

## Supplementary Material

## Superior compatibility of silicon nanowire anodes in ionic liquid electrolytes

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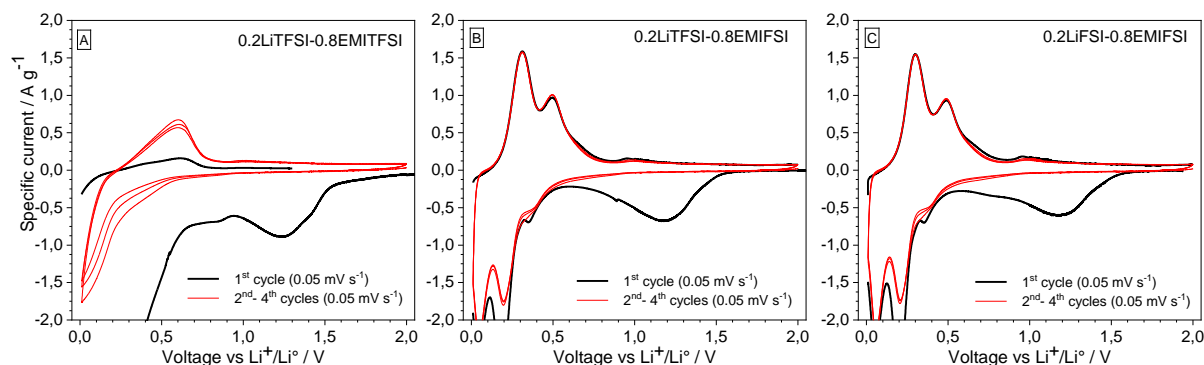
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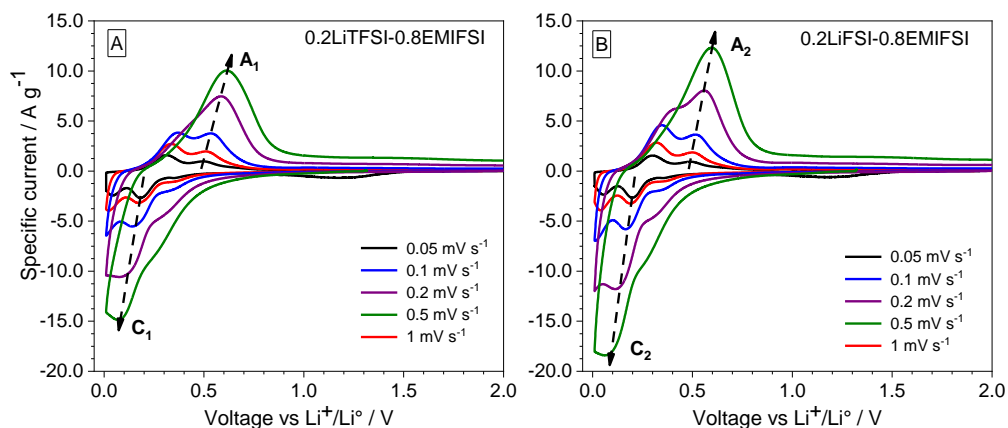
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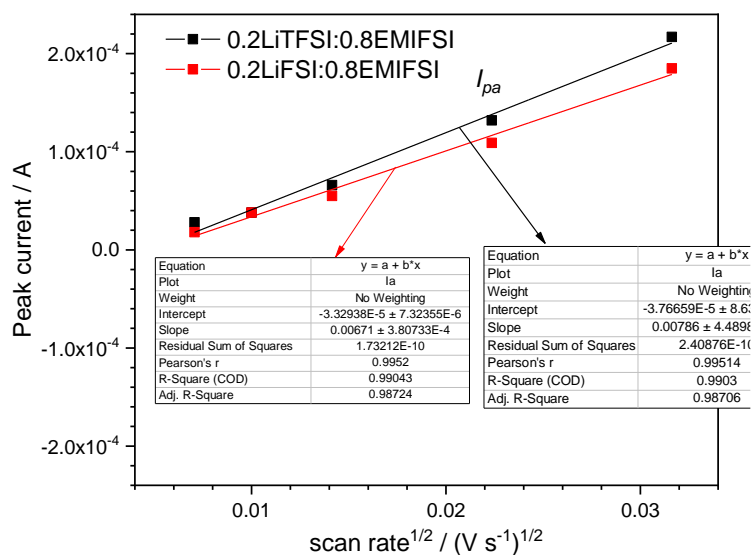
\*Correspondence to: Dr. Giovanna Maresca, Department of Basic and Applied Sciences of Engineering, La Sapienza University of Rome, Piazzale Aldo Moro 5, Rome 00185, Italy. E-mail: giovanna.maresca@uniroma1.it; Dr. Giovanni Battista Appetecchi, ENEA, Technologies and Devices for Electrochemical Storage (TERIN-DEC-ACEL), Via Anguillarese 301, Rome 00123, Italy. E-mail: gianni.appetecchi@enea.it



