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Supporting Information

Influence of Carbonate-Based Additives on the Electrochemical Performance of Si NW Anodes Cycled in an Ionic Liquid Electrolyte

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Experimental

Chemicals Used. All chemicals were used as received. Phenylsilane (PS, 97 %) was supplied by Fluorochem and was stored and dispensed from an Ar-filled glovebox. *N*-methylpyrrolidine (Aldrich, 98 %), 1-bromopropane (Aldrich, 99 %), activated charcoal (Aldrich, Darco-G60), alumina (Aldrich, acidic, Brockmann I), LiTFSI (3 M, 99.9 %), and NaFSI salts (Solvionic, 99.9 %) were used as received. The ethylene carbonate, (EC, 99.9 %), and vinylene carbonate (VC, 97 %) additives were purchased from Merck and used as received.

Substrate Preparation. Stainless steel (SS, 316) foil was purchased from Pi-Kem Ltd. with a thickness of 0.1 mm. The foil was roughened using P600 grit sandpaper to increase the surface area and improve the contact between the current collector and the active material. From this,

substrates of approximately 8 mm x 8 mm were cut and rinsed with acetone. A 20 nm layer of Sn (99.999%, Kurt J. Lesker) was then thermally evaporated onto these pieces in a glovebox-based evaporation unit. The substrates were stored in the Ar filled glovebox prior to reactions to minimize oxidation.

Reaction Setup.

Si NW Synthesis. Si NWs were grown from stainless steel current collectors using a previously published solvent vapour growth system. Reactions were carried out in a long-neck Pyrex 100 mL round bottomed flask containing 7 ml of squalane (Sigma Aldrich, 99%). The growth substrates were placed below the liquid line in the flask, which was attached to a Schlenk line setup *via* a water condenser. This was ramped to a temperature of 125 °C using a three-zone furnace. A vacuum of at least 100 mTorr was applied for 1 h to remove moisture from the system. Following this, the system was purged with Ar. The flask was then ramped to the reaction temperature under a constant Ar flow. A water condenser was used to control the HBS reflux and ensure that the reaction was kept under control. At a reaction temperature (460 °C) 0.75 mL of the phenylsilane precursor was injected, through a septum cap, into the system and the reaction was allowed to proceed for 1 h. Si NW growth proceeded *via* the solution liquid solid growth mechanism. When terminating the reaction, the furnace was opened and the setup was allowed to cool to room temperature before removing the NW coated substrates. The synthetic method allowed for the direct preparation of Li-ion battery electrodes as NWs are grown directly from the CCs, with mass loadings of approximately 0.2 mg/cm² used in this study. This translated to a theoretical area capacity of 0.72 mAh/cm² with the experimental (initial) areal capacities being in the range of: 0.44 – 0.40 mAh/cm². The directly grown active material was advantageous for this study as it allowed the SEI layer to be directly analysed on the Si NW surface, excluding the potential contributions to its composition from binders or conductive additives.

Electrochemical Measurements. The electrochemical performance was evaluated by assembling two electrode Swagelok type cells in an Ar filled glovebox. The cells consisted of Si NWs on a SS current collector (8 mm x 8 mm pieces) as the working electrode, Li foil as the counter and reference electrode and a Celgard separator. For the ionic liquid electrolyte solution *N*-Methyl-*N*-propylpyrrolidinium bis-(trifluoromethanesulfonyl) imide, PYR₁₃TFSI, and *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide, PYR₁₃FSI, ionic liquids were synthesized through a procedure reported elsewhere.⁷⁹ The electrolyte, 0.1LiTFSI–0.3PYR₁₃TFSI–0.6PYR₁₃FSI + 5 wt % EC or 5 wt % VC quaternary mixture, was prepared by dissolving (in the proper proportion and at 40 °C for a few minutes) LiTFSI (vacuum-dried overnight at 120 °C) in the PYR₁₃TFSI-PYR₁₃FSI mixture. Finally, the proper 5 wt. % of either EC or VC was added. A 5 wt. % additive quantity was selected to remain consistent with previous studies in this area, which have shown that 1-5 wt. % of an electrolyte additive is sufficient to influence the electrochemical performance of Li-ion battery. The ionic liquid electrolyte was stored in sealed glass vials within a dry-room. Galvanostatic measurements were carried out in a two electrode Swagelok-type cell using a Biologic MPG-2 in a potential range of 0.01 – 1.0 V *versus* Li/Li⁺. The entire electrochemically active mass was used to calculate the currents applied.

