Supplemental Information for:

In operando Raman Microscopy of Cu/$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ Solid Electrolyte Interface

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Experimental and Methods

Preparation of LAGP Membrane

LAGP membranes were purchased from MSE Supplies (MSE PRO LISICON LAGP Solid State Electrolyte Membrane for Advanced Lithium Batteries, 12 mm diameter). Prior to use in the electrochemical cell, the LAGP was plasma cleaned with Ar and O_2 gas (Tergeo Plus Plasma Cleaner, Pie Scientific) to remove carbon contamination that was present on the LAGP membrane as received. After plasma cleaning, a 25 nm layer of Cu metal was DC sputtered on to the surface of the membrane (3x3" TORUS Mag Keeper sputter guns). XPS (**Figure S1**) of the as received LAGP membrane, LAGP after plasma cleaning, and LAGP after Cu metal deposition confirms the expected composition of LAGP, the removal of carbon contamination and the deposition of Cu on the surface.

In operando cell

The setup of the *in operando* experiment is shown in **Figure S1**. The operando cell was assembled in the following way first 1) a piece of the LAGP membrane was adhered with VHB tape (McMasterCarr, 8127A82) that acted as a sealing O-ring onto the opening of a 20x20 mm 2 mm thick PEEK sheet (McMaster Carr, 8504K72) with a 4 mm hole in the center. Then a thin (0.5 mm thick) stainless steel frame was screwed into the top of the PEEK body which allowed pressure to be applied to the LAGP and make electronic connection with the Cu thin film. The cell was then assembled in an Ar-filled glovebox by cutting a 3 mm diameter piece of Li metal and then placing it on the LAGP membrane. Then a custom machined stainless-steel piston is placed in the cavity and sealed with VHB O-ring (McMasterCarr, 75935A15). Slight pressure is then applied by screwing the bottom of the PEEK body a sheet of the PEEK bottom where the amount of pressure applied can be reproducibly controlled by the thickness of the spacers. Electrical connections were made with Cu tape (3M™ Copper Conductive Tape). After assembly, the cell was sealed in polybag (Sigma-Aldrich, Z183377) with a 0.2 mm thick glass window allowing a view of the exposed Cu/LAGP interface for operando Raman measurements.

Raman spectroscopy

Raman spectroscopy was performed with a Renishaw inVia™ confocal Raman microscope using a 532 nm laser (with an 1800 l/mm grating). By using a 0.5/50 L objective, an energy density of $3.7*10^6$ W/cm^2, a spot size of 1.30 µm in diameter and a laser power of 25 mW was achieved. Spectra in the range of 100 – 1600 cm^{-1} were acquired during *in operando* CV. Single-point spectra were averaged over 60 spectra with an integration time of 2.5 s, while spectra for the mapping were averaged over 10 spectra with an integration time of 1 s on a 17x17 map with 2.3 µm steps. The Raman spectra were baseline corrected using the asymmetrically reweighted penalized least squares smoothing (arPLS) method.[1] An example of the background fitting and subtraction is shown in **Figure S6**. The generation of the Raman maps were created with a custom python code and the interpolations of the generated spectral images were performed with the spline16 within the imshow() function from matplotlib. Inclusion of the python code to generate the images are included along with an example spectrum file.

X-ray Photoelectron Spectroscopy

XPS was performed with a Thermo-Fisher K-Alpha Plus XPS using an Al X-Ray Source (1.486 eV). A flood gun for charge neutralization was used in all experiments. The survey scan was taken from -20 eV to 1400 eV with a pass energy of 200 eV and energy spacing of 1.0 eV. No attempts were made to reference the binding energy of the XPS spectra, which are presented without processing. Ar ions with an energy of 2000 eV with a 200 µm X-ray spot size was used, and the etching dimension was 1 mm x 2 mm. The LAGP after the single electrochemical CV was transferred to the XPS load lock in an air free manner using a K-Alpha Plus vacuum transfer module.

Atomic Force Microscopy

AFM were conducted with a commercial Neaspec n-SNOM microscope using PtIr-coated AFM probes (Neaspec). All experiments were conducted in the N_2 glovebox with a measured O_2 concentration of <20 ppm. AFM images were taken in tapping mode using a tapping amplitude of 90 nm and a resolution of 19.5 nm/pixel for 5 x 5 µm images. Images were processed using the Gwyddion software.

Electrochemical Analysis

To study the electrochemical stability and the initial reaction of LAGP with Li, cyclic voltammetry (CV) was performed using a Biologic SP-300. Single-point *in operando* measurements employed a scan rate of 0.1 mV/s in a range from open-circuit voltage (OCV) approx. 3 V – 0 V, while mapping measurements utilized a scan rate of 0.05 mV/s in a range from OCV approx. 3 V – 0.8 V.

