Supplementary Information

# Surface-Enhanced Raman Spectroscopy (SERS): A powerful technique to study the SEI layer in batteries

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## Experimental

### *Silicon electrodes*

The silicon electrodes used in this study were prepared at the Cell Analysis Modeling and Prototyping (CAMP) facility at Argonne. Commercial silicon (Si) with particle size ca. 70-130 nm from NanoAmor was homogenously mixed with Timcal C45 carbon conductive additive and lithium polyacrylate (LiPAA) binder titrated to pH 7 in a weight ratio of 70.7: 9.4: 19.9, using $H_2O$ as solvent. Then, the mixture was spread onto a 10 µm-thick Cu current collector with a minimal wet gap, resulting in a coating thickness of ~2µm after drying the laminate at 50 $^0$C overnight. The active mass loading was ~0.3 mg cm$^{-2}$.

### *Au-NPs@silicon electrodes*

For the electroplating, a 1400 CellTest® System potentiostat (Solartron Analytical) was used. To obtain the Au-coated silicon electrodes, a three-electrode cell configuration (as shown in **Figure S1**) was used: Pt acted as a counter electrode, Ag/AgCl (4M KCl) as a reference electrode and the silicon as the working electrode. The copper current collector of the Si electrode was covered with consumer-grade polyurethane nail polish to prevent Au deposition onto the Cu. The silicon electrode (ca. 4 cm × 2.5 cm) was immersed in a 1 mM tetrachloroauric acid ($HAuCl_4$) aqueous solution that was polarized at -0.864 V until 0.2 C/in$^2$ (equivalent to 0.031 C/cm$^2$) passed through it. The surface charge and voltage applied here were chosen following previous studies.[1] After the gold deposition, the polyurethane layer was removed with acetone and the electrode was allowed to dry at 150 $^0$C overnight under dynamic vacuum, and from this piece, 11 mm-diameter electrodes were punched and stored in an argon-filled glovebox with < 1 ppm oxygen and water.

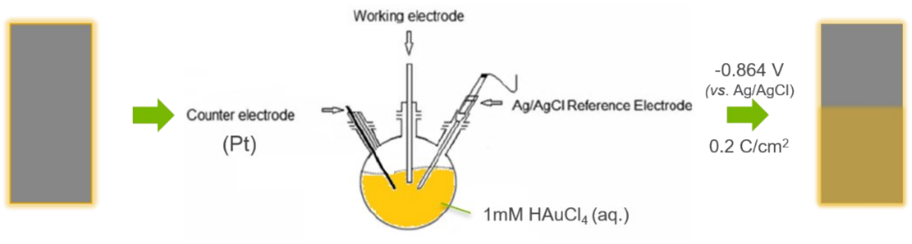

**Figure S1.** Schematic illustration of the electrodeposition process of Au into a silicon electrode. The gray color represents the silicon laminate and the surrounding orange color the Cu laminate in which is casted. After the electrodeposition, the part of the electrode immersed in the 1 mM $HAuCl_4$ solution is coated by Au (gold-color).

It is important to highlight at this point that, although electrodeposition was the technique selected in this occasion, other alternatives such as sputtering may be used for plating Au over the substrate subject of study.

### *Electrochemical tests*

For the electrochemical tests, CR2032 half-coin cells were assembled in an argon-filled glovebox with < 1 ppm oxygen and water. Silicon or Au-coated silicon electrodes acted as the working electrode and lithium metal chips (15.6 mm diameter, from MTI Corp.) as the counter and reference electrodes. 20 µL Gen 2, i.e., 1.2 M $LiPF_6$ in ethylene carbonate:ethyl, methyl carbonate (EC: EMC) in a 3:7 wt % (Tomiyama), was the electrolyte employed and Celgard®2325 dried at 60 $^0$C under vacuum before use was adopted as the separator. The galvanostatic tests were performed in a MACCOR Series 4000 Battery Test System at room temperature. The cells were galvanostatically cycled from 0.01 to 2.0 V *vs.* $Li^+$/Li only twice at a constant current of 450 µA to form the SEI.

