Seminar in the University of Edinburgh

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Title: Novel rechargeable batteries using molecular clusters 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 ($[Mn_{12}O_{12}(RCOO)_{16}(H_2O)_4]$, R = 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, $[PMo_{12}O_{40}]^{3-}$ (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, $[PMo_{12}O_{40}]^{27-}$, 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.

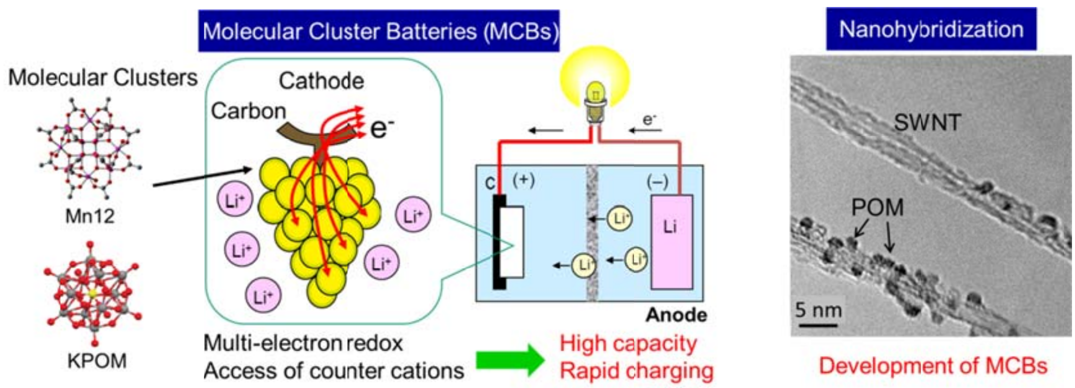

Fig.1. Schematic View of MCBs (Left) and TEM Images of Nanohybrid Materials (Right).

References

1) H. Yoshikawa et al., *Chem. Commun*. **2007,** 3169-3170. 2) H. Yoshikawa et al., *Inorg. Chem.* **2009**, 48, 9057-9059. 3) H. Yoshikawa et al., *Chem. Asian J.* **2011**, 6, 1074-1079. 4) H. Yoshikawa et al., *J. Am. Chem. Soc.* **2012**, 134, 4918-4924. 5) H. Yoshikawa et al., *Angew. Chem. Int. Ed.* **2011**, 50, 3471-3474. 6) H. Yoshikawa et al., *Dalton Trans.* **2012**, 4, 9863-9866. 7) H. Yoshikawa et al., *Chem. Eur. J.* **2013**, 19, 11235-11240. 8) H. Yoshikawa et al., *J. Mater. Chem. A* **2014**, 2, 3801-3807. 9) H. Yoshikawa et al., Chem. *Lett*, in press. 10) H. Yoshikawa, S. Irle et al., *J. Am. Chem. Soc*. in press.