Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information for:

Differentiating Chemical and Electrochemical Degradation of Lithium Germanium Thiophosphate and the Role of Atomic Layer Deposited Protection Layers

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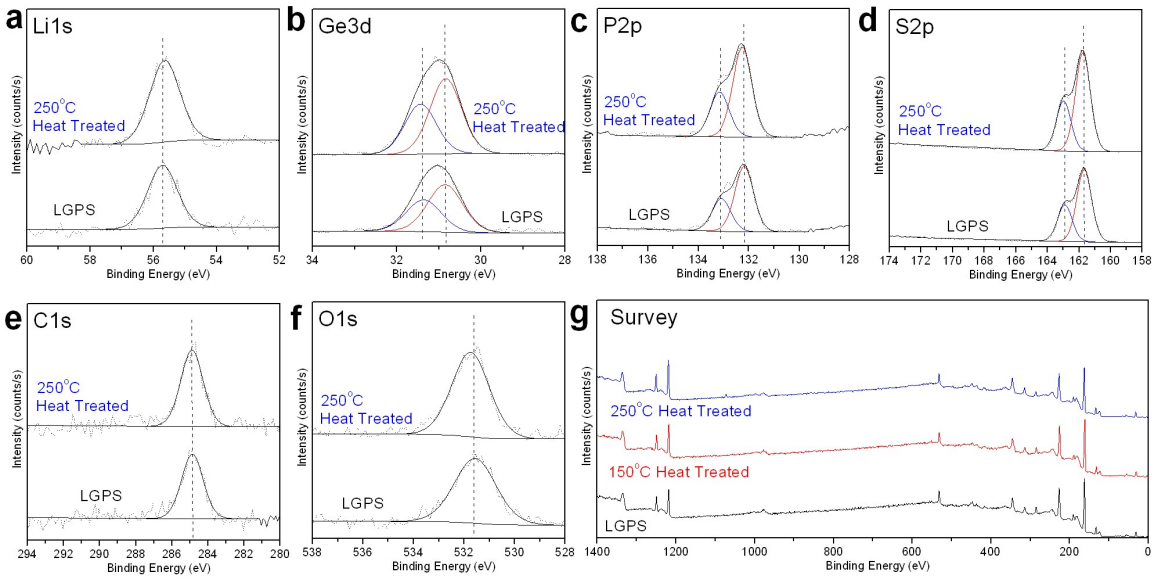

Figure S1: XPS Spectra of as-pressed LGPS pellets and LGPS pellets treated for 8 hours at 250˚C under UHV conditions. High resolution regions for (a) Li1s; (b) Ge3d; (c) P2p; (d) S2p; (e) C1s; (f) O1s; (g) Survey spectra including the intermediate treatment temperature of 150˚C.

