

3. 分子性2次電池における固体電気化学と物性科学

Solid-state electrochemistry and materials science in rechargeable molecule-based batteries

金属クラスター錯体や金属有機構造体(MOF)、共有結合構造体(COF)などの分子性物質を構成成分とする2次電池の研究を進めている。多電子反応による高容量化とともに、クラスター構造やポーラス構造を利用してイオン伝導を確保することによって、エネルギー密度とパワー密度の両方を実現することができるだろう。我々は、このような固体電気化学反応を分子論的に理解したうえで物質開拓を論理的に進めるため、X線吸収スペクトルやNMRなどの電気化学反応下のオペランド計測も開発している。さらに、固体電気化学反応を利用して結晶構造を保ったままバレンス制御することによって、固体物性を自由に制御する研究も進めている。

We have been developing molecule-based rechargeable batteries, using transition-metal cluster complexes, metal-organic frameworks (MOF) and covalent-organic frameworks (COFs). It is expected that their multi-step redox reactions and high ionic conductivities due to their cluster or porous structures would realize both high-energy and high-power densities. To develop material research in a logical way, we have developed various *in operando* measurement systems under electrochemistry for XAFS, NMR, etc. We are also trying to control the valence of these molecule-based materials by solid-state electrochemical reactions, to modulate the physical properties freely.

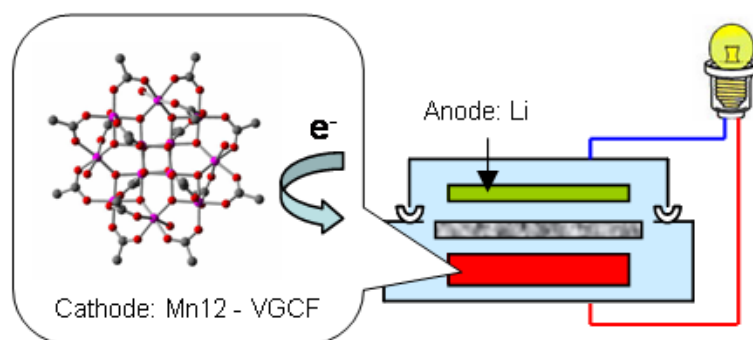


Fig. 1. We fabricated a rechargeable molecular cluster battery, based on a cathode active material, $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$. The charging/discharging experiments revealed rechargeable battery performance with a capacity of ca. 90 Ah/kg, while the first discharging process exhibited an extremely high value of 200-250 Ah/kg.

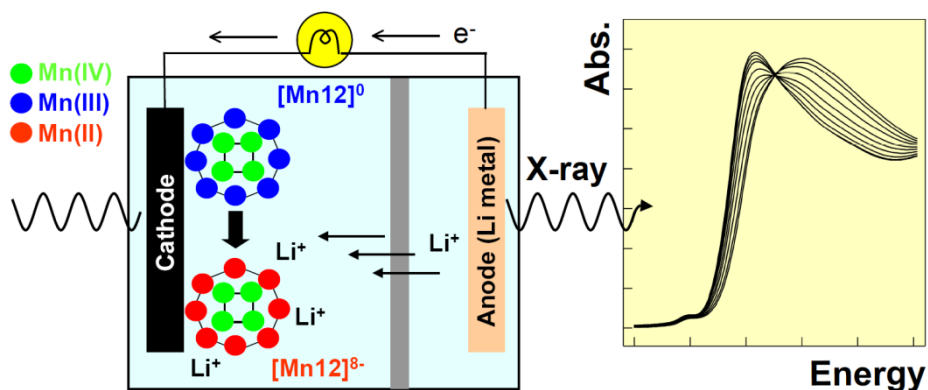


Fig. 2. We carried out *in situ* Mn *K*-edge X-ray absorption fine structure (XAFS) studies of Mn12 molecular cluster batteries to clarify the battery reaction mechanism. The XAFS results confirm that super-reduced species $[\text{Mn}_{12}]^{8-}$ were formed by solid-state electrochemistry during charging/discharging.