### *Characterization techniques*

#### Scanning Electron Microscopy (SEM)

SEM micrographs of silicon and Au-coated silicon electrodes were taken in a scanning electron microscope JEOL JSM-6610LV operated at 10 kV, provided with a secondary electron detector (SED) and a backscattered electron detector (BSED). Elemental mapping analyses were collected using an Energy Dispersive X-Ray Spectroscopy (EDS) unit from Oxford Instruments (model 51-XMX1030), also attached to the microscope, and the extracted EDS data was analyzed with Aztec software. Electrode cross-sections were prepared as follows: while holding the electrodes vertically by the center with tweezers, the electrodes were cut perpendicularly with a sharp blade. Then, each cross-section was glued to carbon-tape adhered to a metallic pin.

In order to prevent them from being exposed to air at any moment, and so avoid possible reactions, the samples were transferred from the glovebox to the microscope in an airtight sample holder.

Below, **Figure S2** shows BSED images of the Au-coated silicon pristine electrode, which are equivalent to those taken with the SED, shown in **Figures 1c** and **1d**.

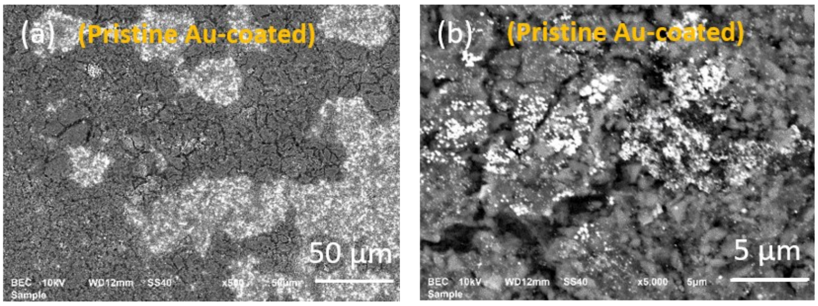

**Figure S2**. BSED images of Au-coated pristine silicon electrodes at two different magnifications, which are equivalent to those shown in Figures 1c and 1d, which were taken with the SED. BSED micrographs allow contrast between elements based on their atomic number (Z). Lighter areas correspond to the heavier element (Au), while darker areas are associated to the lighter element (silicon).

EDS mappings were also collected to further corroborate the presence of Au in the Au-coated pristine silicon electrode (**Figure S3**). Fig. S3 k illustrates the distribution of gold across the electrode surface, where some aggregates are distinguished in certain areas.

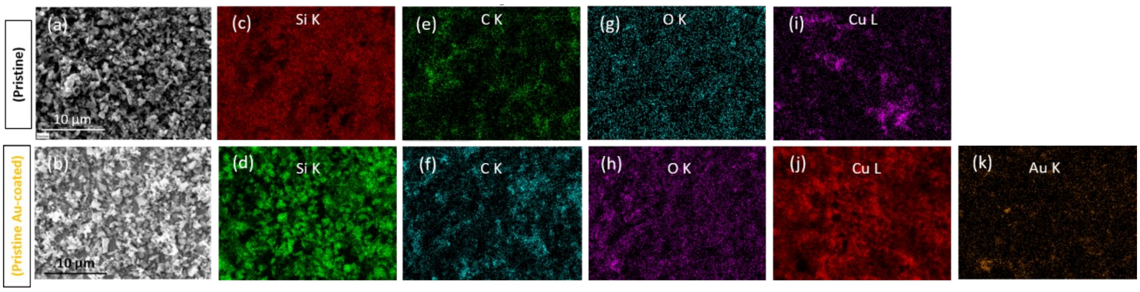

**Figure S3**. SEM images of the pristine (a) and Au-coated pristine silicon (b) electrodes and their corresponding elemental mappings (Si (c and d), C (e, f), O (g, h), Cu (i, j) and Au (k)) obtained using an EDS detector. The colors are different because the software provided them by default.

