

**Electronic Supporting Information:**

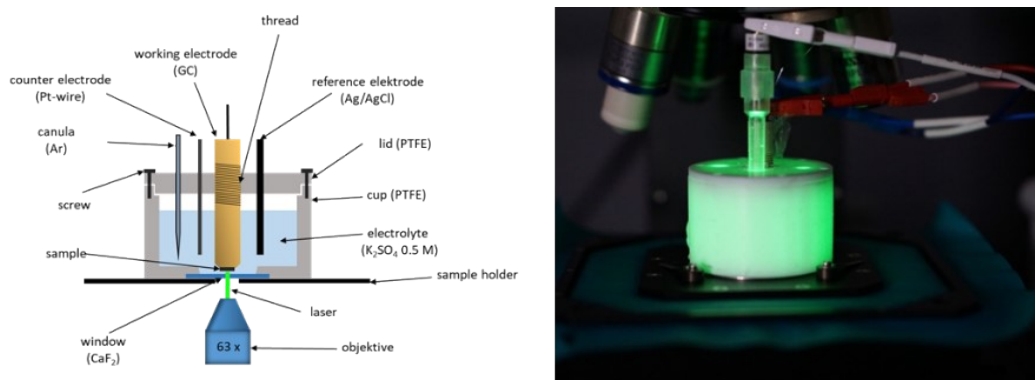


Figure S 1. Sketch (left) and photo (right) of the in situ Raman/CV-cell.

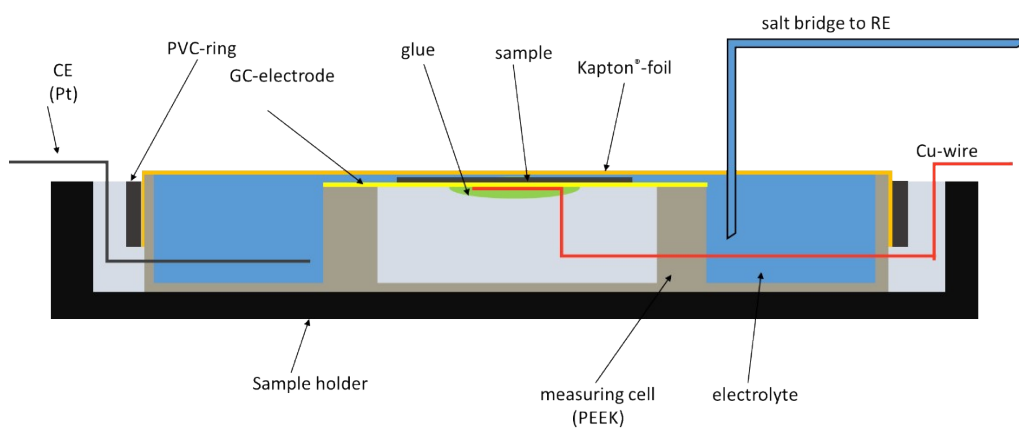
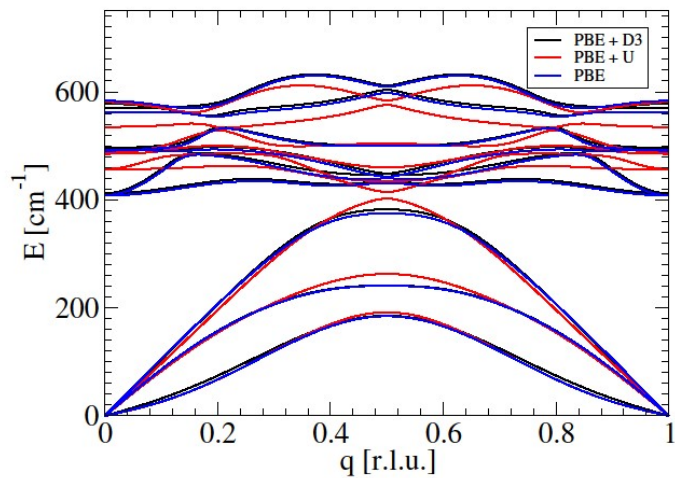
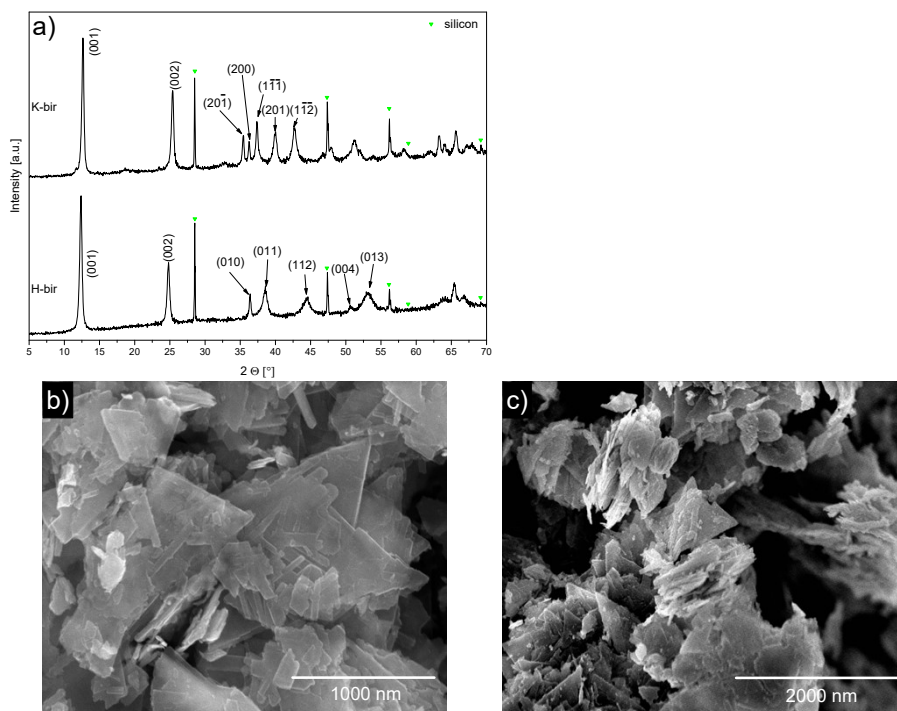


