Ph.D. Thesis Abstract

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Title of the thesis: TIN AND ANTIMONY ALLOY BASED NANOCOMPOSITES AS ANODE MATERIALS FOR SECONDARY LITHIUM-ION AND SODIUM-ION BATTERY

Abstract:

Alkali-ion secondary batteries show promise in electrochemical energy storage applications like portable electronics, electric vehicles, and grid energy storage. Among them, lithium-ion batteries are preferred as they offer high gravimetric and volumetric energy densities compared to other secondary battery chemistries like lead-acid, nickel-metal hydride, etc. However, the scarcity of lithium reserves throughout the globe motivates researchers to explore other alkali-ion secondary battery chemistries (e.g. sodium-ion) as well. Recent developments in alkali-ion battery technologies prefer the use of alloying-type anodes like tin and antimony due to their low-cost, widespread abundance, and comparatively high lithium and sodium-ion storage capabilities than commercially used intercalation-type graphite anodes. Hence, the objective of this thesis is to develop tin and antimony intermetallic based anodes that can be used to fabricate lithium-ion and sodium-ion full-cells with compatible cathodes. In this thesis work, two variants of alloy nanocomposites namely, tin rich and antimony rich are used.

The first alloy variant consisting of tin rich tin-antimony alloy nanoparticles sandwiched between nitrogen-doped reduced graphene oxide nanosheets is prepared using a microwave-assisted hydrothermal process. Among the two nanocomposite variants tested, the 40 wt% graphene content nanocomposite shows the best electrochemical performance and is able to deliver 540 $mAhg^{-1}$ after 200 cycles at 0.1 Ag^{-1} specific current and a good rate capability performance of 305 $mAhg^{-1}$ at 4.0 Ag^{-1} specific current. The sandwich architecture of the nanocomposite, in conjunction with the Ni foam current collector, restricts the grain growth of the Sn and SnSb phases during repeated cycling, introduces pseudocapacitive properties, and eliminates the generation of any semi-infinite diffusion processes. When coupled with LNMO cathode, the resulting lithium-ion full-cell delivers a nominal working voltage of 4.3 V, an energy density of 421 $Whkg^{-1}$ and is able to retain 86.8% of its initial capacity after cycling at

0.5 C rate for 200 cycles. Under higher C rates, the full-cell delivers an energy density of 279.5 $Whkg^{-1}$ at an 8.0 C rate and recovers 90% of its initial capacity when the rate is lowered. The same tin rich alloy nanocomposite is also tested as an anode in a sodium-ion battery. The sodiation behaviour of the pristine alloy nanoparticles, as suggested by ex-situ XRD analysis, follows a diffusion-controlled charge transfer mechanism. However, the introduction of nitrogen-doped graphene imparts extrinsic pseudocapacitance in the resulting nanocomposite which amplifies the electrochemical performance. The 40 wt% graphene content nanocomposite variant shows the best capacity retention and is able to deliver 480 $mAhg^{-1}$ after 200 cycles at 0.1 Ag^{-1} specific current and a good rate capability performance of 200 $mAhg^{-1}$ at 4.0 Ag^{-1} specific current. When coupled with Fe-PBA cathode, the resulting sodium-ion full-cell delivers a nominal working voltage of 2.5 V, an energy density of 262.5 $Whkg^{-1}$ and is able to retain 85.7% of its initial capacity after cycling at 1.0 C rate for 100 cycles. Under higher C rates, the full-cell delivers an energy density of 125 $Whkg^{-1}$ at an 8.0 C rate and recovers 80% of its initial capacity when the rate is lowered. Cyclic voltammetry and EIS studies reveal that coupling a pseudocapacitive anode with a diffusion-controlled cathode is advantageous in designing high-power sodium-ion full-cells.

The second alloy variant comprising of antimony rich tin-antimony alloy nanorods mixed with nitrogen-doped reduced graphene oxide flakes is also prepared via a microwave-assisted hydrothermal process. The pristine nanorods are initially synthesized from nanoparticle precursors in a microwave-assisted hydrothermal environment using CTAB as a growth control agent and subsequently mixed with nitrogen-doped reduced graphene oxide flakes to prepare the nanocomposite. Detailed TEM and XRD studies reveal that the CTAB molecules preferentially adsorb on the 110 planes of both Sb and SnSb nanoparticles and the microwave-hydrothermal environment forces them to arrange accordingly (110 restricted growth) before undergoing local sintering to generate nanorods. The 40 wt% graphene content nanocomposite variant shows the best capacity retention and is able to deliver 500 $mAhg^{-1}$ after 200 cycles at 0.25 Ag^{-1} specific current and a good rate capability performance of 200 $mAhg^{-1}$ at 4.0 Ag^{-1} specific current. When coupled with LNMO cathode, the resulting lithium-ion full-cell delivers a nominal working voltage of 4.3 V, an energy density of 344 $Whkg^{-1}$ and is able to retain 87.5% of its initial capacity after cycling at 0.5 C rate for 200 cycles. Under higher C rates, the full-cell delivers an energy density of 215 $Whkg^{-1}$ at an 8.0 C rate and recovers 90% of its initial capacity when the rate is lowered. The same antimony rich alloy nanocomposite is also tested as an anode in a sodium-ion battery. The 40 wt% graphene content nanocomposite

variant shows the best capacity retention and is able to deliver 350 $mAhg^{-1}$ after 200 cycles at 0.1 Ag^{-1} specific current and a good rate capability performance of 100 $mAhg^{-1}$ at 4.0 Ag^{-1} specific current. When coupled with Fe-PBA cathode, the resulting sodium-ion full-cell delivers a nominal working voltage of 2.5 V, an energy density of 250 $Whkg^{-1}$ and is able to retain 82.5% of its initial capacity after cycling at 0.33 C rate for 100 cycles. Under higher C rates, the full-cell delivers an energy density of 137.5 $Whkg^{-1}$ at a 4.0 C rate and recovers 87% of its initial capacity when the rate is lowered.

Keywords: Tin; Antimony; Microwave-assisted hydrothermal process; Nitrogen-doped reduced graphene oxide; Ni foam; Anode; LNMO; Prussian blue analog; Cathode; Lithium-ion; Sodium-ion; Half-cell; Full-cell;