Supplementary Information

Operando X-ray absorption spectroscopy of phosphomolybdic acid redox mediators for electrochemical conversion of biomass to green hydrogen

Robert Price [a=], Lewis MacDonald [a=], Luke L. Keenan [b=], William Johnson [a], Stephen M. Lyth [a], Jun Li [a] and Edward Brightman [a]

[a.] *Strathclyde Incubator for Green Hydrogen Technologies (SigH_2t), Department of Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow, G1 1XJ.*
[b.] *Diamond Light Source Ltd., Harwell Science and Innovation Campus, Fermi Avenue, Didcot, OX11 0DE.*
E-mail: edward.brightman@strath.ac.uk

XAS Experimental conditions

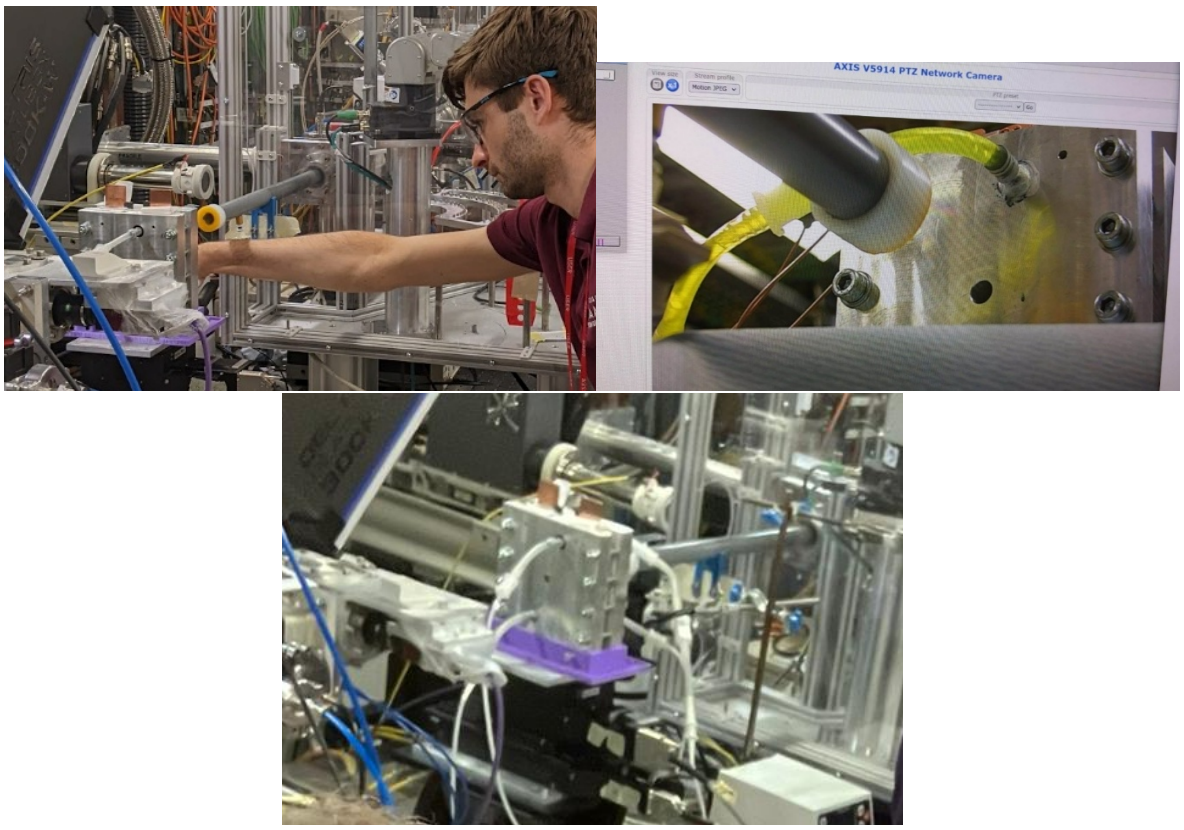

Figure S1. A selection of images of the assembled flow cell, situated in position on the sample stage of the B18 beamline at Diamond Light Source.

