Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

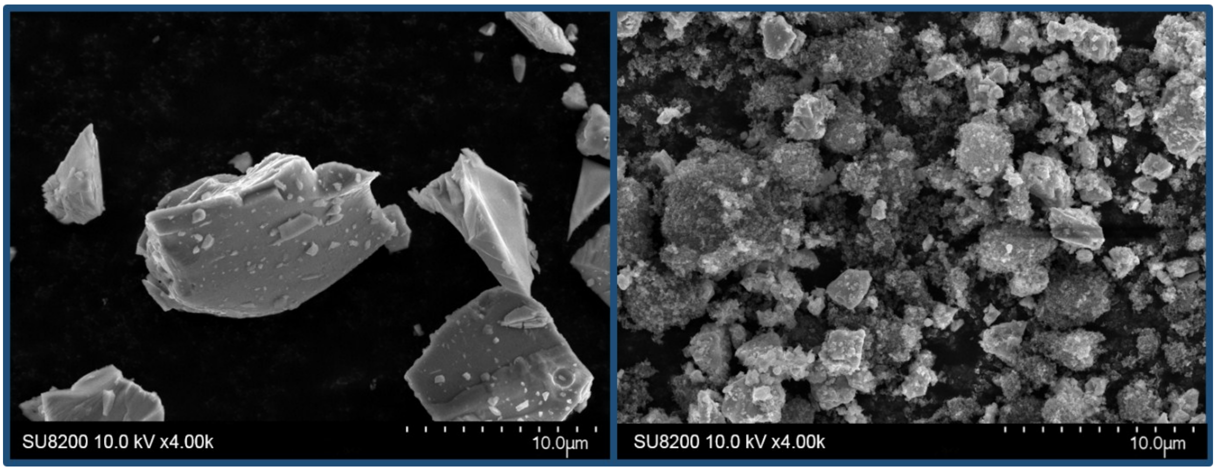

Figure S1: SEM image of pristine $Bi_2(MoO_4)_3$ (left) and $Bi_2(MoO_4)_3$ ball-milled with carbon (right) acquired at 4000 times magnification.

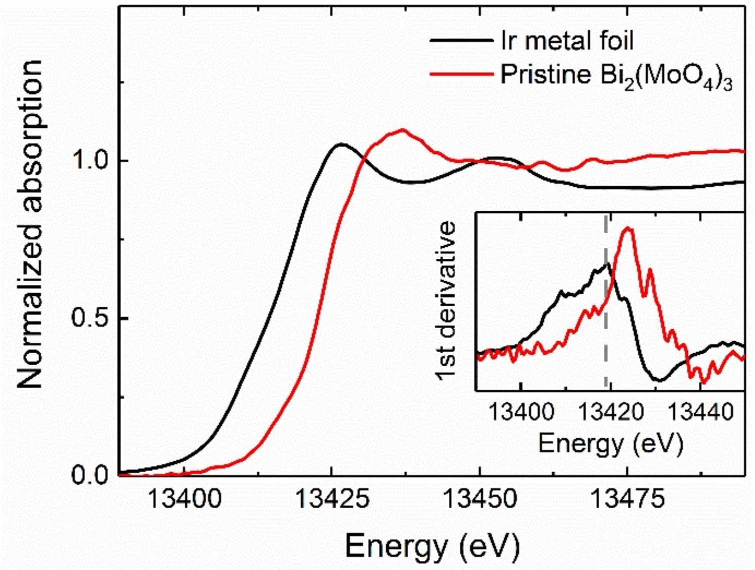

Figure S2: Normalized absorption spectra of Ir foil over the Ir L1-edge, serving as reference for metallic Bi L3-edge (identical edge energy at 13419 eV for Ir L1-edge and Bi L3-edge) and pristine $Bi_2(MoO_4)_3$ for the Bi L3-edge, serving as Bi^{3+} reference. Inset shows the corresponding 1st derivative data, with the peak maximum being used as the reference value. Grey dotted line (inset) shows the position for the theoretical edge energy for the Ir L1-edge and Bi L3-edge at 13419 eV.

XRD of $Bi_2(MoO_4)_3$ was measured in transmission geometry with sample in 0.3 mm capillary. An unknown impurity is also present. A variety of structures have been tested without favourable result. Bismuth molybdate crystallizes in numerous systems (non-stoichiometry and modulated structures on BiMoO-based structures) and the correct one was not possible to obtain. Our sample are still close to 100 % purity, and the unknown structure will have negligible effects on the electrochemistry.