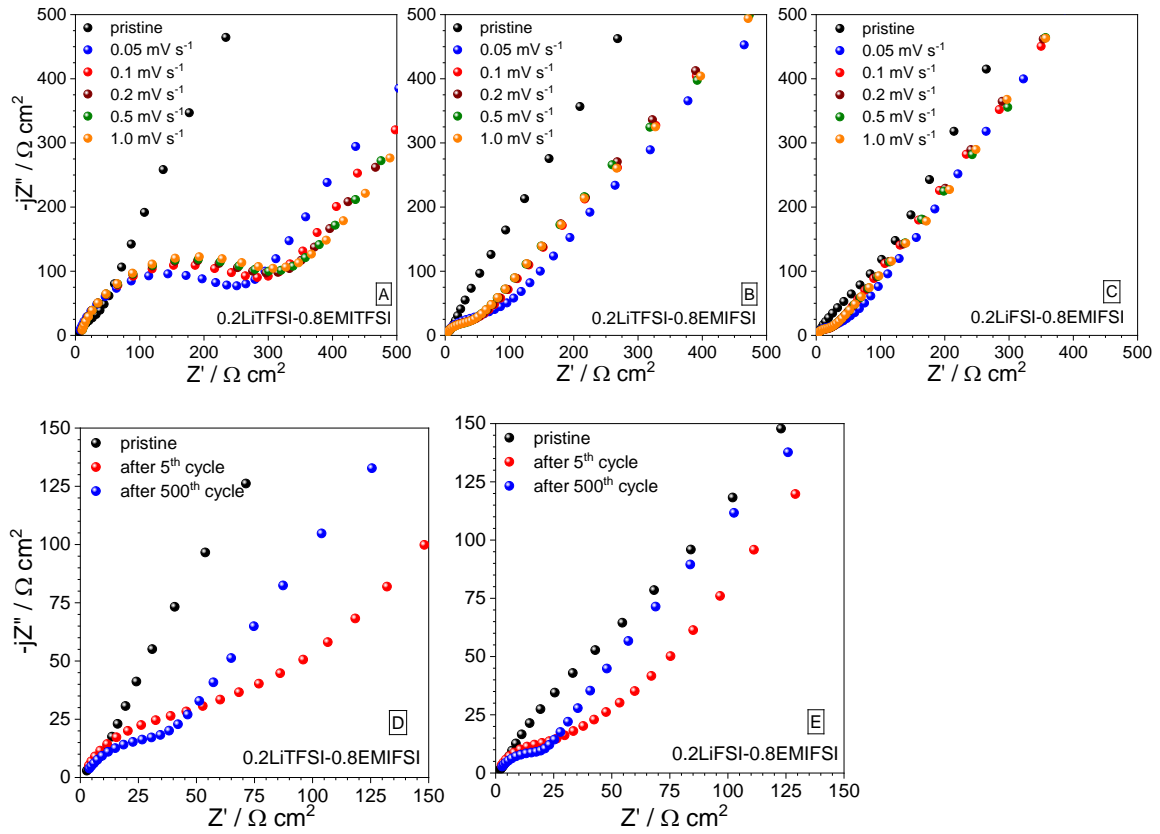
**Supplementary Figure 1:** Magnification of the cathodic sweep, referred to the CV profiles reported in Figure 1, run on Li/Si cells containing 0.2LiTFSI-0.8EMITFSI (panel A), 0.2LiTFSI-0.8EMIFSI (panel B), and 0.2LiFSI-0.8EMIFSI (panel C). T = 20 °C.



