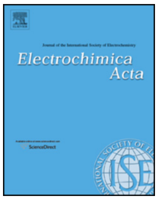
Electrochimica Acta 231 (2017) 247–254

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



Research Paper

High energy lithium ion battery electrode materials; enhanced charge storage via both alloying and insertion processes

Mechthild Lübke[a,b], Dougal Howard[a], Ceilidh F. Armer[b,c], Aleksandra J. Gardecka[a,b], Adrian Lowe[c], M.V. Reddy[d,e], Zhaolin Liu[b], Jawwad A. Darr[a,*,1]

[a] Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK
[b] Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Republic of Singapore
[c] College of Engineering and Computer Science, Australian National University, Canberra, ACT 0200, Australia
[d] Department of Physics, National University of Singapore, Singapore 117542, Republic of Singapore
[e] Department of Materials Science and Engineering, National University of Singapore, Singapore 117576, Republic of Singapore

ARTICLE INFO

Article history:
Received 19 September 2016
Received in revised form 9 February 2017
Accepted 11 February 2017
Available online 16 February 2017

Keywords:
continuous hydrothermal flow synthesis
lithium ion battery
anode
transition metal
alloy

ABSTRACT

A series of nano-sized tin-doped metal oxides of titanium(IV), niobium(V) and vanadium(IV), were directly synthesized using a continuous hydrothermal process and used for further testing without any post-treatments. Each of the as-prepared powders was characterized *via* a range of analytical techniques including powder X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy and Brunauer-Emmett-Teller surface area measurements, as well as being investigated as an electrode material in a lithium-ion coin cell (*vs* lithium metal). All the tin-doped nanomaterials showed higher specific capacities compared to their undoped metal oxide counterparts. The increased charge storage was discussed to originate from the electrochemical activation of the tin dopant as an alloying material. Overall, this work presents a reliable method of combining stable insertion materials with high capacity tin alloying materials under scaled-up conditions.

1. Introduction

Rechargeable lithium-ion batteries represent the dominant energy storage technology in a range of portable devices from smartphones and laptops to cordless power tools. One desirable attribute for a battery in such devices is a high energy density [1]. For high energy batteries, high capacity and low operating potential (*vs* Li/Li$^+$) electrode materials, are desirable for the negative electrode of a lithium-ion battery [2]. There are numerous candidate negative electrode materials in lithium-ion batteries that can be classified as storing charge predominately via insertion/intercalation, pseudocapacitive surface reactions, conversion or alloying processes [3]. Insertion of lithium-ions into 1D or 3D structures (intercalation in between the 2D layers) of an electrode material, can involve relatively small volume changes in some host materials, giving generally high cycle stability and moderate to low specific capacities, *e.g.* graphite = 372 mAh g^{-1}, TiO_2 (0.5 M of lithium-ions per 1 M TiO_2) = 168 mAh g^{-1} and lithium titanate LTO = 175 mAh g^{-1} [3]. TiO_2, Nb_2O_5 and VO_2 have attracted attention as lithium-ion battery negative electrodes, due to their relatively low cost and reasonably high theoretical capacities of 175, 200 and 320 mAh g^{-1}, respectively [4–8].

In a previous report by the authors [7], a mixed phase of VO_2 was cycled in the wide potential range of 0.05 to 3.00 V *vs* Li/Li$^+$ (comparable published literature is usually in the range *ca.* 1.50 to 3.00 V *vs* Li/Li$^+$); the excellent high power performance (*e.g.* specific capacities of 350 mAh g^{-1} at 0.1 A g^{-1} and 95 mAh g^{-1} at 10.0 A g^{-1}, respectively) was suggested to be due to the material displaying (supercapacitor-like) pseudocapacitive charge storage behaviour under these cycling conditions [9–14]. A similar behaviour was found by the authors in further publication for semicrystalline Nb_2O_5 [6]. Cycling nanosized Nb_2O_5 in a wide potential range of 0.05 to 3.00 V *vs* Li/Li$^+$ (comparable published literature is usually in the range of *ca.* 1.00 to 3.00 V *vs* Li/Li$^+$) showed high power performances and additional charge storage at lower potentials, which was largely due to pseudocapacitive charge storage behaviour. In comparison, materials that store charge via conversion and alloying reactions tend to display even

---

[*] Corresponding author at: Christopher Ingold Laboratories, Department of Chemistry, University College London 20 Gordon Street, London, WC1H 0AJ. Tel.:+ +44 0 20 7679 4345; Mobile: +44 0 7941 928875.

