



Probing Interfacial Processes of Lithium Ion Batteries In Situ Non-Linear and Linear Spectroelectrochemical Investigation

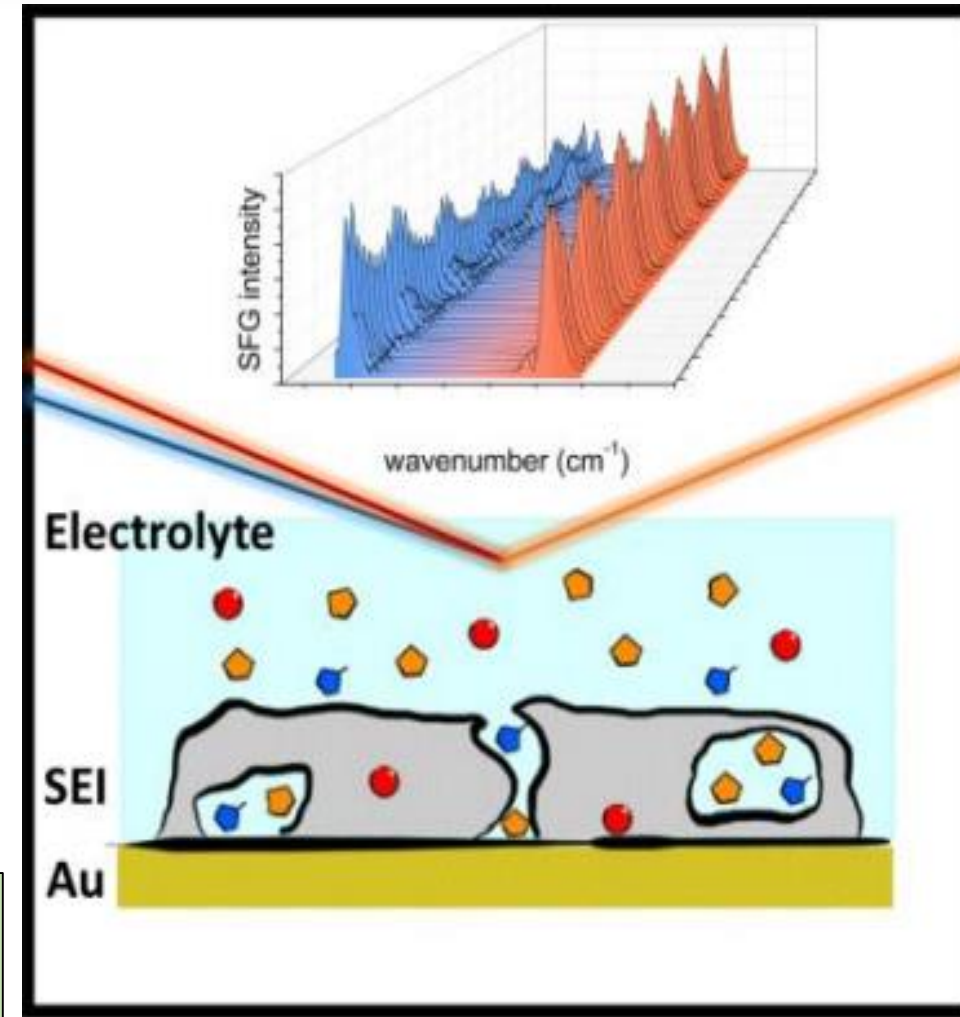
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Introduction