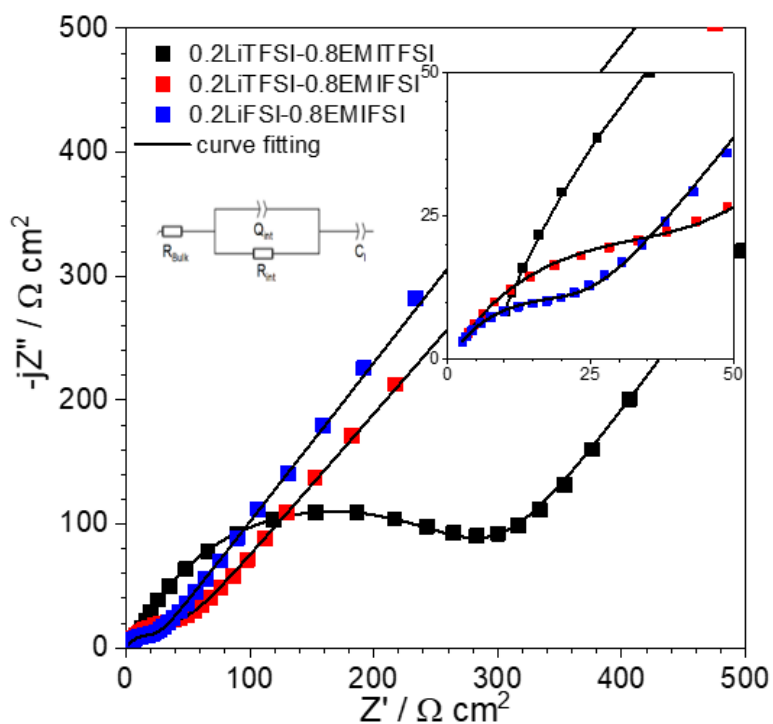
**Supplementary Figure 2:** CV curves of Li/a-Si cells with 0.2LiTFSI-0.8EMIFSI (panel A) and 0.2LiFSI-0.8EMIFSI (panel B) electrolytes at different scan rates. T = 20 °C.



**Supplementary Figure 3:** Peak current vs scan rate square root dependence for the lithiation of a-Si electrodes in 0.2LiTFSI-0.8EMIFSI and 0.2LiFSI-0.8EMIFSI electrolytes. The related linear-fit is also reported. T = 20 °C



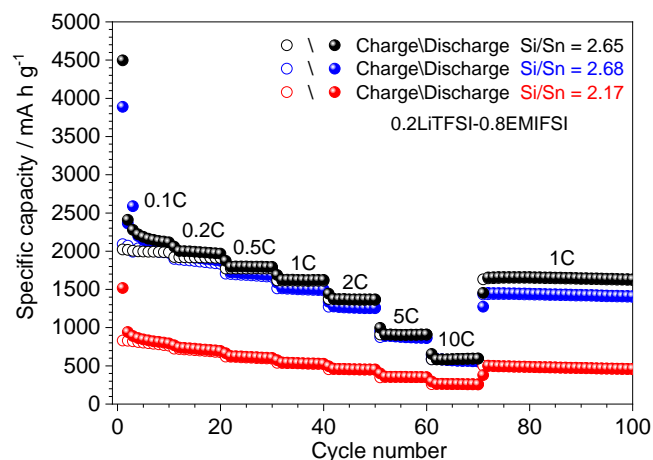
**Supplementary Figure 4:** AC responses, taken under OCV condition, of Li/Si cells containing the 0.2LiTFSI-0.8EMITFSI, 0.2LiTFSI-0.8EMIFSI, and 0.2LiFSI-0.8EMIFSI electrolytes. The impedance measurements were run after the CV tests (reported in Figure 1) were carried out at different scan rates (panels A, B, and C) and CV tests at  $1 \text{ mVs}^{-1}$  (panels D and E). Frequency range: 10 kHz – 1 Hz. Voltage amplitude:  $\Delta V = 10 \text{ mV}$ .  $T = 20 \text{ }^\circ\text{C}$ .