Table S1: Complete list of standard materials characterised as part of this study.

Standard Material:	Purity/Supplier:	Mass of Standard/mg	Mass of Cellulose/mg
MoO_3	Sigma-Aldrich	24.30	56.71
MoO_2	Sigma-Aldrich	21.66	58.34
$H_3[PMo_{12}O_{40}]\cdot xH_2O$	Thermo Scientific Chemicals	32.20	48.87
$Na_2MoO_4\cdot 2H_2O$	Sigma-Aldrich	40.29	40.16
Na_2MoO_4	Sigma-Aldrich	39.64	40.59
$(NH_4)_6Mo_7O_{24}\cdot 2H_2O$	Sigma-Aldrich	29.77	50.42

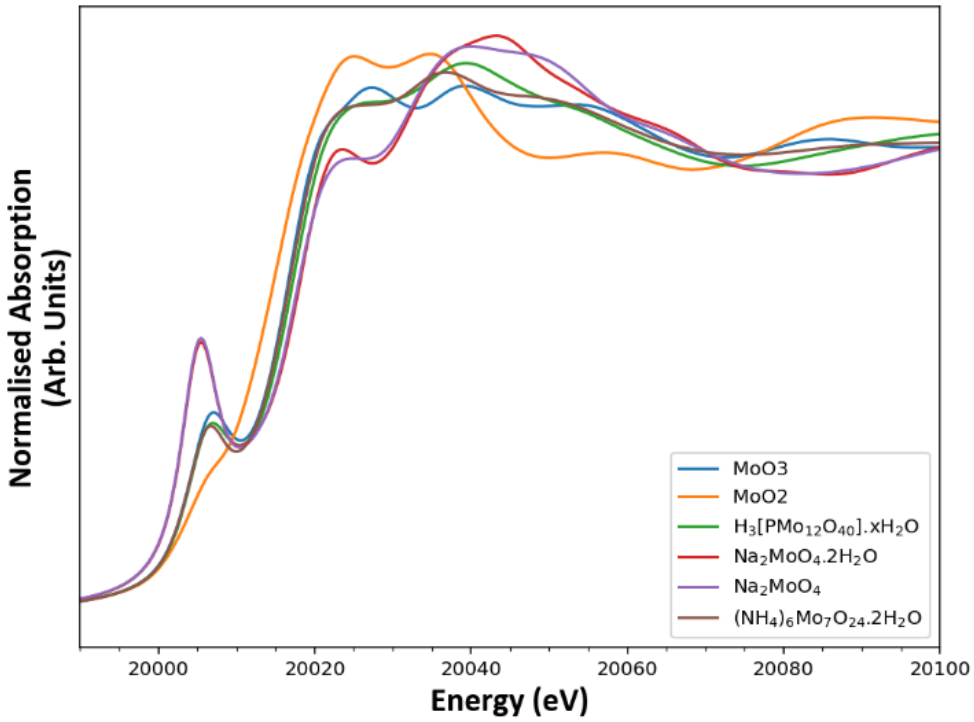

Figure S2: XANES spectra of Calibration Standards listed in Table S1

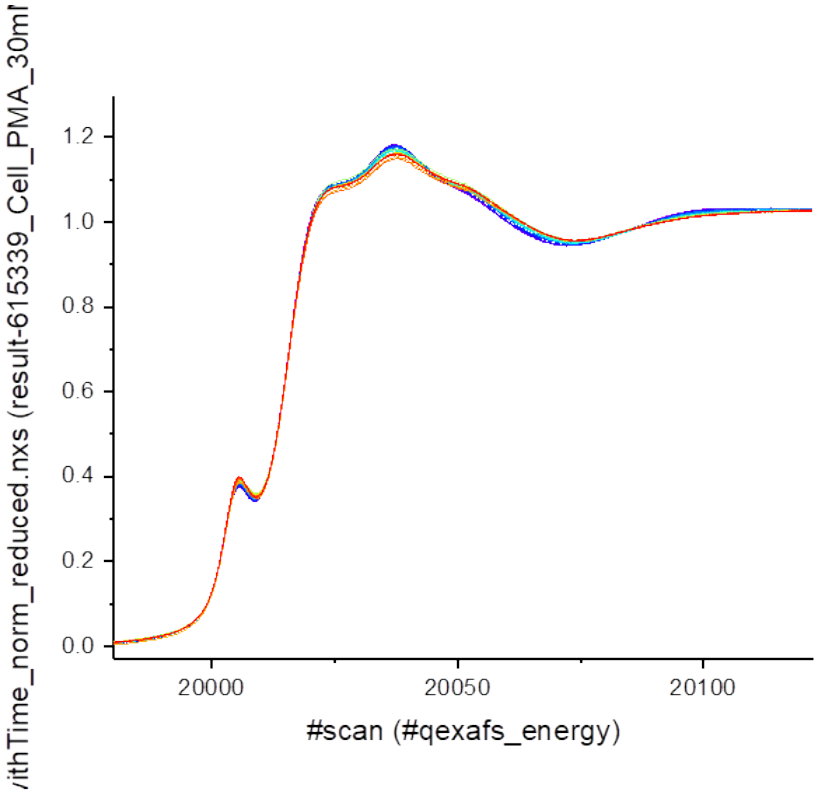

Figure S3: Plot of sequential quick XAS spectra obtained during an *operando* reoxidation of the Electrochemically-reduced sample, plotted over a colour gradient from red to blue. Each spectrum took 31.55 seconds.

