

Electronic supporting information, ESI

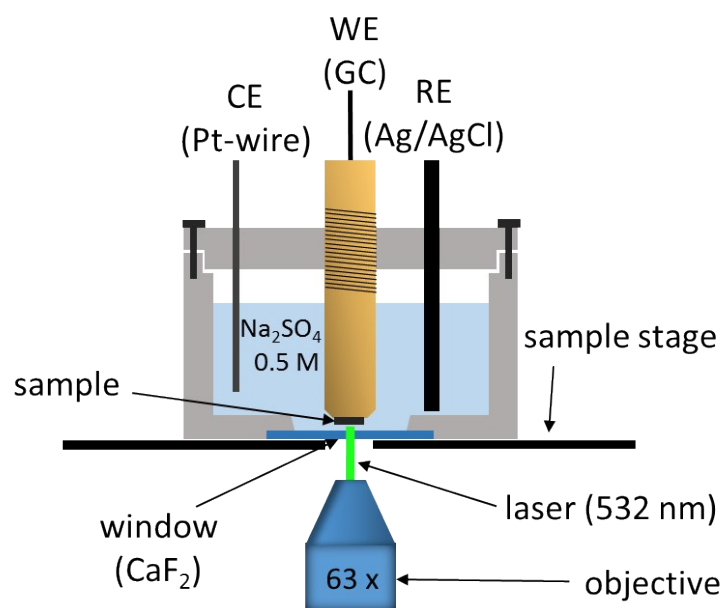


Figure S 1. Sctch of the *in situ* Raman measuring cell.

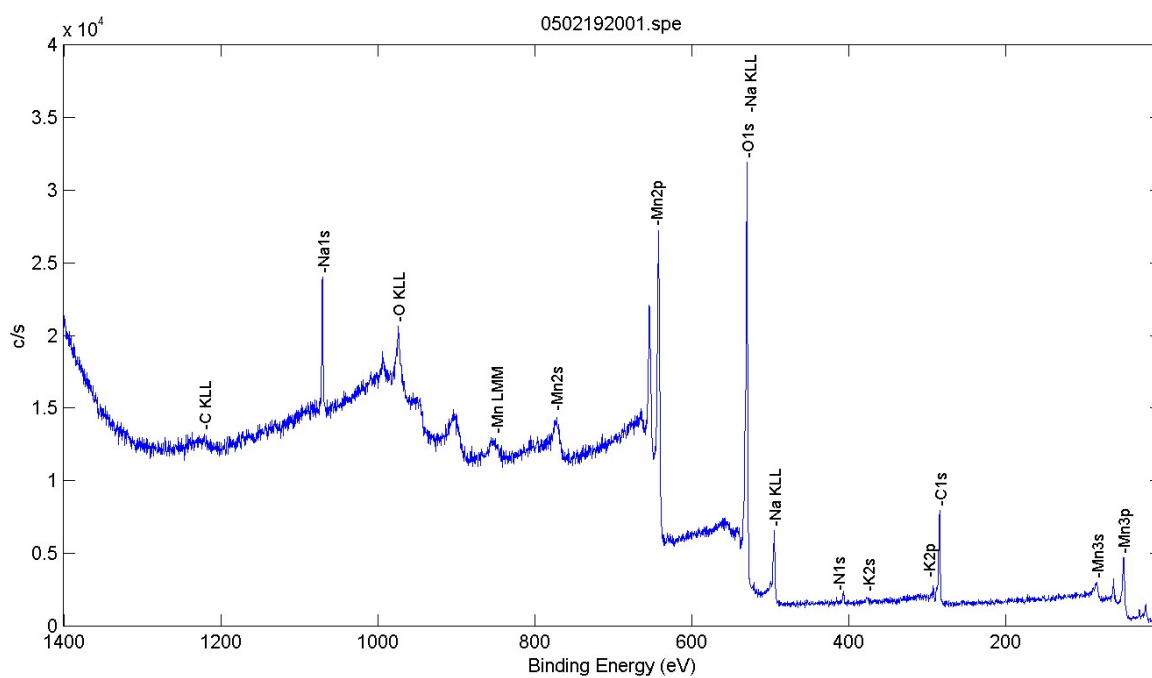


Figure S 2. XPS-spectrum of Li,Na,K-bir.