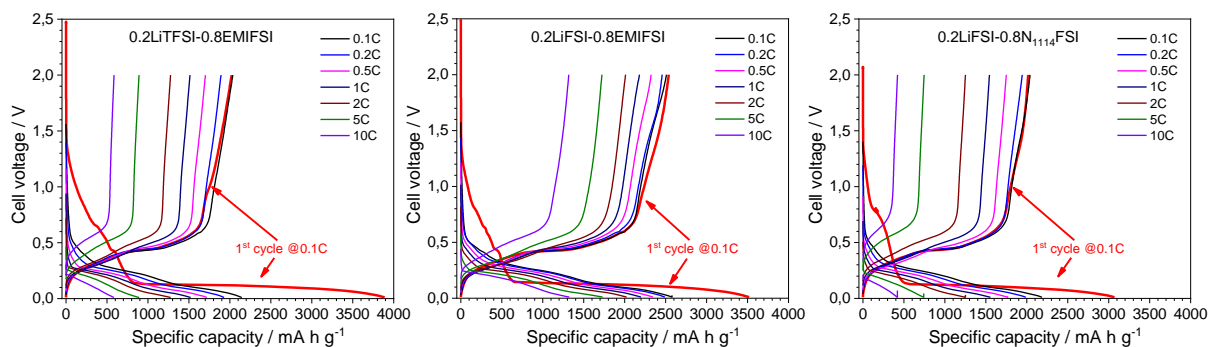
**Supplementary Figure 5:** AC response of Figure S3 of Li/Si cells in 0.2LiTFSI:0.8EMITFSI, 0.2LiTFSI:0.8EMIFSI and, 0.2LiFSI:0.8EMIFSI electrolyte with the equivalent circuit model adopted. The high-medium frequency region (and the related curve fitting) is magnified in the insert.

