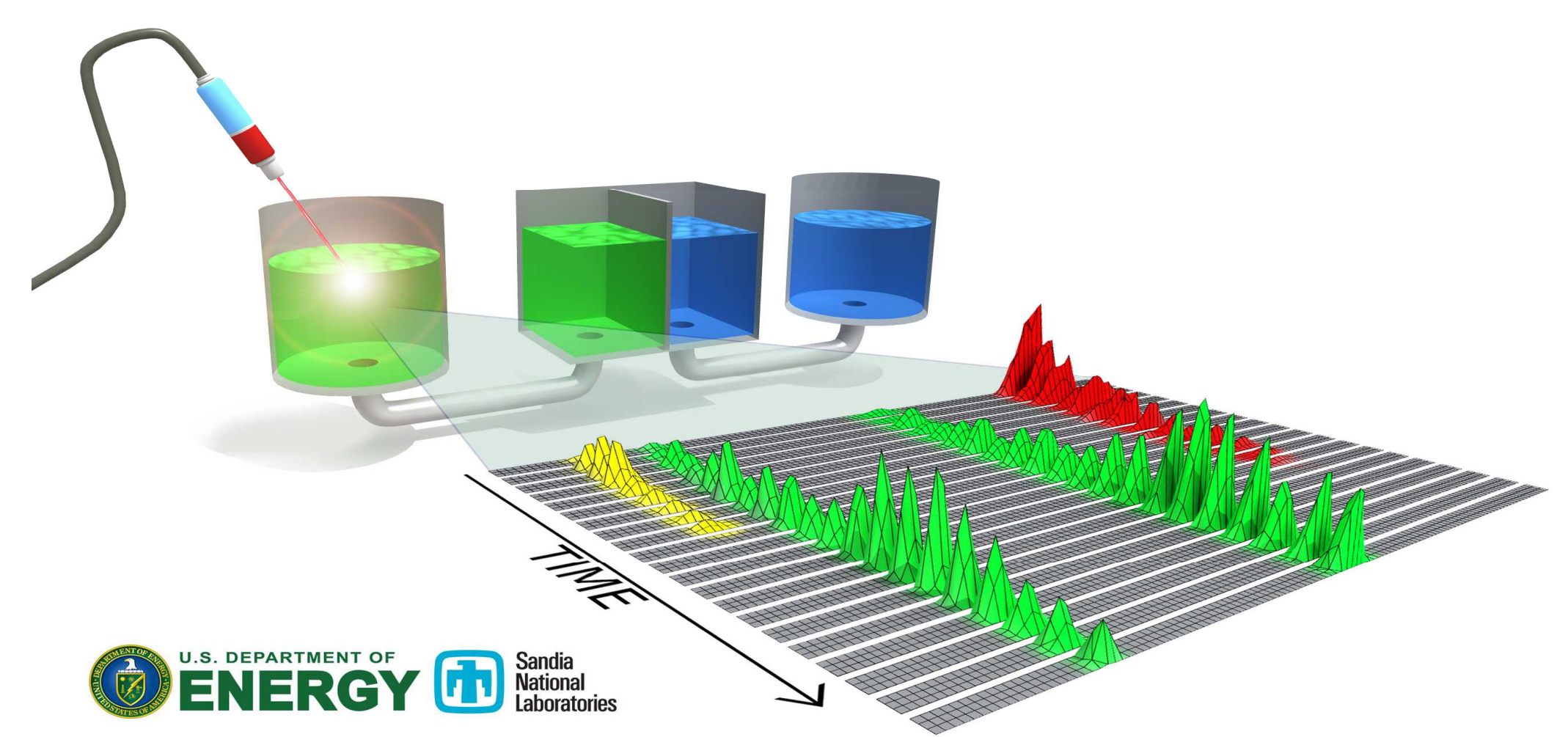
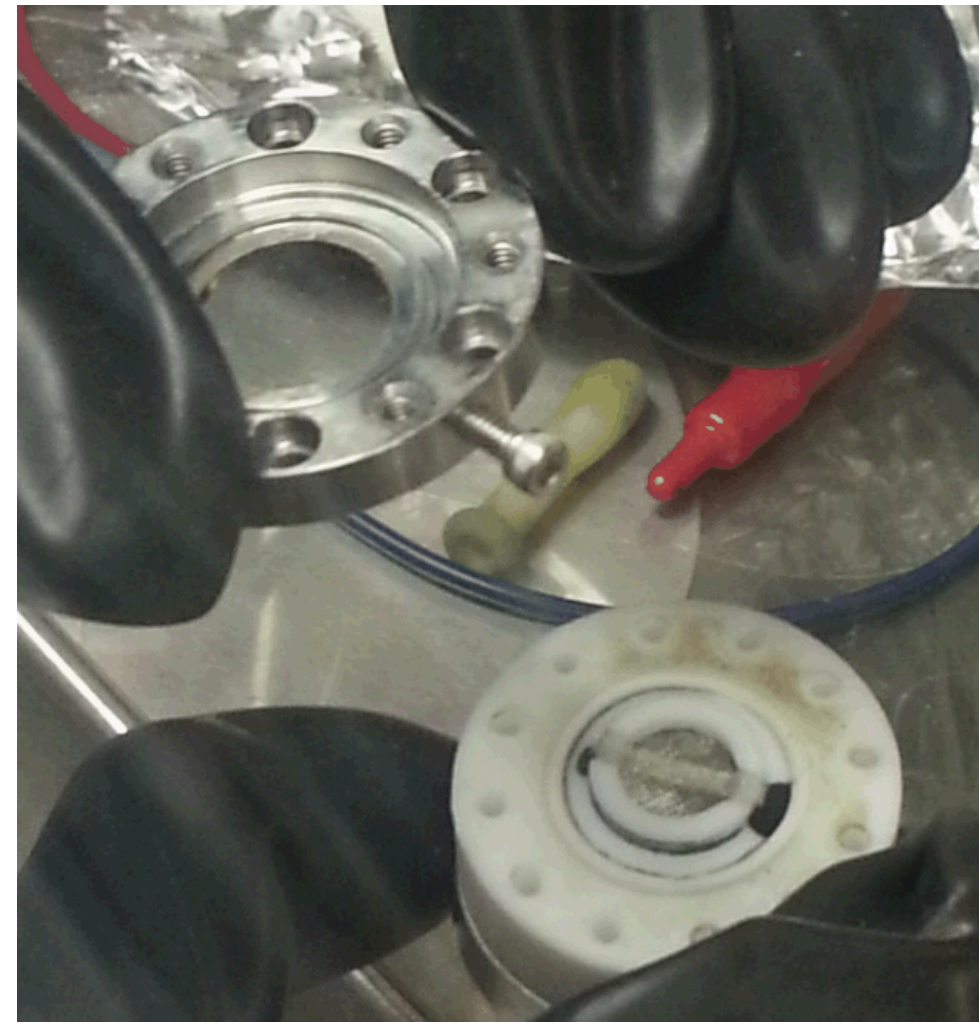
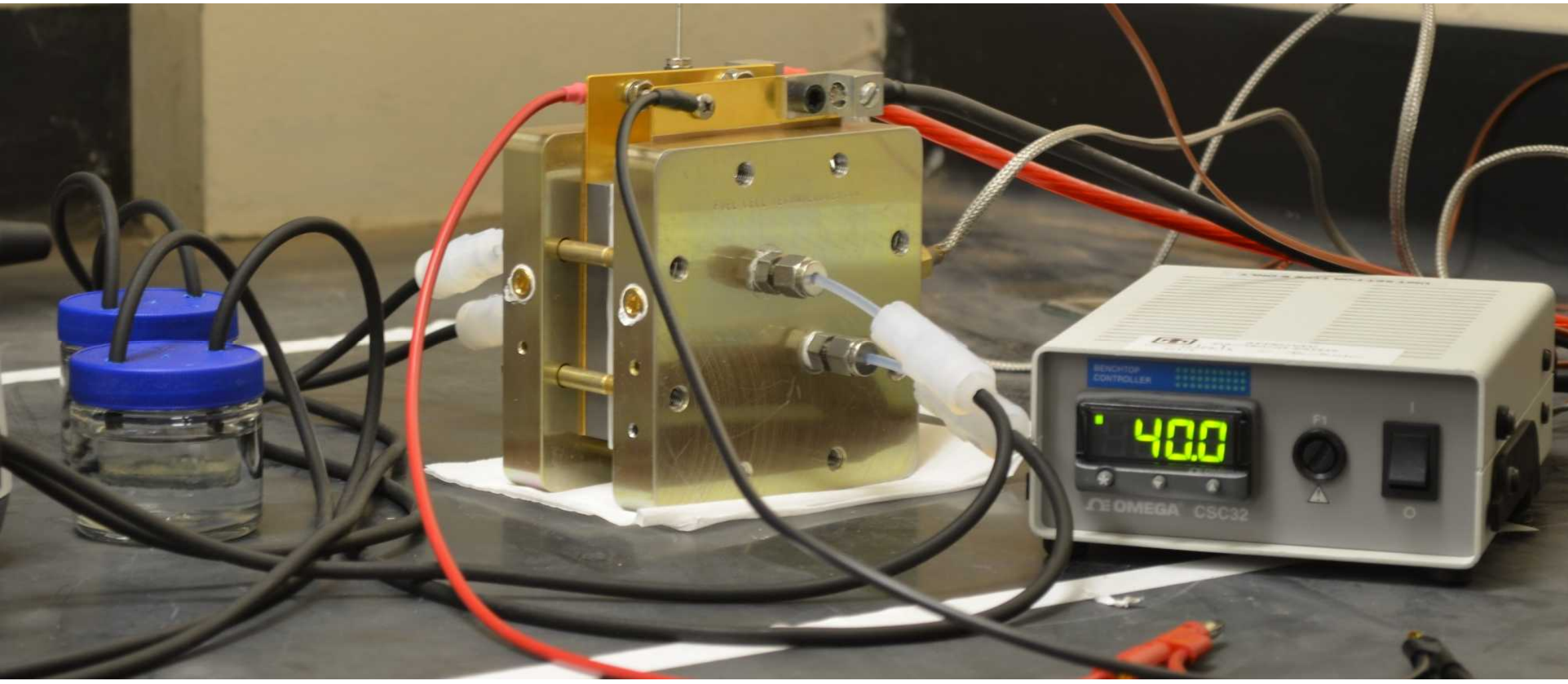


Exceptional service in the national interest



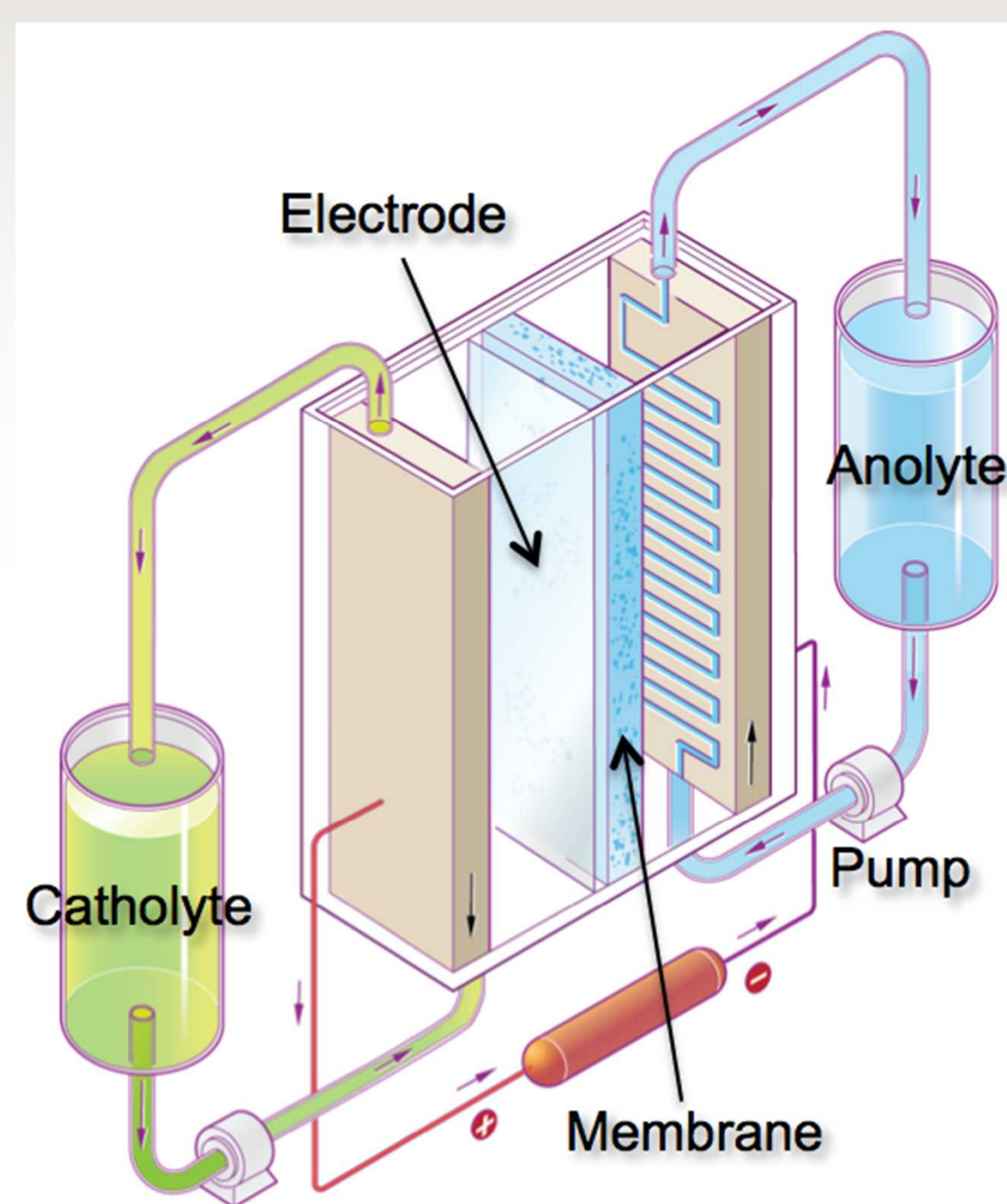
In operando Flow Battery Monitoring for Safety and Reliability

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Our laboratory is investigating the use of Raman spectroscopy as an *in operando* tool for monitoring both aqueous and non-aqueous RFB systems. We have shown this method to be incredibly informative about the chemistry at the electrode's surface and in solution. Monitoring RFB is important because systems of this size are costly and potentially hazardous. "Seeing" inside the battery to examine state-of-charge, decomposition, and potential runaway reactions is of utmost importance as RFB matures.