Figures

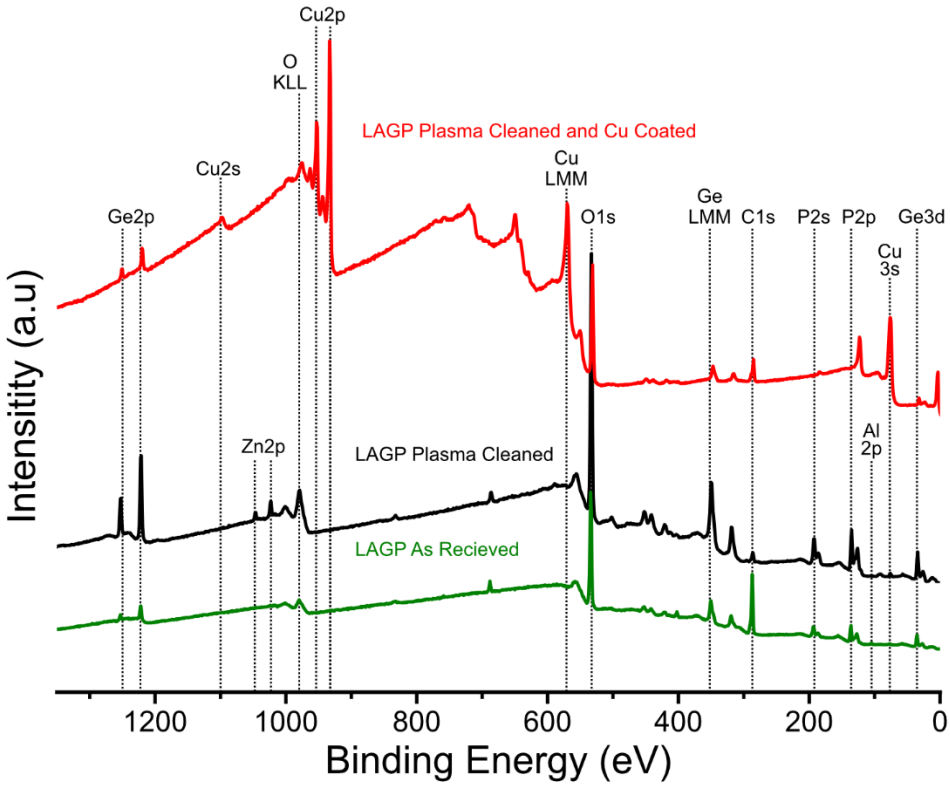

Figure S1: XPS survey scans of the LAGP membrane, as received, after plasma cleaning, and after Cu coating.

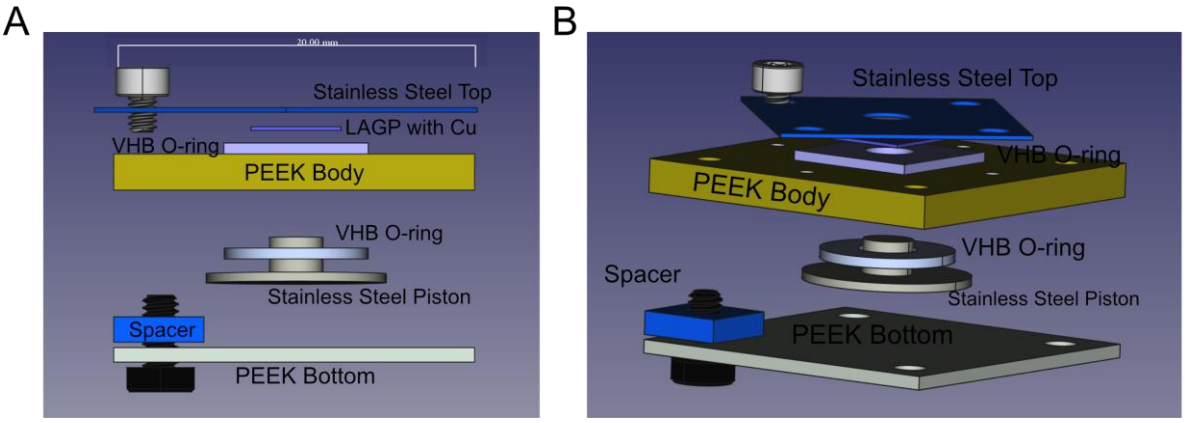

Figure S2: *In operando* spectro-electrochemical cell schematic.

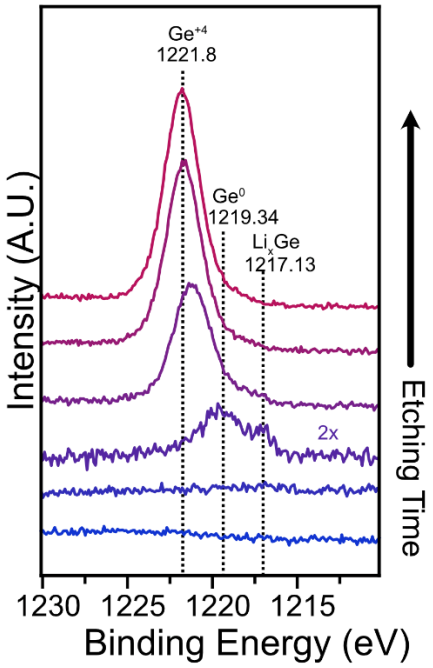

Figure S3: High resolution XPS of the Ge 2p region after etching away the Cu overlayer.