### S.1 Effect of Sn/Si ratio

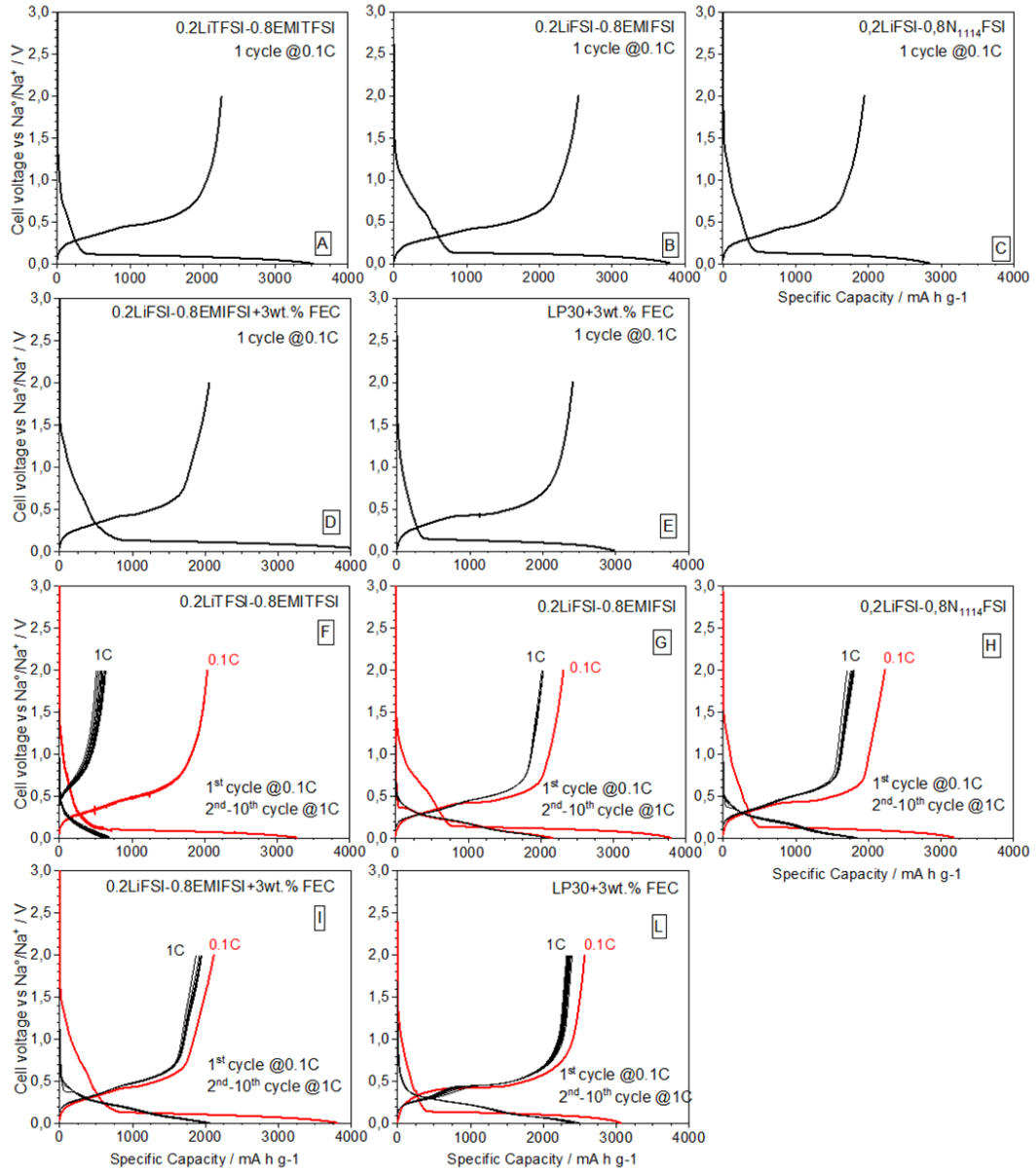
The influence of the Si:Sn weight ratio was preliminarily evaluated through cycling tests. The data, depicted in Figure S5 as capacity (referred to as the overall Si+Sn material weight) evolution as a function of the cycle number, show high and reproducible performance only at Si:Sn ratios above 2.6:1. These results are observed in different electrolyte formulations subjected to various current rates, suggesting that a Sn content above 28 wt.% depletes the overall electrochemical behavior of the electrodes. Further investigation would be needed to better clarify this issue. It is also possible to hypothesize a threshold for the Si:Sn ratio (around 2.6), which must be overcome to allow high cell performance. Therefore, only Si-Sn NW samples having a Si:Sn weight ratio above 2.6 were investigated.



