Mechanochemical Synthesis Of Electron-Rich Polyoxometalates

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The constantly growing demand in renewable energy sources brings the need of new methods to store this energy that can be released when demand exceeds generating capacity. Storage of energy as electrical charge in batteries and storage of energy via the conversion into chemical fuels are the two most promising solutions to this challenge. Polyoxometalates (POMs) are ideal candidates in this regard due to their ability to reversibility accept multiple electrons with no change in their structure.

The study by Awaga and co-workers suggested that the Keggin-type POM, $[PMo_{12}O_{40}]^{3-}$, can undergo to reversible 24-electrons reduction in Li ion batteries.[1] Recently, it has been revealed that the Wells-Dawson anion, $[P_2W_{18}O_{62}]^{6-}$ undergoes to extensive reduction and can be used for rapid H_2 generation or as an electrolyte in a high energy-density redox flow battery.[2] Although a various number of works have reported charge storage and conversion materials based on electron-rich POMs, the formation of 'super-reduced' POMs by chemical reduction neither in solid state nor in solution has hardly been investigated. This prompt us to explore the step-wise chemical reduction of $(TBA)_3[PMo_{12}O_{40}]^{3-}$ using Li metal in order to provide better fundamental understanding of the reactivity and the electronic properties of the resulting electron-rich nanoscale metal oxides as well as the use of them for energy applications.

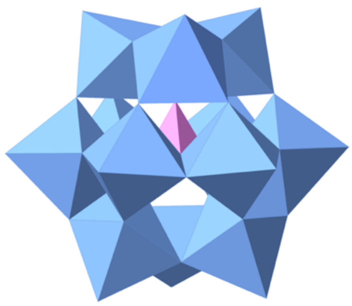

Figure 1. Representation of Keggin-type Polyoxometalate $[PMo_{12}O_{40}]^{3-}$.

[1] Wang H.; Hamanaka, S.; Nishimoto, Y.; Irle, S.; Yokoyama,T.; Yoshikawa,H; and Awaga, K. J. Am. Chem. Soc., **2012**, 134, 4918

[2] Chen, J-J; Symes D. M.; Cronin, L. Nature Chem., **2018**, 10, 1042