Supporting Information

Charge storage mechanism of Li_xWO_3 Hexagonal Tungsten Bronze in aqueous electrolytes

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S1. TGA

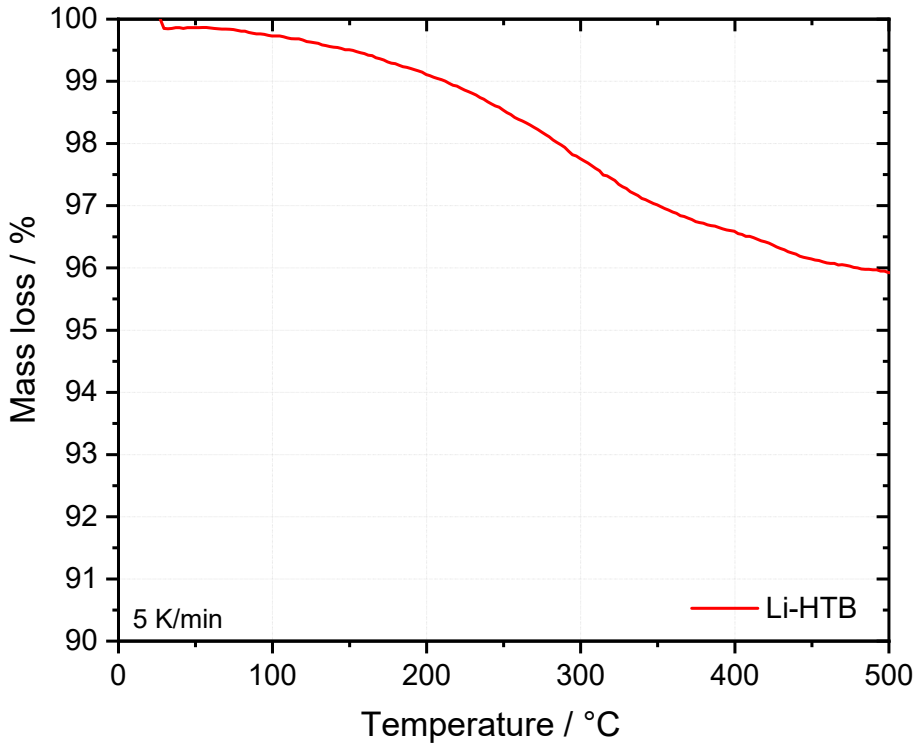

Figure S1. *TGA analysis for the Li-HTB sample.*

S2. Structural Refinement of Li-HTB

The lithium hexagonal tungsten bronze (Li-HTB) compound crystallizes in the same space group P6/mmm as WO_3 [1] with the cell parameters a = 7.3328(3) Å, c = 3.86243(18) Å. The cell volume 179.859(12) Å^3 is close to that of WO_3, V = 179.84(14) Å^3 (Figure S2).

