Supporting Information

High performance of thick amorphous columnar monolithic film silicon

anodes in ionic liquid electrolytes at elevated temperature.

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Experimental

Silicon thin film electrodes were prepared by DC magnetron sputtering (Angstrom Sciences Inc., USA) of n-type silicon (99.999%, Kurt J. Lesker, USA), at a pressure of about $5 \times 10-3$ Torr of argon 99.9995%() onto roughened copper foil (Oxygenfree, SE-Cu58, Schlenk Metallfolien GmbH & Co. KG). The base pressure of the vacuum system was less than 5×10^{-6} torr. The surface density of the a-Si film thus obtained was 0.7 and 1.3 mg/cm² (~6 µm thick).

The electrolyte solution 1M LiPF₆ in FEC/DMC 1:4 by weight, Li-battery grade, was purchased from Merck, KGaA.

[BMP][TFSI] (>98.5%) and Li[TFSI] (99.95%) were purchased from Aldrich. [MPP][FSI] (>99.9%) was purchased from Solvonic (France) and Li[FSI] (>99.95%) from Suzhou Fluolyte Co, Ltd (China).

[BMP][TFSI] and [MPP][FSI] before use were dried in vacuum at 80 °C for 20 hours, and water content after drying comprised 10 ppm for [BMP][TFSI] and 5ppm for [MPP][FSI]. The water content in the ILs was determined by Karl Fischer titration. Li[TFSI] and Li[FSI] were dried in vacuum at 120°C for 20 hours. 0.5M Li[TFSI] solution in [BMP][TFSI], 0.5M Li[TFSI] solution in [MPP][FSI] and 0.5M Li[FSI] solution in [MPP][FSI] were used for the electrochemical measurements.

Li/Si cells were tested galvanostatcally in coin-type cells (2523, NRC, Canada) vs. lithium metal (Chemetall Foote Corporation, USA) using BT2000 battery cycler (Arbin Instruments).

After cycling Si electrodes were fully delithiated during prolonged potentiostatic polarization at 1.2V and withdrawn from the cells. The electrodes which were cycled in

1M LiPF_6 in FEC/DMC electrolyte solution were washed four times with pure DMC and dried. The electrodes cycled in the IL electrolyte solutions were washed in the same manner with pure dimethoxyethane.

HRSEM images and EDS data were obtained using a FEI xHR- SEM Magellan 400L microscope, equipped with the Oxford Industries INCAx-sight energy dispersive spectrometer (EDS) attachment. EDS measurements and mapping were performed at two operating voltages, 5 and 15 kV in order to obtain two different penetration depths of the electron beam into the samples.

X-ray photoelectron spectroscopy (XPS) was used for the surface analysis of the a-Si electrodes. Photoelectron spectra were obtained with a Kratos Axis-HS spectrometer (England) at a residual gas pressure of $\sim 5 \times 10^{-10}$ Torr using monochromatized Al K' α radiation (hv = 1486.68 eV) and a hemispherical analyzer. During the measurements, the vacuum in the analysis chamber was 2 × 10–9 Torr. For transferring the air sensitive electrodes (after cycling) to the spectrometer we used a home-made transfer system which contains a magnetic manipulator and a gate valve.

Raman spectra of the silicon electrodes were measured in a back scattering configuration using micro-Raman spectrometer HR 800 (Jobin Yvon Horiba), with He-Ne laser (excitation line 632.8 nm).

Characterization of the pristine Si electrodes.

The XRD pattern of the silicon film electrodes (Fig. S1) shows a broad peak at about 29° indicating an amorphous form of silicon¹. Fig. S2 shows the Raman spectrum of the Si film electrodes. The peak around 520 cm⁻¹ indicative for crystalline silicon ^{2, 3} was not detected. The bands centered around 155, 310, 475 cm⁻¹, and the weak shoulder at 400

cm⁻¹ are typical features of amorphous silicon vibration modes, associated with TA (transverse acoustic), LA (longitudinal optic), TO (transverse optic) and LO (longitudinal optic) phonons respectively. The presence of these features allows the conclusion that the sputtered thin Si films have an amorphous structure ^{4,5}. The band observed around 630 cm⁻¹ corresponds to the 2LA second order phonon Raman scattering and TO+TA overtone ^{5,6}. Thus, the Si electrodes prepared for this study, should be considered as purely amorphous. Fig. S3 shows a SEM image of a pristine silicon film (~6-7 µm thick) deposited onto roughened copper foil. The left image shows a lateral view of the Si electrode and the right image shows a cross section of these electrodes.

SEM images of the cycled Si electrodes.