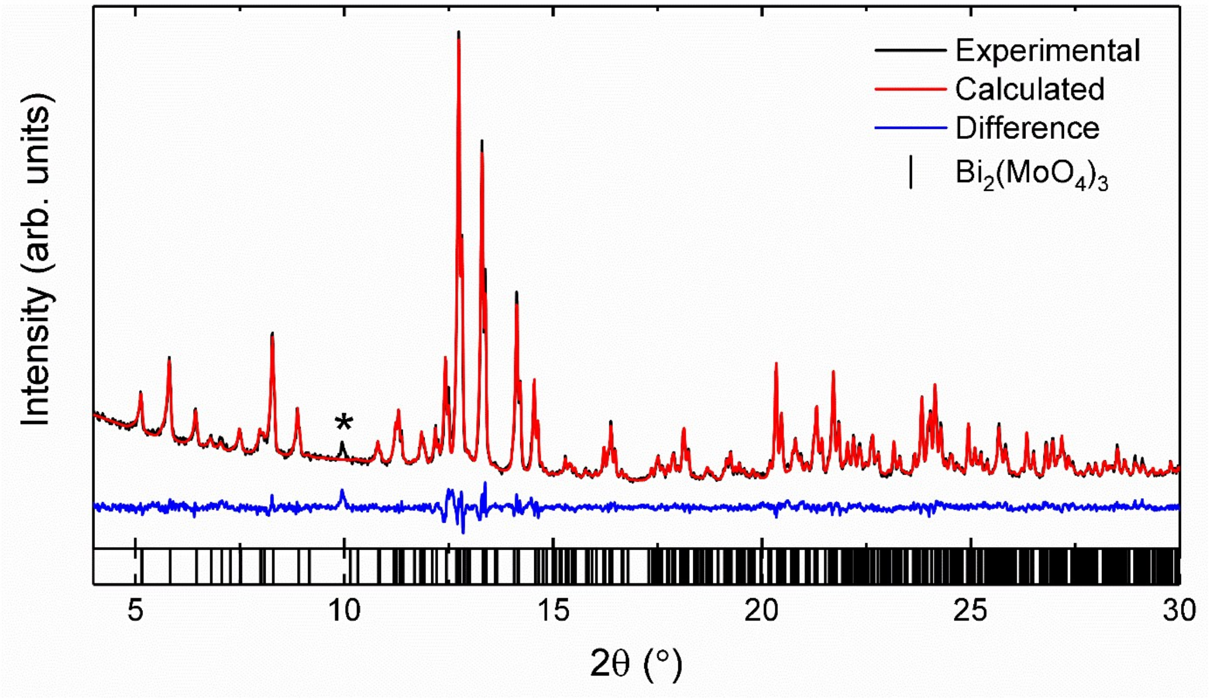

Figure S3. Rietveld refinement of $Bi_2(MoO_4)_3$ showing experimental, calculated and difference profiles; $MoK\alpha_{1,2}$ radiation. Bars in lower panel correspond to positions of Bragg reflections from $Bi_2(MoO_4)_3$. R_{wp} – 7.21 %, R_{exp} – 4.48 %, R_p – 5.44 %, χ^2 – 1.61. Cell parameters (space group $P12_1/c1$): a = 7.718(0) Å, b = 11.515(1) Å, 11.983(1) Å, β = 115.419(5). Impurity phase is marked with asterix (*). Crystallographic data is included in Table S1.

Table S1: Crystal structure data for $Bi_2(MoO_4)_3$ as obtained from Rietveld refinement of XRD data.

