Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for:

Revealing electronic structure changes in Chevrel phase cathodes upon magnesiation using X-ray absorption spectroscopy

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Full cell test

Mg coin cells (Mg metallic anode, polyethylene separator, Mo_6S_8 cathode) were assembled using standard 2032 coin cell hardware (Pred Materials). The Mo_6S_8 was prepared following standard high temperature preparations,[1,2] ground to a powder, and sieved to -100 mesh. 9g Mo_6S_8, 0.5g Denka carbon black, and 0.5g PVDF were mixed in 6.25g NMP for 3 hours in a blade mixer. The resulting slurry was blade coated onto Ni foil (Goodfellow, Huntington, England) at 100um wet film thickness (approximately 4mg/cm^2 active loading) and allowed to dry under a fume hood overnight. The resultant coating was then vacuum dried to 120˚C for 12 hrs in a vacuum oven. Cathodes were then punched and assembled with a separator (Tonen, Toray Corp., Japan) and a Mg foil anode (Leico, New York). Electrolytes were prepared according to published procedures;[3] 0.25M APC in THF was used for all tests. Cells were assembled into test holders in controlled temperature ovens (SPX, Charlotte, NC) at 60˚C. Cells were discharged at 0.3C through 10 charge/discharge cycles, by discharging to 0.5V, then charging to 1.8V, then holding at 1.8V until the current decayed to 0.03C. C rates were calculated based upon the theoretical energy of 122mA-hr/g Mo_6S_8. Cathodes were recovered after 10 cycles in either the charged or discharged state, and then rinsed with THF in an Ar glove box (Vac Atmospheres, <0.5ppm H_2O and O_2) and sealed under Ar and delivered to the beamline for analysis. Typical charge/discharge curves for the 10th cycle of a representative cell are shown in Figure S1.

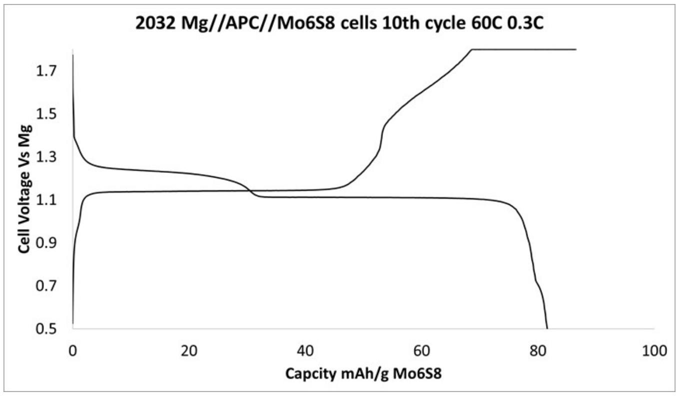

Figure S1: Charge/discharge characteristics for the Mg//APC//Mo_6S_8 coin cells used in the analysis. Conditions: 60C, 0.3C rate.

XAS measurements

Samples at different charging/discharging stage are collected to run ex-situ Mo K-edge XAS experiments at beamline 10-ID at the Advanced Photon Source using fluorescence mode.[4] This line generates an approximate flux of 10^{12} photons/sec at the Mo edge of 20000.48 eV. Measurements were done in transmission mode utilizing N2/Ar filled ionization chambers. Samples were sealed between thin layers of aluminized kapton to prevent air exposure during testing and transport to and from the glovebox. Samples were secured to an appropriate holding configuration that allowed for multiple samples to be done as rapidly as possible to prevent contamination. Scans were performed using a fast scan technique to minimize exposure time. Molybdenum foil was used as a reference calibration for all samples and was located downstream between the second and third ionization chamber to account for any beam changes attributable to absorption by the sample.

Data from the S K-edge of $Mg_xMo_6S_8$ and elemental sulfur were acquired at 9BM using both fluorescence and electron yield modes. The sealed laminates were measured in helium and data were aligned to elemental sulfur's white line (2472.5 eV). Both detection modes gave similar results at each charge state, indicating that the observed changes persist into the bulk. However, fluorescence is prone to self-absorption, so the electron yield is compared to calculation in Figure 3.