E-mail address: j.a.darr@ucl.ac.uk (J.A. Darr).

[1] Research webpages http://www.ucl.me.uk.

http://dx.doi.org/10.1016/j.electacta.2017.02.063
0013-4686/

higher capacities *e.g.* $Fe_2O_3 = 1007\ mAh\ g^{-1}$, $Si = 3579\ mAh\ g^{-1}$, $Sn = 993\ mAh\ g^{-1}$, and $SnO_2 = 782\ mAh\ g^{-1}$ [15], but tend to display poor cycle life at high active loadings, due to extreme volume/structural changes in the active material during cycling, which damages electrode integrity [16,17].

A number of reports in the literature have sought to develop complex or nanocomposite battery electrode materials, which display a combination of different charge storage mechanisms *e.g.* both insertion and conversion/alloying charge storage mechanisms [18,19]. It is envisaged that such materials can provide a balance between moderate structural changes and reasonably high capacities, which should prolong cycle life stability and possibly high power performance.

In a previous report by the authors [20], Sn^{4+} was successfully doped into anatase TiO_2 and the materials were used as a negative electrode material in a lithium-ion half-cell. In the wide potential window of 0.05 to 3.00 V *vs* Li/Li^+, a significant increase in capacity was observed with increased Sn amount (range of 4 to 15 at% Sn with respect to Ti) because of electrochemical activity resulting from the lithium-ion alloying reactions associated with Sn in the material. The following reactions were proposed for some of the electrochemical lithiation/delithiation processes of such insertion and alloying reactions for Sn doped titanias (Eqs. (1)–(4), apply to titania, whilst Eq. (5) is essentially Eq. (2) expressed for niobium or vanadium oxides as will be discussed later) [3,15,21]:

$$xLi^+ + \text{electrolyte} + xe^- \rightarrow \text{SEI}\ (xLi) \quad (1)$$

$$M_yO_z + xLi^+ + xe^- \leftrightarrow Li\ _xM_yO_z\ (0 \leq x \leq 0.5 \text{ for } TiO_2) \quad (2)$$

$$SnO_2\ (\text{doped in } M_yO_z \text{ initially}) + 4\ Li^+ + 4\,e^- \rightarrow Sn + 2\ Li_2O \quad (3)$$

$$Sn + xLi^+ + xe^- \leftrightarrow Li\ _xSn\ (0 \leq x \leq 4.4) \quad (4)$$

$$M_yO_z + xLi^+ + xe^- \leftrightarrow Li\ _xM_yO_z\ (0 \leq x \leq 2{,}1 \text{ for } Nb_2O_5, VO_2) \quad (5)$$

Reaction 1 corresponds to the initial solid electrolyte interphase (SEI) formation during the first and following few cycles. Reaction 2 corresponds to the reversible insertion/deinsertion of lithium-ions into the titania host material. Reaction 4 is the alloying/dealloying reaction of Sn with lithium-ions and this can occur after reaction 3 (formation of metallic Sn and Li_2O). There has been considerable disagreement regarding reaction 3; many researchers support the idea that reaction 3 is irreversible after the first lithiation [22–24]. However, in several electrode materials, higher than expected total reversible lithium-ion charge storage capacities were observed, which suggested partial or fully reversible conversion reactions were likely, *i.e.* the reverse of reaction 3 that would allow SnO_2 to reform during cycling [25–27]. An attempt to confirm this was made by the assistance of ex-situ X-ray photoelectron spectroscopy (XPS) measurements [26,28] and ex-situ high resolution-transmission electron microscopy (HR-TEM) studies [28,29] after the first delithiation step at ca. 3.0 V *vs* Li/Li^+.