Atom	Wyckoff	x	y	z	Occupancy
Bi1	4e	0.2390(7)	0.6368(9)	0.2447(7)	1
Bi2	4e	0.4084(5)	0.3697(2)	0.0831(1)	1
Mo1	4e	0.0800(9)	0.8561(1)	0.3890(3)	1
Mo2	4e	0.2342(4)	0.1355(7)	0.1988(9)	1
Mo3	4e	0.5410(7)	0.3840(4)	0.4149(8)	1
O1	4e	0.0473(1)	0.1831(7)	0.1987(5)	1
O2	4e	0.0376(4)	0.4435(5)	0.2171(9)	1
O3	4e	0.1425(9)	0.3091(4)	0.0534(1)	1
O4	4e	0.2013(7)	0.0431(1)	0.0619(2)	1
O5	4e	0.2282(1)	0.5612(1)	0.0109(1)	1
O6	4e	0.2328(9)	0.8309(1)	0.0358(5)	1
O7	4e	0.3959(3)	0.0629(3)	0.3241(1)	1
O8	4e	0.4031(6)	0.3160(9)	0.4260(9)	1
O9	4e	0.4300(2)	0.4438(1)	0.2396(5)	1
O10	4e	0.4392(2)	0.2195(7)	0.1835(8)	1
O11	4e	0.6202(1)	0.0618(3)	0.0465(1)	1
O12	4e	0.7361(7)	0.3176(2)	0.1326(0)	1

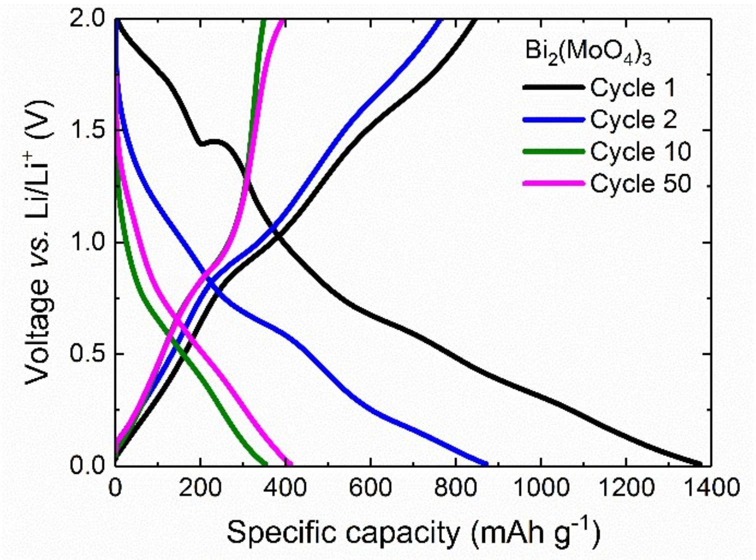

Figure S4. Dis-/charge voltage profiles for selected cycles in the voltage range 0.01 – 2.00 V.

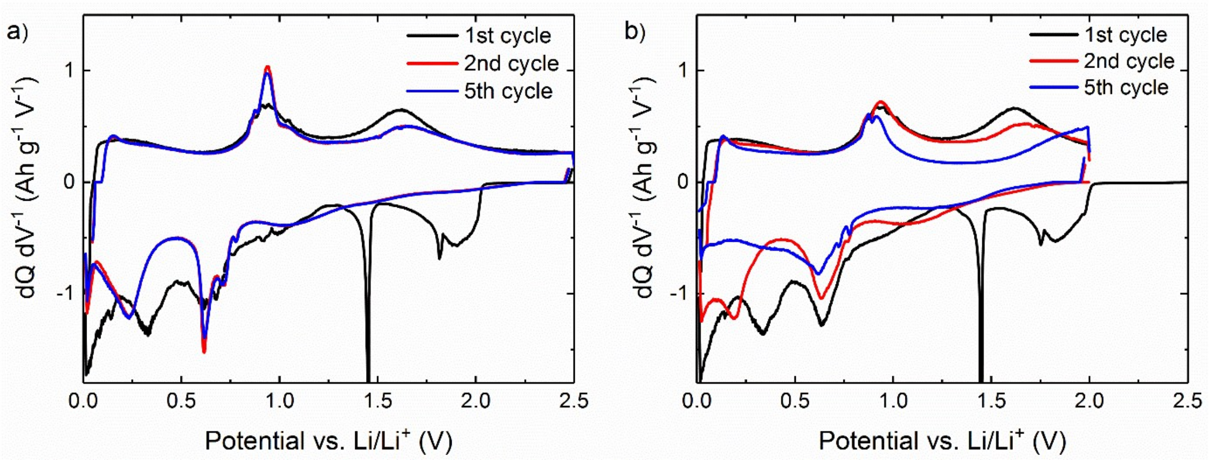

Figure S5. dQ dV^{-1} plots for $Bi_2(MoO_4)_3$ cycled in the voltage range 0.01 - 2.50 V (a) and 0.01 – 2.00 (b) corresponding to the voltage profiles shown in Figure 2 a) and Figure S4, respectively. Signals were smoothed with adjacent averaging (20 points of window) in OriginLabs.