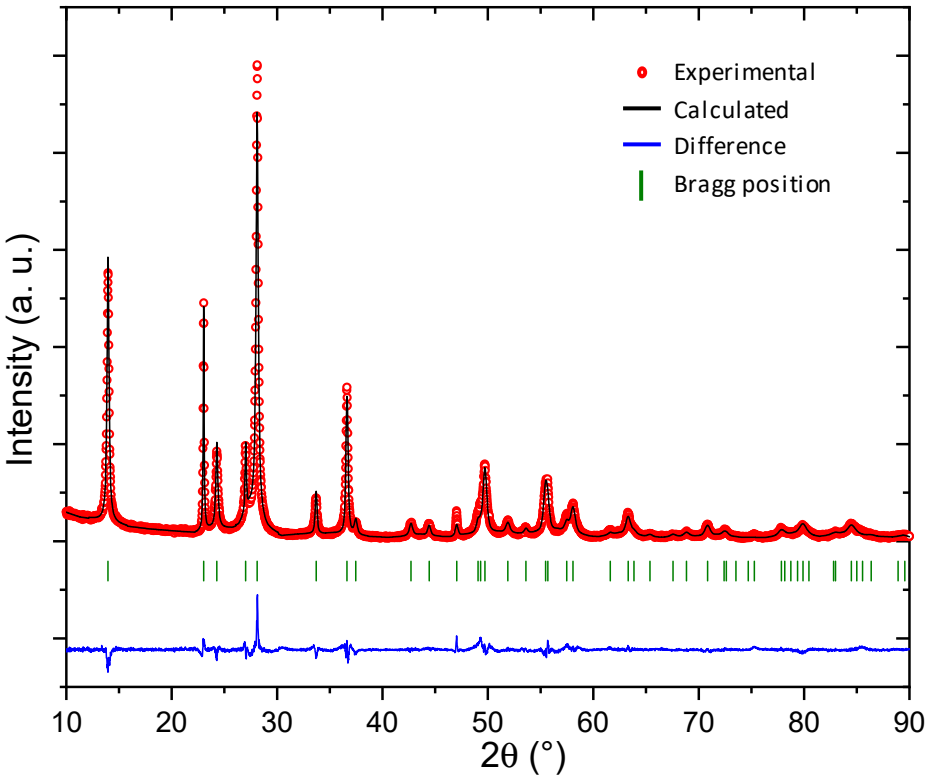

Figure S2. *Rietveld refinement of $Li_{0.167}WO_3(H_2O)_{0.333}$. The final reliability factors are R_p = 0.076, R_{wp} = 0.100, R_{exp} = 0.055, R(F) = 0.046.*

The structural refinement of Li-HTB from the X-ray powder pattern began with the structural model of WO_3 containing the following three atoms: W in 3f (0.5,0,0), O1 in 3g (0.5,0,0.5), and O2 in 6l (x,2x,0) with x ~ 0.21. After refinement of atomic positions and atomic displacement parameters (ADP), the Fourier difference maps (Figure S3) indicated a high electron density (charge = 4.97) in the 2e (0,0,z) site with z ~ 0.30 (position named "max1"). If an atom occupying max1 was too close to another atom occupying max1 (dmax1−max1 = 1.51 Å); the maximum occupancy of max1 is then 0.5. The 2e site occupied by oxygen atoms (= O3) was introduced into the refinement with half-occupancy. Since the ADP of O3 produced a negative result, this was fixed at 0.01, and the site occupation factor of O3 was fixed at its maximum, *i.e.*, 0.5. The TGA analysis showed a mass loss of around 4% of the compound when heating from room temperature to 500°C, corresponding to approximately 0.3 moles of H_2O. Note that the Fourier difference maps did not make it possible to locate the hydrogen atoms. We presumed that the previously introduced O3 atoms corresponded to water in the structure. In addition, the ICP-OES chemical analysis confirmed the presence of 0.16 moles of Li in the compound. Subsequent Fourier difference maps indicated some electron density located at the 4h Wyckoff position (1/3,2/3,z ~ 2/3) with M-O distances of around 2 Å. Therefore, the 4h site occupied by Li atoms was introduced into the refinement with an occupancy of 1/8 and an ADP set to 0.01. The introduction of Li atoms into the refinement served neither to improve nor impair it, although this was expected given the small amount of Li inserted. Lastly, the ADP of W atoms was switched to anisotropy.

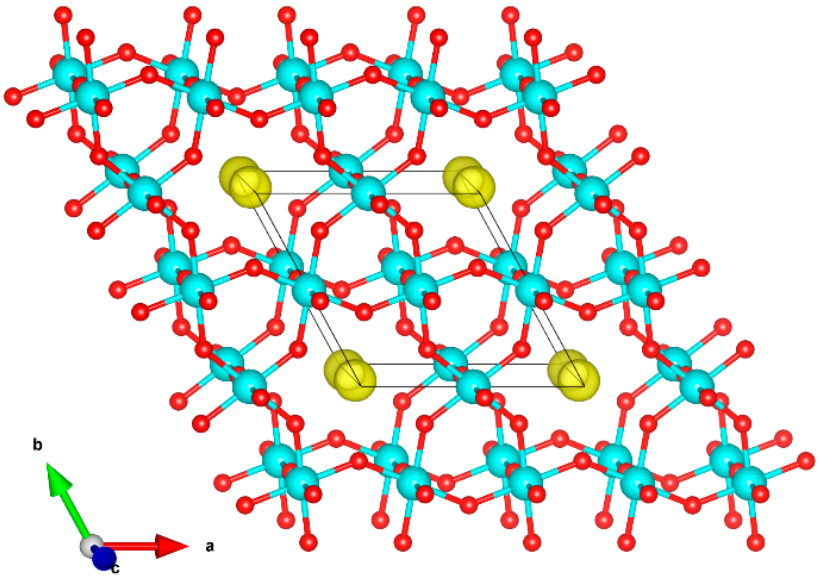

Figure S3. *Electronic density at 2e (0,0,z) with z ~ 0.30 (max1) obtained after refining the* WO_3 *model and performing Fourier difference calculations.*

