

# Super-reduced POM<sup>27-</sup>: An Excellent Molecular Cluster Battery Component and Semipermeable Molecular Capacitor

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One of the most intriguing properties of polyoxometalate (POM) clusters is their highly unusual capability to accept a large number of electrons, a property which finds its expression in the term “electron reservoir” or “electron sponge” that is sometimes applied to them. This means for instance that POM clusters have the potential to play an important role as a cathode-active material. As early as the mid-1970’s Launay [1] reported the preparation and characterization of electrochemically highly reduced metatungstate anions. Based on the observation of irreversible electrode reactions, and simple molecular orbital considerations, these investigators proposed that three joint octahedra comprising each of the four corners of the POM cluster would be reduced by up to six electrons, and that this locally reduced structure would feature W<sup>IV</sup>-W<sup>IV</sup> bonds arranged in the form of triangles [1]. Clearly, these suggestions were highly speculative and lacked any direct evidence. More recently, our team reported that in high-capacity lithium batteries with a molybdate POM [2], each  $\alpha$ -Keggin containing 12 Mo atoms may indeed be reduced by up to 24 additional electrons, as evidenced by *in situ* observed changes of the Mo ion average valences, according to Mo K-edge XANES absorption edge energies. This high uptake of excess electrons (termed “super-reduction” in ref. 1) is the current confirmed record for a single molecular cluster, and is certainly remarkable because usually highly charged anions are prone to break covalent bonds and decompose spontaneously. The POM-MCBs exhibit a large capacity of ca. 270 (A h)/kg in a voltage range between 4.0 and 1.5 V.

In this work, theoretical investigations are presented on the molecular and electronic structure changes of  $\langle$ -Keggin-type POM<sup>3-</sup> clusters [PM<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> (M = Mo, W) occurring towards reaching their super-reduced POM<sup>27-</sup> state during the discharging process in lithium-based molecular cluster batteries (MCBs). Density functional theory (DFT) was employed in geometry optimization and first principles molecular dynamics (FPMD) simulations was used to explore local minima on the potential energy surface of neutral POM clusters, adorned with randomly placed Li atoms as electron donors around the cluster surface. On the basis of structural, electron density, and molecular orbital (MO) studies, we present evidence that super-reduction is accompanied by metal-metal bond formation, beginning from the 12<sup>th</sup> to 14<sup>th</sup> excess electron transferred to the cluster. Afterwards, the number of metal-metal bonds increases nearly linearly with the number of additionally transferred excess electrons. In  $\langle$ -Keggin-type POMs, we observed the formation of metal triangles as a prominently emerging structural feature. The origin of the Mo triangle formation during super-reduction stems from the formation of characteristic three-center two-electron bonds in triangular Mo sites, created under preservation of the original metal skeleton via ‘squeezing out’ of oxygen atoms from M-O-M bridges when the underlying metal atoms form covalent bonds. The

driving force for this unusual geometrical and electronic structure change is a local Jahn-Teller distortion at individual metal octahedral sites, where the triply degenerate  $t_2$   $d$  orbitals become partially filled during reduction, and gain energy by distorting the octahedron such that metal-metal bonds are formed. The bonding orbitals show strong contributions from mixing with M-O antibonding orbitals, thereby “shuffling away” excess electrons from the cluster center to the outside of the cage. The high density of negatively charged, yet largely separated, oxygen atoms on the surface of the super-reduced POM<sup>27-</sup> polyanion allows the huge Coulombic repulsion due to the presence of the excess electrons to be compensated by the presence of Li counteranions, partially penetrating into the outer oxygen shell (see Figure 1). It is concluded that such a “semiporous molecular capacitor” structure is a general requirement for designing effect cathode materials for MCBs [3].

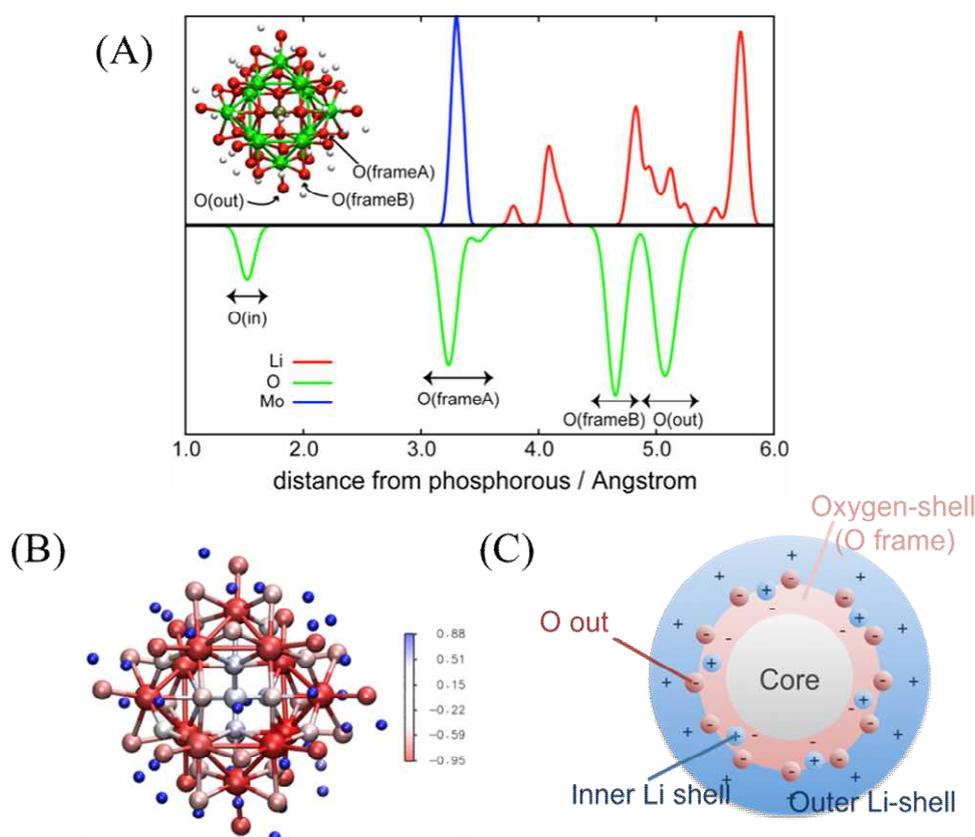


FIG 1. Charge distribution in an optimized POM<sup>27-</sup> structure including 35 lithium atoms. (A) depicts integrated NPA atomic charges in shells around the phosphorous center, (B) shows charge changes during the super-reduction of the POM<sup>3-</sup> cluster by neutral Li atoms, and (C) schematically illustrates the notion of a “molecular capacitor”.

## References

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