Supporting Information

In Situ Neutron Depth Profiling of Lithium Metal-Garnet Interfaces for Solid State Batteries

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Experiments

Synthesis of garnet solid state electrolytes. The garnet solid state electrolytes were synthesized following previous method.[1] Specifically, the garnet ceramic with the chemical formula of $Li_{6.75}La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ was prepared by conventional solid state reaction. Stoichiometric amounts of La_2O_3 (Alfa Aesar, 99.9%), ZrO_2 (Inframat® Advanced Materials, 99.9%), LiOH (Alfa Aesar, 98.0%), $CaCO_3$ (Alfa Aesar, 99.0 %), and Nb_2O_5 (Alfa Aesar, 99.9%) were mixed and ball milled in isopropanol for 24 h. 10 wt% Excess LiOH was added to compensate for Li loss during the calcination and sintering procedures. The dried mixed powder precursors were pressed and calcined at 900 °C for 12 h. Calcined pellets were broken down and ball-milled again in isopropanol for 48 h. The final cubic phase powder was pressed into pellets at 500 MPa and sintered in alumina crucible at 1050 °C for 12 h. The obtained dense garnet pellets were mechanically polished for symmetrical cell assembling. The dimensions of garnet pellets are about 500 μm thick and 8 mm in diameter.

E-beam and atomic layer deposition (ALD). Electron beam deposition of a nickel layer was performed by an Angstrom NexDep Ebeam evaporator. The sample was held on a silicon wafer in the E-beam chamber. Air pressure in the chamber is controlled below $5*10^{-6}$ Torr. Typically, the deposition rate is 0.2 nm/second by controlling current through the metal target. Totally 50 nm of Ni was deposited on the surface of garnet.

ALD of a ZnO coating layer was performed on the Beneq TFS 500. Pure nitrogen was used as carrier gas. The chamber is vacuumed and the temperature is controlled to be 150^{o}C during the whole process. Typically 0.2 nm thickness ZnO was deposited in one ALD cycle. Each cycle included alternating flows of diethyl zinc (DEZ, 1.5 seconds Zn precursor) and water (1.5

seconds, oxidant) separated by flows of pure nitrogen gas (4 and 10 seconds, as carrier and cleaning gas, respectively).

Cell assembly. The Li/Garnet/Li symmetric cells were prepared by sandwiching the ZnO-coated garnet pellet between two thin Li disks (~0.5 cm^2, 150 μm thick) following by heating at 250^oC for 30 min in argon filled glovebox. Three pieces of stainless steel coin cell spacers (1 mm thick, 15.8 mm diameter) were placed on the top to press the molten Li onto the garnet surface to ensure a good contact. After Li was melted on to garnet, a stainless steel spacer and a center punched (~0.5 cm^2) Ti foil strip were attached to bottom and top melting Li, respectively, to serve as the current collector.

For Li/Garnet/CNT asymmetric cells, Li metal was melted on one side of garnet pellet following the same process. Then ~30 μL 3mg/mL P3 CNT (Carbon Solutions, Inc) in N-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich, 99%) solution was coated onto the other side of garnet pellet to form 2-3 μm CNT film. To ensure good electrical contact, a center punched (~0.5 cm^2) Kapton tape (Uline, 1 Mil, 1" x 36 yds) was stuck onto CNT film, which was then coated with 50 nm Ni using e-beam technique. Both symmetric cells and asymmetric cells were covered by a 7.6 μm thick Kapton film and sealed with epoxy glue to separate air during transportation. The Kapton film also served as the mask to block ^4He signal during NDP measurement.

Materials characterization and measurement. The morphologies of the solid state cells were conducted on a Tescan XEIA Plasma FIB/SEM at 10 kV. Neutron depth profiling measurement were conducted at the NIST Center for Neutron Research (NCNR) at the NG1 Cold Neutron Depth Profiling station following the previous protocol.[2,3] Specifically, the cells were mounted on a Al hot plate on a Al disc holder and exposed to cold neutrons (<4 meV) beam. The whole set up was in an ultra-high vacuum chamber. The NDP spectra were recorded every 300 s during

battery cycling. A BioLogic VSP potentiostat was used to conduct the *in situ* battery cycling. Galvanostatic stripping-plating cycling at different current densities was recorded at 90 ^{o}C.

