Materials Letters 140 (2015) 115–118

Contents lists available at ScienceDirect

Materials Letters

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

Facile one pot molten salt synthesis of nano $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In)

M.V. Reddy [a,b,*], V.H. Khai [a,c], B.V.R. Chowdari [a]

[a] Department of Physics, Solid State Ionics/Advanced Batteries Lab, National University of Singapore, Singapore 117542, Singapore
[b] Department of Materials Science & Engineering, National University of Singapore, Singapore 117546, Singapore
[c] Anglo-Chinese School (Independent), Singapore 139650, Singapore

ARTICLE INFO

Article history:
Received 28 July 2014
Accepted 25 October 2014
Available online 4 November 2014

Keywords:
Molten salt synthesis
Ceramic oxides
X-ray diffraction
Scanning electron microscope
Surface area
Energy storage

ABSTRACT

Novel mixed metal oxides, $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) were successfully prepared for the first time using the molten salt method (MSM) at low temperature. Compounds were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM) and Brunauer, Emmett and Teller surface area technique. $(M_{1/2}Sb_{1/2}Sn)O_4$ has significantly large specific surface area of 694, 210 and 81 $m^2 g^{-1}$ for M=V, Fe and In respectively. Preliminary energy storage studies were carried out under identical conditions and electrochemical reaction mechanism involving alloying–de-alloying reactions of Sn, In and Sb with Li using M=V, Fe as matrix elements were proposed.

1. Introduction

Recent synthesis of nanomaterials has attracted major attention from the material research community due its interesting physical, chemical, electrochemical and biomedical properties [1–8]. Among different applications, energy storage [9] is one important area, with many advances on nanostructured materials for Li-storage being made recently. Sn-based oxides are one of the attractive candidates studied in different applications [9,10]. Very recently, mixed oxides, $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) have been prepared using the solid state-reaction method at high temperature of about 700 °C, 1150 °C and 800 °C respectively [11,12]. Their reaction mechanism was proposed based on alloying–de-alloying reaction of Sb, In and Sn with Li were proposed [9]. The theoretical reversible capacity of the alloy, $Li_{4.4}Sn$ is as high as 993 mA h g^{-1} in comparison to the theoretical value of 372 mA h g^{-1} for commercial graphite. In these metal composites, the initial reaction with Li-metal will give rise to the respective elements, which will subsequently form the alloy of $Li_{4.4}Sn$, Li_3Sb and In_3Sb respectively [9,13], while the remaining metal (M=In, Fe) or metal oxide (VO) act as matrix element for Li-cycling process of the electrodes.

Despite the promising Li-cycling properties, the compounds prepared using the solid state-reaction method appeared to have low specific surface area. For novel functional properties like catalytic, sensing, photocatalytic, conversion and storage properties, high surface area materials are needed. There is urgent need for novel synthesis of the above materials that can produce high surface area and phase pure form. In this aspect, one pot molten salt synthetic approach is taken for the preparation of mixed metal oxides $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) at low temperature of 280 °C using the molten salt method, something that is first of its kind. Furthermore, the produced material showed a single phase-tetragonal type crystal structure and high specific surface area of 694 $m^2 g^{-1}$ (M=V).

2. Experimental

Preparation: The compounds $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) were prepared by the molten salt method. Stoichiometric ratios of respective metal salts (0.5 $MVOSO_4 \cdot 5\,H_2O$, 0.5 M $FeSO_4 \cdot 7\,H_2O$ and 0.5 M $In(NO_3)$) are mixed with 0.5 M Antimony Sulfide (Sb_2S_3), 1 M Tin Chloride ($SnCl_2 4\,H_2O$) and the mixture 8.8 M $LiNO_3$–1.2 M LiCl in molten salt at 280 °C for 3 h in air in a box furnace heating rate 3 C min^{-1} and cooled to room temperature at heating rate of 5 °C min^{-1}. The resulting mixture of produced

* Corresponding author at: Department of Physics, Solid State Ionics/Advanced Batteries Lab, National University of Singapore, Singapore 117542, Singapore. Tel.: +65 65162607; fax: +65 67776126.
E-mail addresses: msemvvr@nus.edu.sg, phymvvr@nus.edu.sg, reddymvvr@gmail.com (M.V. Reddy).

http://dx.doi.org/10.1016/j.matlet.2014.10.145
0167-577X/

Table 1
Color, lattice parameter values, BET surface area and density values of $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe and In).

Parameter	$(V_{1/2}Sb_{1/2}Sn)O_4$
Color	Light yellowish green
Lattice parameter (Å)	a=4.718 (5) c=3.169 (4)
Crystal size (nm)	3.7
BET surface area ($m^2\ g^{-1}$)	694.59
Pore volume ($cm^3\ g^{-1}$)	0.385
Average pore diameter (nm)	2.22
Density ($g\ cm^{-3}$)	5.0076 (8)
	$(Fe_{1/2}Sb_{1/2}Sn)O_4$
Color	Light reddish brown
Lattice parameter (Å)	a=4.645(5), c=3.149(4)
Crystal size (nm)	2.9
BET surface area ($m^2\ g^{-1}$)	210.4
Pore volume ($cm^3\ g^{-1}$)	0.134
Average pore diameter (nm)	2.54
Density ($g\ cm^{-3}$)	3.7340 (5)
	$(In_{1/2}Sb_{1/2}Sn)O_4$
Color	Grayish white
Lattice parameter (Å)	a=4.757(5), c=3.192(4)
Crystal size (nm)	4.8
BET surface area ($m^2\ g^{-1}$)	80.8
Pore volume ($cm^3\ g^{-1}$)	0.055
Average pore diameter (nm)	2.75
Density ($g\ cm^{-3}$)	4.6303(5)