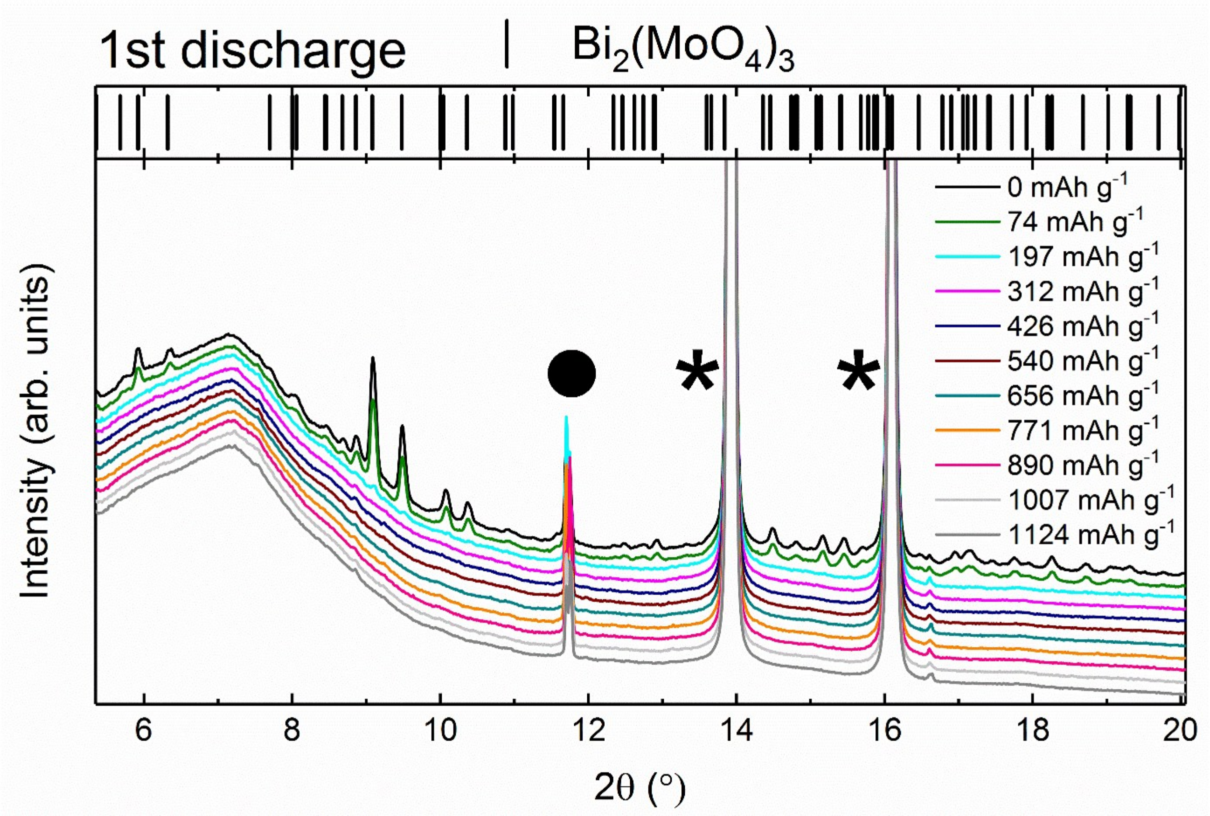

Figure S6. Cascading diffractograms from pristine state (top) to fully lithiated during 1st discharge. Top panel shows calculated hkls for $Bi_2(MoO_4)_3$. Bragg reflections from copper current collector and lithium counter electrode are marked with asterix (*) and circle (•), respectively. The large background at around 7deg is due to glass fiber separator and liquid electrolyte. $\lambda = 0.5053$ Å.