Material Characterization. Scanning electron microscopy (SEM) analysis was performed on a Hitachi SU-70 system operating between 5 and 20 kV. The uncycled substrates required no prior treatment before SEM analysis. For transmission electron microscopy (TEM) analysis the NWs were removed from the growth substrate through sonication before being drop cast onto a lacy carbon TEM grid. TEM analysis was conducted at 200 kV on a JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector. For *ex-situ* analysis the SEI layer was removed, by soaking the electrodes in acetonitrile for 24 h before rinsing with 0.1 mM acetic acid, deionized H₂O and ethanol in that

order, prior to imaging. The respective mass of Si and Sn was determined through measurement using a Sartorius Ultra-Microbalance SE2 (repeatability $\pm 0.25 \mu\text{g}$). X-ray diffraction (XRD) analysis was carried out using a PANalytical X'Pert PRO MRD instrument with a Cu K R radiation source ($\lambda = 1.5418 \text{ \AA}$) and an X'celerator detector. XPS was performed using a Kratos ULTRA spectrometer using monochromatic Al K α 1486.58 eV. C 1s at 284.8 eV was used as the charge reference to determine the core level binding energies. The pass energy 160 eV was used for the survey spectra and 20 eV for the narrow regions. Construction and peak fitting of synthetic peaks in narrow region spectra used a Shirley type background and the synthetic peaks were of a mixed Gaussian-Lorentzian type. XPS examination of the SEI layer the electrodes were briefly rinsed with dimethylcarbonate (DMC) to remove excess IL prior to analysis. For XPS analysis of the post-cycled Si NWs the SEI was removed by first rinsing with acetonitrile, followed by 1 mM acetic acid, deionized water and ethanol before allowing to air dry.