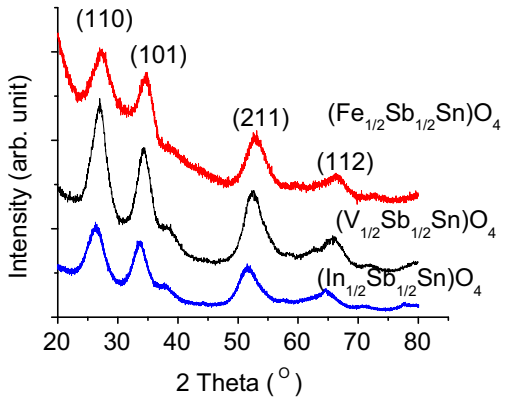

Fig. 1. Powder X-ray diffraction (XRD) patterns of $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) Cu-Kα radiation.

insoluble compound and remaining soluble reactants of excess Li-salts were washed with excess de-ionized water. It was then mixed thoroughly using a magnetic stirrer, filtered using a vacuum pump and dried in a vacuum oven at 90 °C for 12 h.

Fabrication of coin cell: Prepared materials $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) are mixed with Super P carbon black and binder (Kynar 2801) in the weight ratio 70:15:15 using N-methyl pyrrolidinone (NMP) as the solvent and etched Cu-foil acts as a current collector. Coin-type cells of size CR2016 were fabricated in a glove box. Li metal was used as counter and reference electrode and solution of 1 M $LiPF_6$ in ethylene carbonate (EC)+diethyl carbonate (DEC) (1:1 v/v) as the electrolyte with a glass fiber membrane as the separator. Further details on cell fabrication can be found in other reported data [14,15].

Characterization: The powder X-ray diffraction (XRD) patterns taken and they were refined using TOPAS software version 3.1. The morphology was examined by scanning electron microscopy. The Brunauer, Emmett and Teller (BET) technique was used to measure the surface area. Galvanostatic cycling was carried out in the range 0.005–1.0 V vs. Li at current rate of 60 mA g^{-1} using the Bitrode battery tester [16].

3. Results and discussion

Molten salt method is one of the facile low temperature synthesis approach to prepare nano mixed oxides $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) and other metal oxides [15,17,18]. In this process respective metal salts ($VOSO_4 \cdot 5\ H_2O$, $FeSO_4 \cdot 7\ H_2O$ and $In(NO_3)$), Antimony Sulfide (Sb_2S_3) and Tin Chloride ($SnCl_2 4H_2O$) were nicely dissolved at molten salt, 0.18 $MLiNO_3$:0.12 MLiCl. Here $LiNO_3$ acts a good oxidizer, LiCl act as a mineralizing agent, and it slightly improves the crystallinity of the sample. The formation of mixed oxides is determined by the X-ray diffraction technique and the color of the obtained compounds are shown in Table 1.

The powder X-ray diffraction (XRD) patterns of all materials are shown in Fig. 1. Rietveld refinement of the XRD data identifies single phase for all compounds (M=V, Fe, In) and a structure corresponds to tetragonal type structure and lattice parameter values of the compounds are shown in Table 1. The BET surface area values of $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=V, Fe, In) are also given in Table 1. Samples prepared using the molten salt method have remarkably high surface area when compared to those prepared by the solid state method [11,12] (M=V; M=In; and M=Fe). The average crystallite sizes of all compounds are in the range, 3–5 nm, which is in good agreement with broad (hkl) lines observed in the XRD pattern. This is supported by their SEM images shown in Fig. 2. The SEM photographs indicated that nano-sized agglomerates formed by the shown porous compounds are about 10–20 nm. The isotherm data of the three compounds obtained from the BET test is shown in Fig. 3. It shows porous structures that are responsible for the high specific surface area of the compounds and the isotherms are similar to type II.

The galvanostatic charge–discharge profile of $(M_{1/2}Sb_{1/2}Sn)O_4$ (M=In, Fe, In) at low current density (60 mA g^{-1}) and low voltage range (0.005–0.3 V vs. Li) is presented in Fig. 4. It is seen that for $(V_{1/2}Sb_{1/2}Sn)O_4$ and $(In_{1/2}Sb_{1/2}Sn)O_4$, the first discharge profile displays no clear voltage plateau regions due to nanosize nature of the materials (Fig. 1), which indicates that the processes of formation of Sn and Sb metal nano-particles, and subsequent alloy formation with Li-metal overlap each other. The reaction mechanism proposed is similar to what has been previously reported [11,12]. $(Fe_{1/2}Sb_{1/2}Sn)O_4$ however shows a main voltage plateau at ~1.25–1.3 V and a small voltage plateau at ~0.55–0.60 V. This result is also very similar to that of the ballmilled nano-sized $(Fe_{1/2}Sb_{1/2}Sn)O_4$ [12]. At the end of the main plateau, a capacity of 420 mA h g^{-1} is reached.

The first discharge total capacity is 1755 mA h g^{-1}, 1454 mA h g^{-1} and 1395 mA h g^{-1} for M=V, Fe and In respectively. In all three cases, the subsequent charge and discharge cycles overlap well, indicating good cyclability and capacity retention. The capacity vs. cycle number plots are shown in Fig. 4d, which shows very stable capacity from the 5th cycle upto 48th, 52nd and 60th cycle with capacity fading of only 5% (10–48th cycle), 18.2% (10–52nd cycle) and 18 (10–60th cycle) for M=V, Fe and In respectively. On the last cycle, the cells were able to retain a capacity of 355, 147 and 253 mA h g^{-1} respectively. During the first discharge cycle, the excessive formation of the