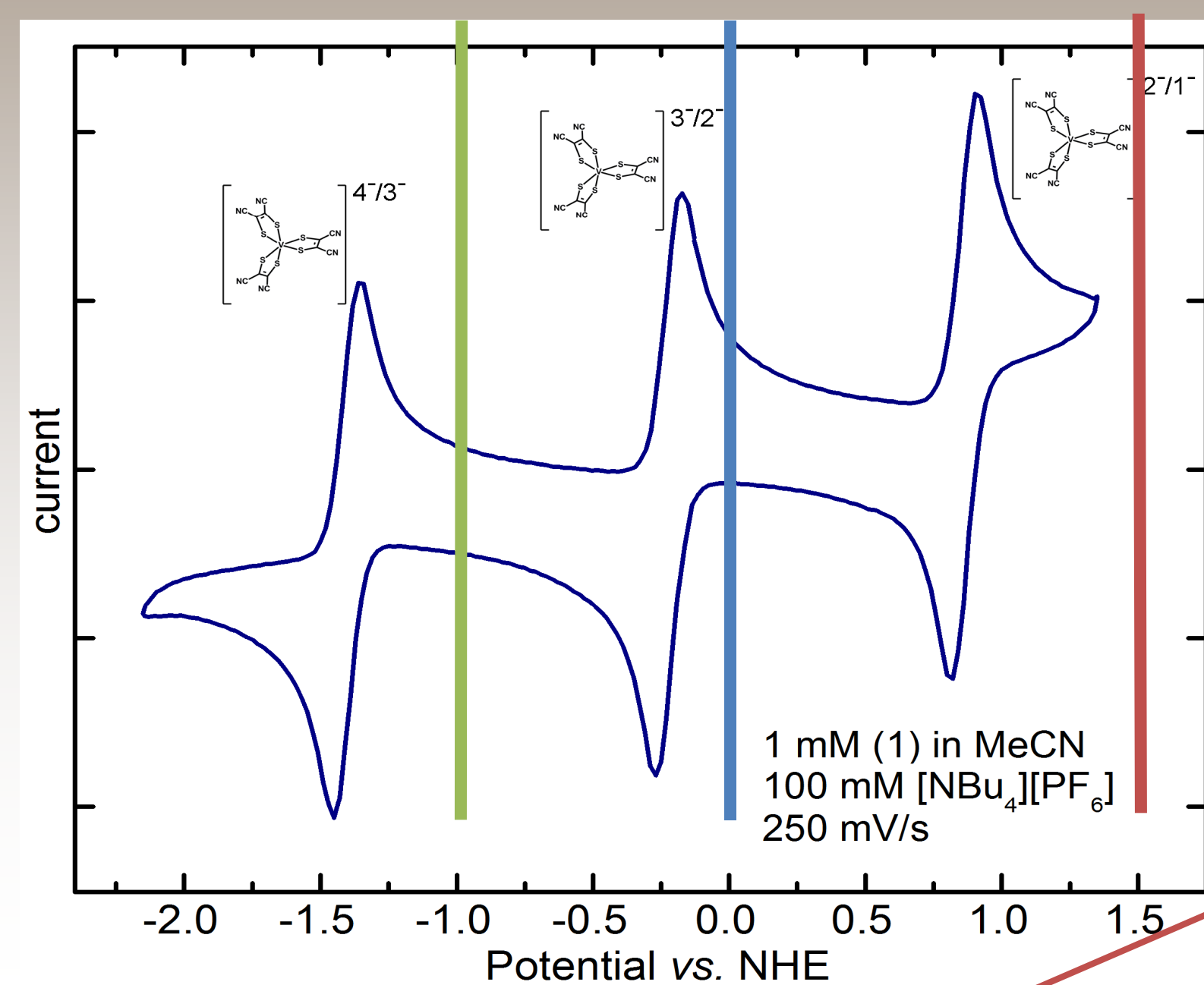
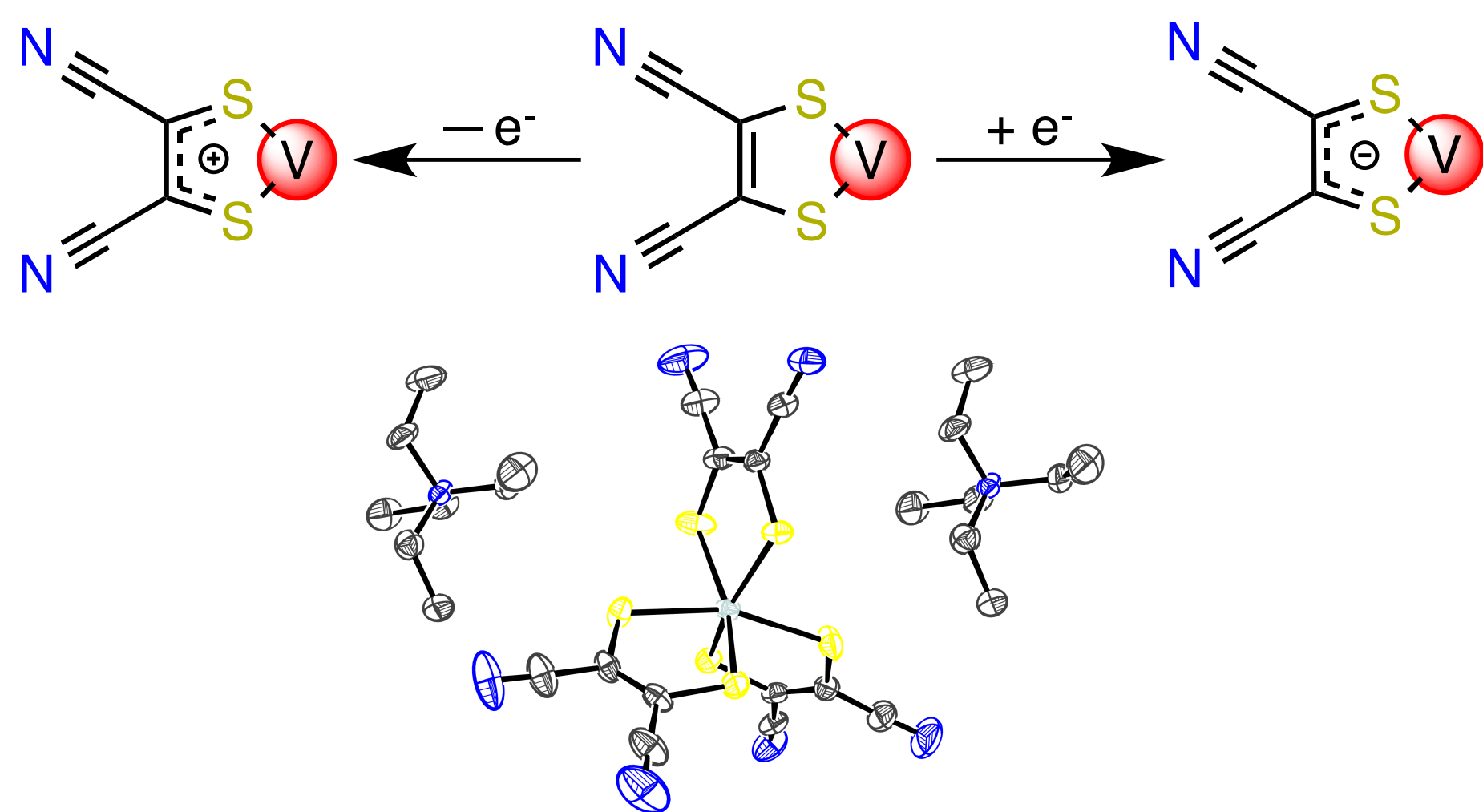


Limitations of other monitoring methods:

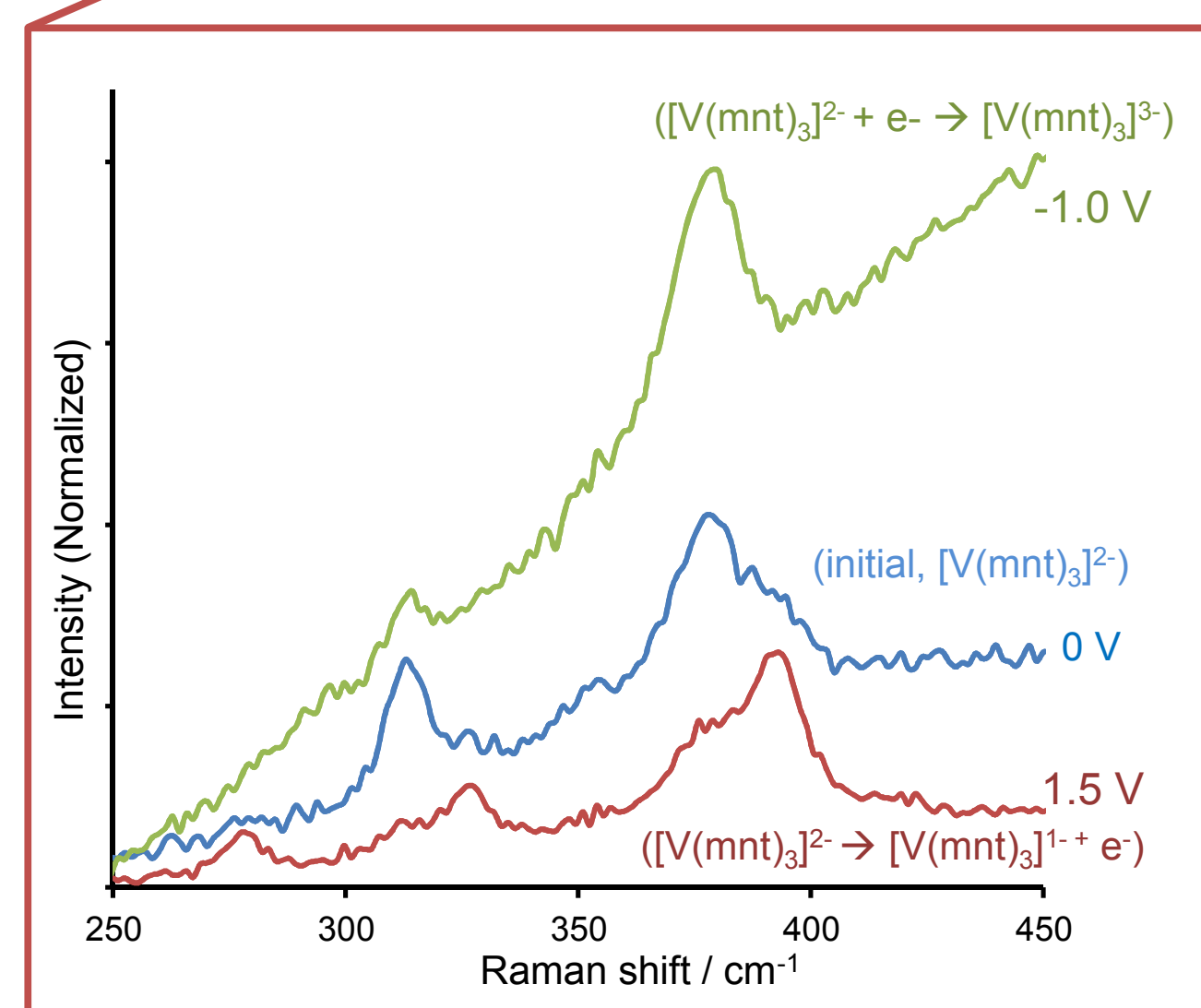
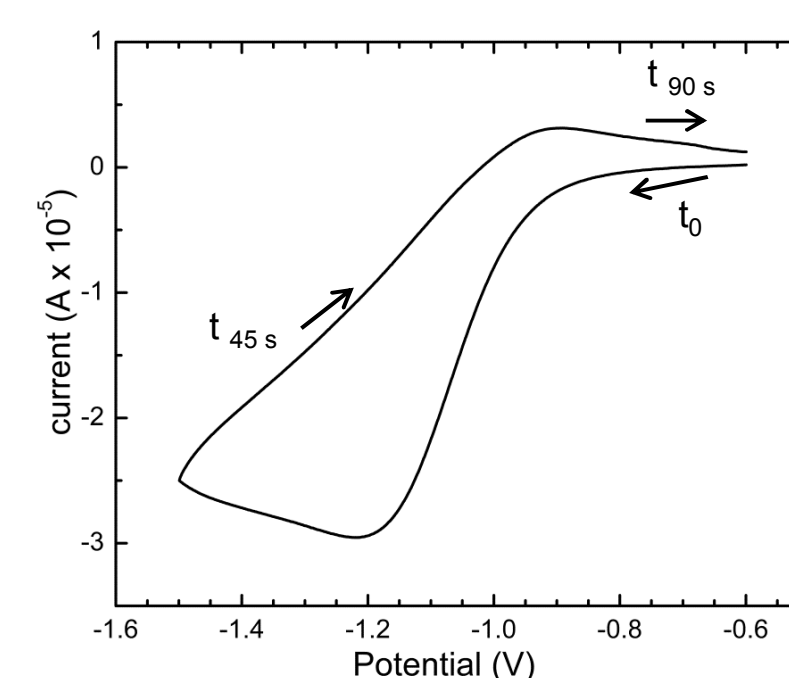
- Open Circuit Voltage (OCV) fails if cells become imbalanced; each half-cell's potentials should be monitored independently but is difficult