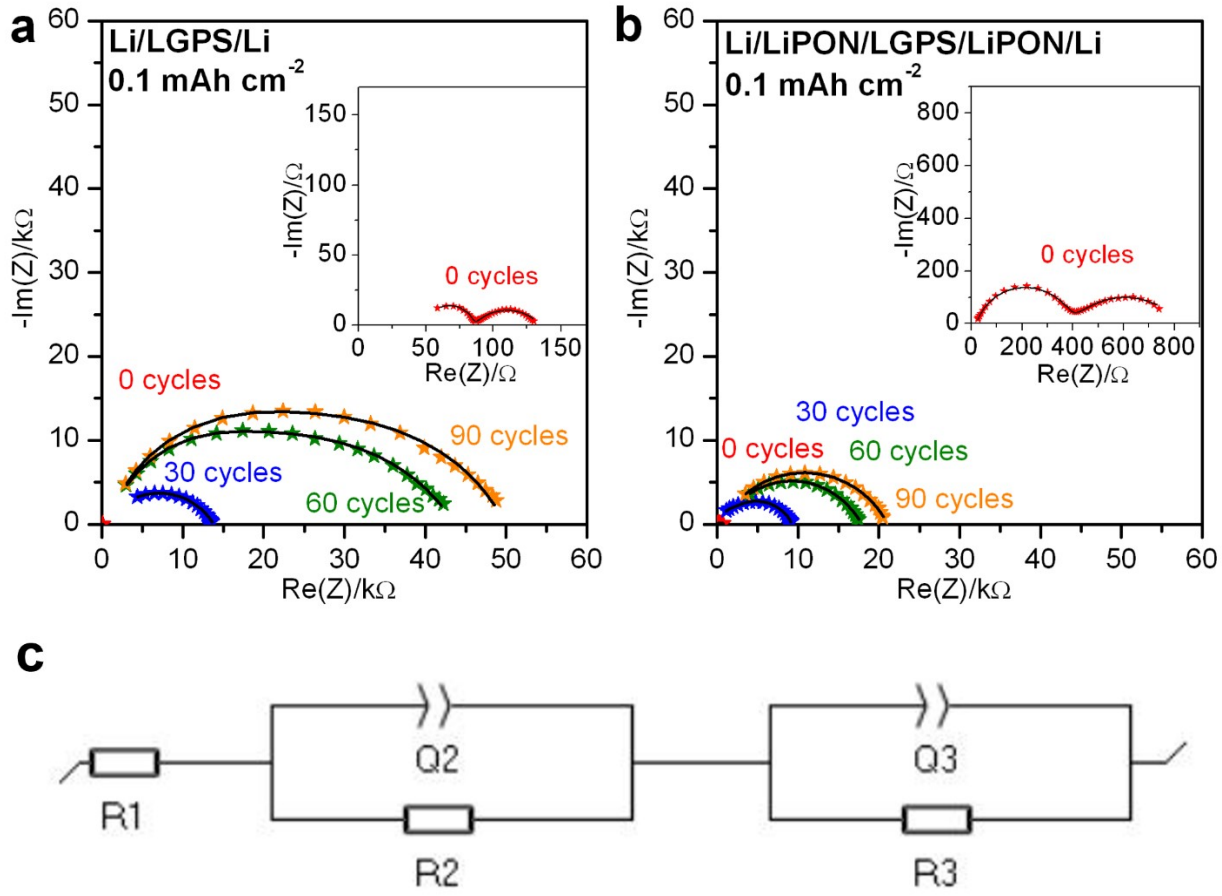

Figure S2: EIS spectra of Li/LGPS/Li symmetric cells with a) bare LGPS pellet and b) 20 nm LiPON coated LGPS pellet measured before electrochemical cycling started (0 cycles), and after 30, 60, and 90 cycles. The insets show the zoomed in view of EIS spectra of 0 cycles. c) The equivalent circuit used for simulation of EIS spectra of the symmetric cell system.

