TUNING THE REDOX-PROPERTIES OF PHOSPHOMOLBDATE-POLYOXOMETALATES BY INCORPORATION OF MANGANESE (II)

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Polyoxometalates (POMs) are a class of polyanionic inorganic materials composed of corner- and edge-linked metal-oxygen octahedra MO₆. POMs are capable of accepting or donating one or more electrons without structural changes. This opens up the potential for POMs to be used as RedOx catalysts. The RedOx activity of a POM can be controlled by incorporating a suitable transition metal. Vanadium with its RedOx pair V(V)/V(IV) represents the best-known example, whereby the Keggin structures of the type $[PV_xMo_{12-x}O_{40}]^{(3+x)-}$ have already been used in numerous oxidative applications.^[1,2] However, the greatest challenge is to find the transition-metal of choice for a desired application. In our study presented here, the influence of the respective substitution metal on the RedOx activity of the resulting POM is investigated using the example of Mn(II) and Mn(II)/V(V) mixed-substituted POMs.



Figure 1: Square-Wave Voltammogram of different V(V) and Mn(II) substituted POM species in comparison to the unsubstituted Keggin-species H₃[PMo₁₂O₄₀].

In addition to spectroscopic and crystallographic methods, electrochemical measurements were used to explore the influence of the respective elements on the RedOx activity of our synthesized POMs. From our results we could conclude that the additional incorporation of Mn(II) causes the RedOx potentials to shift to lower potential values, which is a promising approach for the synthesis of tailored POM catalysts for a specific application.^[3]

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^[2] M. J. Poller, S. Bönisch, B. Bertleff, J.-C. Raabe, A. Görling, J. Albert, Chem. Eng. Sci. 2022, 264, 118143.

^[3] J.-C. Raabe, J. Albert, M. J. Poller, *Chem. – A Eur. J.* 2022, 28, 1–12.