- Conductivity, UV-Vis, and IR have all been proposed as alternatives but concentrations must be low (!) and no chemical information is learned (useful for SOC only)

Raman is a good method for SOC *and* health monitoring:

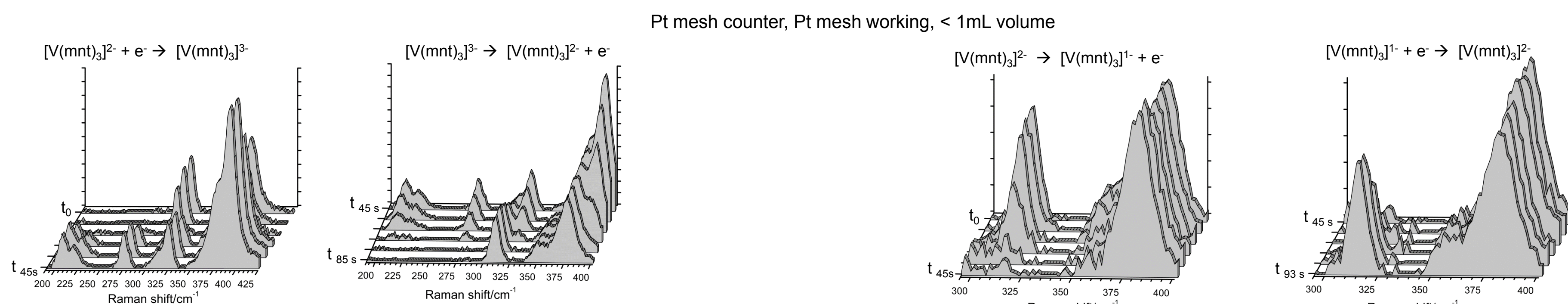
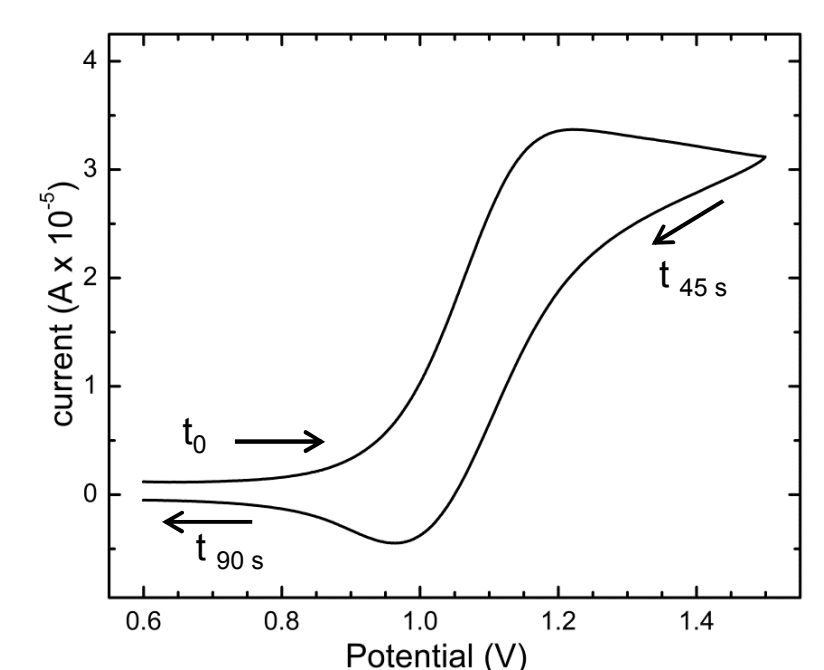
- Higher the concentration, the better the measurement
- Peaks are very responsive to changes in oxidation state