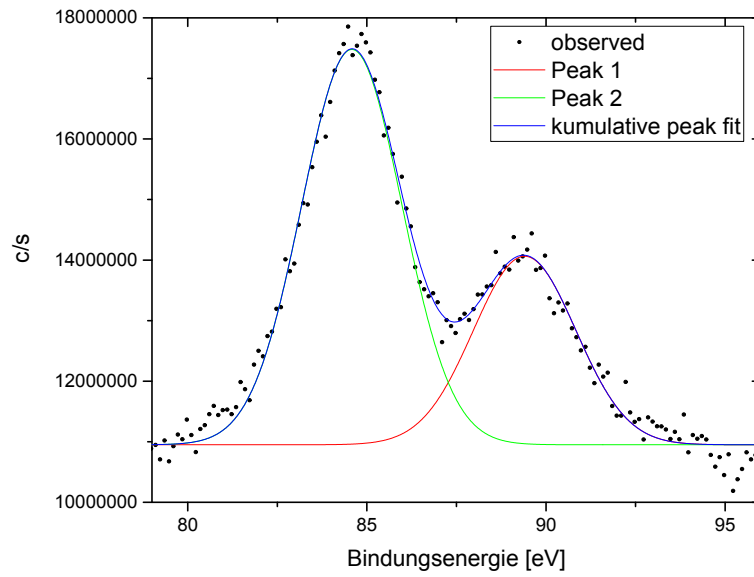


Figure S 3. Detail view of the Mn_{3s} peaks of Li,Na,K-bir. $\Delta E_{Mn3s} = 4,82$ eV.

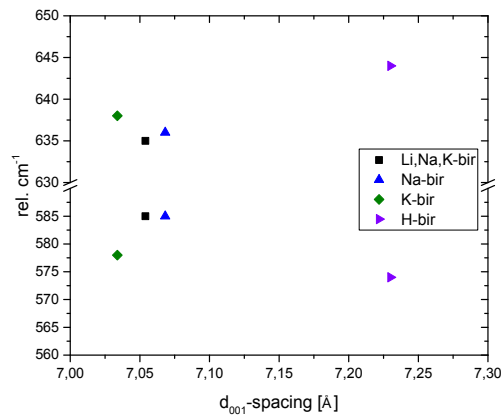


Figure S 4. Korrelation between d_{001} -spacing and spectral position of ν_1 and ν_2 .

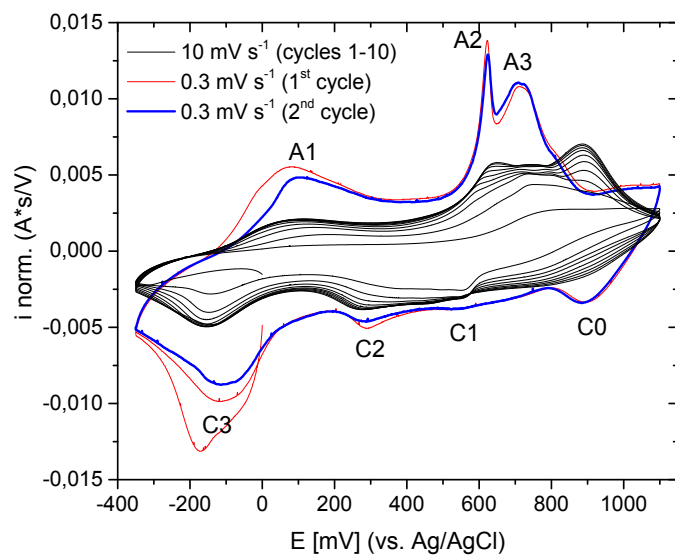


Figure S 5. Normalized Cyclic voltammograms of Li,Na,K-bir in 0.5 M Na₂SO₄ aqueous electrolyte (potential window: -350 mV – 1100 mV (vs. Ag/AgCl)) measured at different scan rates. Electrochemical activation at 10 mV s⁻¹ (black) and 0.3 mV s⁻¹ (red and blue).