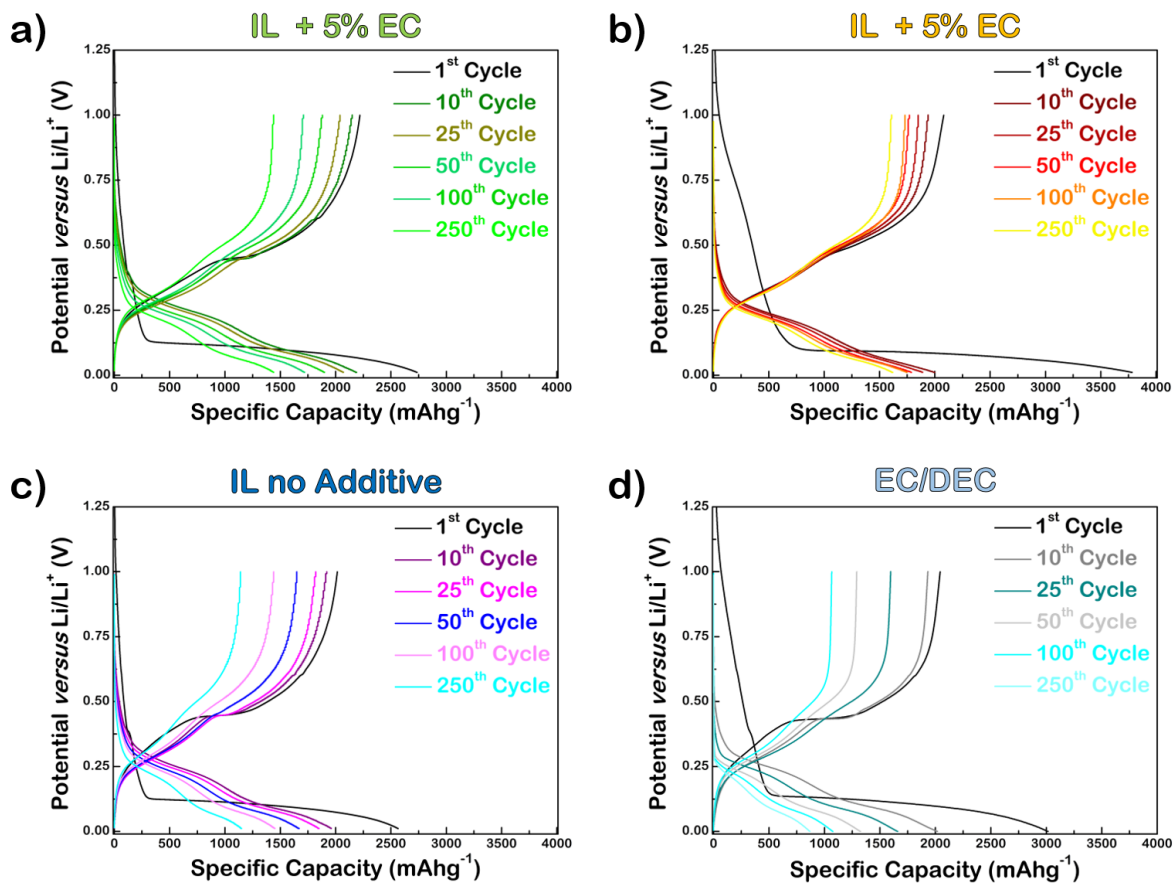


Figure S1. Voltage profiles of the 1st, 10th, 25th, 50th, 100th, and 250th charge and discharge cycles for the Si NWs cycled in a) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% EC, b) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% VC, c) and 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI ionic liquid electrolytes, d) as well as in EC/DEC carbonate electrolyte

EC/DEC + No Additive

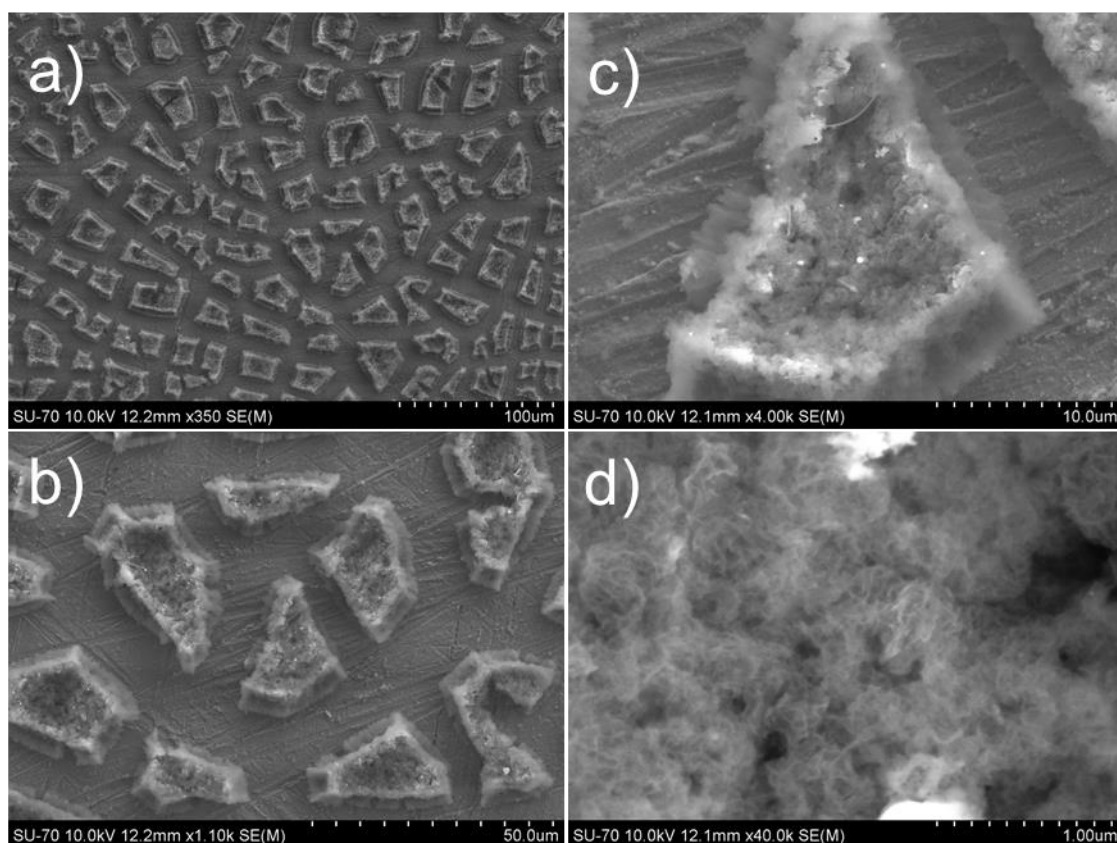


Figure S2. SEM images at different magnifications of the Si NW morphology after 100 cycles in a 1 M LiPF₆ in EC/DEC (1:1 v/v) electrolyte.