The formula obtained was $Li_{0.167}WO_{3.333}$,or $Li_{0.167}WO_3(H_2O)_{0.333}$ if one considers the water molecules in the structure. In the latter case, the oxidation state of tungsten is 5.83+. The final atomic coordinates and ADPs, as well as the selected interatomic distances and bond valence sum (BVS) calculations, are given in Table S1. Figure S2 shows the observed and calculated diffractograms and the differences between them. During refinement, a preferential orientation along the [001] direction was introduced due to the elongated shape of the as-prepared rod-shaped particles. An anisotropic size broadening treated by spherical harmonics of the order 2 [2] was also introduced. Moreover, having taken into account the fundamental parameters of the powder X-Ray diffractometer, the crystallite size and lattice strain were obtained and found to be 54.2(8) nm and 0.379(8), respectively.

Table S1. *Atomic coordinates of the* $Li_{0.167}WO_{3.333}$ *compound with a = 7.3328(3) Å, c = 3.86243(18) Å, V = 179.859(12) Å³, SG P6/mmm. Atomic displacement parameters (Å²), selected interatomic distances (Å) and bond valence sum calculations.*

Atom	**Wyck. pos.**	***x***	***y***	***z***	**SOF**	**U_{eq}* / U_{iso} (Å²)**
W1	3f	0.5	0	0	1	0.0422(10)*
O1	3g	0.5	0	0.5	1	0.010(5)
O2	6l	0.1964(6)	0.3928(11)	0	1	0.030(4)
O3	2e	0	0	0.339(7)	0.5	0.01
Li1	4h	0.3333	0.6667	0.6769	0.125	0.01
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W1	0.0270(9)	0.0192(11)	0.078(2)	0.0096(5)	0	0
W1–O1	2 x 1.931	**Li1–O2**	3 x 2.140	**Li1–Li1**	1.367	
W1–O2	4 x 1.955	**Li1–O1**	3 x 2.224	**Li1–W1**	2.457	
BVS W1	5.59	**BVS Li1**	0.87			

The structure of the lithium hexagonal tungsten bronze can be described in terms of layers of corner-sharing WO_6 octahedra arranged in six-membered rings, giving rise to two kinds of tunnels along the *c* axis, triangular and hexagonal, as shown in Figure S4.

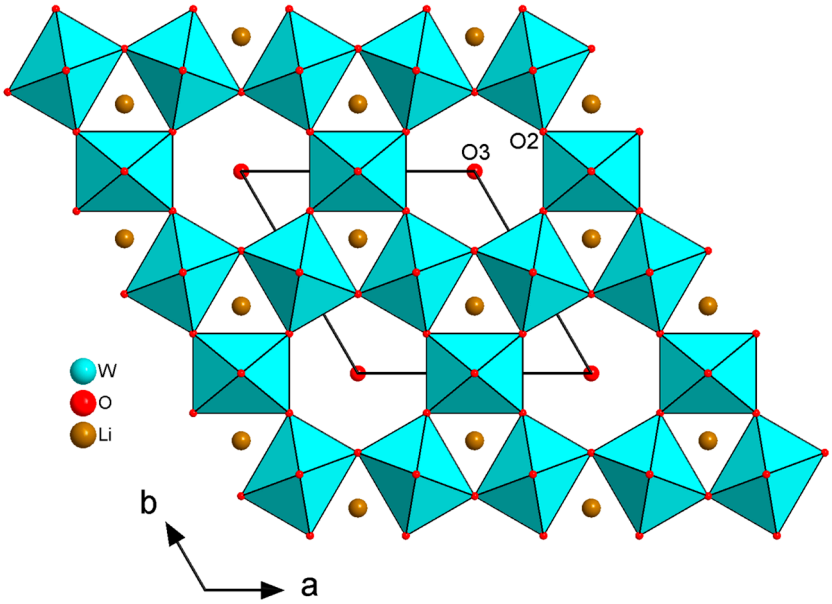

Figure S4. *Structure of the $Li_{0.167}WO_{3.333}$ compound.*

The O3 atoms, which are related to water molecules, are in the hexagonal cavity and are disordered along the *c* axis (Figure S5a). The trigonal prismatic cavities are partially filled with lithium atoms (Figure S4). The occupation of trigonal tunnels by small cations was confirmed in previous studies [3,4]. Lithium atoms occupy distorted octahedra with Li–O distances ranging from 2.140 to 2.224 Å (Figure S5b). Similarly distorted LiO_6 octahedra are observed in other compounds (Li_4WO_5 [5], $LiNbWO_6$ [6]). The shortest Li–W distances are d(Li–W) = 2.457 Å. Such short distances are also to be found in some Li-W-O compounds (d(Li–W) = 2.494 Å as in $Li_5W_2O_7$) [7].