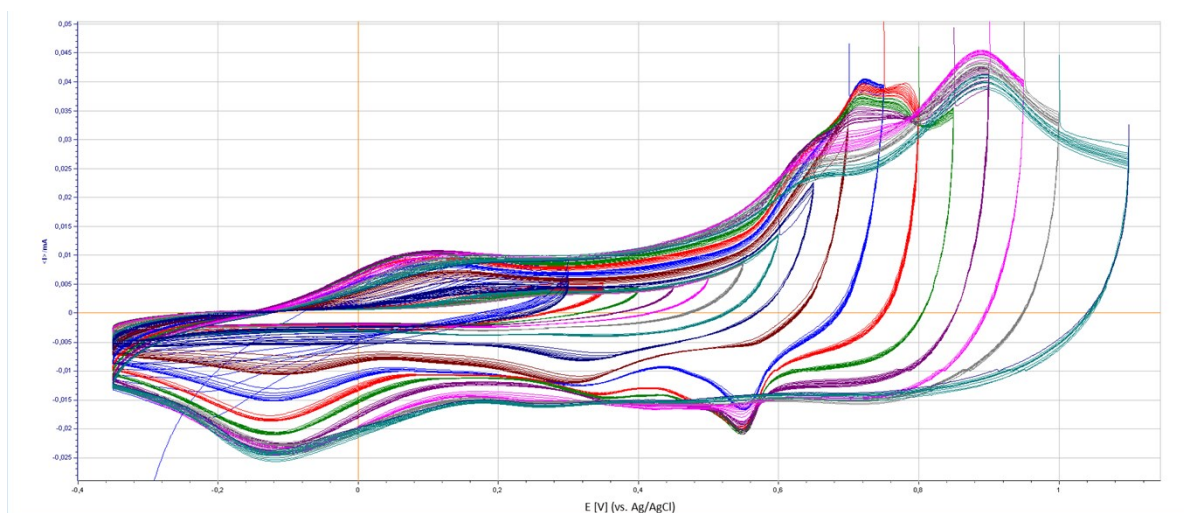


Figure S 6. Dependence of the electrochemical behaviour of Li,Na,K-bir on the applied potential window. Lower reverse potential always -350 mV (vs. Ag/AgCl). Gradual increase of the upper reversal potential to 1100 mV. Electrolyte: Na₂SO₄ (0.5 M). Scan rate 10 mV s⁻¹.