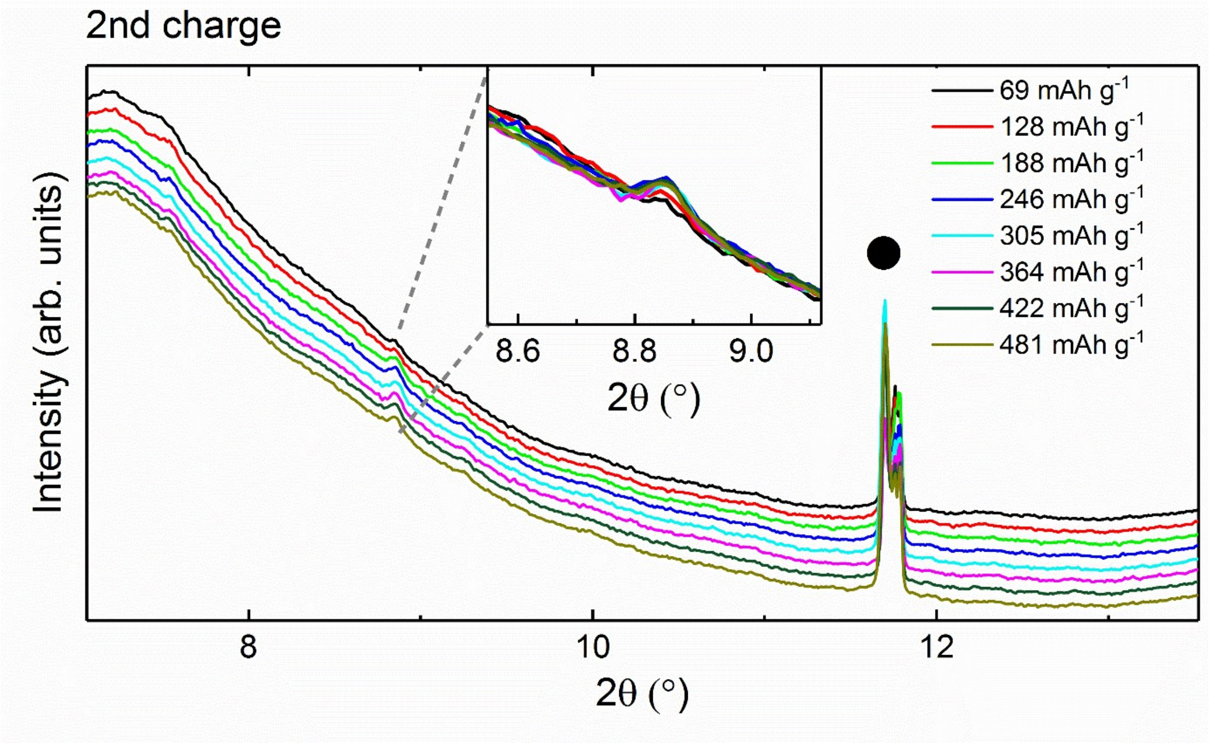

Figure S7. Cascading diffractograms of 3rd discharge with inset showing evolution of theBi (1 0 -2) reflection (space group R -3 m) during 2nd charge. The circle (•) marks a lithium metal reflection. The wavelength was 0.5053 Å.