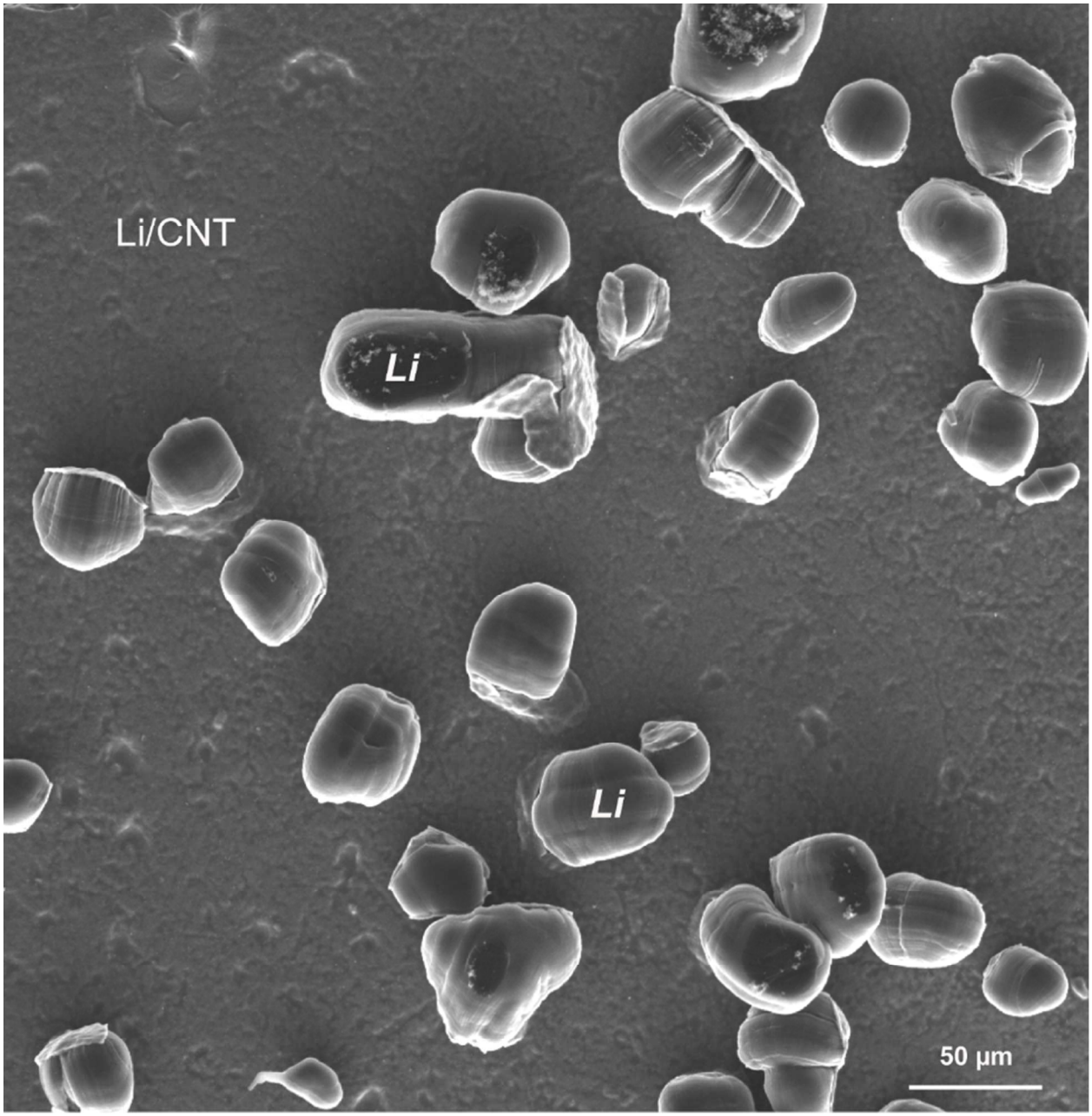

Figure S1. The top-view SEM image of the mushroom-like Li metal on the shiny area of the Li plated CNT film.