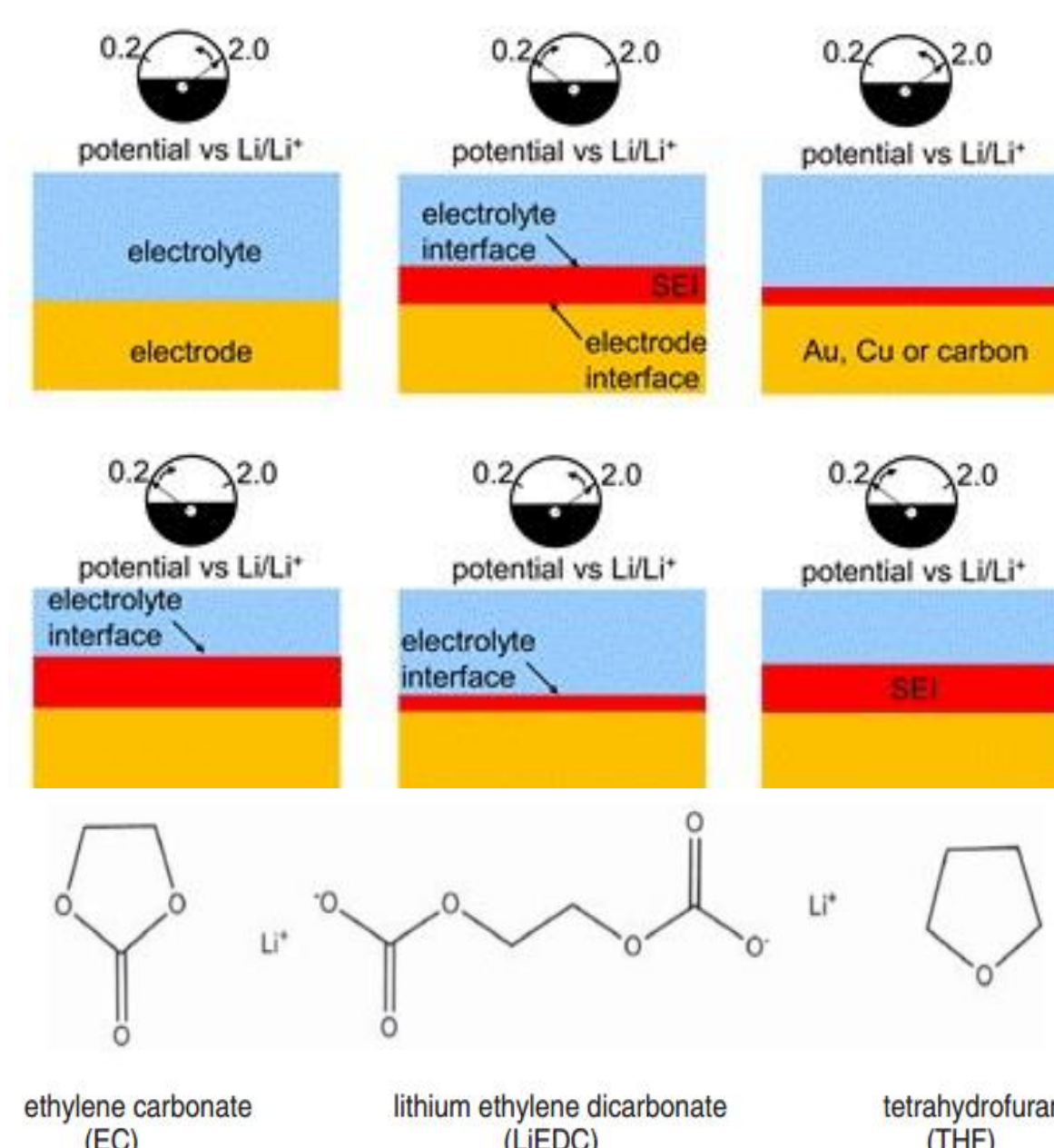
Lithium Ion Batteries

Lithium ion batteries hold a major role in personal electronics due to being a lightweight high energy density. However, due to inherent instability, lithium ion batteries are known to have issues with safety and capacity loss. Our goal is to advance the understanding of the electrochemical processes, specifically the interfacial processes at the anode.



Solid Electrolyte Interphase (SEI)

At the interface of the electrolyte and anode, during the first several charging and discharging cycles, appears a protective layer by interaction of decomposed electrolyte. This protective layer, termed the solid electrolyte interphase, is of particular importance as it increases the stability, impeding dendrite growth, and ultimately leading to improved capacity and safety. Our electrolyte is a lithium salt (LiClO₄) with ethylene carbonate (EC) in a tetrahydrofuran (THF) solvent, leading, primarily, to the SEI contributor, lithium ethylene dicarbonate (LiEDC). By spectroscopically probing the interface with sum-frequency generation and simultaneously scanning with cyclic voltammetry, we are able to see the SEI contribution formation in real time!



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Sum-Frequency Generation (SFG)