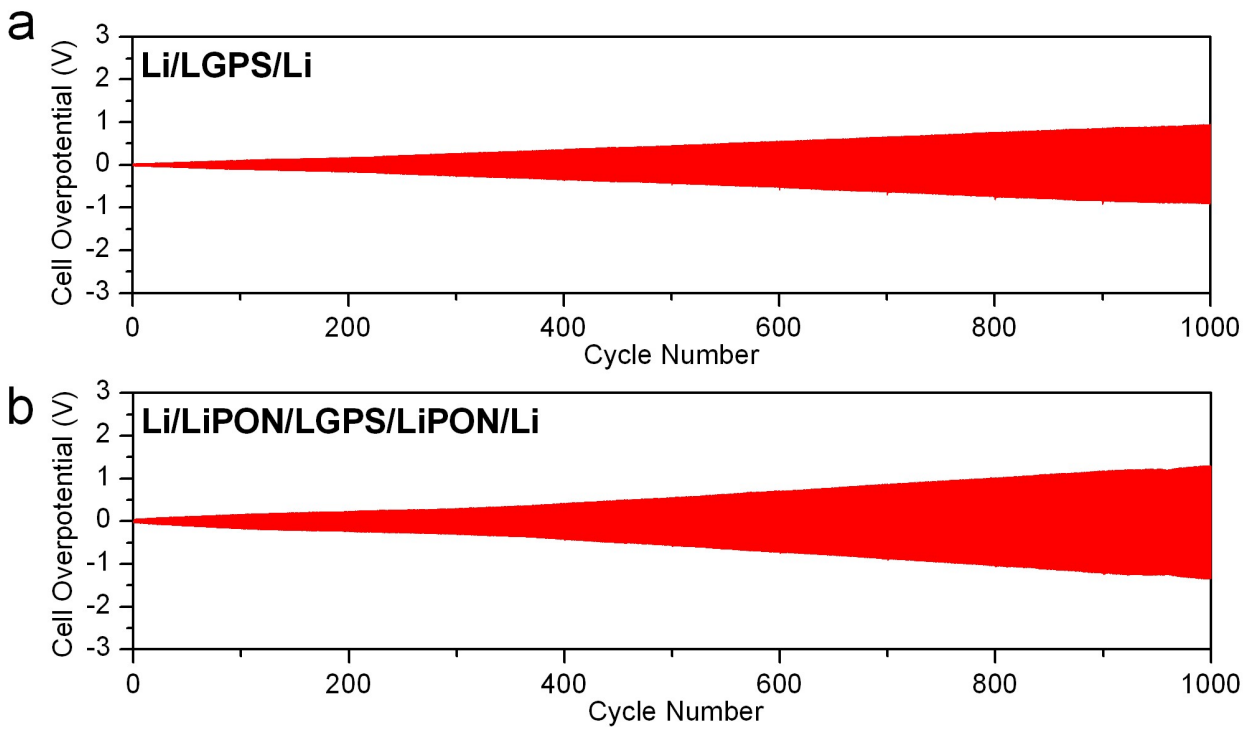

Figure S3: Galvanostatic charging and discharging profiles of Li/LGPS/Li symmetric cells with a) bare LGPS pellet and b) 20 nm LiPON coated LGPS pellet. The current density is 0.1 mA cm^{-2} and hold time is 6 min per half cycle. Total charge capacity for 1000 cycles is 10 mAh cm^{-2}.

