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## Supercapacitive Behaviour of Manganese Dioxide/Tungsten Bronze Composites

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Polyoxometalates (POMs), nanosized-oxide clusters, have received much attention over recent years as an electrode material due to their unique characteristics including high protonic conductivity, acid tolerance, multi-electronic redox properties etc. In this study, the capacitive behavior of aluminum counter cation-based tungsten bronze (POM-Al) and its composites with  $\text{MnO}_2$  was studied. The as-synthesized materials were characterized by Fourier-transform infrared spectroscopy (FTIR), UV-Vis. reflectance spectroscopy and electrochemical techniques. POM-Al exhibited inferior capacitive performance, which dramatically changed upon the fusion of  $\text{MnO}_2$  with it. Only 5% of  $\text{MnO}_2$  in the composites enhances the specific capacitance of POM-Al by more than 7-times. This shows high promise of highly robust POMs for fabrication of acid electrolyte-based supercapacitors.

### Introduction

The focus of energy storage experiences a sharp transition from consumer electronics to electric cars and grid infrastructure. This shift in technical landscape not only encourages battery development, but also the revival of new generations of supercapacitors (SCs) and promotes further research into novel materials that might deliver game-changing advancements in energy storage. The energy in a supercapacitor can be stored by an electric double layer or a redox process between electrode/electrolyte interfaces, or they can be combined (1). However, the electrochemical performance of SCs is largely determined by the electrode materials used. A possible approach for electrode materials is to combine suitable active materials such as polyoxometalate (POMs) with a current collector (2, 3).

The first POMs was discovered in 1826, but the structure has been verified by powder X-ray diffraction in 1934 by Keggin and his group (4). POMs have a peculiar structure made up largely of oxygen atoms and transition metals with a central addenda heteroatom such as X= Si, P, As, Ge, and so on (3). Because of their well-defined, massive, adjustable metal oxygen cluster structures, quick reversible multi-electronic redox activities, and excellent protonic conductivity with great stability (5), POMs, as early transition metal anionic clusters, have been widely attracted in catalysis (6), electrochemistry (7), and energy conversion (8). Wang et al. first pointed out that POMs can also act as an "electron sponge" because of its large electronic transfer capability which makes it suitable as an ideal supercapacitor material (9). Karina Cuentas-Gallegos et al. synthesised and successfully fabricated composite bulk electrodes of molecular hybrid material based on polyaniline (PAni) and POMs such electrode on graphite which was repeatedly cycled for