## Raman spectroscopy

Raman spectra were acquired with a Renishaw inVia™ Raman microscope, which was located inside an argon-filled glovebox with oxygen and water levels below 1 ppm. The measurements were performed with a 785 nm ($\lambda_{exc}$) diode laser and a 1200 line/mm grating, using 20X focal optics and a laser power below 1 mW/µm$^2$. Several 100 µm × 80 µm areas were scanned for each sample with a 20-µm step size, obtaining maps of 20 points, with 20 accumulations per point. The spectra of all these points were baseline corrected and averaged with the help of WiRE 4.1 software and are presented in this manuscript as a single spectrum. For each Au-coated sample, as not all the surface was covered with gold, only the points exhibiting Au where taken into account. Also, on the occasions when normalization was necessary, $Na_4Fe(CN)_6\cdot 10H_2O$ from Sigma Aldrich was added to the electrode without further purification. The enhancement factor was calculated as described previously by some of us,[1] using the most intense band of $Na_4Fe(CN)_6\cdot 10H_2O$ as a pseudo-intensity standard. The spectrum of $Na_4Fe(CN)_6\cdot 10H_2O$ is shown below in **Figure S4**.

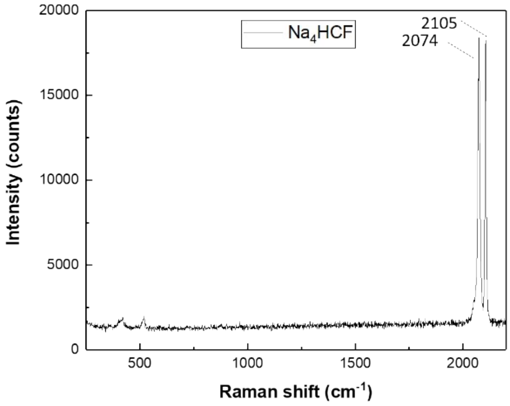

**Figure S4**. Raman spectrum of $Na_4[Fe(CN)_6]\cdot 10H_2O$. The bands labeled with the corresponding Raman shift correspond to the cyanide bands of the material.

The Raman bands observed in the cycled Au-coated silicon electrode are collected in **Table 1**. Please see main text for a further discussion of these results.

**Table S1.** Tentative assignment of the Raman bands encountered in the cycled Au-coated silicon electrode. a-Si stands for amorphous silicon, TA for transversal acoustic mode, and C for C-45 conductive carbon.

| **Raman shift (cm$^{-1}$)** | **Assignment** |
|---|---|
| 298 | a-Si (TA mode) |
| 467 | a-Si |
| 980 | $\nu_{Si\text{-}O}$ or Si-OH or Si (2nd TO mode) |
| 1084 | $\nu_{Si\text{-}O\text{-}Si}$ |
| 1217 | $\nu_{C\text{-}C}$ ($C\text{-}CO_3^{2-}$) or $\nu_{P=O}$ ($(CH_3)_2P(=O)OCH_3$) |
| 1244 | $\rho_{sym, C\text{-}H}$ (HC=CH) or $\nu_{P=O}$ ($P(=O)O_2^{2-}$) |
| 1280 | Si-O |
| 1336 | D-band (C-45) |
| 1396 | $\delta_{C\text{-}H}$ ($=CH_2$) or $\nu_{P=O}$ ($P(=O)F_3$) |
| 1450 | $\delta_{C\text{-}H}$ ($-CH_2-$) |
| 1580 | G-band (C-45) |
| 1848 | $Li_2C_2$ |

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[1] A. Tornheim, V. A. Maroni, M. He, D. J. Gosztola, Z. Zhang, *J. Electrochem. Soc.*, 2017, **164**(13), A3000-A3005.