Theory

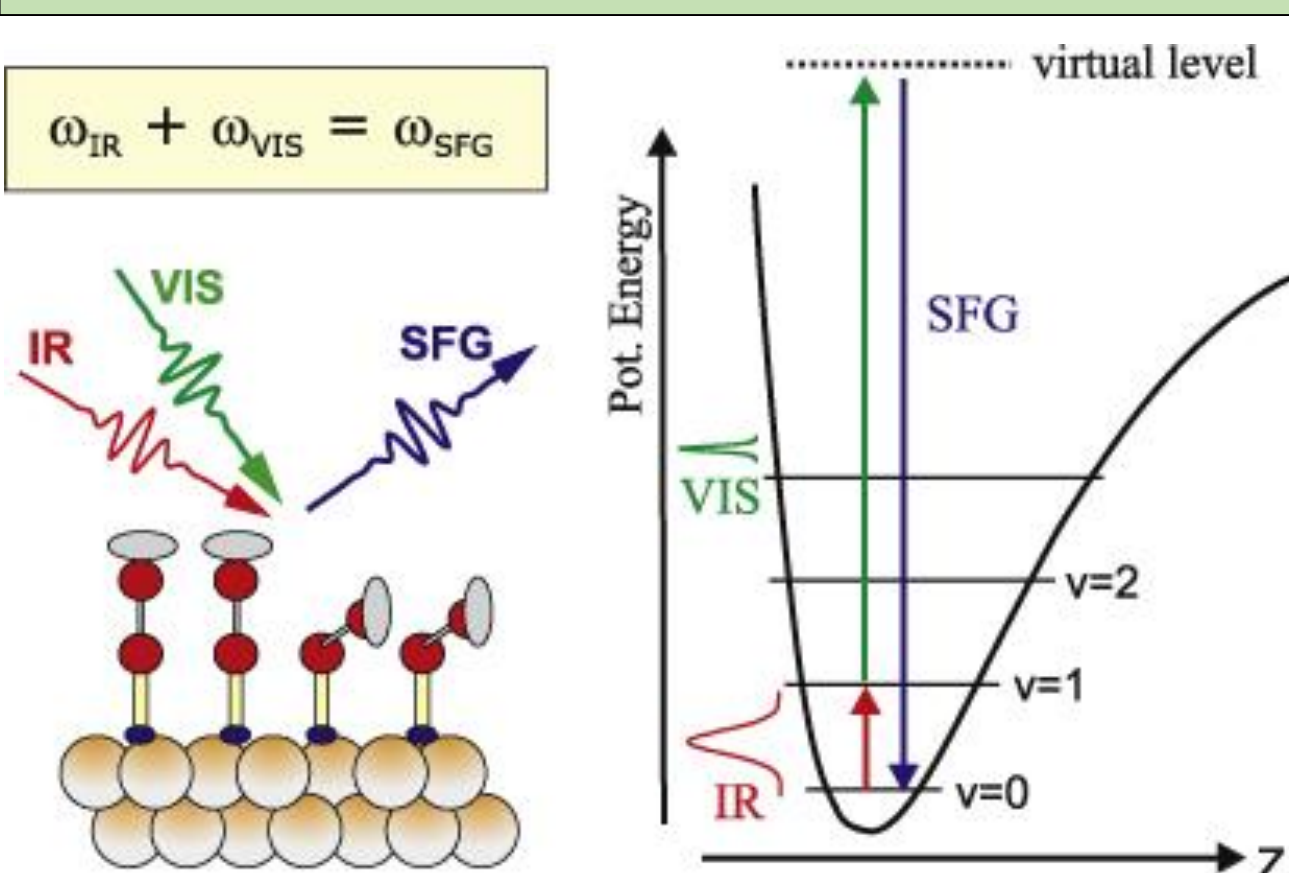


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Nonresonant Suppression

Intensity of the SFG signal originates from a nonresonant signal, the metal-adsorbate's electronic response, and a resonant signal, the adsorbate's molecular response. For