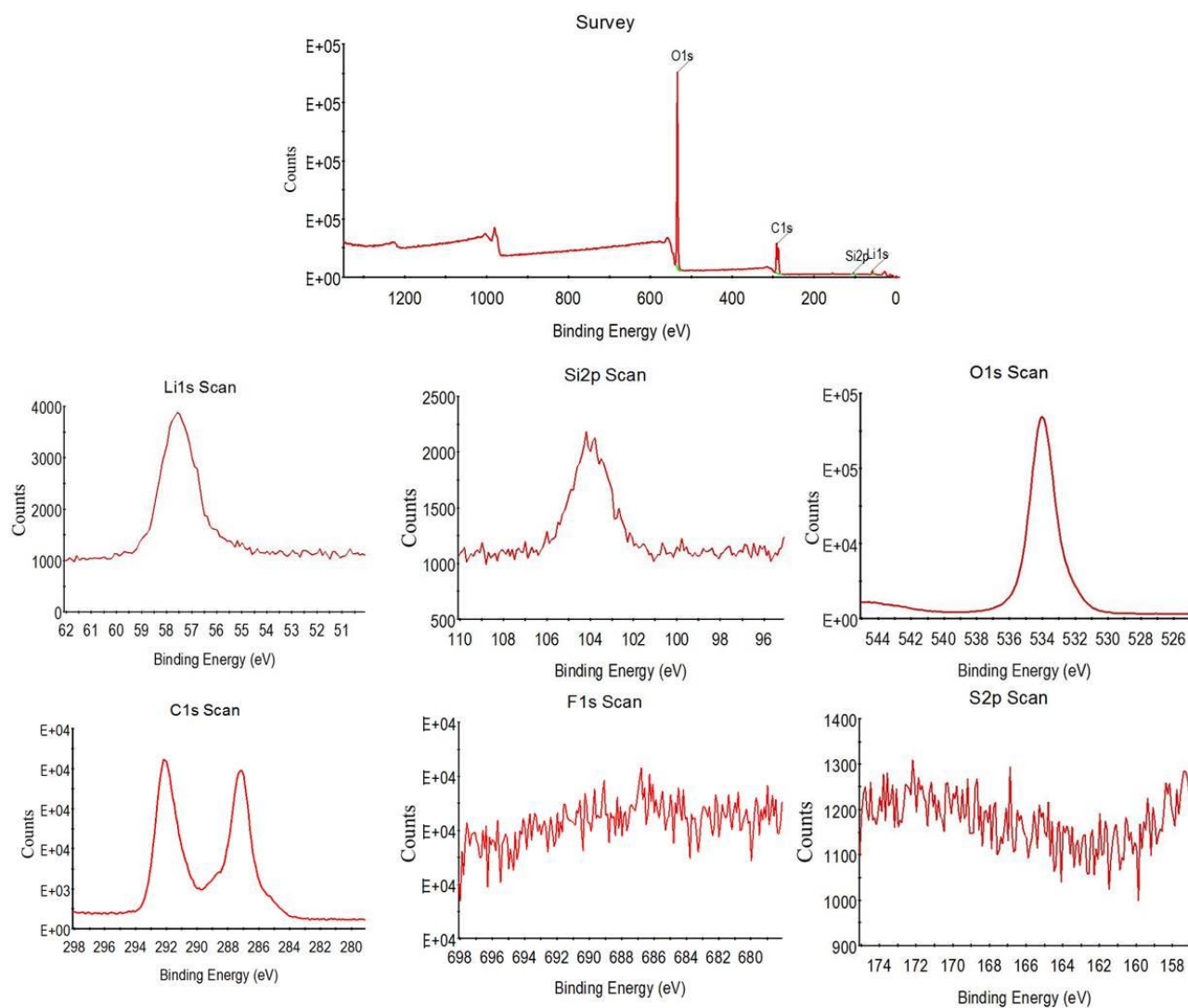
Figure S13. Survey and high resolution x-ray photoelectron spectra of silicon electrode with organic electrolyte (discharged state)
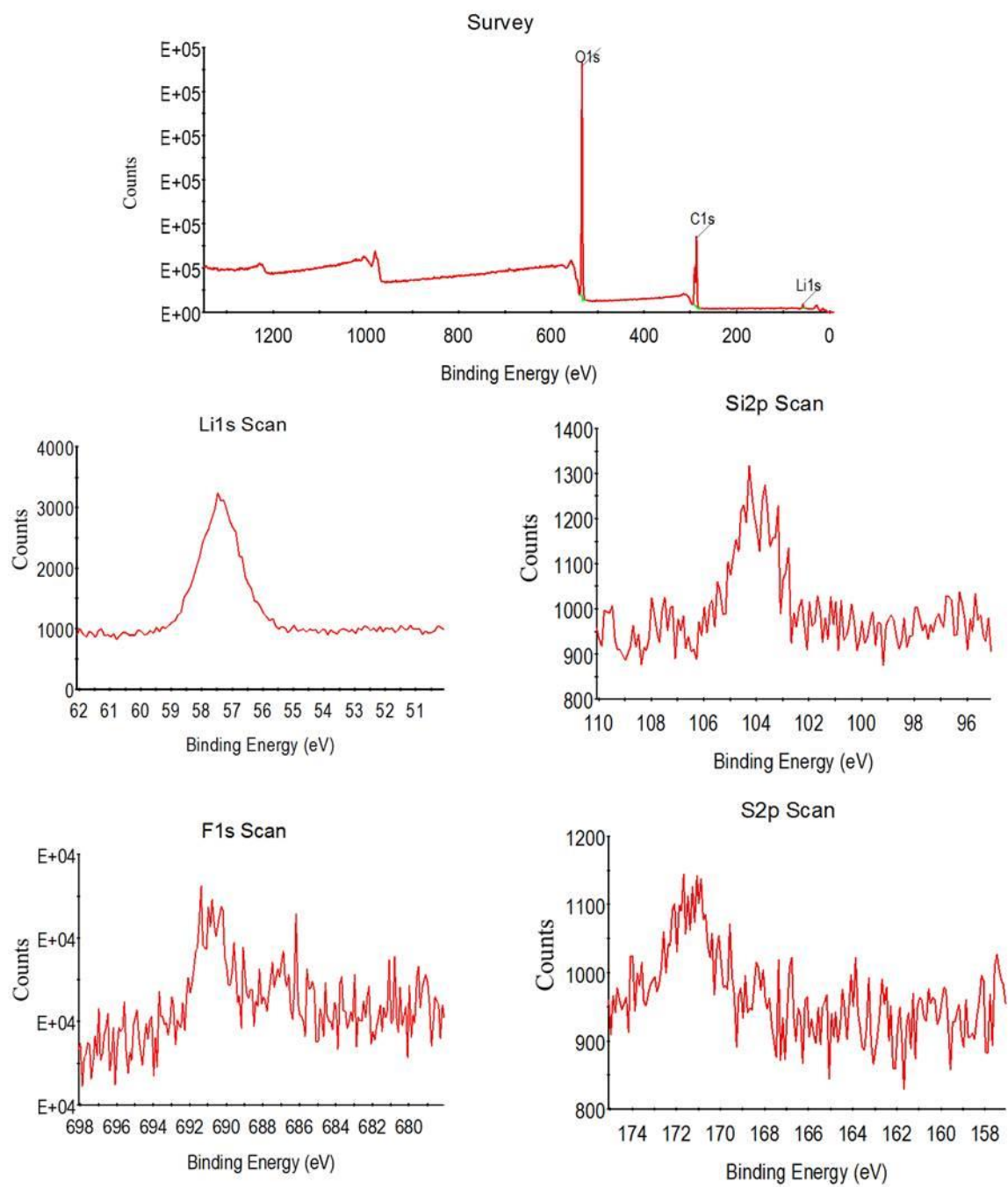
Figure S14. Survey and high resolution x-ray photoelectron