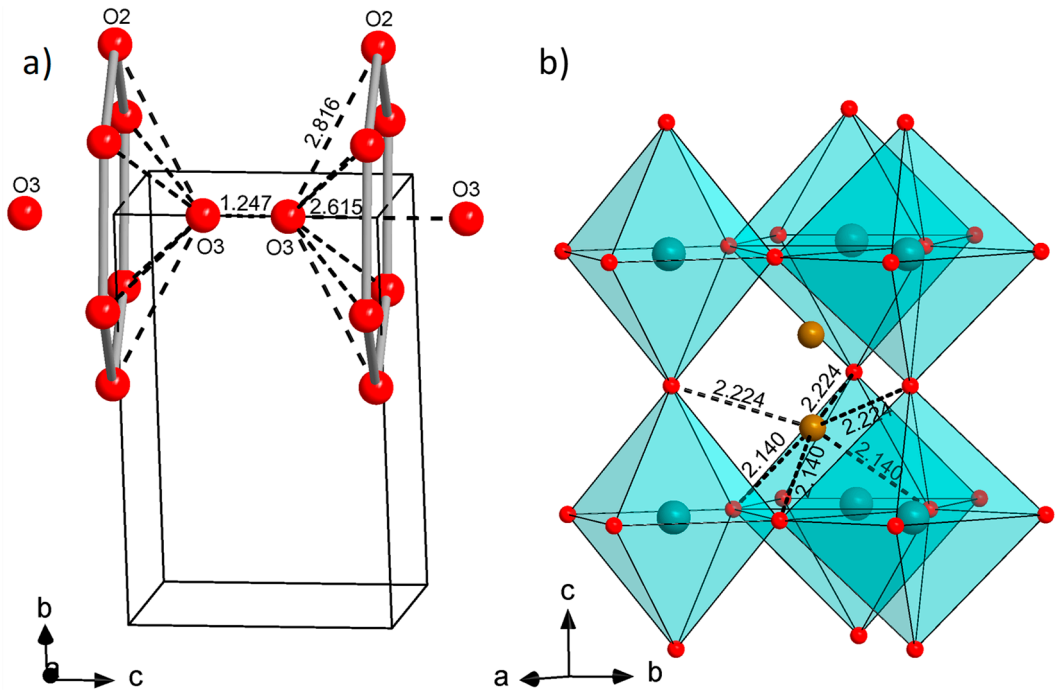

Figure S5. *a) O3 atoms in the hexagonal cavity along the c-axis and O-O distances, and b) Li-O distances (Distances in Angstroms).*

