Monodisperse porous Na$_2$Fe$_2$(PO$_4$)$_3$/CNT nanocomposites for a new high energy sodium ion battery cathodes

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With large energy storage systems (ESSs) developing, sodium ion batteries (SIBs) have attracted considerable attentions in recent years.$^1$ However, it is still a big challenge to look for an appropriate cathode material for SIBs. Fortunately, there is a large number of cathode materials being tested recently, such as layered oxides, carbon nanotubes (CNT) and Na$_x$FePO$_4$ microspheres. Among these candidates, the Fe-based polyanion cathodes are becoming the focus as expected, because of its environmentally friendly and abundant resources. This is especially true for the Fe-based alluaudite (A$_x$M$_{2/3}$P$_{2/3}$O$_5$) type, because it demonstrates great potential as a promising cathode for SIBs.$^{2,3}$

To the best of our knowledge, there is no report about Na$_2$Fe$_2$(PO$_4$)$_3$ applied in the field of SIBs. Herein, we present a monodisperse porous Na$_2$Fe$_2$(PO$_4$)$_3$/micro-sized spheres and a networked nanocomposite combined with carbon nanotubes (CNT) and Na$_2$Fe$_2$(PO$_4$)$_3$/microsphere as new excellent cathodes in SIBs via a solvothermal method.

Figure 1: Typical SEM and TEM images for Na$_2$Fe$_2$(PO$_4$)$_3$/CNT nanocomposites. (a-c) the SEM images show the morphology of the products, these monodisperse porous microspheres are connected with CNT forming a three dimensional network; (d) HRTEM presents a characterized crystal plane of (2−40).

The size and morphology of porous Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres are confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as depicted in figure 1. These target products are consisted of monodispersed porous spherical micro-particles. Most importantly, these microspheres are indeed composed of numbers nanorods with a diameter of about 20 nm. Such a small size structure can make sure a successful transport of the Na ion during the charge/discharge process. The HRTEM characterizations demonstrate a clear crystal plane with d-spacing of 0.53nm corresponding to the (2−40) plane. The energy dispersive X-ray spectroscopy (EDX) mapping analysis reveals these monodisperse Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres includes of Na, Fe, P, O, and provides a direct evidence for the composition of target product.

Figure 2 (a) the formation energy plot of Na$_2$Fe$_2$(PO$_4$)$_3$/C from first principle calculations with a x value ranging from 1 to 2; (b) Galvanostatic charg/discharge profiles of Na$_2$Fe$_2$(PO$_4$)$_3$/C nanocomposites at 5 mA/g for different cycles; (c) a comparison of the cycle performance for Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres and Na$_2$Fe$_2$(PO$_4$)$_3$/C nanocomposites at 5 mA/g; (d) the rate capability comparison of Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres and Na$_2$Fe$_2$(PO$_4$)$_3$/C nanocomposites with various different current rates.

The electrochemical testing indicate that this sodium insertion is a typical solid solution process, see figure2b. Figure 2c and d show that both of the Na$_2$Fe$_2$(PO$_4$)$_3$/microsphere and the corresponding nanocomposite can provide a high discharge capacity and keep a well excellent capacity retention, but the nanocomposite can give a better performance in the high current rate. This is benefited from the outstanding electron transportation feature of the CNTs.

In summary, a solvothermal method is used to prepare monodisperse porous Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres and Na$_2$Fe$_2$(PO$_4$)$_3$/CNT nanocomposites. These porous Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres are consisted of numbers of 20 nm nanorods with an open three dimensional framework. And the Na$_2$Fe$_2$(PO$_4$)$_3$/CNT nanocomposites is actually a network combined with porous Na$_2$Fe$_2$(PO$_4$)$_3$/microspheres and CNT. This specific morphology not only provides a short and efficient pathway for Na ion diffusion, but makes sure a sufficient contact between electrode and electrolyte. Furthermore, the existence of CNT in the nanocomposite system also accelerates the electronic diffusion between electrode particles. All of these result in this kind of electrode having an outstanding capacity and rate capability. Therefore, the Na$_2$Fe$_2$(PO$_4$)$_3$/CNT nanocomposites is a new promising cathode material for high energy SIBs.

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References