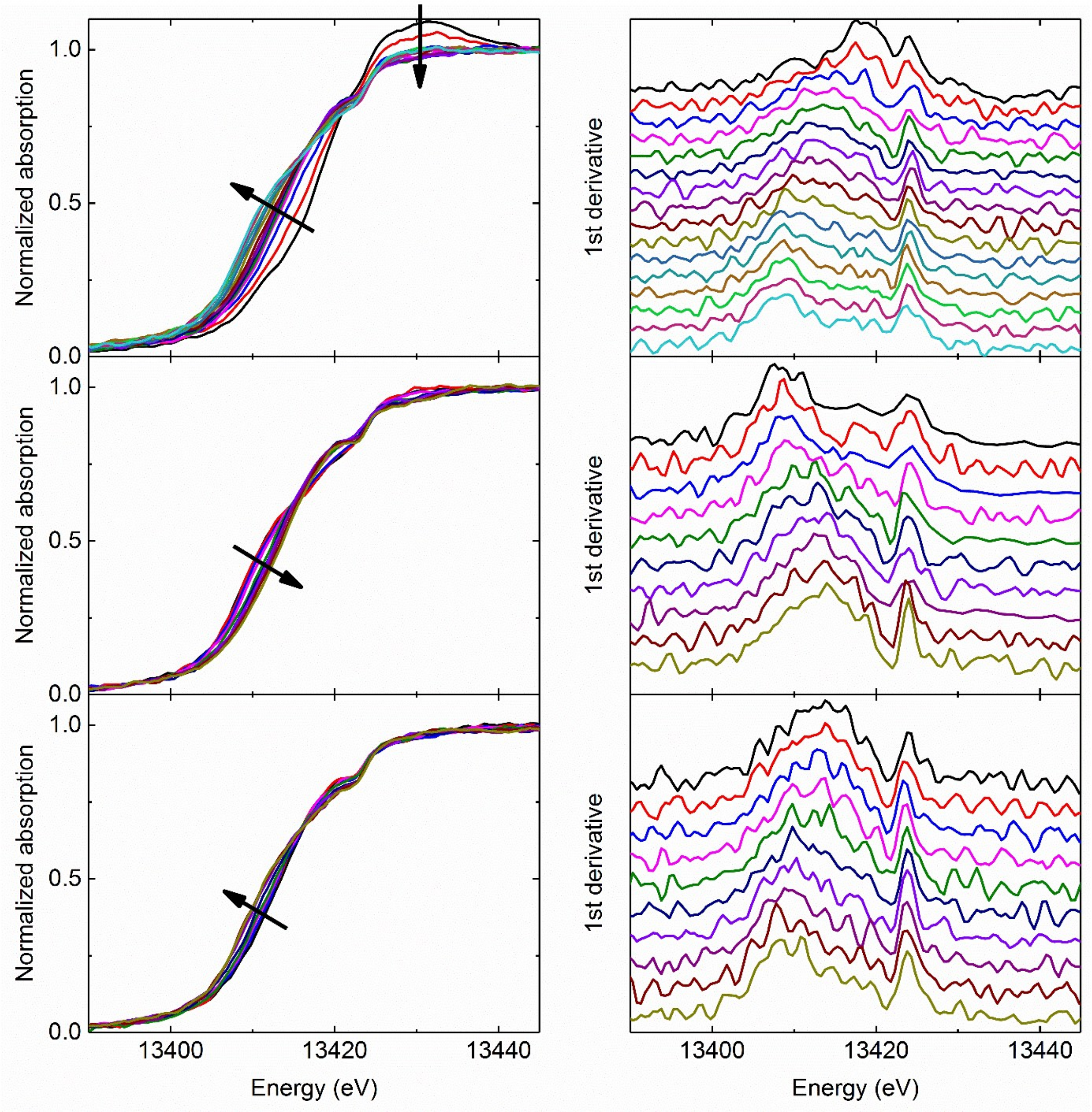

Figure S8. Left side panels shows normalized absorption scans of the Bi L3-edge with corresponding 1st derivative curves on the right hand side for 1st discharge, 1st charge and 2nd discharge in top, middle and bottom panels respectively. Arrows in left side panels indicate the progression of absorption scan from initial to final state in each half cycle (charge or discharge). 1st derivative curves on right side panels are presented in a cascading manner with top scan being the initial scan. Corresponding electrochemical date is shown in Figure 4a.