- Metal compounds are active in the UV/Vis region, can lead to resonance enhancement of Raman (specific enhancement over solvent or supporting electrolyte!)



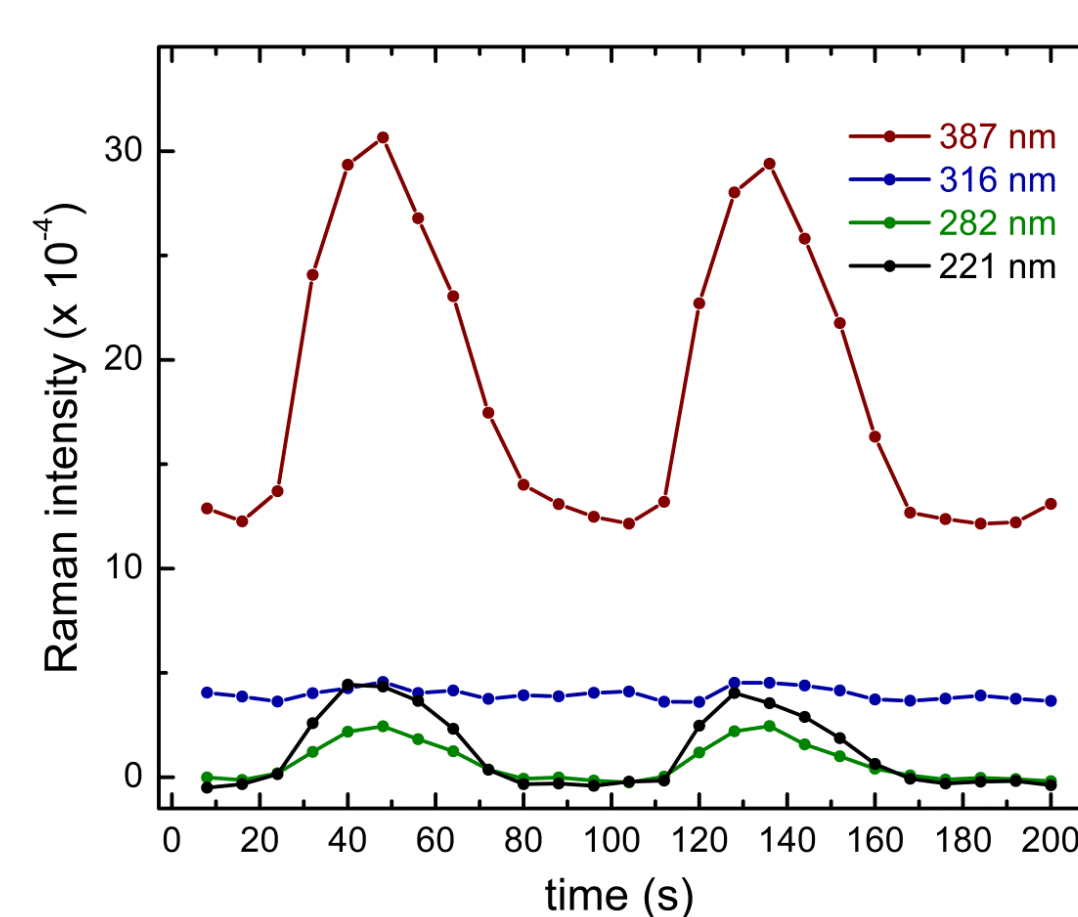
Reduction Process



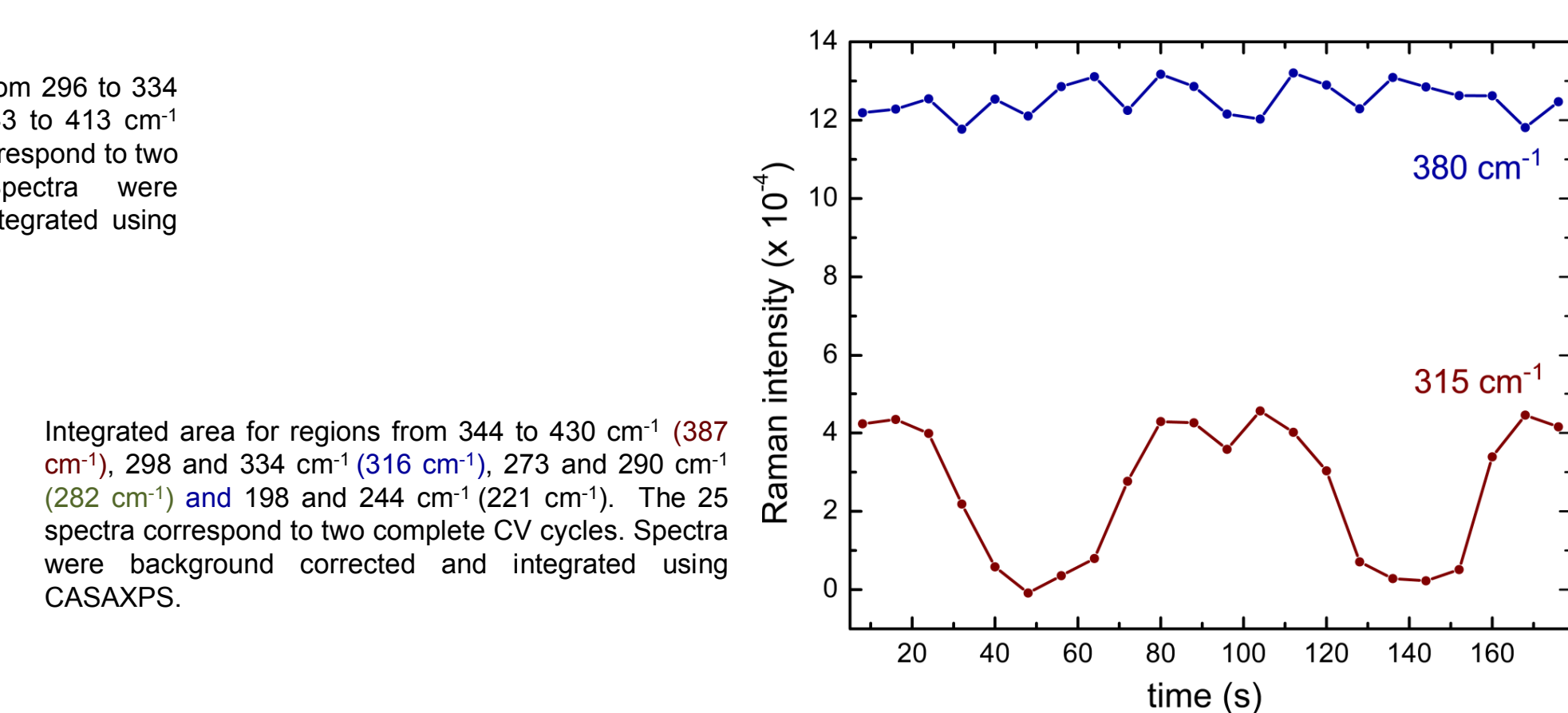
Oxidation Process



Above are two cyclic voltammograms, accompanying real-time Raman spectra, with maxima plotted v. time pictured below. These plots demonstrate the power and precision of this technique as a method for monitoring the state-of-charge and presence of the electrolyte and possible contaminants and decomposition products.



Integrated area for regions from 296 to 334 cm^{-1} (315 cm^{-1}) and from 343 to 413 cm^{-1} (380 cm^{-1}). The 22 spectra correspond to two complete CV cycles. Spectra were background corrected and integrated using CASAXPS.



Integrated area for regions from 344 to 430 cm^{-1} (387 cm^{-1}), 298 and 334 cm^{-1} (316 cm^{-1}), 273 and 290 cm^{-1} (282 cm^{-1}) and 198 and 244 cm^{-1} (221 cm^{-1}). The 25 spectra correspond to two complete CV cycles. Spectra were background corrected and integrated using CASAXPS.