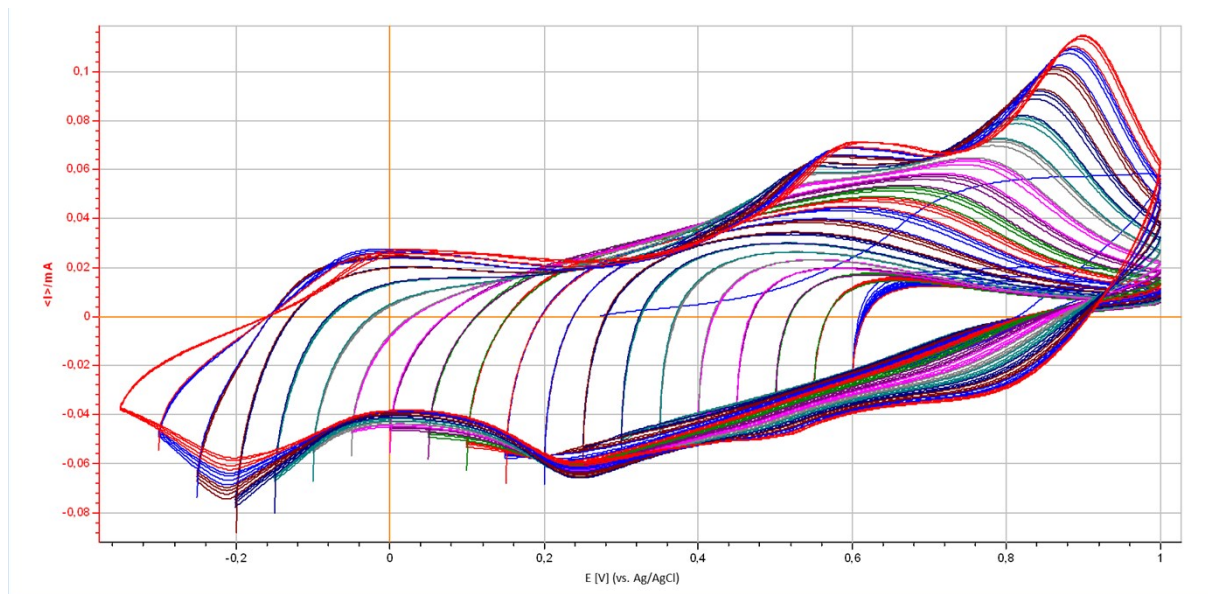


Figure S 7. Dependence of the electrochemical behaviour of Li,Na,K-bir on the applied potential window. Upper reverse potential always 1000 mV (vs. Ag/AgCl). Gradual increase of the upper reversal potential to 1100 mV. Electrolyte: Na_2SO_4 (0.5 M). Scan rate 10 mV s^{-1} .

