

Development of rechargeable batteries using coordination compounds as cathode active materials

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Solid-state electrochemistry is a wide research area covering various topics from fundamental sciences to applications. At present, one of the most important goals is to develop high-performance rechargeable batteries due to the ever-increasing energy demands and pressing environmental concerns. We have recently proposed a new type of lithium battery, “the molecular cluster battery (MCB)”, in which the cathode active materials are polynuclear metal complexes (molecular clusters) such as Mn12 clusters ($[\text{Mn}_{12}\text{O}_{12}(\text{RCOO})_{16}(\text{H}_2\text{O})_4]$, $\text{R} = \text{CH}_3$, C_6H_5 , etc.) and polyoxometalates (POMs), in order to achieve both high battery capacity and fast charging/discharging. It is expected that MCBs would show a high capacity and a rapid charging/discharging due to multi-electron redox reactions of the molecular clusters and quick lithium-ion diffusion, respectively (the left of Fig. 1).

In this seminar, I talk about the performance of the MCBs based on “solid-state electrochemistry of molecular clusters”. Actually, using a Keggin-type POM, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (KPOM), which is well known as catalysts, as a cathode-active material, we achieved a higher battery capacity of ca. 270 Ah/kg, which was larger than those of the lithium ion batteries (ca. 148Ah/kg), and a more rapid charging. Operando Mo K-edge X-ray absorption fine structure (XAFS) analyses on the KPOM-MCBs demonstrated that KPOM underwent twenty four electrons reduction in the discharging process, which indicated that all of Mo^{6+} ions in KPOM changed into Mo^{4+} . This means the formation of a super-reduced state, $[\text{PMo}_{12}\text{O}_{40}]^{27-}$, and the super-reduction electron number of twenty four can explain the large capacity of the KPOM-MCBs. This electron sponge behaviour indicates that molecular clusters are promising cathode active materials for high-performance rechargeable batteries. Furthermore, we exhibited nano-hybrid materials between KPOMs and single-walled carbon nanotubes (SWNTs), in which KPOMs are individually adsorbed on the SWNT surfaces for application to the cathode active materials of MCBs (the right of Fig. 1). The charging/discharging measurements for the KPOM-SWNT hybrid MCBs indicated a higher battery capacity and a faster charging/discharging compared with those of the initial KPOM MCBs.

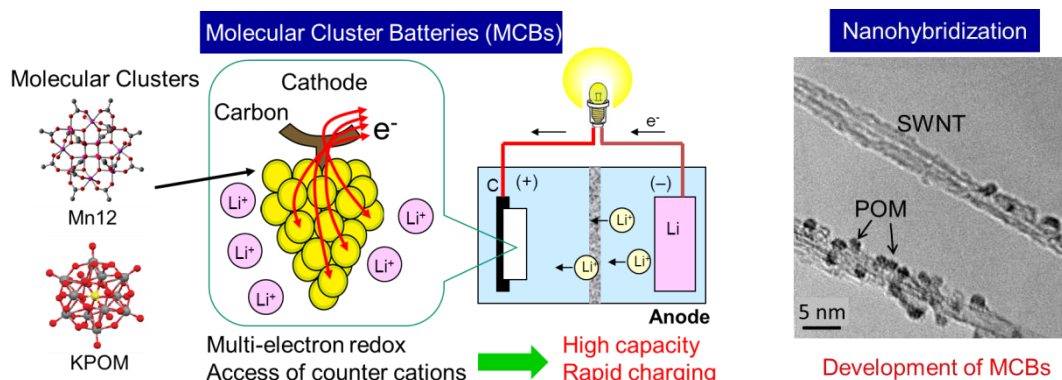


Fig.1. Schematic View of MCBs (Left) and TEM Images of Nano-hybrid Materials (Right).

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