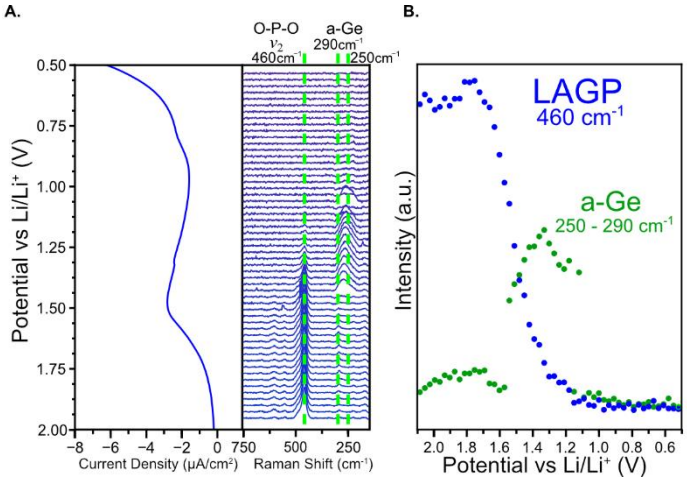

Figure S4: (A) In operando Raman spectra of the Cu/LAGP interface during the initial cathodic CV scan at 0.1 mV s^{-1}. **(B)** Progression of the intensities of 460 cm^{-1} (LAGP) and 250–290 cm^{-1} (a-Ge) bands as a function of the voltage 2.0 – 0.5 V.

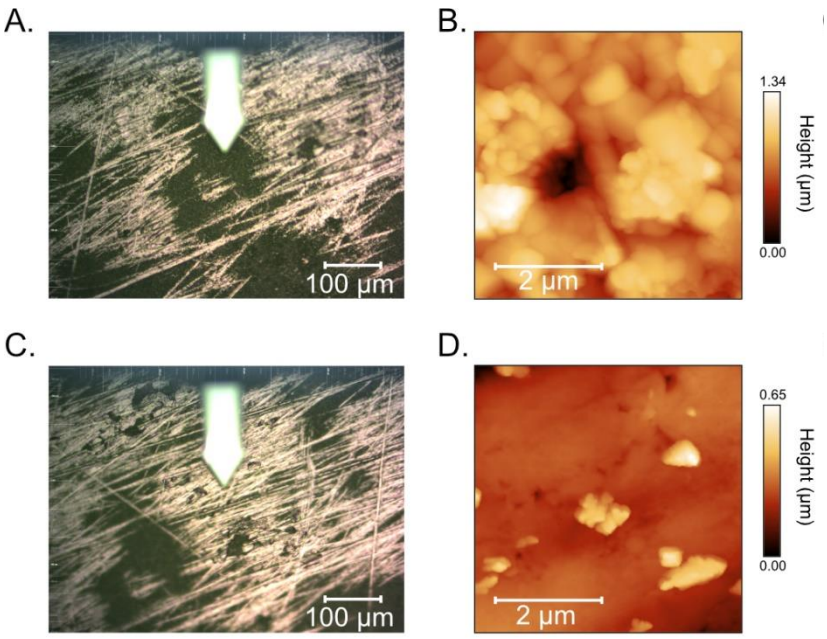

Figure S5: (A) Optical image and **(B)** AFM image of the black colored region of the Cu coated LAGP. **(D)** Optical image and **(E)** AFM image of the Cu-colored (white) region of the Cu coated LAGP.

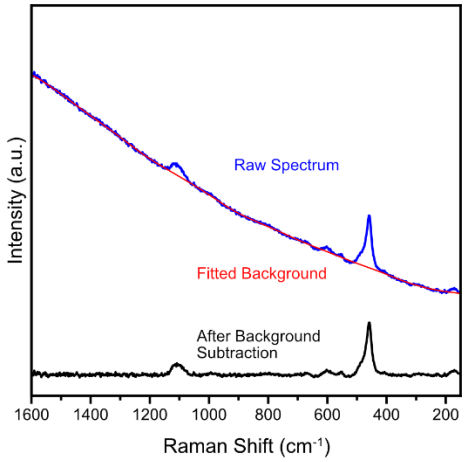

Figure S6: Example of the raw LAGP spectrum collected through the 25 nm copper current collector, the fitted background using the arPLS method and the spectrum after background subtraction.

References.

1 S.-J. Baek, A. Park, Y.-J. Ahn and J. Choo, *Analyst*, 2014, **140**, 250–257.