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Antimony oxychloride/graphene aerogel composite as anode material for sodium and lithium ion batteries

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ABSTRACT

Herein, we report on the synthesis of phase-pure antimony oxychloride ($Sb_4O_5Cl_2$) microstructures and studies on their electrochemical properties as new and potential anodes for sodium and lithium ion batteries. We demonstrate that pristine $Sb_4O_5Cl_2$ based electrode exhibits promising electrochemical behaviour, with a reversible discharge capacity of 830 mAh g^{-1} for the first cycle when cycled against sodium at a current rate of 30 mA g^{-1}. Further, a composite of graphene aerogel is prepared with $Sb_4O_5Cl_2$ microstructures, which are uniformly anchored on the graphene aerogel matrix ($Sb_4O_5Cl_2$-GA), resulting in interconnected networks which facilitate better charge transfer and effective buffering to alleviate the structural variation of $Sb_4O_5Cl_2$ during cycling. We show that $Sb_4O_5Cl_2$-GA electrode exhibits excellent electrochemical properties with much improved cyclic stability and high rate capability. In addition, $Sb_4O_5Cl_2$-GA delivers excellent performance as anode material for lithium ion batteries, with a reversible capacity of 600 mAh g^{-1} obtained over 50 cycles, at a current rate of 50 mA g^{-1}. The obtained results are promising and demonstrate 3D networked antimony oxychloride/graphene composite as a potential anode material for both lithium and sodium ion batteries.

1. Introduction

With the increase in energy demand and quest for efficient storage devices, lithium-ion batteries (LIBs) have successfully been demonstrated as potential power sources for various applications in portable electronics, transport sector, *etc*. However, with the concerns over limited lithium resources, several other battery chemistries are being explored and sodium-ion battery (SIB) seems to be an ideal alternative to LIB, owing to the abundance of sodium in the earth's crust and similar electrochemical properties to that of lithium [1–3]. There are several challenges ahead to realise the practical implementation of these battery systems. For instance, development of efficient electrode materials for Na-ion battery with higher energy and power densities along with long cycle life still remains a key issue.

Graphite, the anode material used in commercial LIBs, however, is not suitable for sodium ion batteries due to its limited performance on sodium intercalation caused by the larger ionic radius of Na [1]. On the other hand, carbonaceous materials such as hard carbon [2], expanded graphite [3] has been studied as stable anodes for SIBs. Apart from the conventional choices of carbonaceous materials, considerable effort has been devoted to exploring metal oxides [4,5], and intermetallics that have the potential to deliver excellent gravimetric capacities against sodium and lithium [6–8].

Recently Sb based materials have attracted attention owing to their high theoretical capacity against sodium (660 mAh g^{-1}). Sb based materials such as Sb_2O_3 [9,10], Sb/C [11], Sb_2O_4 [12], Sb_2S_3 [13], and Sb based intermetallics such as SnSb [14], Bi-Sb [15] have been studied as promising anode materials for SIBs. Sb based materials typically undergo conversion and alloying reactions with Na, involving multiple electrons [16,17]. Huge volume expansion associated with these materials causes pulverisation and cracking of the material, resulting in poor cycling stability [18]. This motivates further exploration of Sb based materials for Na-ion batteries as an effort to improve their overall electrochemical performance. Recently, Xie et al., studied the electrochemical properties of antimony oxychloride based microrods, wherein the material consisted of a mixed phase of $Sb_4O_5Cl_2$, $Sb_8O_{11}Cl_2$ and Sb_2S_3 [19]. Achieving phase-pure growth of antimony oxychloride plays an important role in determining its electrochemical properties.