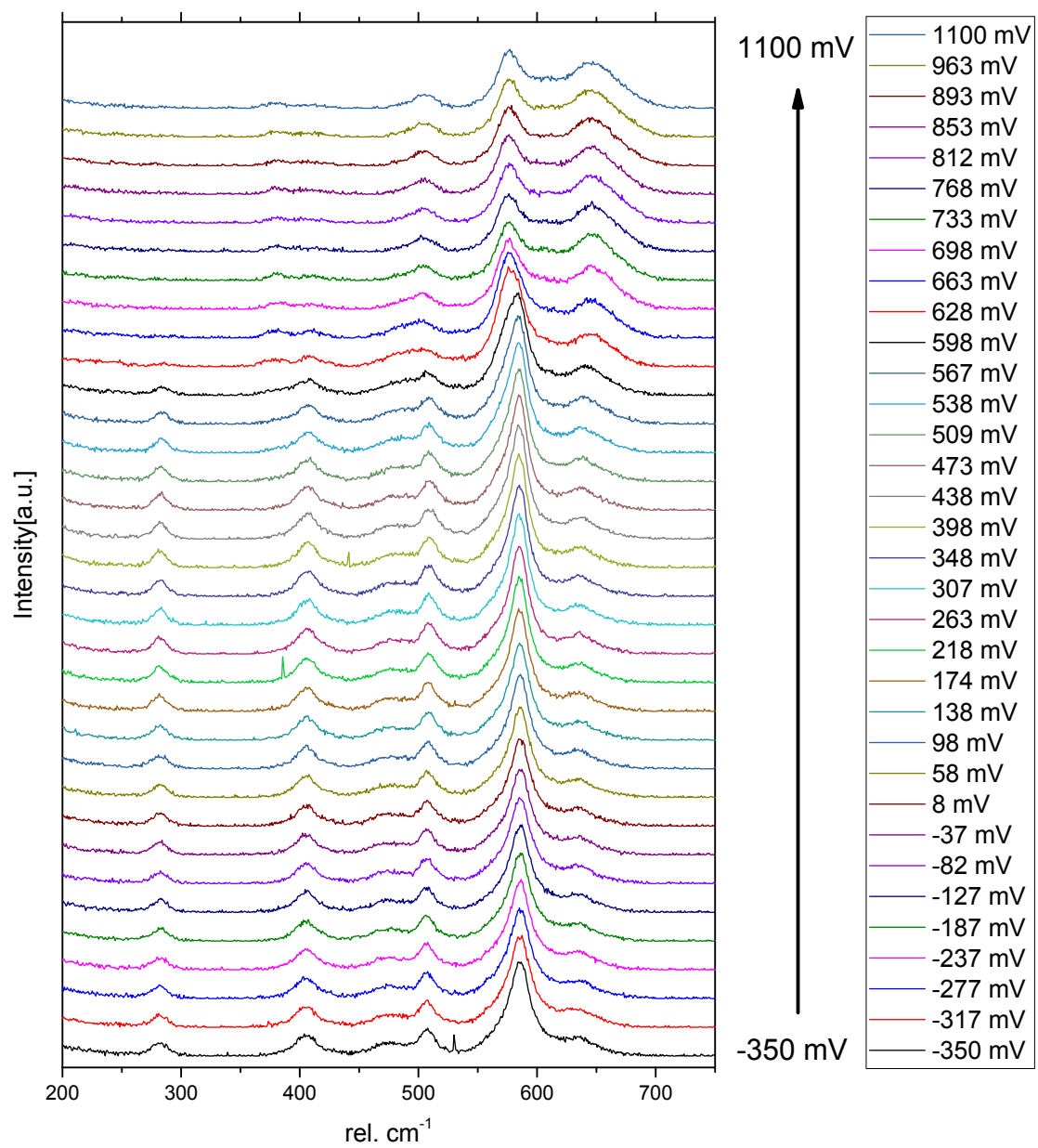


Figure S 8. Potential dependent evolution of the Raman spectra during positive-going potential scan.