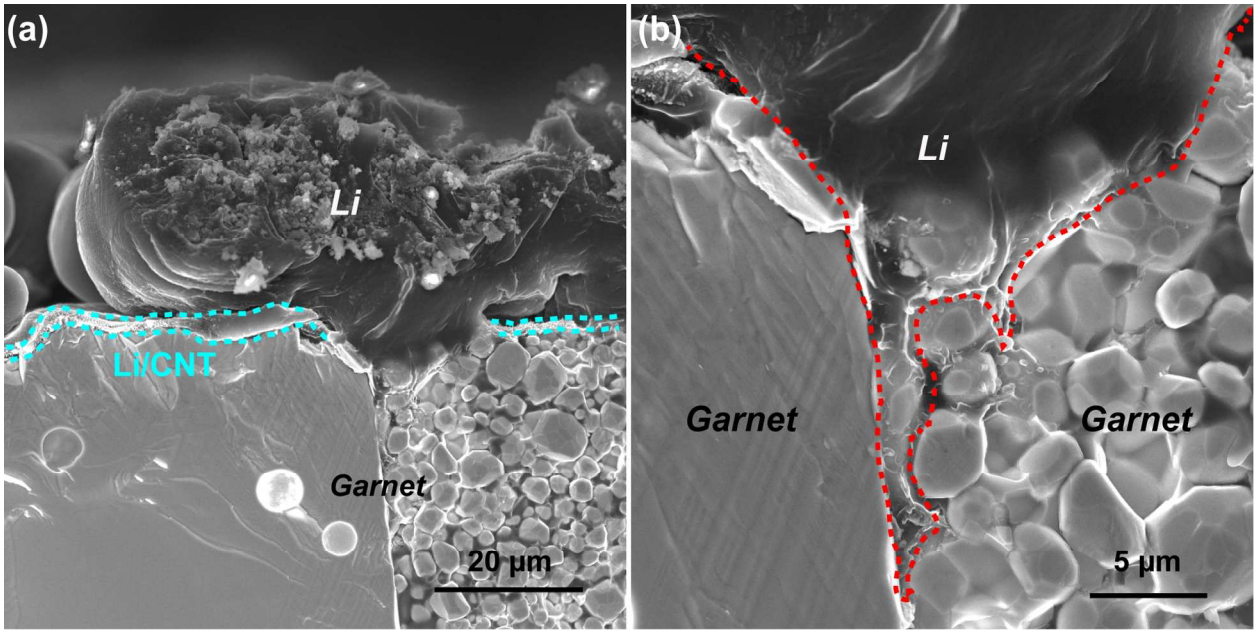

Figure S2. The cross-section SEM images of the mushroom-like Li metal on the shiny area of the Li plated CNT film at different magnifications. At the root of the mushroom-like Li metal, Li grows into garnet pellet along the grain boundaries.

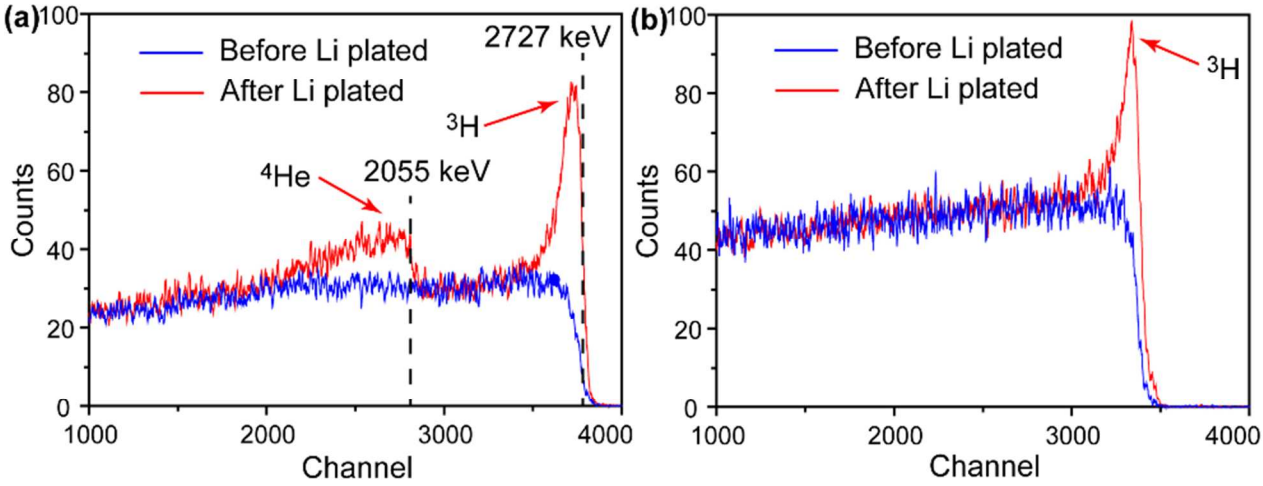

Figure S3. Typical NDP spectra of Li/Garnet/CNT asymmetric cells before and after Li plated to CNT film without (a) or with (b) Kapton film cover. The Kapton film blocks ^{4}He signal and causes the spectra to shift toward smaller channels.

References

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