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ABSTRACT

The use of supercapacitors for energy storage is an attractive approach considering their ability to deliver high levels of electrical power, unlimited charge/discharge cycles, green environmental protection and long operating lifetimes. Despite the satisfactory power density, supercapacitors are yet to match the energy densities of batteries and fuel cells, reducing the competitiveness as a revolutionary energy storage device. Therefore, the biggest challenge for supercapacitors is the trade-off between energy density and power density. This presents an opportunity to enhance the electrochemical capacitance and mechanical stability of an electrode. Previous attempts to get around the problem include developing porous nanostructured electrodes with extremely large effective areas.

One of the emerging high-power supercapacitor electrode materials is molybdenum disulfide (MoS_2), a member of the transition-metal dichalcogenides (TMDs). Its higher intrinsic fast ionic conductivity and higher theoretical capacity have attracted a lot of attention, particularly in supercapacitors. In addition to double-layer capacitance, diffusion of the ions into the MoS_2 at slow scan rates gives rise to Faradaic capacitance. Analogous to Ru in RuO_2, the Mo center atom displays a range of oxidation states from +2 to +6. This plays an important role in enhancing charge storage capabilities. However, the electronic conductivity of MoS_2 is still lower compared to graphite, and the specific capacitance of MoS_2 is still very limited when used alone for energy storage applications. As evident in several literature reports, there is a need to improve the capacitance of MoS_2 with conductive materials such as carbon nanotubes (CNT), polyaniline (PANI), polypyrrole (PPy), and reduced graphene (r-GO). Carbon nanospheres (CNS) have, in the past, improved the conductivity of cathode material in Li-ion batteries, owing to their appealing electrical properties, chemical stability and high surface area.

The main objective of this dissertation research is to develop nanocomposite materials based on molybdenum sulphide with carbon nanospheres for pseudocapacitors with simultaneously high power density and energy density at low production cost. The research was carried out in two phases, namely, (i) Symmetric pseudocapacitors based on molybdenum disulfide (MoS_2)-modified carbon nanospheres: Correlating physico-chemistry and synergistic interaction on energy storage and (ii) The effects of morphology re-arrangements on the pseudocapacitive properties of mesoporous molybdenum disulfide (MoS_2) nanoflakes. The physico-chemical properties of the MoS_2 layered materials have been interrogated using the surface area analysis (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), Raman, fourier-transform infrared (FTIR) spectroscopy, and advanced electrochemistry including cyclic voltammetry (CV), galvanostatic cycling with potential limitation (GCPL), repetitive electrochemical cycling tests, and electrochemical impedance spectroscopy (EIS).

In the first phase, Molybdenum disulfide-modified carbon nanospheres (MoS_2/CNS) with two different morphologies (spherical and flower-like) have been synthesized using hydrothermal techniques and investigated as symmetric pseudocapacitors in aqueous electrolyte. The two different MoS_2/CNS layered materials exhibit unique differences in morphology, surface areas, and structural parameters, which have been correlated with their electrochemical capacitive properties. The flower-like morphology (f-MoS_2/CNS) shows lattice expansion (XRD), large surface area (BET analysis), and small-sized nanostructures (corroborated by the larger FWHM of the Raman and XRD data). As a contrast to the f-MoS_2/CNS, the spherical morphology (s-MoS_2/CNS) shows lattice contraction, small surface area with relatively large-sized nanostructures. The presence of CNS on the MoS_2 structure leads to slight softening of the characteristic Raman bands (E^1_{2g} and A_{1g} modes) with larger

FWHM. The MoS_2 and its CNS-based composites have been tested in symmetric electrochemical capacitors in aqueous 1 M Na_2SO_4 solution. CNS improves the conductivity of the MoS_2 and synergistically enhanced the electrochemical capacitive properties of the materials, especially the f-MoS_2/CNS-based symmetric cells (most notably, in terms of capacitance retention). The maximum specific capacitance for f-MoS_2/CNS-based pseudocapacitor show a maximum capacitance of 231 F g^{-1} with high energy density 26 Wh kg^{-1} and power density 6443 W kg^{-1}. For the s-MoS_2/CNS-based pseudocapcitor, the equivalent values are 108 F g^{-1}, 7.4 Wh kg^{-1} and 3700 W kg^{-1}. The high-performance of the f-MoS_2/CNS is consistent with its physico-chemical properties as determined by the spectroscopic and microscopic data.

In the second phase, Mesoporous molybdenum disulphide (MoS_2) with different morphologies have been prepared via a hydrothermal method using different solvents, water or water/acetone mixtures. The MoS_2 obtained with water alone gave graphene-like nanoflakes (g-MoS_2) while the other with water/acetone (1:1 ratio) gave a hollow-like morphology (h-MoS_2). Both materials are modified with carbon nanospheres as conductive materias and investigated as symmetric pseudocapacitors in aqueous electrolyte (1 M Na_2SO_4 solution). Interestingly, a simple change of synthesis solvents confers on the MoS_2 materials different morphologies, surface areas, and structural parameters, correlated by electrochemical capacitive properties. The g-MoS_2 exhibits higher surface area, higher capacitance parameters (specific capacitance of 183 F g^{-1}, maximum energy density of 9.2 Wh kg^{-1} and power density of 2.9 kW kg^{-1}) but less stable electrochemical cycling compared to the h-MoS_2. These findings have opened doors for further exploration of the synergistic effects between MoS_2 graphene-like sheets and CNS for energy storage.