S3. EQCM Experimental Setup

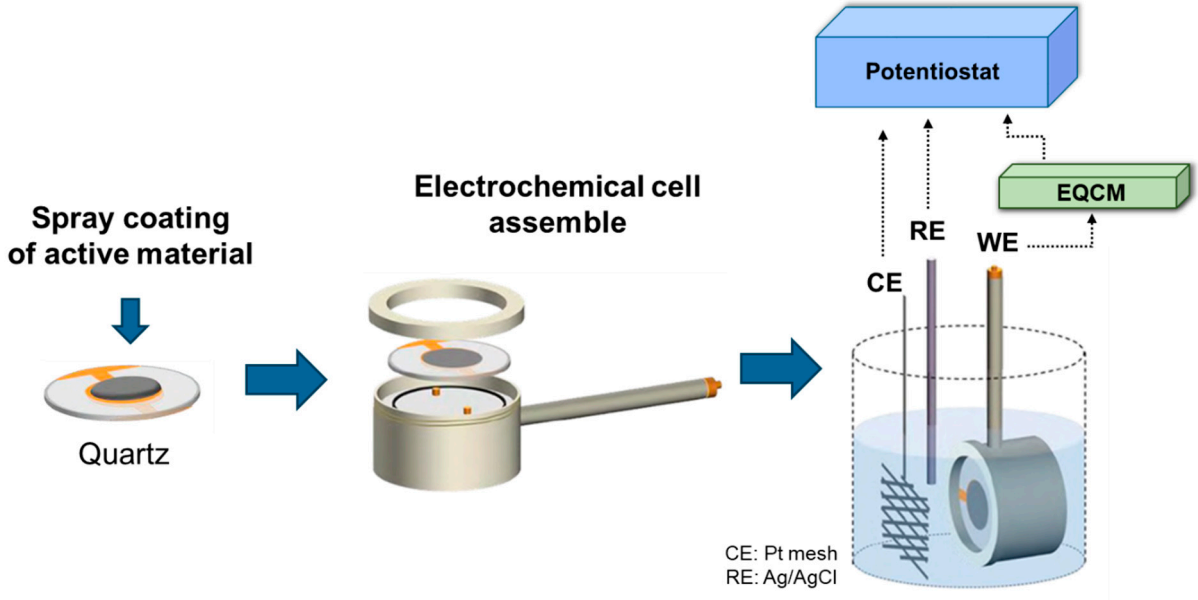

Figure S6. *Schematic of EQCM setup, adapted from reference [8].*

$$\Delta m = -C_f \, \Delta f \qquad \text{Eq. S1}$$

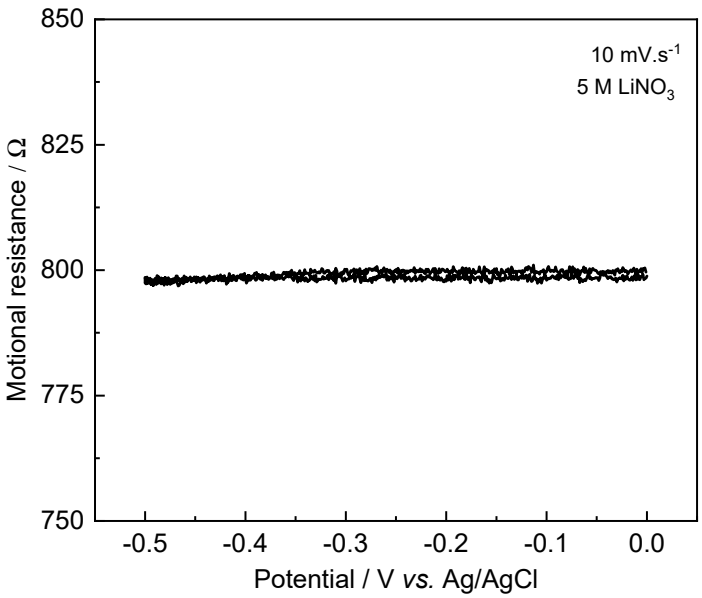

Figure S7. *Change of the motional resistance of Li-HTB on a Ti substrate in 5 M $LiNO_3$ at 10 $mV.s^{-1}$.*

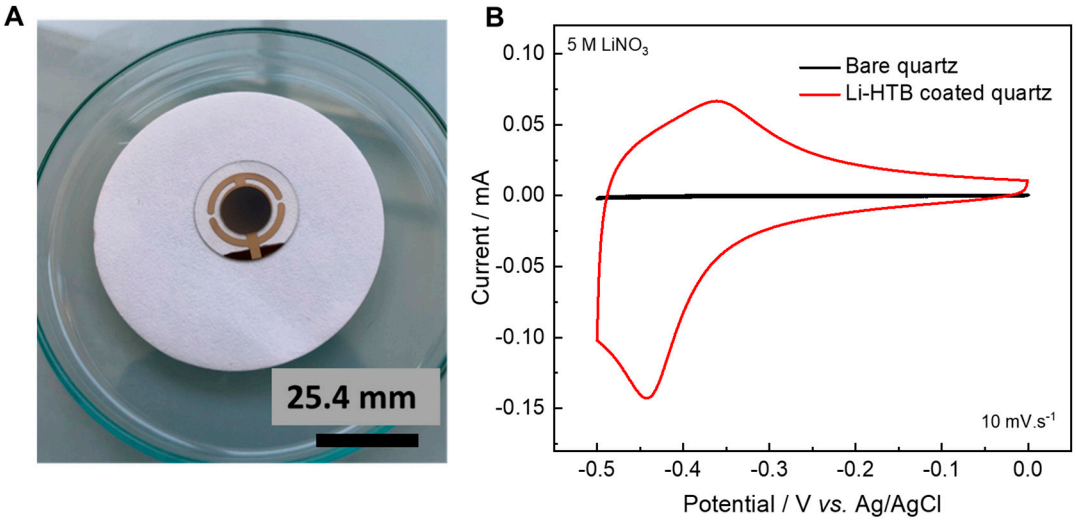

Figure S8. *A) Homogeneously coated quartz and B) CV of bare quartz vs.CV of coated quartz with Li HTB in 5M $LiNO_3$ at 10 $mV.s^{-1}$.*