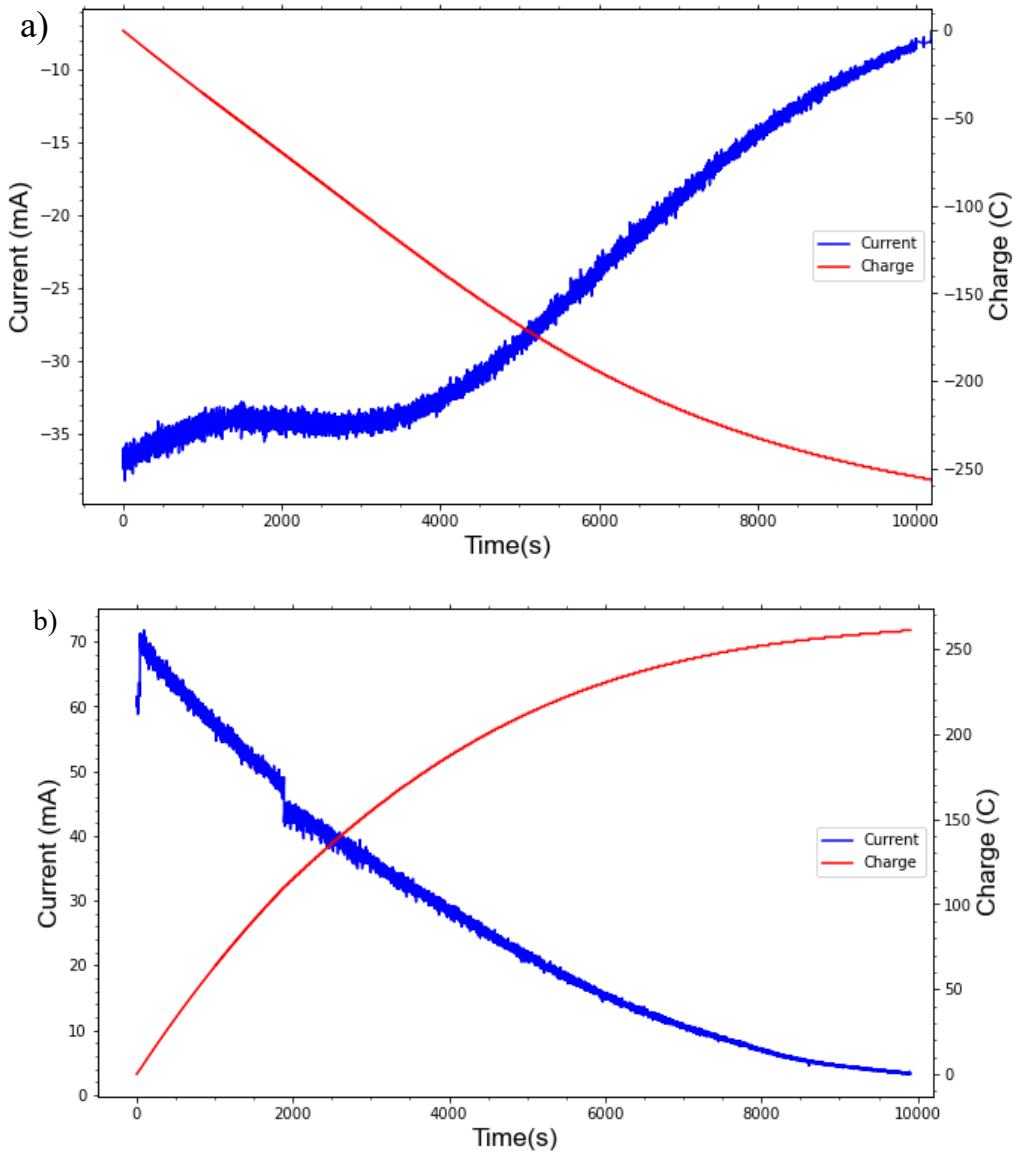

Figure S4. Plots of current and charge passage as a function of time for an H-cell operating with a PMA anolyte in a) reduction mode and b) oxidation mode.