spectra of silicon electrode with Pip RTIL electrolyte (discharged state)
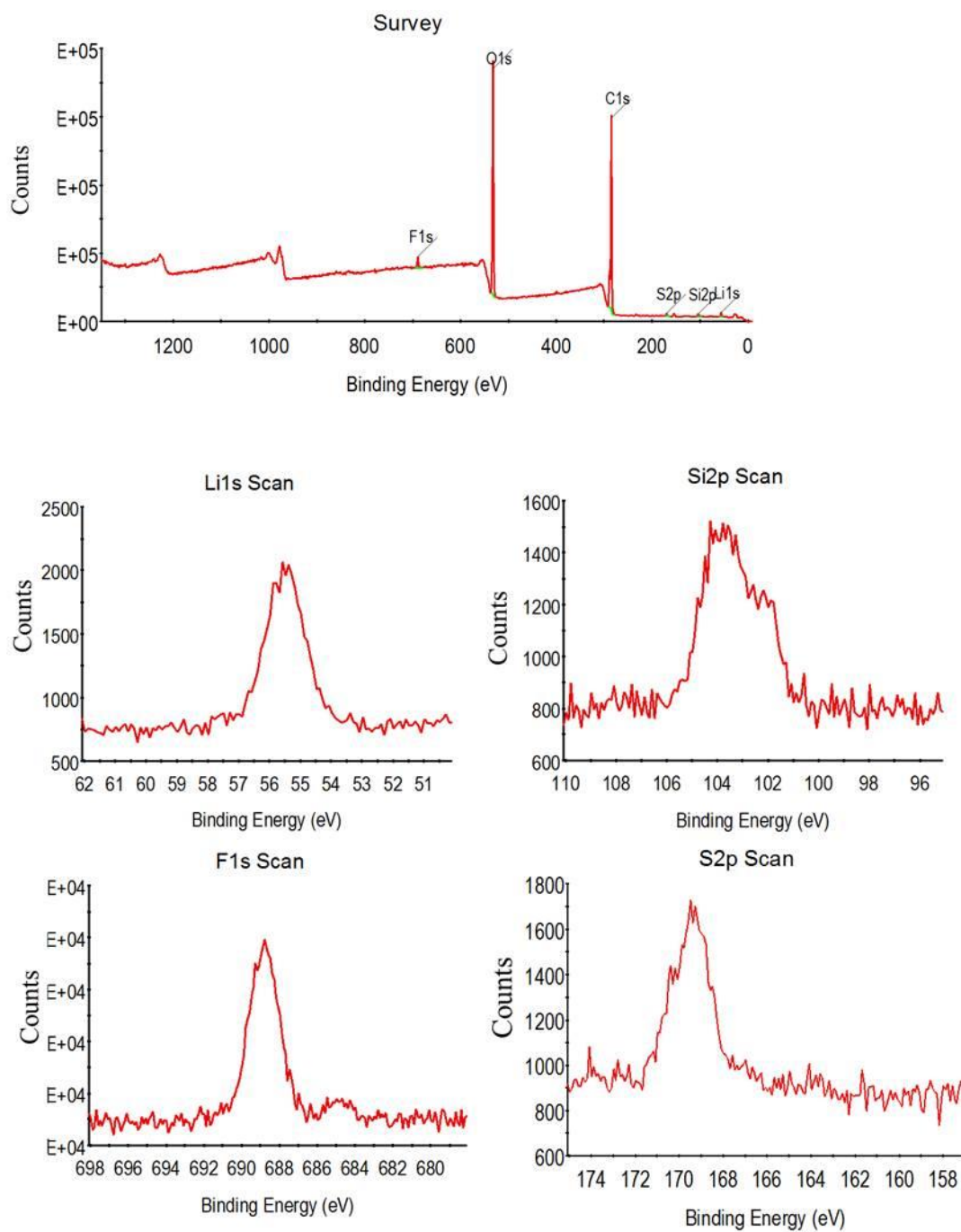
Figure S15. Survey and high resolution x-ray photoelectron spectra of silicon electrode with Pip RTIL-20%PC electrolyte mixture (discharged state)

