

# **Discrete Metal-Oxide Clusters with Organofunctionalization as High-Performance Anode Materials.**

## **Abstract:**

Molybdenum trioxide ( $\text{MoO}_3$ ) with a theoretical specific capacity of  $1117 \text{ mA h g}^{-1}$  is widely considered a promising anode material for lithium-ion batteries. However, the irreversible conversion reactions, low electrical conductivity, and detrimental volume expansion upon Li intercalation between the one-dimensional layered structures of  $\text{MoO}_3$  hinder its practical implementation. Herein, we report a facile synthetic protocol that allows surficial modification by replacing the terminal and bridging oxo groups of molybdenum oxide clusters. Successful organoimido functionalization resulted in a large cathodic shift in  $\text{Mo(VI/ V)}$  reduction by 0.45 to 0.6 V depending upon the functional group attached, pronounced electronic communication between the organic moiety and the metal–oxide unit, and significant increase in electrical conductivity (70–100  $\Omega$  interfacial charge-transfer resistance). Combined with the enlarged active surface area due to the structural hindrance induced by the organic functionality. Taking advantage of both the electronic and structural influence of the surficial imido groups, the organo-functionalized molybdenum oxide clusters exhibited a greater capacity performance. The steady specific capacity was greater than  $1800 \text{ mA h g}^{-1}$  at  $900 \text{ mA g}^{-1}$  at the end of 360 cycles, where the best value of  $1860 \text{ mA h g}^{-1}$  was achieved for the methoxyaniline-substituted species. The steady capacity of  $660 \text{ mA h g}^{-1}$  was achieved in the fast charge–discharge process ( $3000 \text{ mA g}^{-1}$ ) over 1400 cycles. Higher conductivity, accommodation of more Li, and faster  $\text{Li}^+$  diffusion kinetics are achieved. The results indicate that the surficial modification of metal oxides with organo moieties using our facile synthetic method has broad application potential for metal oxides to be used as high-capacity electrode materials in the future.