Fig. S4 shows SEM images of Si electrodes cycled in 1M LiPF₆ in FEC/DMC and ILbased electrolyte solutions at 60°C, as indicated. It is seen, that in all cases cycling of Si electrodes changes the uniform surface morphology of the pristine Si electrodes into separate islands of about 10-30 μ m in lateral size. The Si electrodes cycled in the FECbased electrolyte solutions are coated with very thick irregular coating layers (Fig. S4a and b). It should be noted, that in the case of Si electrode that underwent 870 cycles in the IL electrolyte containing only FSI anions, the quartz separator was partially adhered to the surface of the electrode (Fig. S4c). However, higher magnification enables to observe thick surface layers which cover the islands (Fig. S4d). Si electrodes cycled in the IL electrolyte containing both FSI and TFSI anions are shown in Fig. S4e. The islands are coated with relatively thin surface films which permit to distinguish among the domes of the single Si columns.

XPS and EDS analysis of the surface films

XPS spectra of the pristine Si electrodes and the electrodes cycled in the three different electrolyte solutions are shown in Fig.S5, and the surface chemical compositions of these electrodes are compared in Table S1. Note, that the signal of Si is absent in all the XPS spectra due to the formation of surface films. According to the EDS results, cycling of Si electrodes in $LiPF_6/FEC/DMC$ solution at 60°C leads to the formation of much thicker surface films compared to that formed at 30°C. Indeed, the content of Si detected by EDS in the latter case was much higher both at 5 and 15keV. Much higher content of F and P was measured in the surface composition of the electrode cycled at 60°C compared to 30°C, what suggests that at elevated temperatures the surface layer comprises mainly decomposition products of the LiPF₆ salt. Judging from the content of the Si measured by EDS at both values of the electron beam energy, the surface films that are formed on Si electrode cycled in 0.5M Li[TFSI] / [MPP][FSI] IL at 60° C are relatively thin (even thinner than those formed in the FEC-DMC 1:4/1M LiPF₆ at 30°C). According to the EDS results, the main elements detected in these films are C, N, O and S. Thus, one can suggest that the main components of these films are the products of the decomposition of the IL anions $(LiNSO_2, Li_2NS_2O_4, Li_2SO_2, Li_2S_2O_4)^7$. The content of F in these surface products is much lower than in the case of organic carbonates based solutions.



Fig. S1 XRD pattern of pristine silicon film (~6-7 µm thick) deposited onto roughened copper foil.



Fig. S2 Raman spectrum of pristine silicon film (~6-7 µm thick) deposited onto roughened copper foil.



Fig. S3 SEM images of pristine silicon film deposited onto roughened copper foil. Left image – lateral view, right image – cross section.











Fig. S4 SEM images of the cycled at 60°C silicon electrodes.

a) and b) – after about 700 cycles and failure in 1M LiPF₆ in FEC/DMC 1:4 (curves 5 in Fig. 2), c) and d) – after about 870 cycles and failure in 0.5M Li[FSI] in [MPP][FSI] (curves 6 in Fig. 2), e) – after about 1300 cycles in 0.5M Li[TFSI] in [MPP][FSI] (Fig. 3).



Fig. S5 XPS spectra of Si electrodes.

- a) Pristine Si electrode,
- b) Si electrode cycled for 700 cycles in 1M LiPF₆ in FEC/DMC 1:4 at 30°C,
- c) Si electrode cycled for 700 cycles in 1M LiPF₆ in FEC/DMC 1:4 at 60°C (curves 5 in Fig.2),
- d) Si electrode cycled for about 870 cycles in 0.5M Li[FSI] in [MPP][FSI] (curves 6 in Fig. 2),
- e) Si electrode cycled for about 1300 cycles in 0.5M Li[TFSI] in [MPP][FSI] (Fig. 3).

Element	1M LiPF ₆ in FEC/DMC						0.5M Li[TFSI] in [MPP][FSI]		
	30°C			60°C			(60°C)		
	XPS	EDS 5 keV	EDS 15keV	XPS	EDC 5 keV	EDS 15keV	XPS	EDS 5 keV	EDS 15keV
Li	21.14	-	-	-	-	-	20.79	-	-
С	33.47	17.72	23.25	28.99	22.03	30.85	26.1	6.78	11.19
Ν	0	-	-	-	-	-	4.99	3.72	-
0	20.8	39.41	28.29	24.49	26.9	30.88	35.26	37.56	20.79
F	22.22	7.45	3.46	42.65	39.54	20.14	3.68	-	-
Si	-	35.42	44.59	-	7.29	15.48	-	39.84	63.38
Р	2.37	-	-	3.87	4.24	2.65	-	-	-
S	0	-	-	-	-	-	9.18	5.73	1.45

Surface composition (atomic %) determined by EDS and XPS of a-Si electrodes cycled in organic carbonate-based and IL electrolyte solutions.

References

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