investigation of the adsorbate's molecular response, we can suppress the nonresonant SFG signal.

Simplified SFG Signal:

$$I_{SFG}(\omega) \propto |\chi_R^{(2)}(\omega) + \chi_{NR}^{(2)}(\omega)|^2 E_{IR} E_{VIS}^2$$

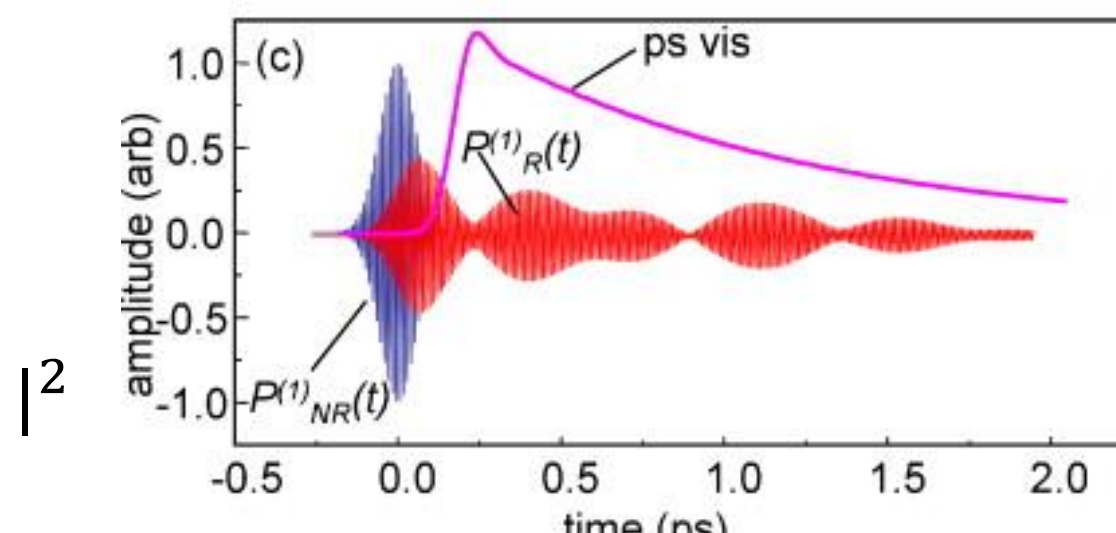
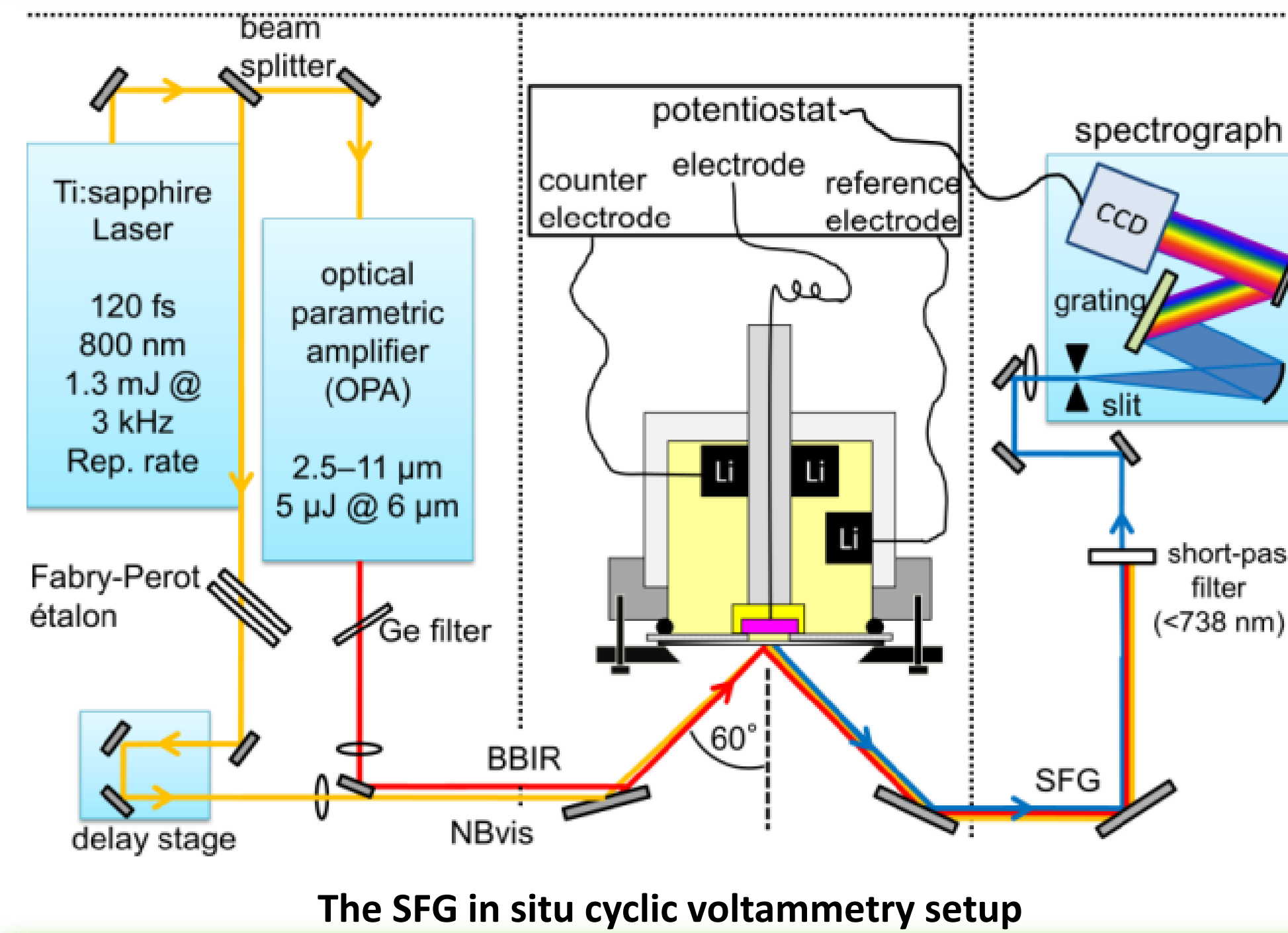