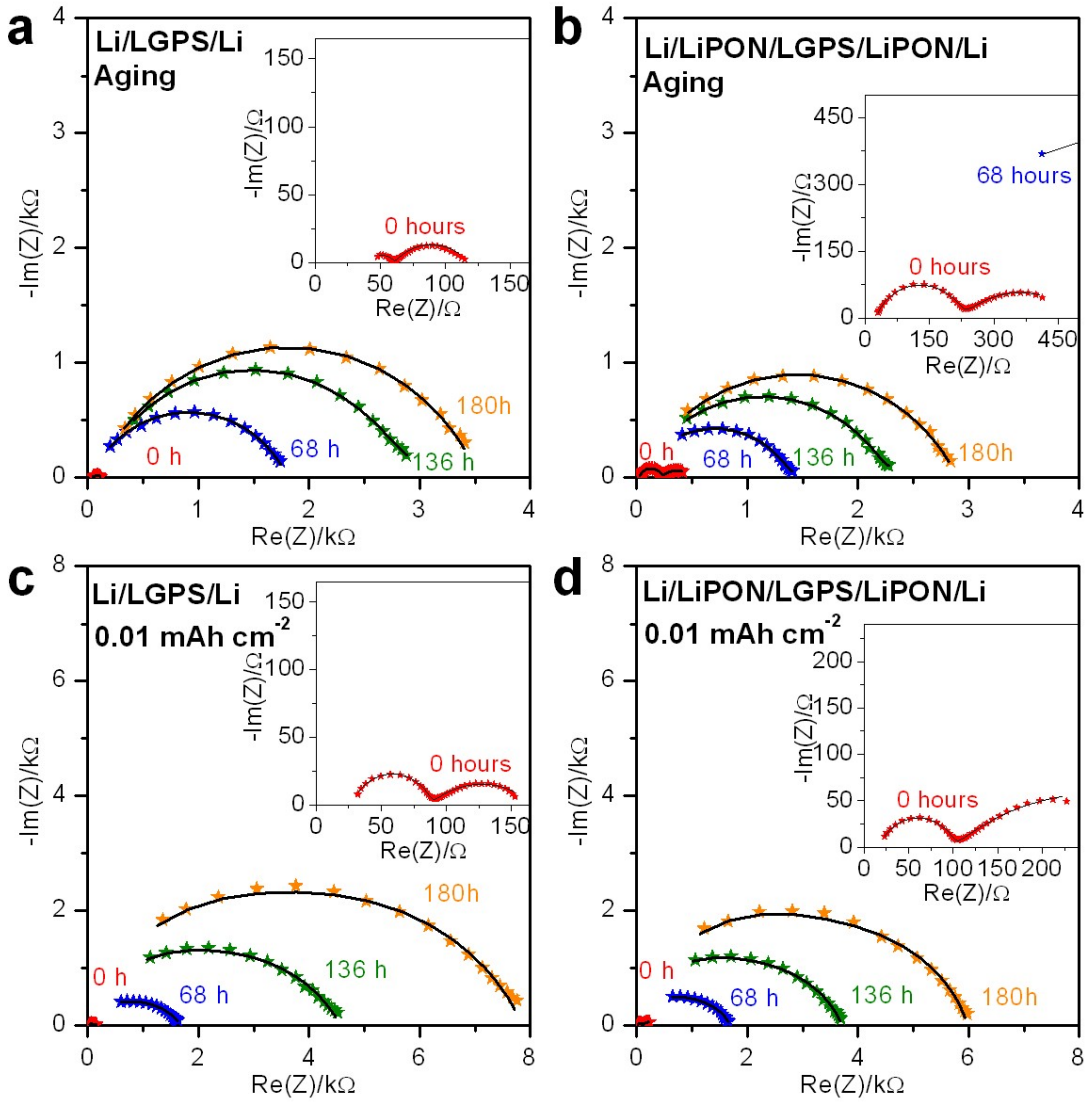

Figure S4: EIS spectra of Li/LGPS/Li symmetric cells with a) bare LGPS pellet and b) 20 nm LiPON coated LGPS pellet in aging test, with EIS measured at the beginning (0 h) and after 68 hours, 136 hours, and 180 hours. And EIS spectra of Li/LGPS/Li symmetric cells with c) bare LGPS pellet and d) 20 nm LiPON coated LGPS pellet in galvanostatic charging and discharging, with EIS measured before cycling (0 h) and after roughly 68 hours (300 cycles), 136 hours (600 cycles), and 180 hours (900 cycles) of cycling equivalent to same stage of aging test.

Computational Methods

We performed DFT calculations within the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) [1] functional using the Vienna Ab initio Simulation Package (VASP) [2]. The projected augmented wave (PAW) method with a plane-wave basis set was used to describe the interaction between core and valence electrons. A energy cutoff of 350 eV was used for geometric optimization with (2 x 2 x 2) k-point mesh (except for Li metal BCC unit cell where an increased cutoff energy of 400 eV and (12 x 12 x 12) k-point mesh was employed). Periodic boundary conditions were employed in all three directions.

The LGPS ($Li_{10}GeP_2S_{12}$) model structure has dimensions of 8.788 Å x 8.788 Å x 12.658 Å.

The relative energies on the degradation path were calculated by,

$$E_{initial} = E_{LGPS}$$

$$E_{intermediate} = E_{LGPS + Li\ cation} - E_{LGPS} - E_{Li\ cation}$$

$$E_{final} = E_{LGPS + Li\ atom} - E_{LGPS} - E_{Li\ metal\ BCC}$$

where E_{LGPS} is the energy of pure LGPS system that was prepared for this paper, $E_{LGPS + Li\ cation}$ is the energy of LGPS inserted a Li cation, $E_{Li\ cation}$ is the energy of a Li cation in the LGPS, $E_{LGPS + Li\ atom}$ is the energy of LGPS inserted Li atom, and $E_{Li\ metal\ BCC}$ is the energy of a Li atom in Li metal body-centered cubic unit cell. We used the average values of more than six configurations for Li inserted LGPS.