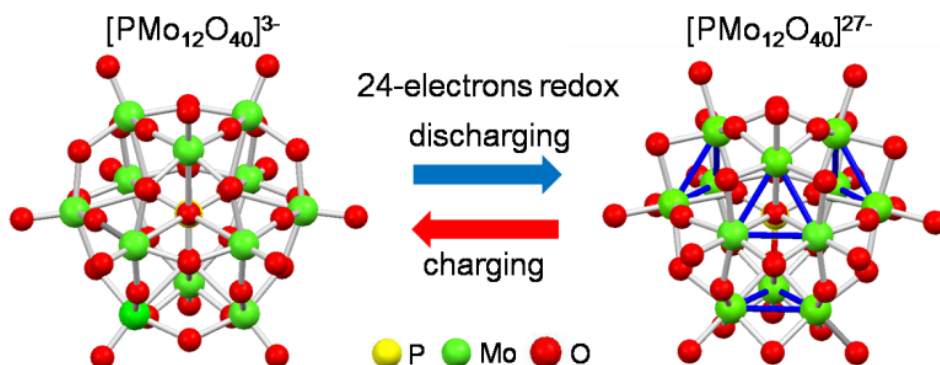


Fig. 3. We carried out *in operando* XAFS studies on the cathode materials of the POM-MCBs. We found that this battery includes a solid-state electrochemical reaction between the original $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and the super-reduced state $[\text{PMo}_{12}\text{O}_{40}]^{27-}$, which results in a twenty-four-electron reduction/oxidation. The molecular structure of $[\text{PMo}_{12}\text{O}_{40}]^{27-}$, estimated from EXAFS analyses, showed that Mo^{4+} metal-metal bonded triangles are formed due to the large number of additional electrons in the super-reduced state.

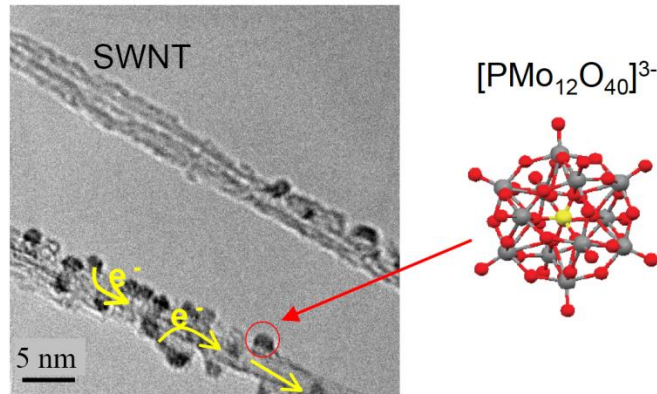


Fig. 4. POM/SWNT hybrid materials, in which the POM molecules are individually adsorbed onto the surfaces of SWNTs, can be used as a cathode-active material in rechargeable lithium batteries. This POM/SWNT battery exhibits a very high capacity (> 300 Ah/kg) with a short charging/discharging time (< 2 hours), suggesting smooth electron transfer between the POMs and the electrode through SWNTs, and smooth access of lithium ions to the POMs.

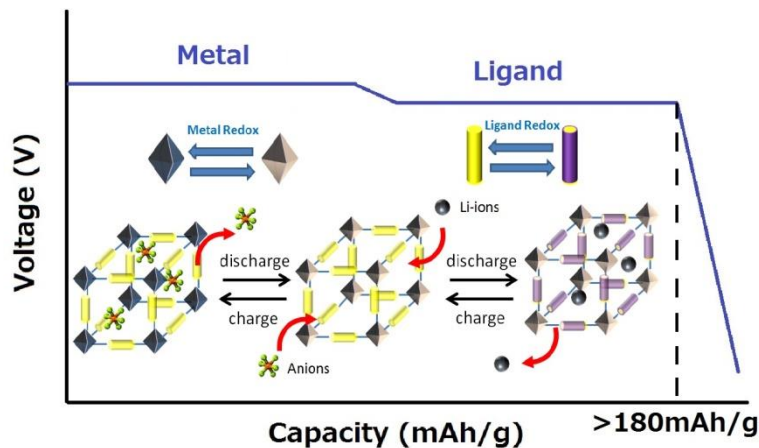


Fig. 5. Metal-organic frameworks (MOFs) are well known for their application to various types of energy storage; nevertheless, their potential in electron storage has scarcely been investigated. We discovered a new electrochemical mechanism, namely “bipolar charging” mechanism by analyzing the solid-state electrochemical process of a flexible redox active MOF. In a single redox cycle, not only the Li-ions but also the bulky anions are separately intercalated into the pores of the MOF and contribute to the total capacity. With this “bipolar charging” mechanism, a general synthetic strategy could be proposed. Furthermore, MOF materials employing this mechanism may exhibit remarkable reactivity and high cyclic stability, and be adopted as versatile electrode materials in various battery architectures.

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