XAS simulations

The ground-state structures of $Mg_xMo_6S_8$ are optimized based on density functional theory,[5,6] which is realized in the Vienna Ab initio simulation package.[7,8] The electron-ion interactions are described using the pseudopotential approach [9,10] and the exchange-correlation effects are approximated using standard generalized-gradient approximations (PBE-GGA).[11] A planewave energy cutoff of 300 eV is used and a k-point grid of 6×6×6 for the primitive cell (or equivalent for supercells) is used to ensure numerical convergence.

The S K-edge XANES are calculated using the wavefunction based eXcited electron and Core-hole (XCH) approach, which is built upon PWSCF, part of the Quantum ESPRESSO suite.[12] A detailed description and justification of this method can be found elsewhere.[13,14] The Mo K-edge XAS, including both near-edge (XANES) and extended structure (EXAFS), are simulated based on the Green's function representation of the golden rule. Compared to the wavefunction approach, this real-space Green's function formalism without the need to explicitly calculate the final states provides a computationally efficient means to access excitation energies that are far above the absorption edge. In this work, we use the FEFF code to compute the Mo K-edge XAS.[15,16] It is known that XAS, especially EXAFS can be very sensitive to structural disorder and thermal vibrations. To test these effects, we also carry out a set of ab initio molecular dynamics (AIMD) simulations and compute the ensemble-averaged spectra for various $Mg_xMo_6S_8$ structures. In all AIMD simulations, the systems (comprising 2×2×2 supercells of $Mg_xMo_6S_8$) are equilibrated at 300 K with a Nosé thermostat.[17] A timestep of 0.5 fs is used and the systems are typically equilibrated for 2 ps before beginning sampling for XAS calculations.

Sensitivity of Mo K-edge EXAFS

From the ex-situ Mo K-edge EXAFS measurement, we found that the samples after cycles are very sensitive to measurement conditions, which has not been fully discussed in the literature. In Figure S2, Mo K-edge EXAFS are presented for samples initially collected at fully charged and discharged states, yet kept in the sealed Ar glovebox for a month before measurement. It is shown that all spectra relax to some intermediate state that can be a mixture of incomplete magnesiated phases. Currently the exact causes of this "relaxation" are unknown. Air and/or moisture exposure might be one cause – supposedly happening during cell opening and transport between experiments. Future work aims to address this unexpected "relaxation" behavior by carefully controlling measurement procedures to ensure the seals made with kapton are secure and the storage environment is oxygen and moisture free. Nevertheless, this is surprising because the general consensus in the literature is that the $Mg_xMo_6S_8$ compound is air stable, i.e. no electrochemical activity. From our Mo K-edge EXAFS data, we argue that this is not necessarily true and one should be extremely careful with future ex-situ measurements.

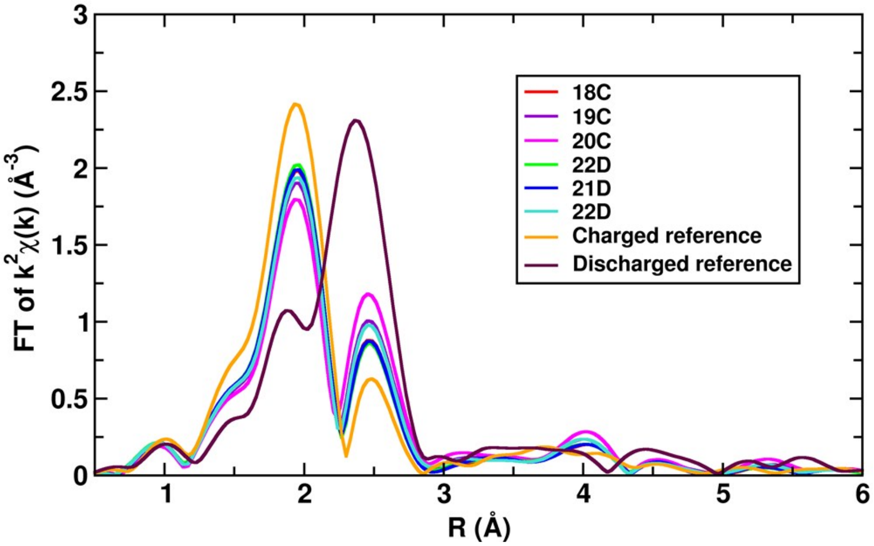

Figure 2: Mo K-edge EXAFS collected for samples with different degree of air exposure. "C" and "D" denote charged and discharged state, respectively. The reference spectra are measured for samples with minimal air exposure.

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