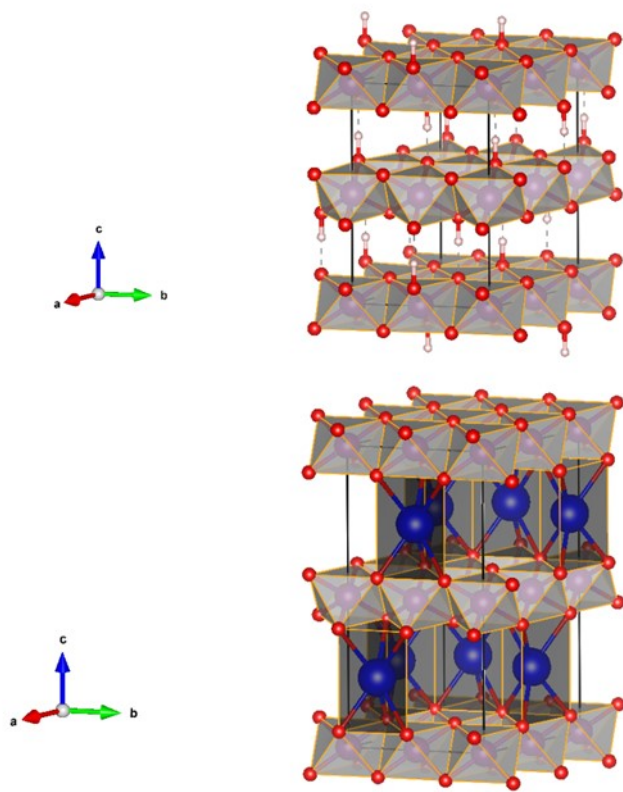
Figure S 2. Schematic representation of the in situ XRD/CV-cell.



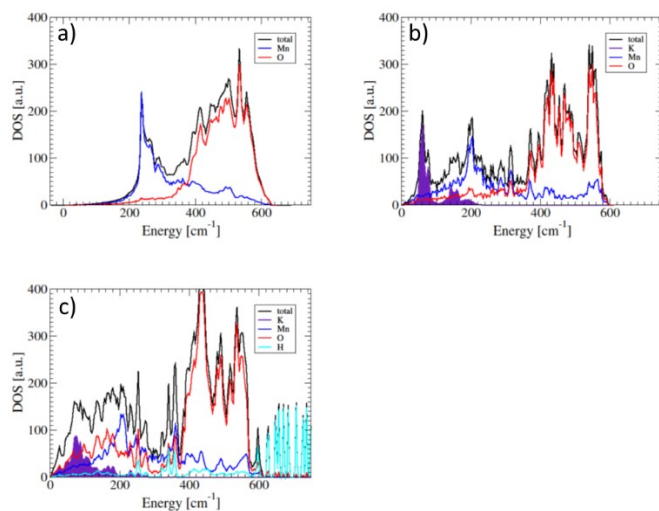
**Figure S 3.** Phonon dispersion curves for  $\text{MnO}_2$  as obtained by applying the PBE functional as compared to a PBE + U and a dispersion corrected PBE + D3 calculation. The impact of the dispersion correction on the dispersion curve is negligible, while the U correction results in a frequency shift of certain bands. Notably, the Raman active mode that is found at about  $560 \text{ cm}^{-1}$  for the case of the PBE and the PBE+D3 calculation is shifted to lower frequencies for the PBE+U calculation, hence yielding less good agreement with experiment.



