Nasicon structure materials as cathode electrode for Na-ion battery

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Sodium-ion batteries (SIBs) are a viable alternative to lithium-ion batteries (LIBs) for large-scale electrical storage due to their low cost and higher sodium abundance. Cathode materials are crucial to the energy density of NIBs and optimizing their electrocatalytic properties is critical. High energy density values have been obtained by using cathode materials based on polyanionic solids characterized by high thermodynamic stability thanks to the high energy value of their polyanionic covalent bonds. An important class of polyanionic materials is represented by NaSICON (Natrium Super Ionic CONductors) with formula NaxMM'$(XO_4)_3$, where M and M' are metallic and have proven to be interesting for the development of cathode materials for NIBs thanks to their high mobility of Na^+ ions and the structural versatility that allows working on a wide range of potentials. An interesting material belonging to this category is $Na_4CrMn(PO_4)_3$ which presents the highly reversible Mn^{4+}/Mn^{3+} redox couple which can develop a voltage value of 4.15 and 3.52 V with respect to Na^+/Na and a capacity of 108 $mAhg^{-1}$. In the present work, a composite material based on $Na_4CrMn(PO_4)_3$ (NMCP)and carbon nanofiber (CNF) was synthesized by electrospinning using a polymer such as polyacrylonitrile (PAN) as a precursor of the CNFs to obtain a material with a one-dimensional structure (1D) characterized by a high number of active sites and high resistance to deformation, improving the electrode reaction kinetics and cyclic stability. The material obtained with this process is characterized by flexibility that allows it to be used directly as a "free-standing" working electrode, without conductive additives, binders, and current collectors, with consequent simplification of the electrode preparation process and improvement of the battery energy density. The synthesized material was subjected to chemical-physical characterization. The DSC-TGA analysis allowed to evaluate the amount of active material on the composite sample equal to 40wt%. The XRD profiles of all samples show the main diffraction peaks typical of a rhombohedral NaSICON structure with R-3c space groups and also a broad centered peak at $2\theta=25°$ attributable to the presence of amorphous carbon. The SEM images show a dense fibrous structure characterized by the presence of small clusters of a few tens of nanometers and aggregates of particles up to 50-100 nm in size. The high-magnification image highlights the porosity of the nanofibers with a pore diameter between 50 and 100 nm. The surface area value, determined by the BET method, is about 169 $m^2 g^{-1}$. The porosimetric analysis revealed a prevalent presence of mesopores confirming the SEM analysis which can favor ionic diffusion and the intercalation-deintercalation processes of Na ions. The half-cell charge-discharge tests, produced an initial reversible capacity of about 107 mA h g^{-1} at 0.1C within 1.4 ~ 4.3 V, high-rate capability up to 2 C, and well capacity retention of about 70% after 500 cycles at 1C. These results showed that NMCP is a promising self-standing and binder-free cathode material for SIBs.

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