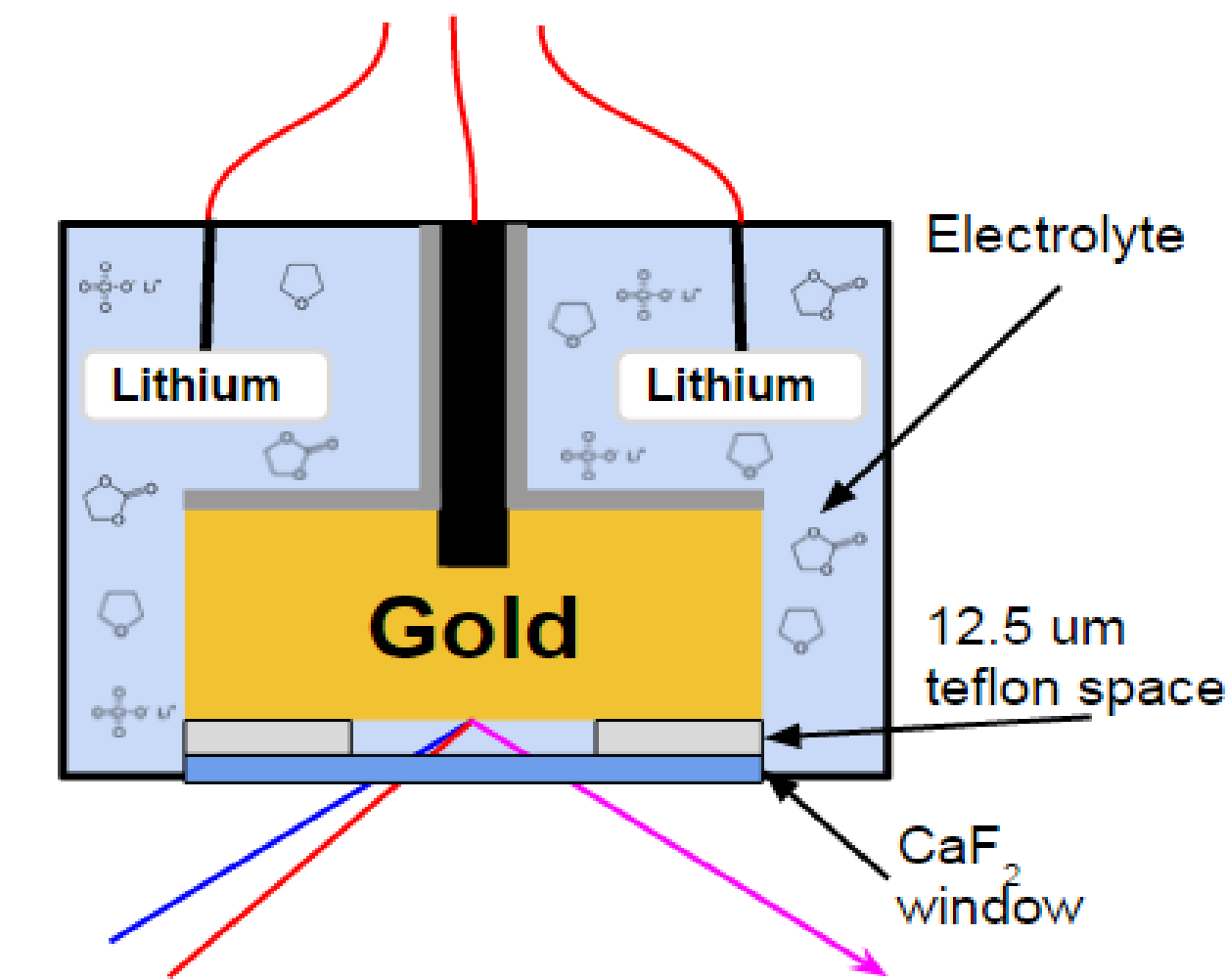
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Through time-windowing, i.e. time delaying the VIS pulse the duration of excitation as given by free-induction decay, we are able to separate the two contributions, and therefore, suppress the nonresonant signal from our investigation.