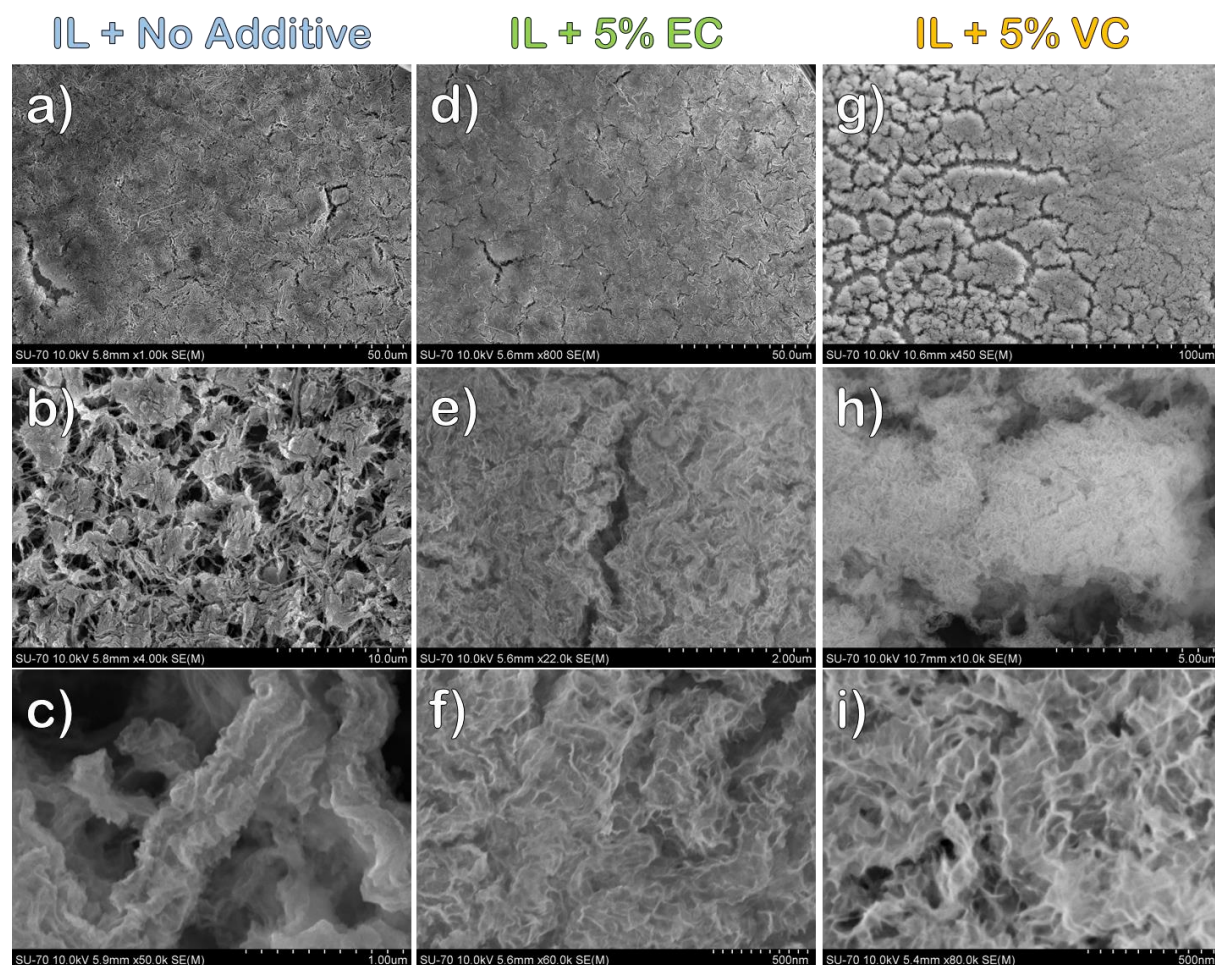


Figure S3. SEM images at different magnifications of the Si NW morphology after 100 cycles in (a-c) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI, (d-f) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% EC and (g-i) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% VC electrolyte.