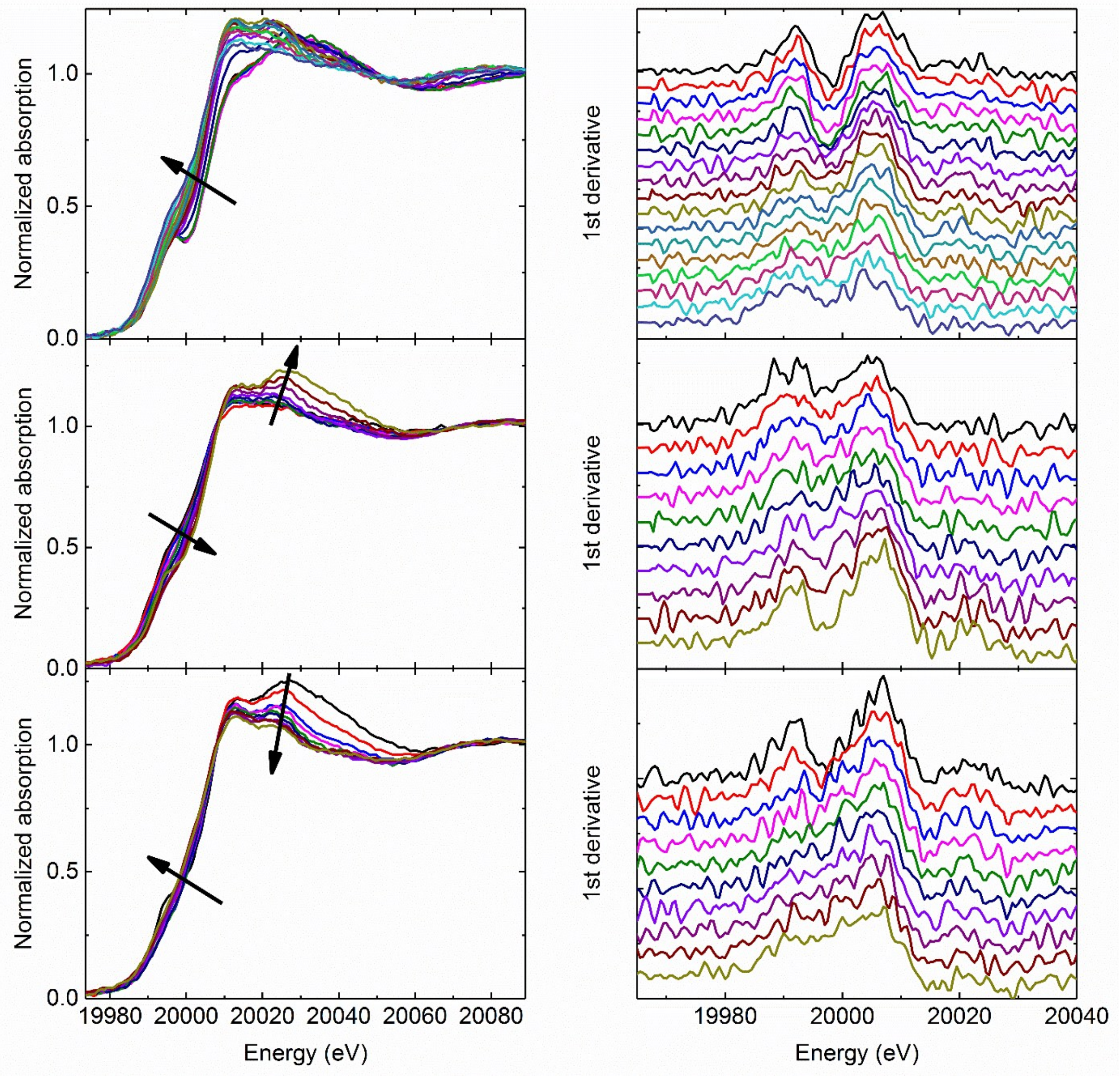

Figure S9. Left side panels shows normalized absorption scans of the Mo K-edge with corresponding 1st derivative curves on the right hand side for 1st discharge, 1st charge and 2nd discharge in top, middle and bottom panels respectively. Arrows in left side panels indicate the progression of absorption scan from initial to final state in each half cycle (charge or discharge). 1st derivative curves on right side panels are presented in a cascading manner with top scan being the initial scan. Corresponding electrochemical date is shown in Figure 4a.

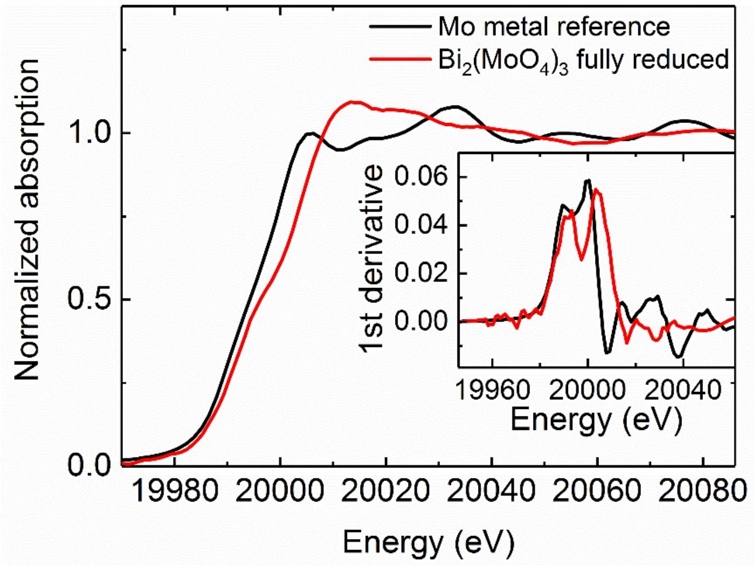

Figure S10: Comparison of Mo K-edge XANES spectra of Mo metal foil and fully reduced $Bi_2(MoO_4)_3$ after 1st discharge. Inset shows the 1st derivative curves of the normalized data.