Table S2. Atomic composition of the SEI formed on silicon electrodes using different electrolytes.

Element	Atomic Composition / %		
	1:1 EC/DEC + 1M LiPF$_6$	RTIL + 0.8M LiTFSI	RTIL + 20 vol% PC + 0.8M LiTFSI
O	44.29	37.06	26.08
C	31.51	40.23	56.25
Si	2.78	0.23	1.05
Li	22.96	21.79	15.54
F	0.13	0.26	0.59
S	-	0.05	0.07
N	0.18	0.38	0.42

SEM
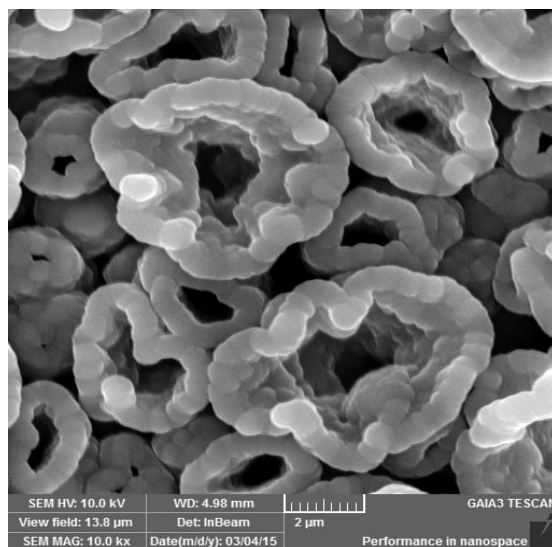
Figure S16. Scanning electron images of 3D silicon electrodes at lithiated state with conventional organic electrolyte

References

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3. Montanino, M.; Moreno, M.; Carewska, M.; Maresca, G.; Simonetti, E.; Lo Presti, R.; Alessandrini, F.; Appetecchi, G. B. Mixed organic compound-ionic liquid electrolytes for lithium battery electrolyte systems. J. Power Sources. 2014, 269, 608-615.