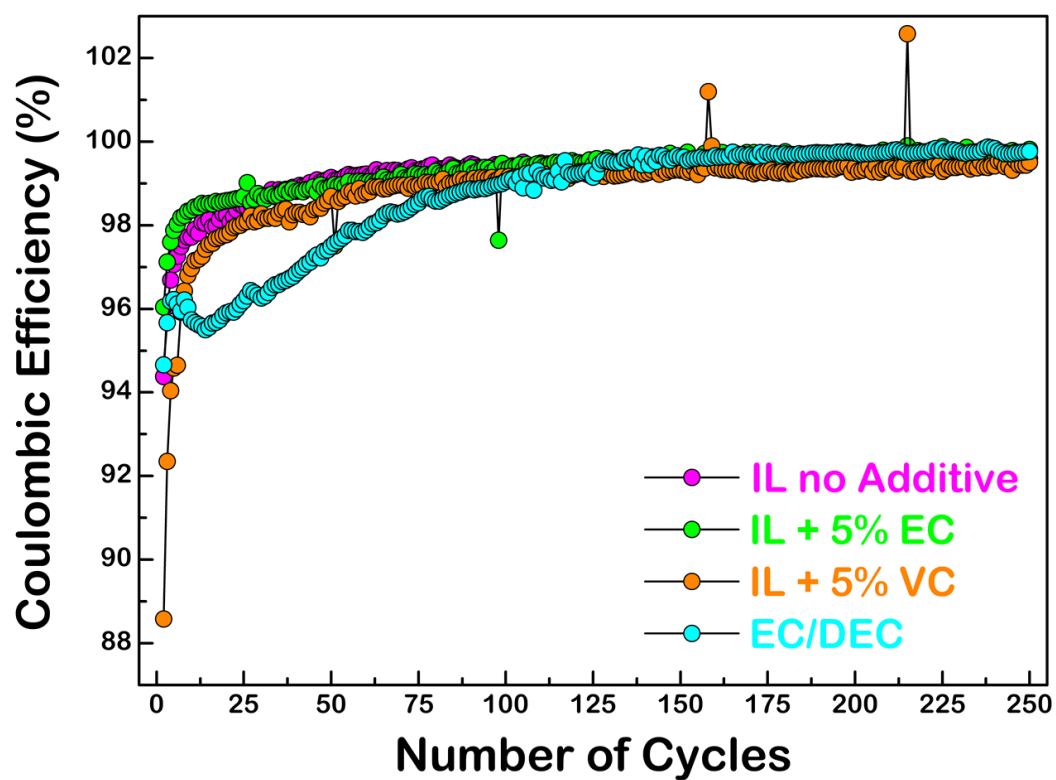


Figure S4. Coulombic efficiencies for the Si NWs cycled in 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% EC, 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% VC, and 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI ionic liquid electrolytes, as well as in EC/DEC carbonate electrolyte. For clarity the plot begins with the 2nd CE value. The initial CE values were 78.59 % (IL), 81.14 % (IL + 5% EC), 55.01 % (IL + 5% VC) and 67.78 % (EC/DEC)