SFG in Synchronization with Cyclic Voltammetry

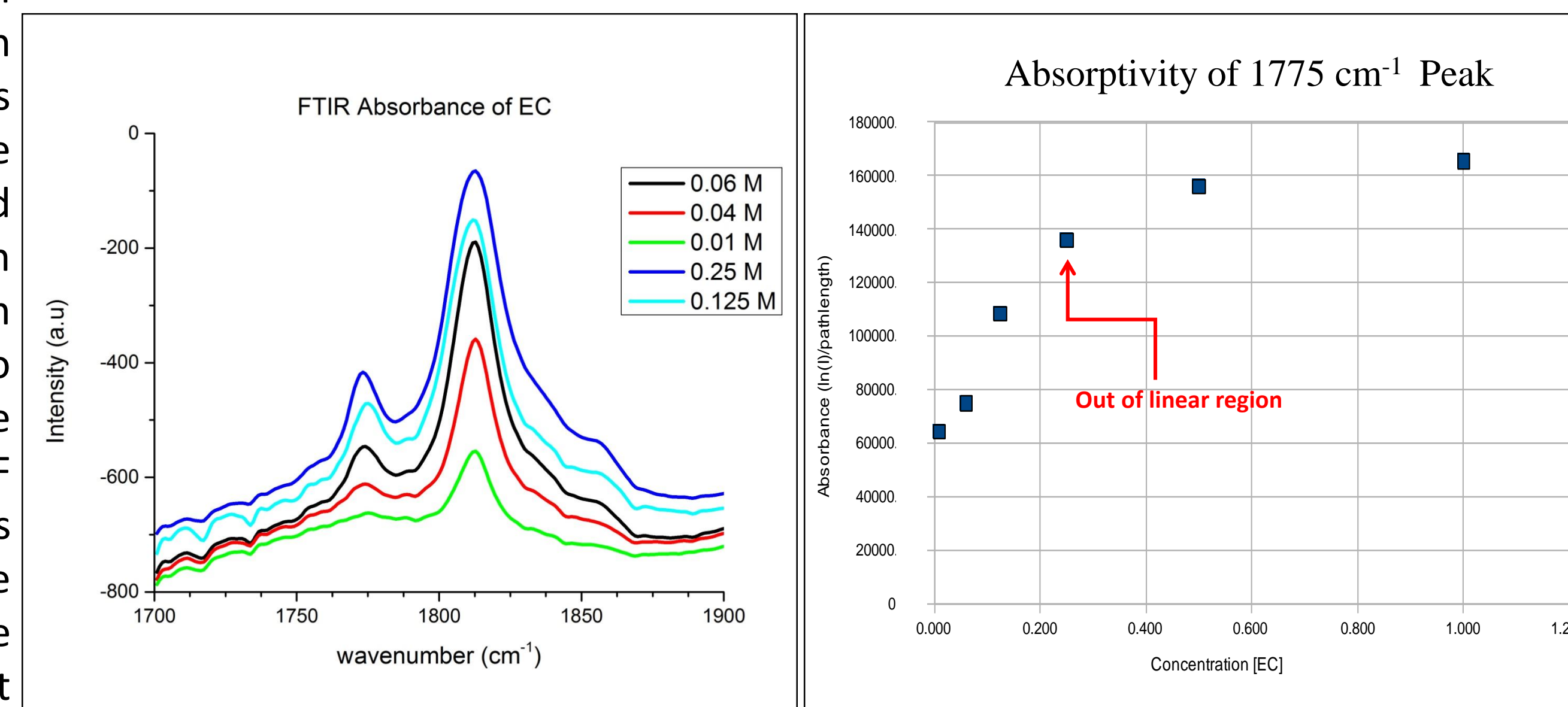


This system, developed in the Dlott group, allows us to "see" the molecular interaction at the surface of the anode, during the charging and discharging of a lithium ion battery.