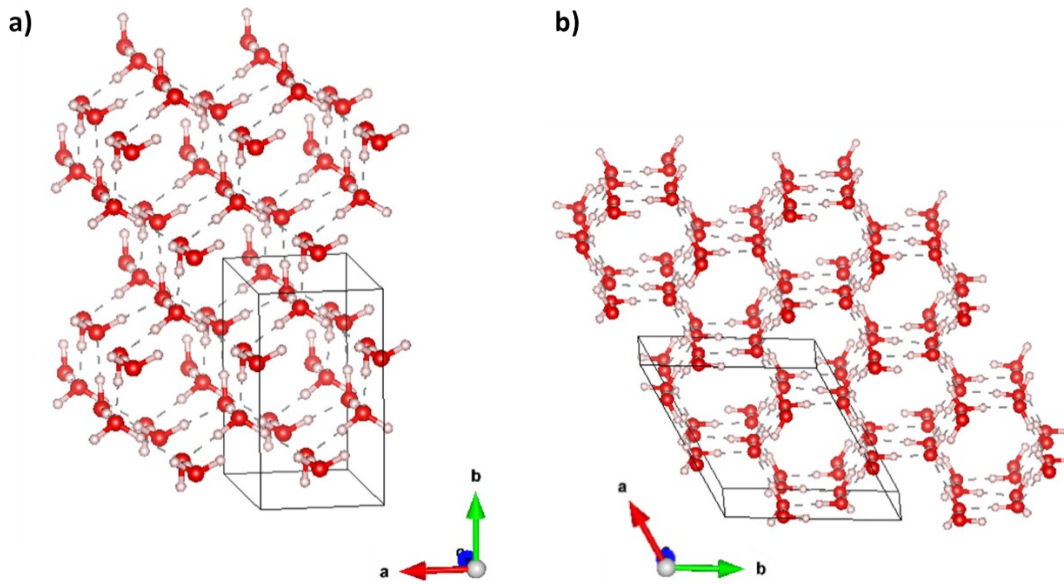
**Figure S 4.** a) XRD-pattern of the birnessites obtained via ion exchange K-bir (monoclinic) (top) and H-bir (hexagonal) (bottom). SEM images of b) K-bir and c) H-bir.



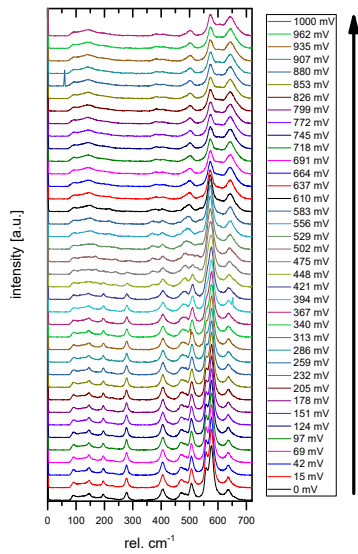
**Figure S 5.** a) H-bir ( $\text{H}_{0.5}\text{MnO}_2$ ), b) K-bir ( $\text{K}_{0.5}\text{MnO}_2$ ) based on the hexagonal ( $P6_3/mmc$ ) structure as obtained from DFT structure optimization, without considering interlayer water.