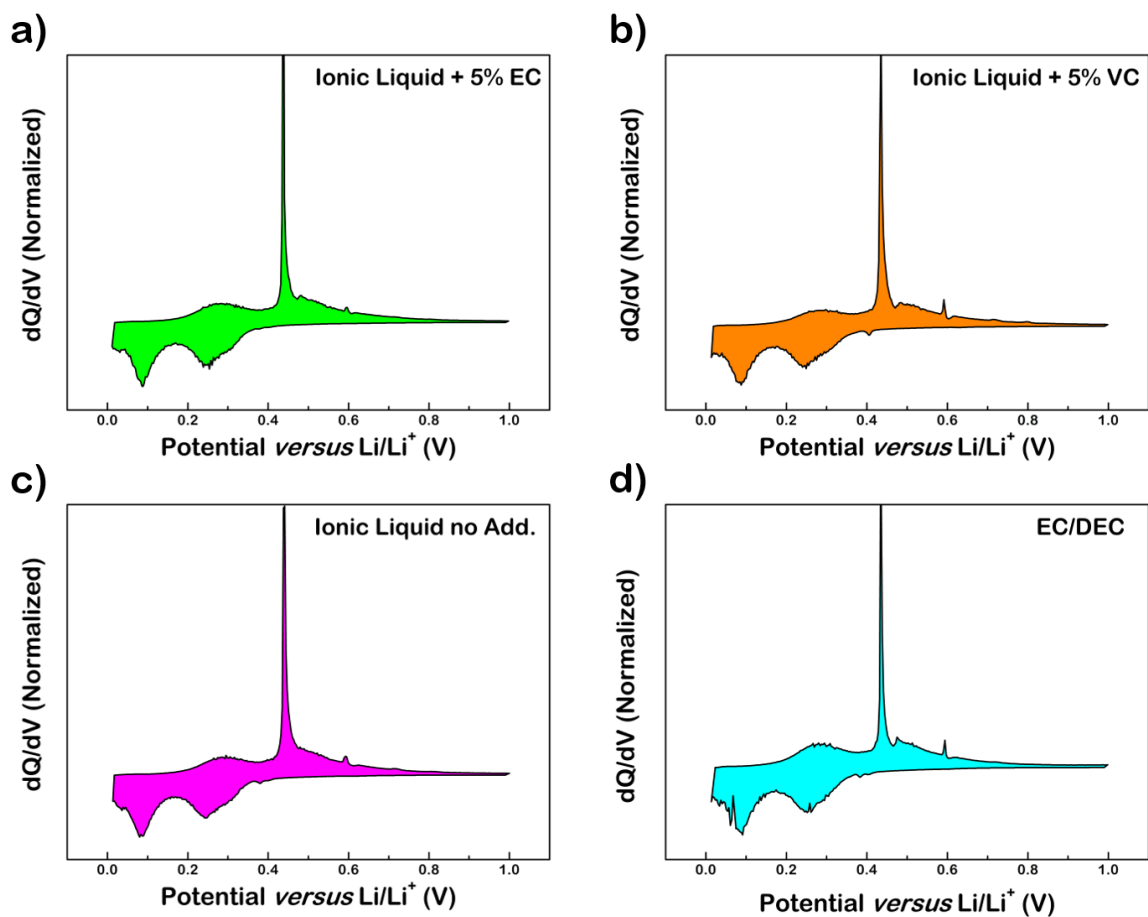


Figure S5. Comparison of differential capacity plots (of the 2nd cycle) for the Si NWs cycled in a) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% EC, b) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% VC, c) and 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI ionic liquid electrolytes, d) as well as in EC/DEC carbonate electrolyte.