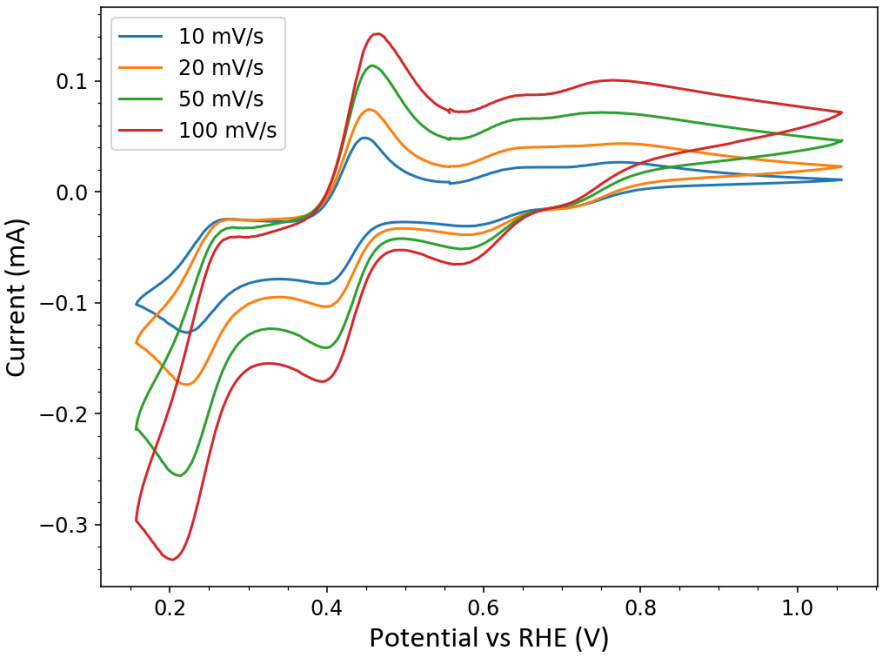

Figure S5. Plots of cyclic voltammetry of 0.01 mol dm^{-3} PMA at scan rates ranging from 10 to 100 mV/s.