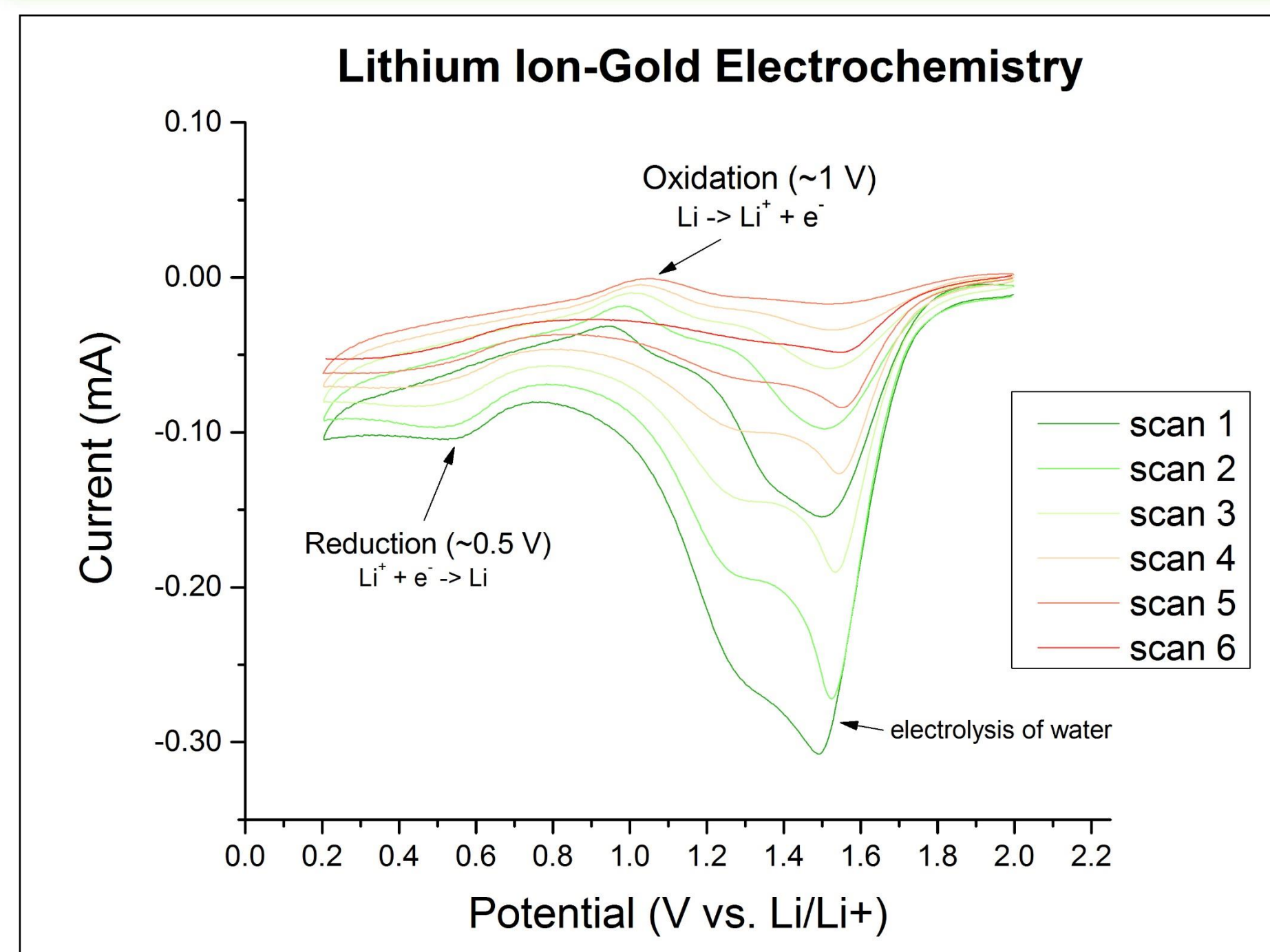


Investigation of the Electrolyte IR Absorption

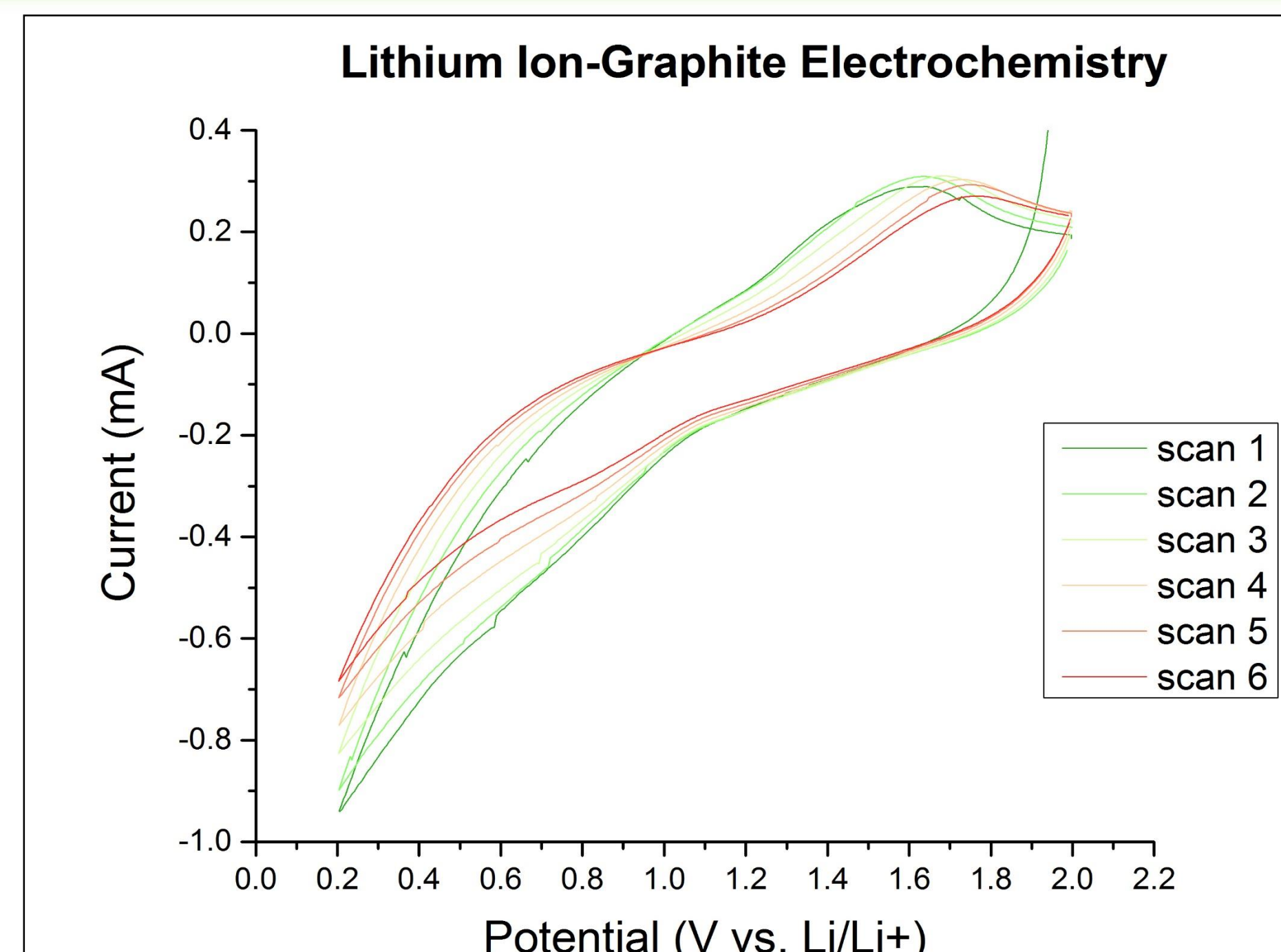
From the nonresonant suppression figure in the previous section, we can see the separation of the curves. However, if absorption was to occur the blue curve becomes as long as the red curve and non resonant suppression cannot work. Fourier Transform Infrared spectroscopy (FTIR) is used to observe the IR absorption of ethylene carbonate which was diluted in a THF solvent. Complete IR absorptive effects are seen with 0.5 M [EC] leading to the realization that previous results¹ were bulk contributions and not the resonant interfacial molecular response.