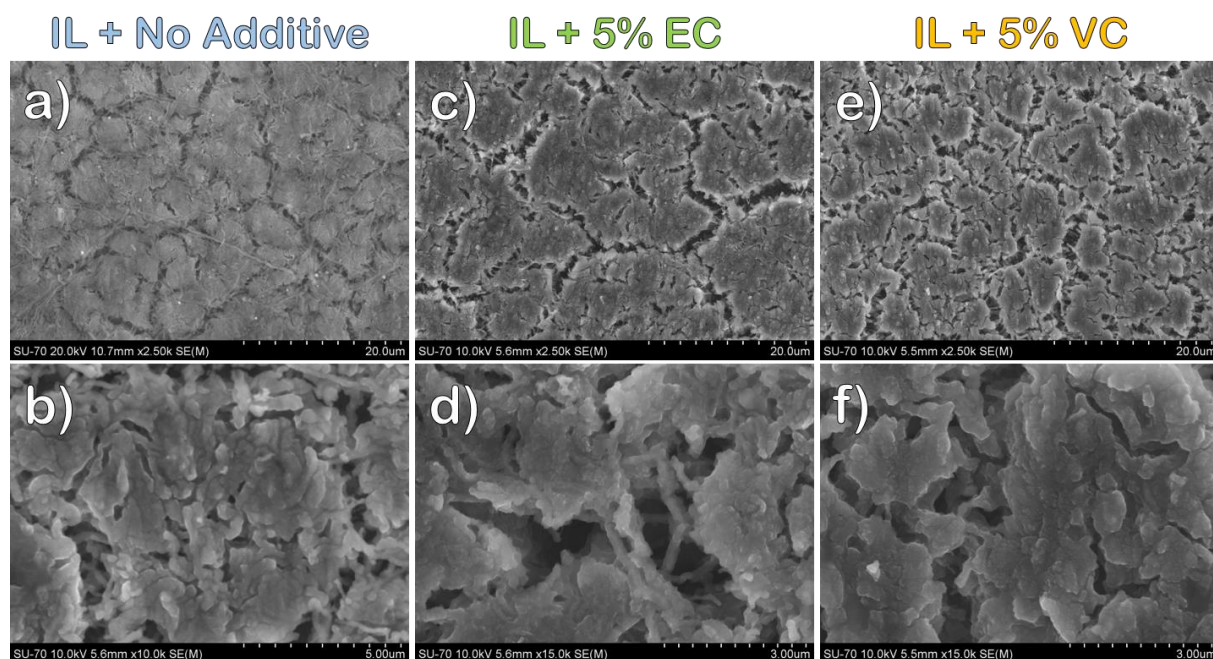


Figure S6. SEM images of the SEI layer formed on Si NWs after 100 cycles in (a-b) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI, (c-d) .1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% EC and (e-f) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% VC electrolyte.

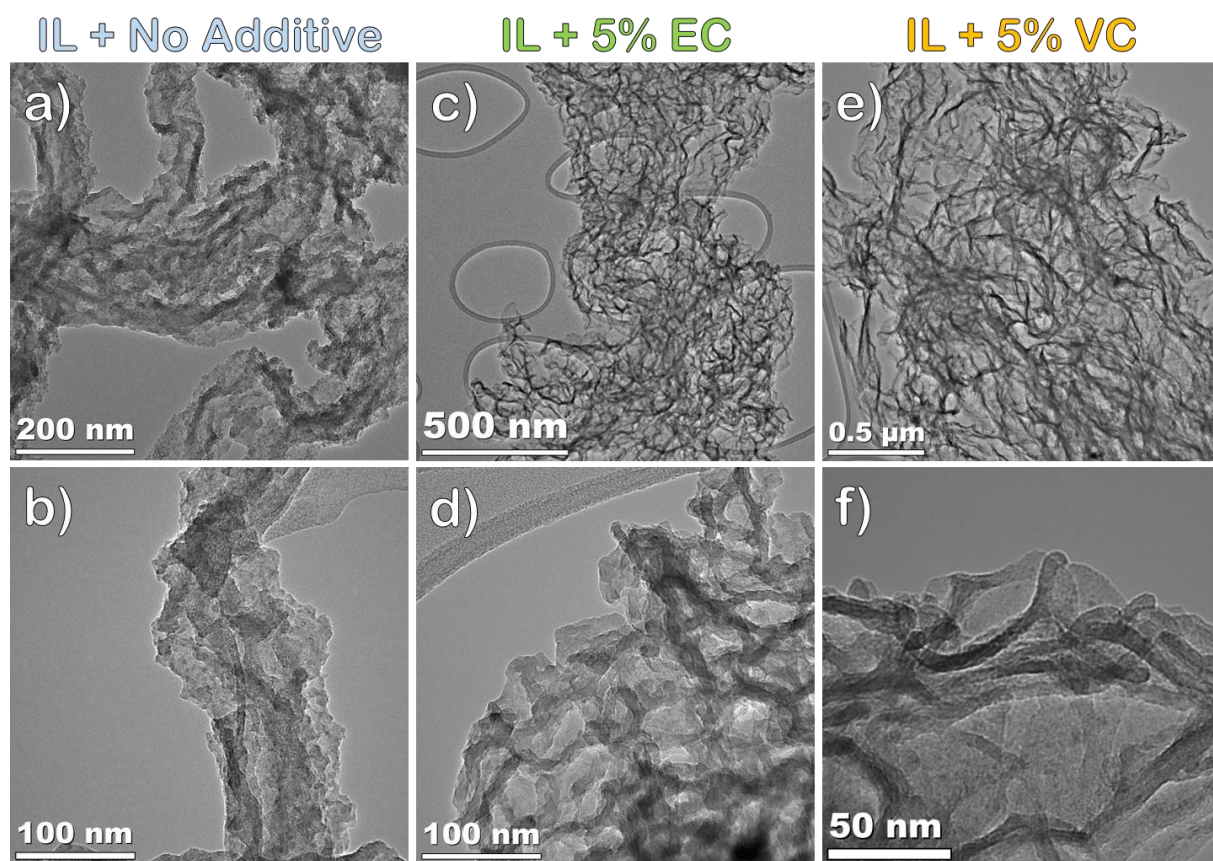


Figure S7. TEM images at different magnifications of the Si NW morphology after 100 cycles in (a-b) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI, (c-d) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% EC and (e-f) 0.1LiTFSI-0.6PYR₁₃FSI-0.3PYR₁₃TFSI + 5% VC electrolyte.