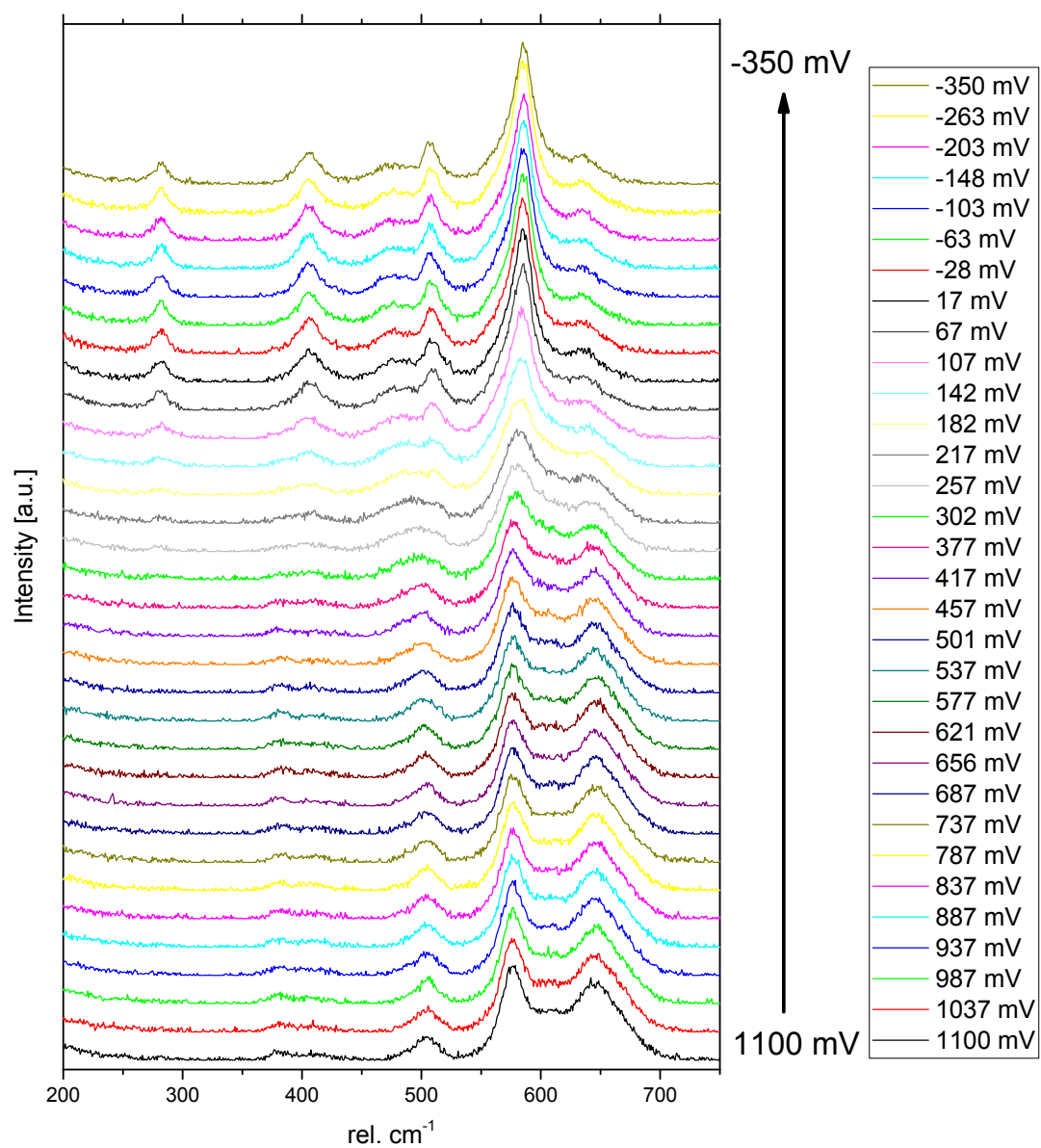


Figure S 9. Potential dependent evolution of the Raman spectra during negative-going potential scan.