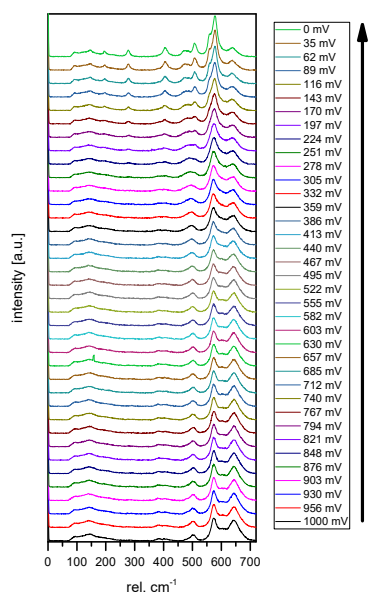
**Figure S 6.** Phonon density of states (DOS) for a)  $\text{MnO}_2$ , b)  $\text{K}_{0.25}\text{MnO}_2$  and c)  $\text{K}_{0.25}\text{MnO}_2 \cdot 0.5 \text{H}_2\text{O}$ . The partial density of states of Mn, O, K and H are depicted together with the total DOS. In panel c) there are additional, water related modes outside the depicted energy range. The K-related vibrations are centered at around  $100 \text{ cm}^{-1}$  with not contributions above  $280 \text{ cm}^{-1}$ .



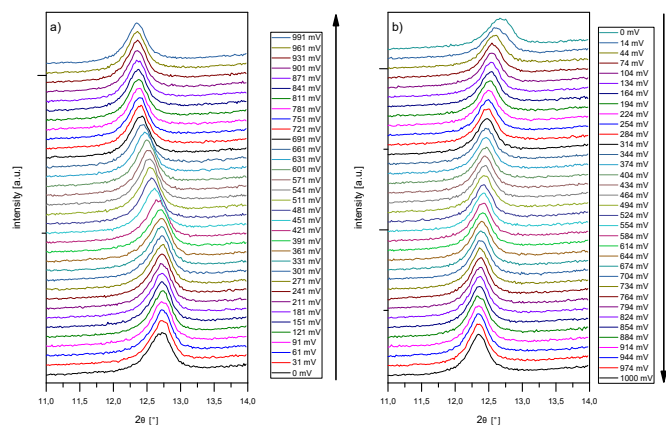
**Figure S 7.** The two different structural modifications of solid water that were used as reference structures. a) space group  $Cmc2_1$  b) space group  $P6_3cm$ .



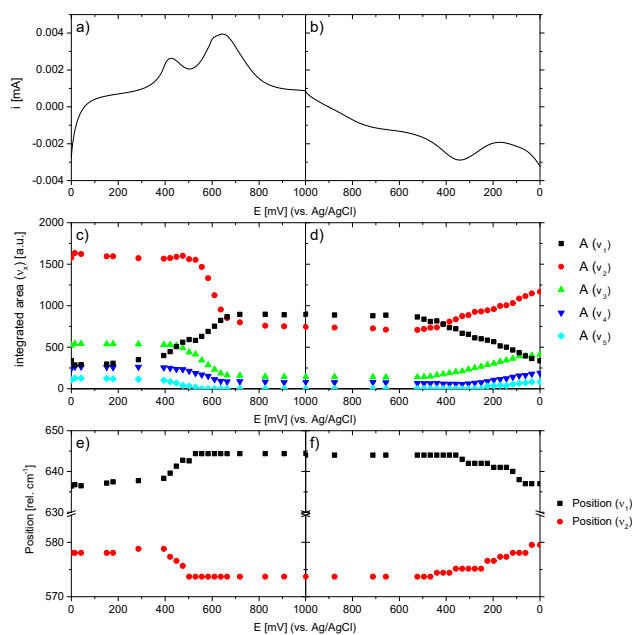
**Figure S 8.** Raman spectra (in situ) anodic. Electrolyte: 0.5 M  $K_2SO_4$ , scan rate  $0.3\text{ mV s}^{-1}$ .



**Figure S 9.** Raman spectra (in situ) cathodic. Electrolyte: 0.5 M  $K_2SO_4$ , scan rate  $0.3 \text{ mV s}^{-1}$ .



**Figure S 10.** Change of the position of the 001-Reflection as a function of potential. a) anodic and b) cathodic. Electrolyte: 0.5 M  $K_2SO_4$ , scan rate  $0.05 \text{ mV s}^{-1}$ .



**Figure S 11.** a) and b) CV-curve of LNK-bir, measured in 0.5 M K<sub>2</sub>SO<sub>4</sub> (scan rate 0.3 mV s<sup>-1</sup>). c) and d) Potential-dependent integrated areas of the respective Raman bands, e) and f) potential dependencies of the positions of the Raman bands  $v_1$  and  $v_2$ .