Here we demonstrate that pure-phase antimony oxychloride ($Sb_4O_5Cl_2$) microstructures, prepared *via* hydrothermal technique,

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exhibit promising electrochemical performances as potential electrode for both sodium and lithium-ion batteries. Lithium ion intercalation into MOCl (M = Fe,V,Cr,Ti) was first reported by Whittingham [20,21], and recently, other metal oxychlorides such as Vanadium oxychloride [22,23] and Bismuth oxychloride [24] have been explored as electrode material for sodium and lithium ion batteries. $Sb_4O_5Cl_2$ exibits excellent Na-ion storage performance by delivering a high initial reversible capacity of 830 mAh g^{-1}. Further, we prepared $Sb_4O_5Cl_2$-graphene aerogel composite electrode ($Sb_4O_5Cl_2$-GA) *via* low temperature self assembly process, which showed much improved rate capability by retaining a stable capacity of over 200 mAh g^{-1} at 2 A g^{-1} (~3 C; 1 C corresponding to 450 mA g^{-1}). $Sb_4O_5Cl_2$ microstructures, which are uniformly anchored on the graphene aerogel matrix result in interconnected networks which facilitate better charge transfer and effective buffering to alleviate the structural variation of $Sb_4O_5Cl_2$ during cycling. Further, we demonstrate that $Sb_4O_5Cl_2$-GA delivers excellent performance as anode material for lithium ion batteries, with a reversible capacity of 600 mAh g^{-1} obtained over 50 cycles, at a current rate of 50 mA g^{-1}.

2. Experimental section

2.1. Synthesis of $Sb_4O_5Cl_2$ microstructures

$SbCl_3$ (2 mmol) and PVP (315 mg) dissolved in 10 mL of DI water was stirred for 30 min to get a homogenous solution. Appropriate amount of 2M H_2SO_4 was added to the above solution and stirred well to get a uniform solution. The resultant solution was transferred to a Teflon-lined autoclave and was kept at 180 °C for 2 h. The autoclave was allowed to cool down to room temperature and the product was washed several times with ethanol and DI water to remove the impurities.

2.2. Preparation of $Sb_4O_5Cl_2$ -GA

20 mg of GO prepared by modified hummer's method was uniformly dispersed in 10 mL of DI water by ultrasonication for 1 h. 1.5 mL of 2 M ascorbic acid was added to the above solution and sonicated for few sec. The as-synthesized $Sb_4O_5Cl_2$ microstructures were mixed with the above solution by stirring. The solution was kept in an oil bath at 60 °C for 24 h without being disturbed. The black cylindrical aggregate thus formed was washed for several times in DI water. The product was freeze dried for 24 h to obtain $Sb_4O_5Cl_2$-GA.

2.3. Morphological and structural characterization

The surface morphology was examined by using scanning electron microscope (SEM; Nova NanoSEM 450, FEI) and transmission electron microscope (TEM; FEI TECNAI 30 G2 S-TWIN microscope with an accelerating voltage of 300 kV). Structural characterization has been done using X-ray diffraction (XRD) with Cu-K_α radiation within Bragg's angle ranging from 10° to 80° (Emperean, PANalytical XRD system). Thermogravimetric analysis of samples has done in the presence of oxygen using SDT-Q-600, TA Instruments. The porosity characteristics including BET surface area were studied using N_2 adsorption-desorption isotherms measured at 77 K up to a maximum relative pressure of 1 bar, with the Micromeritics 3-Flex surface characterization analyzer.

2.4. Electrochemical characterization

For pristine $Sb_4O_5Cl_2$ samples, the electrodes were prepared by mixing the active material, Super-P and CMC binder (carboxymethyl cellulose) in the weight ratio of 70:20:10. For $Sb_4O_5Cl_2$-GA, slurry was prepared with active material, Super-P and CMC binder in the ratio 80:10:10. The slurry was uniformly coated onto a Cu foil and vacuum dried at 120 °C for 12 h. For the electrochemical studies, galvanostatic charge-discharge measurements on the fabricated electrodes were carried out in a CR2032 type coin cell assembled in an argon filled glove box with moisture and oxygen level maintained at less than 0.1 ppm. 1M $NaClO_4$ in PC (with 10 wt % FEC) was used as the electrolyte and with Na metal as both reference and counter electrodes. Typical mass loading of the active material is 1.5 mg cm^{-2}. Cyclic voltammetry was performed for all the samples in the voltage range between 0.05 and 2 V versus Na/Na^+. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a sinusoidal signal of 10 mV amplitude, between frequencies ranging from 10 mHz to 40 kHz. For lithium ion battery measurements, 1M $LiPF_6$ in EC:DMC (1:1 vol ratio) was used as the electrolyte and all the electrochemical measurements were carried out in the voltage range between 0.01 and 3 V versus Li/Li^+.

