# In Operando X-ray Studies of High-Performance Lithium-Ion Storage in Keplerate-Type Polyoxometalate Anodes

Chia-Ching Lin, Chi-Ting Hsu, Han Yi Chen*

*Department of Material Science and Engineering, National Tsing Hua University,*

*No. 101, Sec. 2, Kuang-Fu Road, Hsinchu 30013, TAIWAN*

*hanyi.chen@mx.nthu.edu.tw*

## Abstract

In this study, a Keplerate-type polyoxometalate (POM) $Na_2K_{23}\{[(Mo^{VI})Mo^{VI}_5O_{21}(H_2O)_3(KSO_4)]_{12}[(V^{IV}O)_{30}(H_2O)_{20}(SO_4)_{0.5}]\}$ ca200$H_2O$ (**{$Mo_{72}V_{30}$}**) was utilized as an anode for lithium-ion batteries (LIBs) because of its unique transition metal cluster structure. **{$Mo_{72}V_{30}$}** has a high capacity of 1300 mA h $g^{-1}$ without significant cycling fading up to 100 cycles due to the multiple-electron transfers and stable molecules structure. Ex situ X-ray diffraction result shows that the lithiation/delithiation process undergoes with amorphous **{$Mo_{72}V_{30}$}**, which is lack of long-range order, resulting in excellent cycling stability. The energy-storage mechanisms was also studied through *in operando* synchrotron X-ray absorption near edge structure (XANES), *ex situ* extended X-ray absorption fine structure (EXAFS), and potentiostatic intermittent titration technique (PITT) measurements. Based on the above results, we propose that the **{$Mo_{72}V_{30}$}** molecular cluster is similar to an ion sponge with diverse Li ion diffusion channel. Lithium ions react with polyanions by surface adsorption reactions and continuously intercalation processes. These results indicate that **{$Mo_{72}V_{30}$}** is a promising anode material for LIBs.

***Keywords*** - Polyoxometalate, Lithium-ion batteries, Anode materials, Charge storage mechanism