Comparison of Electrochemistry on Au and Graphite



The expected lithium underpotential deposition and stripping occurring at ~0.5 V and ~1 V, respectively, can be seen. What was previously thought to be the SEI formation (~1.5 V), is now known to be electrolysis of H₂O (~50 ppm) and O₂ impurity in the THF.



The transition from using a gold electrode to a graphite electrode is a work in progress. Deposition of lithium on the surface of the electrode was visible during testing but peak intensities are low. Still, the CV is indicative of reversibility.

Observing SEI on Gold *in situ*

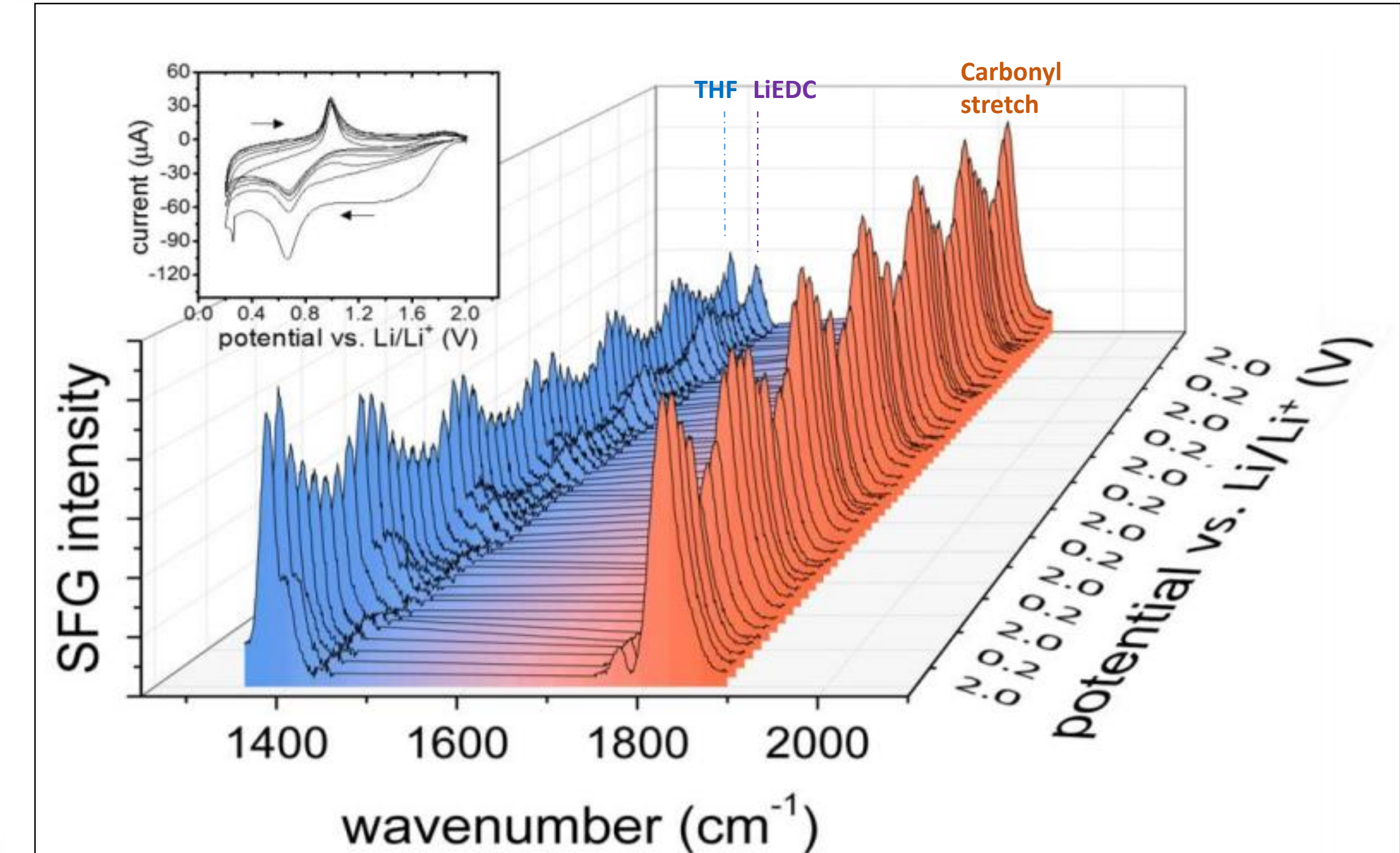


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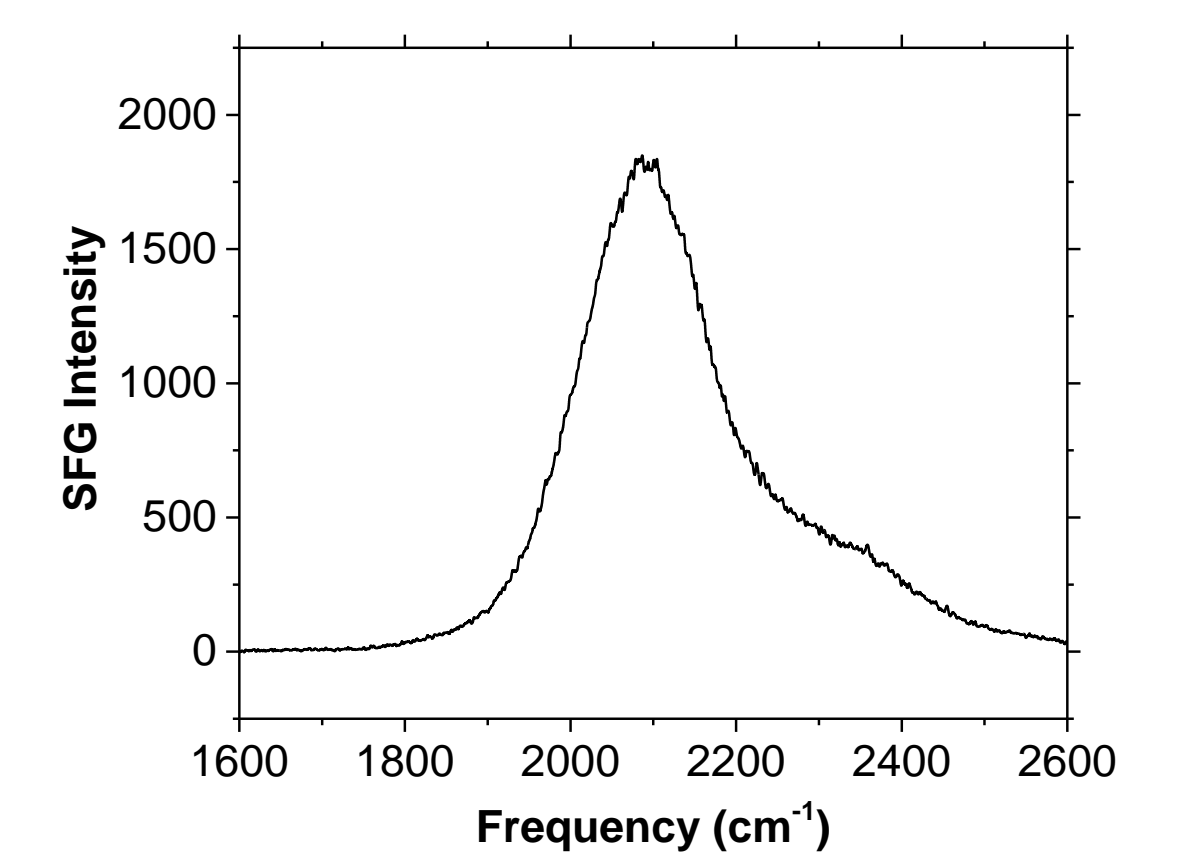
The SEI (LiEDC) and THF region at ~1400 cm⁻¹ and ethylene carbonate region at ~1800 cm⁻¹ are shown over six cycles. The THF peak decays while the LiEDC peak appears and grows over the duration of the experiment. The EC peak does not change.

Future Plans

Typically, lithium ion batteries use active carbon (graphite) electrodes. Carbon's advantageous intercalation properties leads to a higher capacity. Moving from the model system to a realistic system, i.e. from a gold electrode to a graphite electrode, is a crucial step for this project. The first challenge was to fabricate a graphite electrode that may be used optically, and after some tinkering, a mechanically polished carbon slurry (10% carbon black, 10% carboxymethyl cellulose, 80% graphite) layering a copper electrode achieved optically suitability, as shown by the SFG spectrum below. The next steps are to understand the new electrochemistry and *in situ* probe the SEI with SFG so to identify the molecular structures and evolutions at the interface.



Left: polished graphite electrode
Right: dried slurry (pre-polish)



1st SFG signal of graphite electrode (clean)

References

- Prabuddha Mukherjee, Alexei Lagutchev and Dana D. Dlott, *J. Electrochem. Soc.* 159, pp. A244-A252 (2012)
- Interfacial Processes of a Model Lithium Ion Battery Anode Observed, *in situ*, with Vibrational Sum-Frequency Generation Spectroscopy, Bruno Giuliano Nicolau, Natalia Garcia-Rey, Bogdan Dryzhakov, Dana D. Dlott. *The Journal of Physical Chemistry C* Just Accepted Manuscript.
- Optically and thermally induced molecular switching processes at metal surfaces. Petra Tegeder 2012 *J. Phys.: Condens. Matter* 24 394001