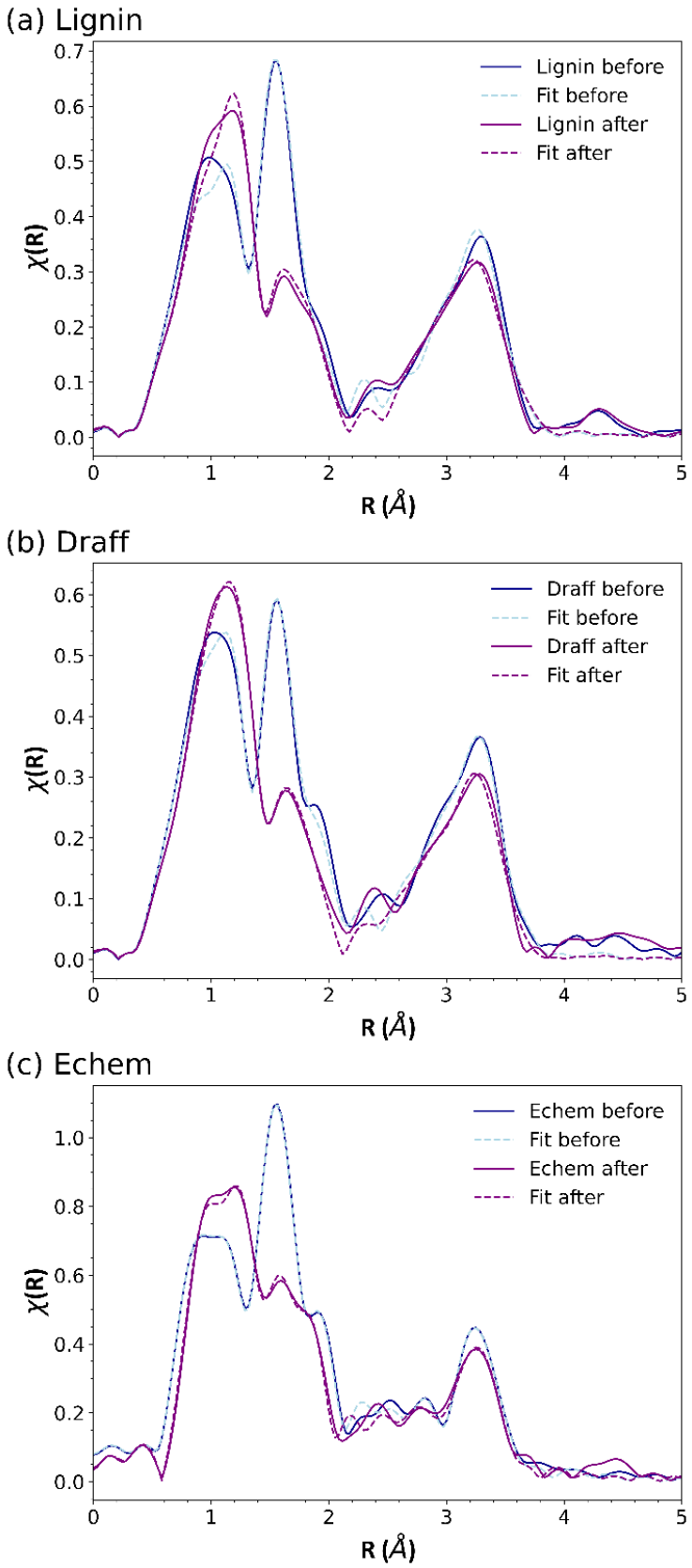

Figure S6. Fitting of EXAFS spectra (in R-space) of Lignin, Draff and Echem samples before and after re-oxidation of reduced PMA (starting photoelectron scattering paths obtained from geometrically relaxed DFT calculations and modelled using Artemis software)