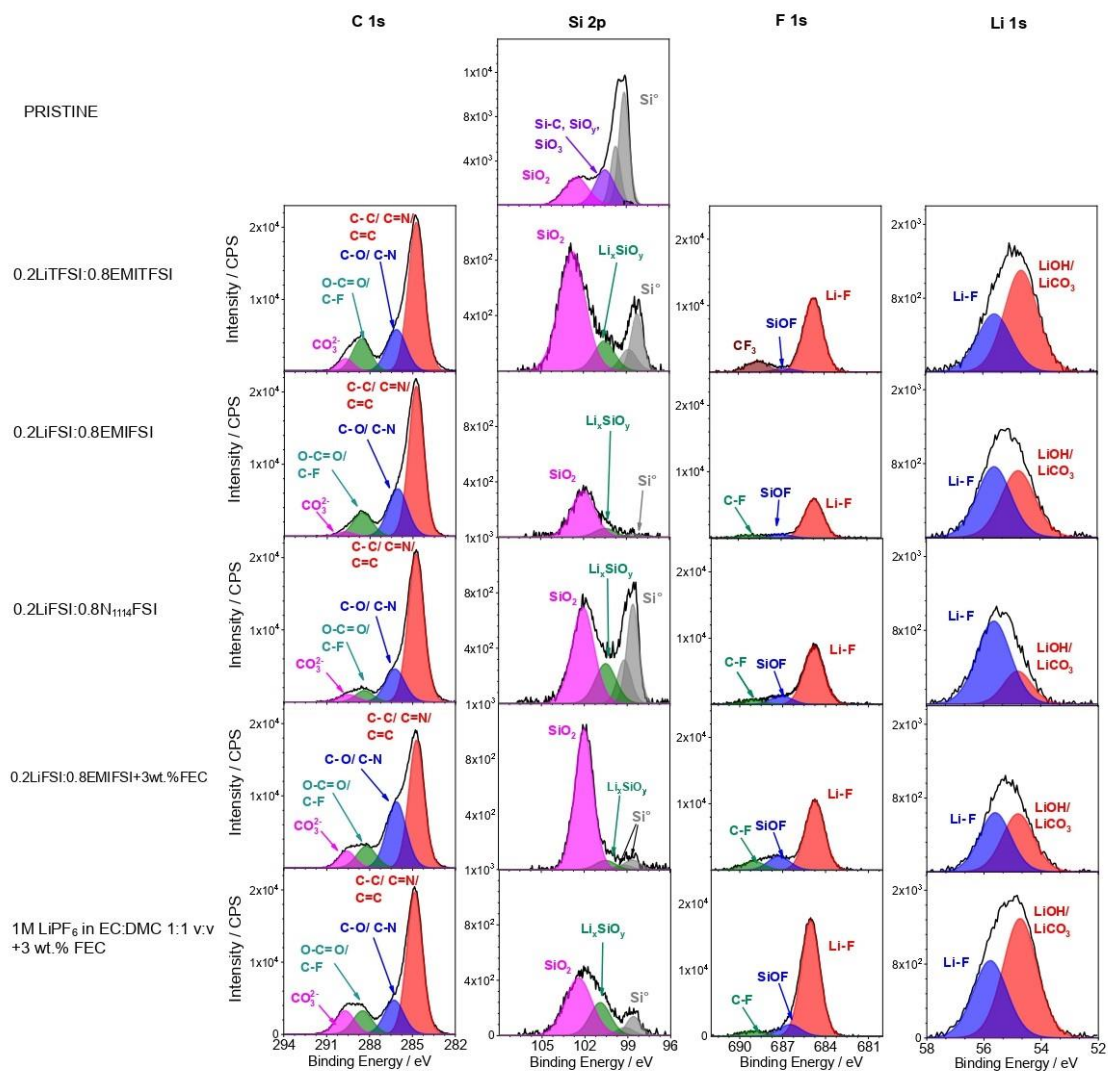
**Supplementary Figure 6:** Cycling performance of Li/Si cells in 0.2LiTFSI-0.8EMIFSI, comparing Si-Sn NW anodes with different Si:Sn weight ratios. Current rates from 0.1 to 10C. T=20°C.