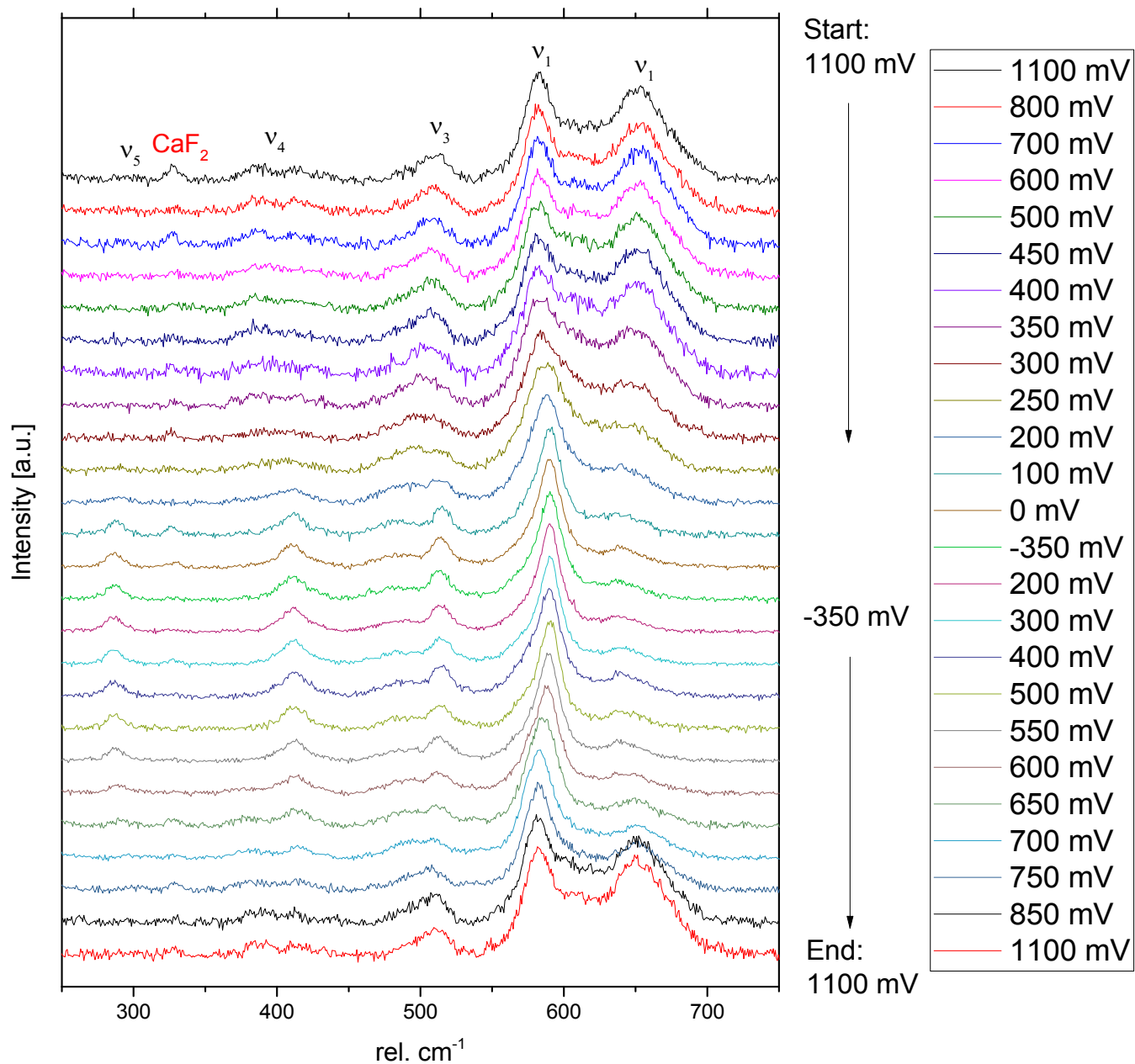


Figure S 10. Potential dependent evolution of the Raman spectra (normalized to the intensity of ν_1) during ex situ measurements.