For the DOS calculation, we prepared the amorphous systems of Li_4Ge, Li_3N, Li_3P, Li_2S, and Li_2O with 32 atoms of Ge, N, P, S, and O, respectively. The systems were fully relaxed and then annealed at 1500 K for at least 3ps to allow sufficient atomic rearrangement, followed by

geometry optimization. A time step of 1 fs was used while the temperature was controlled via Nose-Hover thermostat [3].

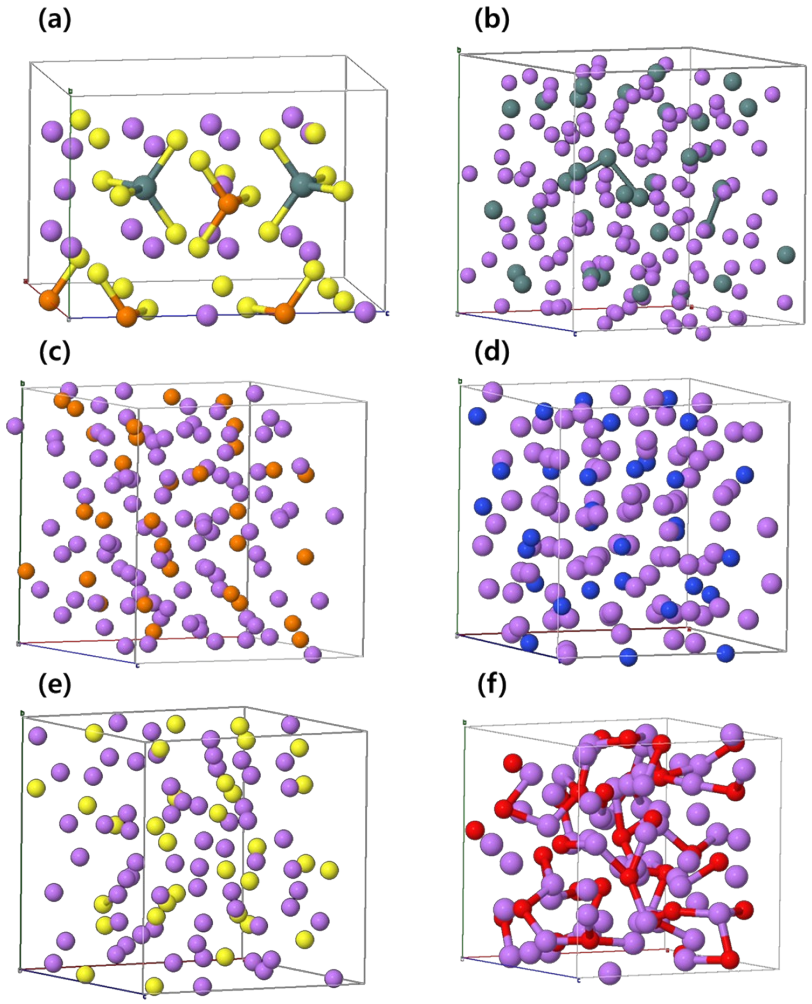

Figure S5: Atomistic ensembles used for the simulation volume: (a) LGPS (8.788Å×8.788Å×12.658Å); (b) Li_4Ge (13.948Å×13.948Å×13.948Å); (c) Li_3P (12.676Å×12.676Å×12.676Å); (d) Li_3N (10.093Å×10.093Å×10.093Å); (e) Li_2S (11.639Å×11.639Å×11.639Å); (f) Li_2O (8.503Å×8.503Å×8.503Å).

1. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868

2. G. Kresse and J. Furthmuller, Phys. Rev. B: Condens. Matter Mater. Phys., 1996, 54, 11169–11186

3. W. G. Hoover, Phys. Rev. A: At., Mol., Opt. Phys., 1985, 31, 1695–1697.