S4. XAS – setup

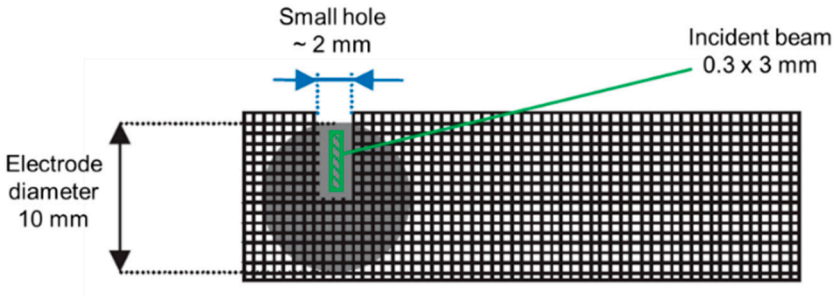

Figure S9. *Electrode drawing to be used in an operando cell for XAS.*

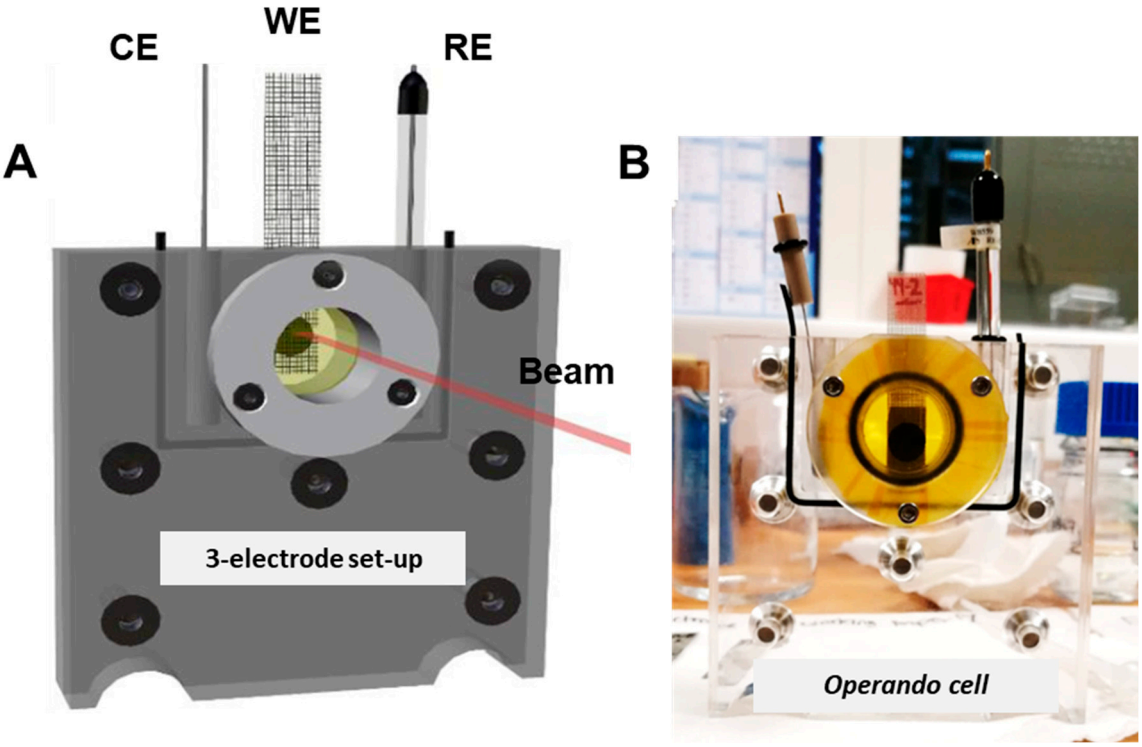

Figure S10. *Operando XAS cell. A) Scheme of the cell indicating the 3-electrode setup, and B) Frontal view of the operando cell.*

References

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