

Nanostructured NaMnPO₄ based supercapacitors-Electrochemical performances under ambient and non-ambient conditions

Abstract

Supercapacitors are high-power energy storage devices, which have hundreds of thousands cycle life, capacity to absorb surge/ spikes, with easy fabrication, maintenance and disposal strategies. For the major part of the last four decades, Na-ion based energy storage systems remained under the shadow of their more illustrious counterparts based on Li-ion. Even after large-scale commercialization of Li-batteries, it was always known that sodium, with similar oxidation state and electronic configuration, can deliver characteristics close to Li⁺ based energy storage devices. The growing understanding and expertise to develop novel nanoparticles ranging from solid, hierarchical to hollow, has allowed the resurgence of Na-ion based energy storage systems. Compared to other sodium-based structures, Na-based phosphates have delivered exciting results due to their thermal stability and higher operating voltage window. In this work, sodium manganese phosphate (NaMnPO₄) is chosen as the active electrode material because of its high electrochemical potential, large theoretical specific capacitance, greater structural and thermal stability. A successful synthesis strategy to obtain single phase NaMnPO₄ is established. The materials are characterised using a large number of techniques such as: XRD, XPS, SEM, TEM, BET, Zeta, DLS, etc.

It is shown that NaMnPO₄ can be used as an effective electrode material for Na-ion supercapacitors, with specific capacitance values that are comparable or higher than those reported in literature pertaining to such materials. To induce quantum jump in the specific capacitance value, a strategy based on the use of redox additive modified electrolytes is proposed. The fruitfulness of the strategy is established using two redox additives in 2 M NaOH electrolyte viz., K₃Fe(CN)₆ and KI. Performance improvement of >40% is shown to prove the correctness of the hypothesis. The electrochemical studies under various external factors like: temperature, external frequency, magnetic field, etc. have remained ignored for Na-ion supercapacitors. In the temperature dependent study in the fabricated Na-ion supercapacitor device, an enhancement of >65% is reported, on increasing the temperature from 25 to 65 °C. Similarly, the magnetic field dependent study can also lead to appreciable changes in the device performance. A new theoretical model is proposed for the first time to explain the magnetic supercapacitors.

Keywords: Na-ion supercapacitor, redox additive, asymmetric device, electrochemical activity, non-ambient conditions