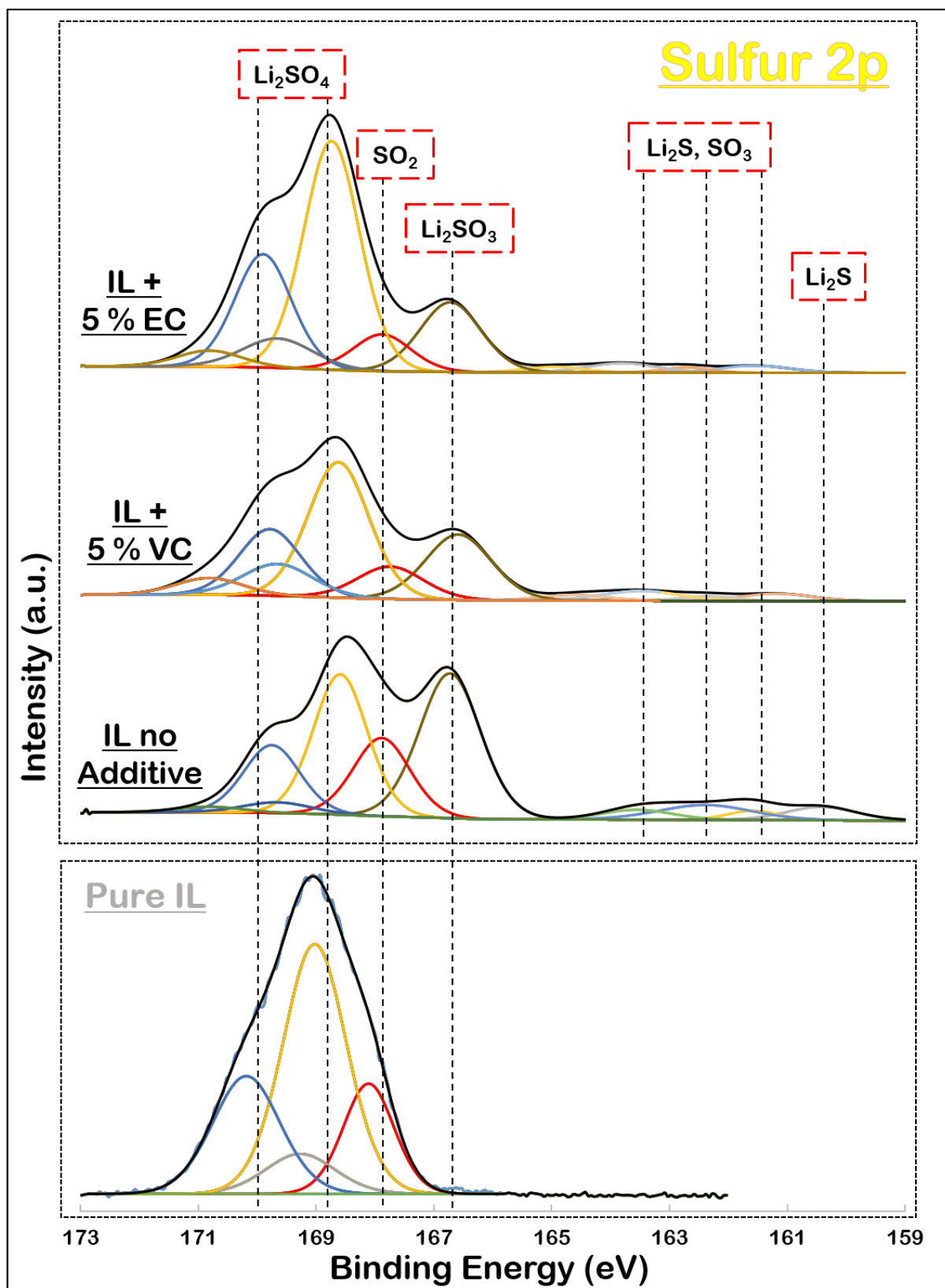


Figure S8. High resolution S 2p spectra of the Si NWs after 100 cycles using each additive as well as the XPS obtained for the IL directly.