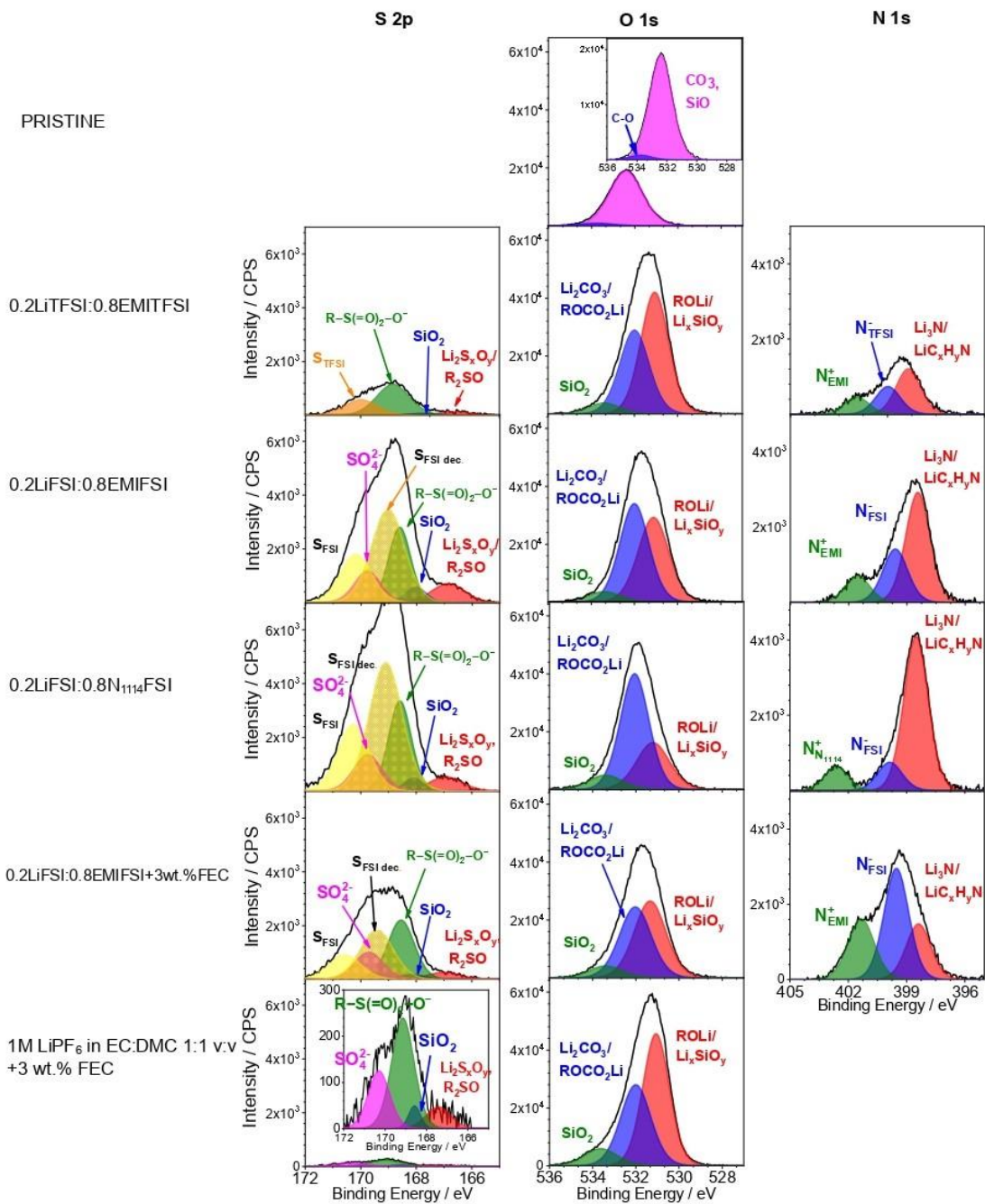
**Supplementary Figure 7:** Selected voltage vs. capacity profiles of Li/Si-S NW cells in 0.2LiTFSI-0.8EMIFSI (panel A), 0.2LiFSI-0.8EMIFSI (panel B) and 0.2LiFSI-0.8N<sub>1114</sub>FSI (panel C) electrolytes at different current rates (from 0.1C to 10C). T=20°C.



**Supplementary Figure 8:** Voltage vs. capacity profiles, referred to selected charge-discharge cycles, of Li/Si-Sn NW cells cycled in different electrolytes.  $T = 20^{\circ}\text{C}$ .



**Supplementary Figure 9:** High-resolution C 1s, Si 2p, F 1s, and Li 1s core level spectra obtained on pristine Si-Sn NW anodes and after one charge-discharge cycle in different electrolyte formulations.



**Supplementary Figure 10:** High-resolution S 2p, O 1s, and N 1s core level spectra obtained on pristine Si-Sn NW anodes and after one charge-discharge cycle in different electrolyte formulations.