

### Supplementary Information

#### **Ag nanoparticles modified porous Si microspheres as high-performance anode for Li-ion batteries**

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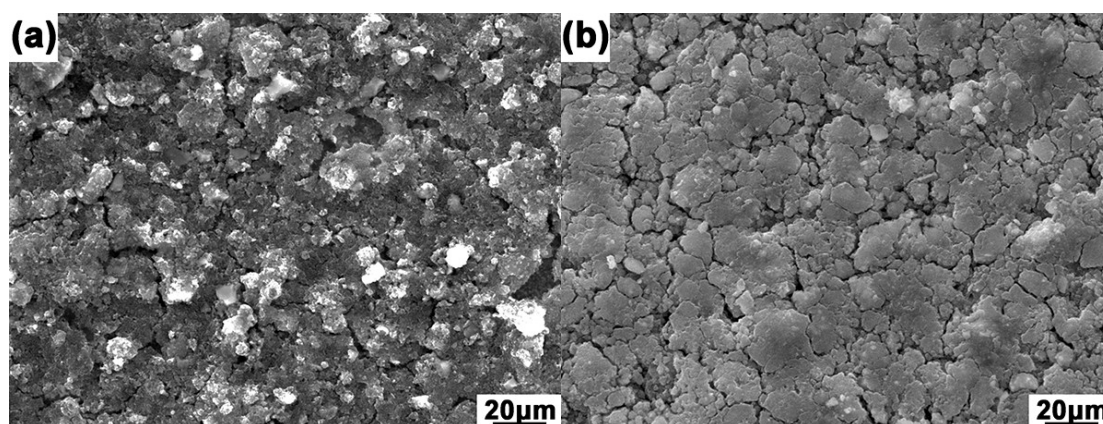
## Discussion

The mass ratio of Ag to Si in pSi/Ag microspheres is measured by X-ray Fluorescence (XRF) Spectrometer in Table S1. After the removal of O and N elements during reduction, there was a slight increase in the mass ratio of Ag to Si in pSi/Ag microspheres compared to that of AgNO<sub>3</sub> to SiO<sub>2</sub> in the raw.

**Table S1.** Mass ratio of Ag to Si in pSi/Ag microspheres.

Samples	Mass ratio of Ag to Si
pSi/Ag-1	1.3:98.7
pSi/Ag-5	6.3:93.7
pSi/Ag-10	12.3:87.7

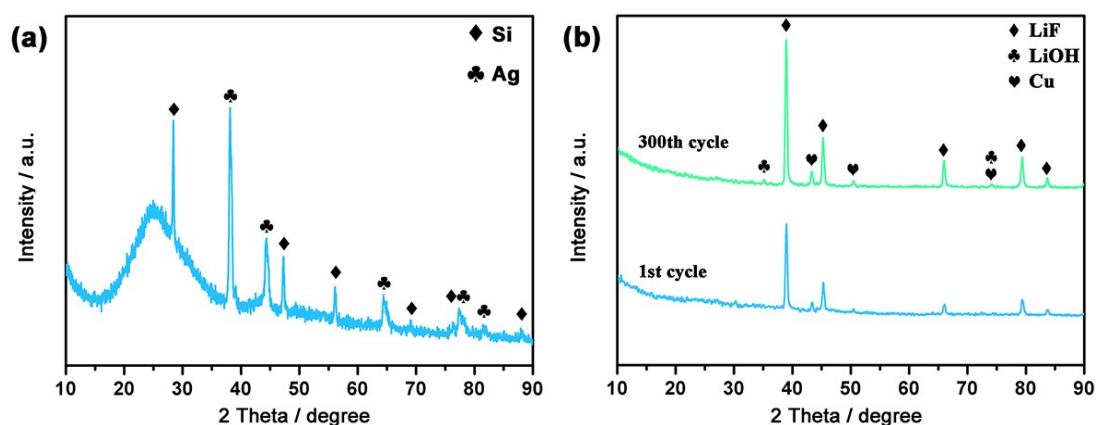
Fig. S1 shows the comparison of surface morphology of pSi/Ag-5 electrode surface before and after cycle. As the Fig. S1a shown, there are pre-existing cracks on the electrode surface before cycle. However, following volume effect of Si during cycling, the cracks on the electrode surface increase obviously, causing the formation of additional SEI films, and may also leading a small amount of Si particles to detach the electrode. Moreover, no distinct electrode pulverization was observed, indicating overall stability of the electrode structure.



**Fig. S1.** SEM images of the surface of pSi/Ag-5 electrode (a) before and (b) after 300 cycles.

The XRD analysis in Fig. S2a revealed that the active materials after cycles still comprised of Si and Ag, akin to the pSi/Ag-5 powder before the cycle. However, the intensity of the diffraction peaks of Si were significantly reduced compared to that before the cycle, and an evident broad peak appeared near the Si (111) plane, indicating the amorphization of porous Si after delithiation. A

small proportion of Si maintained its crystal structure, which can be accounted for the fact that this part of the Si was not involved in the charge-discharge processes due to detachment caused by volume expansion. As shown in Fig.S2b, The GIXRD diffraction pattern revealed a strong LiF peak, indicating that the F element detected in pSi/Ag-5 electrode corresponds to LiF. The formation of LiF was attributed primarily to the decomposition of solvents and  $\text{LiPF}_6$  in the electrolyte, with the addition of FEC additives during decomposition contributing to the formation of a stable LiF layer on the active material surface. In addition to LiF, electrolyte decomposition also yielded LiOH, evidenced by the diffraction peak at  $35.5^\circ$  corresponding to the (110) crystal plane of LiOH. The Cu diffraction peak was attributed to interference caused by the copper foil current collector at the electrode edge. When comparing the GIXRD patterns of pSi/Ag electrodes with 1 and 300 cycles, it can be observed that the diffraction intensity of LiF remains stable, suggesting the stable structure of LiF SEI film.



**Fig. S2.** XRD patterns of (a) pSi/Ag-5 after 300 cycles, (b) the surface of pSi/Ag-5 electrode after 1 and 300 cycles.