Layered and polyanion based electrode materials for sodium rechargeable cells

Abstract

Now a day's sodium ion batteries(SIBs) are emerging as promising alternative of lithium ion battery, owing to similar electro-chemistry and high natural abundance. But the inadequacy of suitable anode, attracts researcher's attention towards the development of stable and economically viable high performance anodes. Hard carbon the only active anode for SIB, poses very low intercalation voltage which may causes Na-plating like serious issues and raise safety issues and also the low initial coulombic efficiency is another associated with this anode. Whereas, Titanium based anodes seem to be attractive as negative electrodes for sodium ion rechargeable cells. In view to this layered sodium titanate ($Na_2Ti_3O_7$/NaTO) and poly-anionic sodium titanium phosphate ($NaTi_2(PO_4)_3$/ NTP) are more attractive among researcher, for their low operation redox voltage which making it suitable for high energy density anode together with higher structural stability and faster ionic mobility respectively. However, poor intrinsic electronic conductivity of NTP and low initial coloumbic efficiency, fast capacity fading associated with NaTO limits their practical use. Various strategies have been adopted to address these issues related to both the anodes. These include but not limited to surface modification, bulk modification and making composites with carbonaceous additives. Surface properties of the anodes are improved by coating with carbon using different carbon source including citric acid, sucrose, poly-ethylene glycol, ploy-vinyl alcohol, poly-aniline, poly-vinyl pyrrolidone etc. Carbon coating is imparted ex-situ, in-situ carbonization, polymerization etc. Factors such as carbon source, quality of the carbon, the thickness of coating, nature of the coating play important role to improve columbic efficiency, rate performance and cycling stability by increasing the electronic conductivity and making a protective barrier on the material surface. The specific capacity of 76mAhg^{-1}, 107mAhg^{-1},119mAhg^{-1} after 100 cycle is obtained using sucrose, PVA, PEG has been used as carbon source respectively, showing a great improvement of cycleability compare to bare NaTO. Again, a discharge capacity of 114mAhg^{-1} is obtained after 100 cycles when it is cycled at 100mAg^{-1} and after 500 cycle a 1.5Ag^{-1} current density delivers 82mAhg^{-1} of discharge capacity and at a current density of 2mAg^{-1} a discharge capacity of 78mAhg^{-1} is obtained for NaTO@PaNI anode which justify its improvement in high rate sustainability. Inert surface coating also proven efficient to retard the unwanted side reaction on the electrode-electrolyte interface. In addition, to impart the structural stability of the NaTO, by synthesizing the dopant variants of NaTO anode has been proven effective to improve electronic conductivity and variation in unit cell volume enhance the Na^+ ion transportation. The impact of making carbonaceous composite of NaTO and NTP with rGO and CNT offers faster electronic conduction by lowering charge transfer resistance(R_{ct}) and increasing the Na^+ diffusion co-efficient by proving a conductive path. The excellent electrochemical performance of the composite may be ascribed to the synergetic interaction between the carbonaceous additives and the material which introduce some pseudo-capacitive nature into it. The combine effect of structural integrity, high electronic conductivity as well as high ionic diffusivity in NTP-rGO10-CNT10 leads to excellent electrochemical performance in terms of high specific capacity (124 mA h g^{-1} at 100 mA g^{-1}), remarkable high-rate cycling stability (62.5% capacity retention after 400 cycles at 10 C), and excellent rate capability (87 mA h g^{-1} at 25C) Finally, to investigate the full cell characteristics of these anodes, $Na_3V_2(PO_4)_3$/NVP is chosen as cathode. Incorporation of electronegative F atom resulting the increase of nominal voltage of the cathode and as a result energy density of the full cell is increased. Tape casting the conventional coating technique doesn't provide a good mixing of active material, binder and conductive agent. Whereas, by adopting an efficient electrode fabrication technique i.e., electrophoretic deposition, a good adhered, porous electrode is obtained which provides high rate performance of the NVP cathode. Finally, using optimized anodes composition and modified cathode, a reasonable full cell performance is obtained. All these electrochemical performances validate the application of above mentioned anodes and cathodes in sodium ion based energy storage applications.

Keywords: $Na_2Ti_3O_7$, $NaTi_2(PO_4)_3$, Surface coating, Carbonaceous composite, Doping, Sodium ion cells.