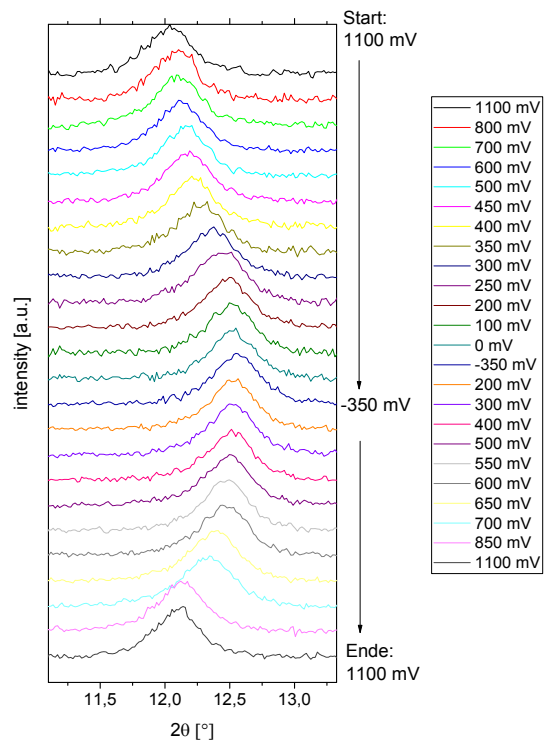


Figure S 11. Potential dependent evolution of the d_{001} -spacing

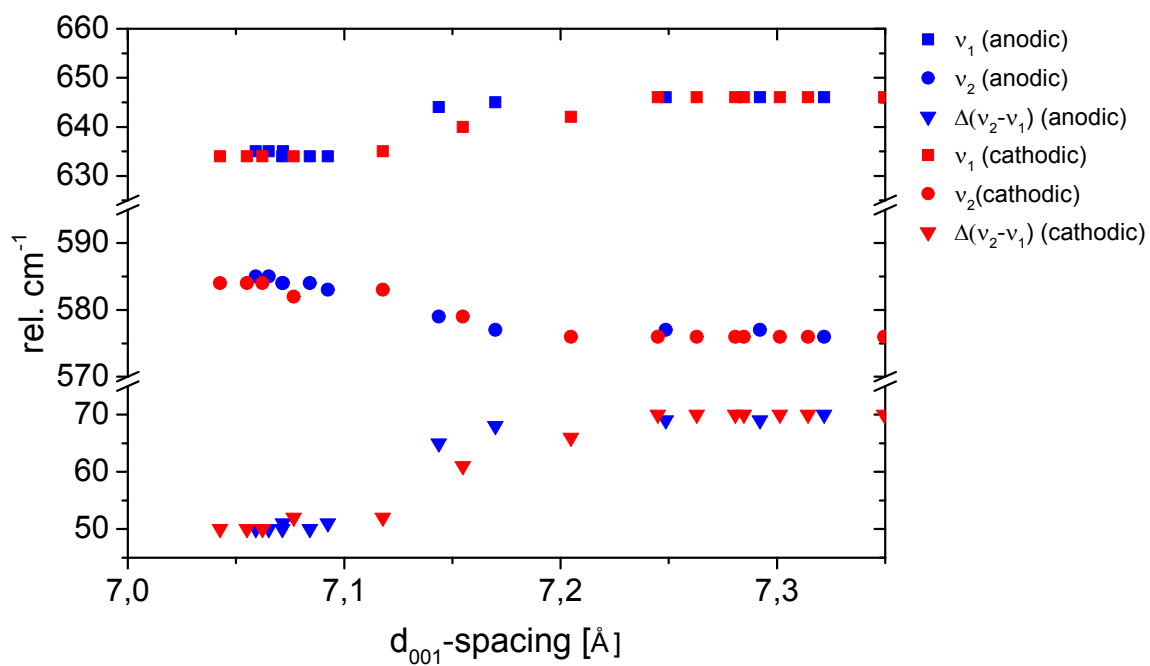


Figure S 12. Correlation between positions of ν_1 , ν_2 and $\Delta(\nu_1-\nu_2)$ and the d_{001} -spacing.

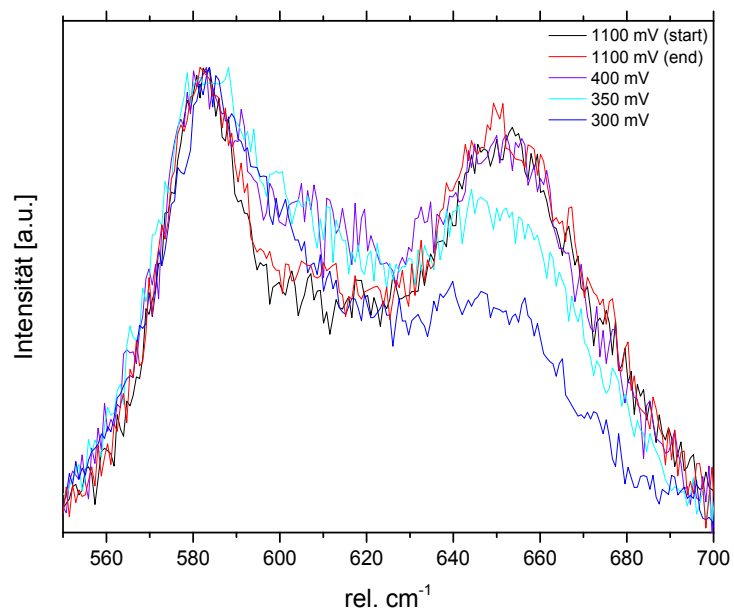


Figure S 13. Selected Raman spectra obtained from *ex situ* Raman measurements in 0.5 M Na₂SO₄. Normalized to the intensity of ν_2 .