3. Results and discussion

$Sb_4O_5Cl_2$ microstructures were synthesized by a simple hydrothermal method. As-synthesized $Sb_4O_5Cl_2$-GA composite is obtained as a black cylindrical aggregate with monoclinic $Sb_4O_5Cl_2$ microstructures trapped inside three dimensionally connected thin reduced graphene oxide sheets (Fig. S1). $Sb_4O_5Cl_2$ microstructures (~4 μm in size) exhibit a unique flower shaped morphology which is formed by the aggregation of $Sb_4O_5Cl_2$ nanoflakes, ~200 nm in size, as shown in Fig. 1A (See Figs. S1A and B for details). Fig. 1C shows the SEM image of $Sb_4O_5Cl_2$-GA composite clearly revealing $Sb_4O_5Cl_2$ microstructures encapsulated within few-layered graphene sheets, forming three dimensionally oriented cross linked networks. Fig. 1B,D represent high resolution TEM (HRTEM) images of $Sb_4O_5Cl_2$ microstructures and $Sb_4O_5Cl_2$-GA composite, respectively, showing an inter planar distance of 0.31 nm corresponding to (002) plane of $Sb_4O_5Cl_2$ [25]. Presence of few-layered graphene surrounding $Sb_4O_5Cl_2$ domains is clearly evident in the HRTEM image (Fig. 1D). X-ray diffraction (XRD) was employed for the structural characterization of materials (Fig. 1E) and XRD patterns clearly indicate all the reflections which are indexed to the monoclinic phase of $Sb_4O_5Cl_2$ (JCPDS No-30-0091) [25].

The graphitic peak at ~26° is not visible in the XRD pattern of $Sb_4O_5Cl_2$-GA, which could be due to high crystallinity of the pristine material [26]. Thermogravimetric analysis (TGA) was performed in a temperature range of 40 °C-1000 °C in presence of oxygen. $Sb_4O_5Cl_2$ remains stable till ~400 °C, beyond which it decomposes releasing $SbCl_3$ gas (Fig. 1F) [27]. This in turn gets converted to Sb_2O_3 phase above 475 °C. An increase in sample weight can be observed above 600 °C due to oxidation of Sb_2O_3 particles. TG curve of $Sb_4O_5Cl_2$-GA shows a slight weight loss around 100 °C due to evaporation of surface absorbed water. Weight loss till 400 °C can be attributed to the elimination of carboxyl groups and surface absorbed moisture [18], as observed for the pure graphene aerogel (Fig. S4A). A drastic weight loss between 400 °C to 600 °C can be attributed to the thermal decomposition of rGO in air, in addition to the decomposition of $Sb_4O_5Cl_2$ and the accompanied phase change of $Sb_4O_5Cl_2$ to Sb_2O_3. A similar weight gain is observed beyond 600 °C, corresponding to the oxidation of Sb_2O_3. $Sb_4O_5Cl_2$-GA showed an altogether different thermal decomposition behaviour when compared to the pristine $Sb_4O_5Cl_2$, indicating better stability of the graphene composite [28,29]. From the TG analysis, the amount of graphene in $Sb_4O_5Cl_2$-GA was estimated to be ~10 wt%.

It has been shown that pH of the reaction mixture is very critical for the controllable synthesis of $Sb_4O_5Cl_2$, which are typically