Recently, the origin of additional stored capacity for SnO_2 was shown to be a reactive Li_2O layer in the potential range 0.9 to 3.0 V *vs* Li/Li^+ [30]. It was reported that ex-situ TEM measurements were performed at different potentials during cycling, and the highest delithiation activity was observed for $Li_2O/LiOH$ layers with only moderate activity of SnO_x phases. This might be related to the work of Grey et al., who investigated the origin of additional capacity for conversion materials, in this case for RuO_2 [31]. It was shown that the reactivity of lithium hydroxides can provide additional charge storage during the first lithiation, *e.g.* from the reaction for LiOH ($2Li + LiOH \rightarrow Li_2O + LiH$) [31]. The origin of these reactive lithiated layers can be found in the conversion reaction (Eq. (3)) and can also be found in the initial irreversible decomposition of the electrolyte, from which products are adsorbed at the electrode surface (initial formation of LiOH) [32].

In the current study, nanosized $Ti_{0.88}Sn_{0.12}O_2$, $Nb_{1.66}Sn_{0.34}O_5$ and $V_{0.8}Sn_{0.2}O_2$ powders were directly synthesized using a pilot scale continuous hydrothermal flow synthesis (CHFS) reactor and the freeze-dried nano-powder was investigated as potential negative electrode materials for lithium-ion batteries (without any further processing or heat-treatment of the powder whatsoever). The CHFS process is described later, and can be thought of as a rapid and continuous process that mixes supercritical water (in an engineered mixer) with appropriate metal salts in ambient temperature water, to instantly form nanoparticles of the corresponding metal oxides (via a rapid hydrolysis and dehydration reaction) which are collected downstream after in-flow cooling in the process. There are many negative electrode materials for lithium-ion batteries that have been made *via* CHFS type processes, including TiO_2 [8,20], Fe_3O_4 [33], $Li_4Ti_5O_{12}$ [34], semicrystalline Nb_2O_5 [6], VO_2 [7], and layered titanates [35]. The main advantages of using CHFS processes is that materials with small dimensions and narrow size distributions are attainable, which can improve charge transfer/transport processes. The synthesis process also allows very homogenous doping, which can alter the electronic and physical properties of the material under cycling [36]. Different from our previous studies for TiO_2, Nb_2O_5 and VO_2 [6,7,20], where a lab scale reactor was used (production rate $<7\ g\ h^{-1}$), the materials were synthesized herein using a pilot scale CHFS reactor (used production rate up to $200\ g\ h^{-1}$ but process capability of 6 Kg per day has been demonstrated for other materials [36]). The nano-sized doped-materials were all investigated electrochemically *via* potentiodynamic and galvanostatic methods in order to assess their performance as stable high energy negative electrode materials. The main aim of the work was to identify if doping high amounts of Sn into different nanosized insertion materials, could increase the specific capacity (due to electrochemical alloying reactions of the dopant at lower potentials vs Li/Li^+).

2. Experimental

2.1. Materials

0.25 M Titanium oxysulphate hydrate ($TiOSO_4$: 29 wt% TiO_2 and 17 wt% H_2SO_4, Sigma Aldrich, Steinheim, Germany) and 0.325 M base potassium hydroxide (KOH, >85%, Fisher Scientific, Loughborough, UK) were used as precursors for titanium oxide synthesis. 0.1 M Ammonium niobate(V) oxalate hydrate (Sigma-Aldrich, >99.99%, Steinheim, Germany) was used for the synthesis of the niobium oxides (no base added). Ammonium metavanadate (0.1 M, >99%, Sigma Aldrich, Steinheim, Germany) was mixed with oxalic acid dehydrate (0.2 M, >99%, Sigma Aldrich, Steinheim, Germany) until the color changed from yellow to dark blue and then used as a V^{4+} precursor solution for the vanadium oxides synthesis [37], (no base added). Tin(IV) sulphate (97%, Acros Organics, Geel, Belgium) was used as a Sn^{4+} precursor in concentrations of 0.055 M, 0.02 M and 0.013 M for the synthesis of $Ti_{0.88}Sn_{0.12}O_2$, $Nb_{1.66}Sn_{0.34}O_5$ and $V_{0.8}Sn_{0.2}O_2$, respectively.

2.2. General synthesis process

Nanosized transition metal oxides were synthesized using a pilot-scale continuous hydrothermal flow synthesis (CHFS) reactor utilizing a confined jet mixer (CJM), the design of which is fully