Nanostructured Metal Oxides for Anodes of Li-Ion Rechargeable Batteries

Ming Au* and Thad Adams

Savannah River National Laboratory, Aiken, SC, USA

Abstract

The aligned nanorods of Co_3O_4 and nanoporous hollow spheres (NHS) of SnO_2 and Mn_2O_3 were investigated as the anodes for Li-ion rechargeable batteries. The Co_3O_4 nanorods demonstrated 1433 mAh/g reversible capacity. The NHS of SnO_2 and Mn_2O_3 delivered 400 mAh/g and 250 mAh/g capacities respectively in multiple galvonastatic discharge-charge cycles. It was found that high capacity of NHS of metal oxides is sustainable attributed to their unique structure that maintains material integrity during cycling. The nanostructured metal oxides exhibit great potential as the new anode materials for Li-ion rechargeable batteries with high energy density, low cost and inherent safety.

1. Introduction

Recently, the plug-in hybrid or electric vehicles are proposed as the near term solution for energy independence and clean environment transportation. The lighter, cheaper and safer Li-ion batteries are the key for migration from petroleum propulsion to electrification. The theoretic capacity of carbon intercalation anodes currently used in Li-ion rechargeable batteries is limited to 372 mAh/g [1]. The new anode materials that can meet major criteria such as high energy density, long cycling life, low cost and safety will change the whole landscape of Li-ion rechargeable batteries. A number of metals have been investigated for next generation of high capacity anodes [2-10]. However, the large volume expansion (300-400%) during metal lithiation causes material pulverization resulting in rapid decrease of initial high capacity. In other hand, the volume of the most metal oxides shrink slightly during lithium conversion expansion. For example, the volumes of Co_3O_4 and Mn_2O_3 are reduced 87% and 94% after conversions of $Co_3O_4+8Li \rightarrow 3Co+4Li_2O$ and $Mn_2O_3+6Li \rightarrow 2Mn+3Li_2O$. Although the theoretic energy densities of the metal oxides are generally not as high as metals, they have the inherent edge to deliver sustainable high capacity if their structures are finely tuned.

Table.1 The candidates of anode materials for Li-ion rechargeable batteries

Anode Materials	C	Al	Si	Sn	SnO_2	Co_3O_4	Mn_2O_3
Lithiated phase	LiC_6	Li_9Al_4	$Li_{21}Si_5$	$Li_{17}Sn_4$	Li_2O/Sn (Li_2O/SnO)	Li_2O/Co (Li_2O/CoO)	Li_2O/Mn (Li_2O/Mn)
Theoretic specific capacity (mAh/g)	372	2235	4010	959	711 (356)	890 (223)	1017 (339)
Theoretic volumetric capacity (mAh/cm3)	833	6035	9340	7000	4941	5438	4577
Volume changes (%)	12	238	297	257	51	-87	-94

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* Corresponding author: ming.au@srnl.doe.gov, 803-507-8547

The aligned nanorods and hollow microspheres of metal oxides were synthesized for various applications such as gas absorption [11], magnetic materials [12], gas sensors [13], photocatalysis [14], capacitors [15] and batteries [16,17]. To assess their potentials for Li-ion rechargeable batteries application, the Co_3O_4 nanorods and hollow nanoporous spheres of SnO_2 and Mn_2O_3 were investigated.

2. Experimental

A thin film of Co_3O_4 nanorods (NRs) were grown on a titanium substrate (10 x 40 x 1 mm) and the hollow nanoporous spheres (HNSs) of SnO_2 and Mn_2O_3 were synthesized by hydrothermal processes as reported by literature [15,17,18]. The morphology and structure of Co_3O_4 NR and HNSs of SnO_2 and Mn_2O_3 were characterized by Hatichi C430 Scanning Electron Microscope (SEM) and Panalytical X'Pert Pro X-ray diffractometer (XRD) respectively.

A half cell of Li/Co_3O_4 NRs was constructed in VAC argon filled glove box. The Co_3O_4 NR strip and a Li foil (Aldrich) were inserted in the cell as the anode and cathode respectively. The 1M $LiPF_6$ in PC/DMC (Propylene Carbonate and Dimethyl Carbonate) was purchased from Ferro and used as the electrolyte. Princeton Applied Physics' VersaSTAT-3 was used for measurement of electrochemical properties of the new anodes. The galvanic charge-discharge was carried out at 700 mA/g from 0.01V to 3.00 V. Cyclic voltammetry (CV) was measured at 0.1mV/s from 0.01 V to 3.00 V.

The 20mm Li/SnO_2 and Li/Mn_2O_3 coin cells were fabricated in the argon filled glove box. The anodes were made by 70% of active materials (SnO_2 and Mn_2O_3), 20% acetylene carbon black and 10% polyvinylidene fluoride (PVdF) in typical slurry-pasting-baking process. The Celgard 200 polymer membranes were used as the separators. The 1M $LiPF_6$ in PC/DMC was used as the electrolyte. CV was measured at 0.5mV/s from 0.01 V to 1.50 V. The galvanic charge-discharge cycles were carried out at 500 mA/g from 0.01V to 1.50 V.

After 20 and 100 cycles, the anodes were taken out of the cell for SEM, XRD and XPS characterization.

3. Results and Discussion

3.1. Co_3O_4 nanorods

Co_3O_4 nanorods were grown on Ti sybstrate by hydrothermal process and used as the anode directly. XRD confirmed the formation of Co_3O_4 (Fig.1). SEM shows that the Co_3O_4 thin film consists of hollow nanorods (NR) with average diameter of 70 nm and length of 200 nm (Fig.2). Most of NR were perpendicularly grown from Ti substrate with hollow channels open to outside. This morphologic feature may facilitate shuttling of Li ions.

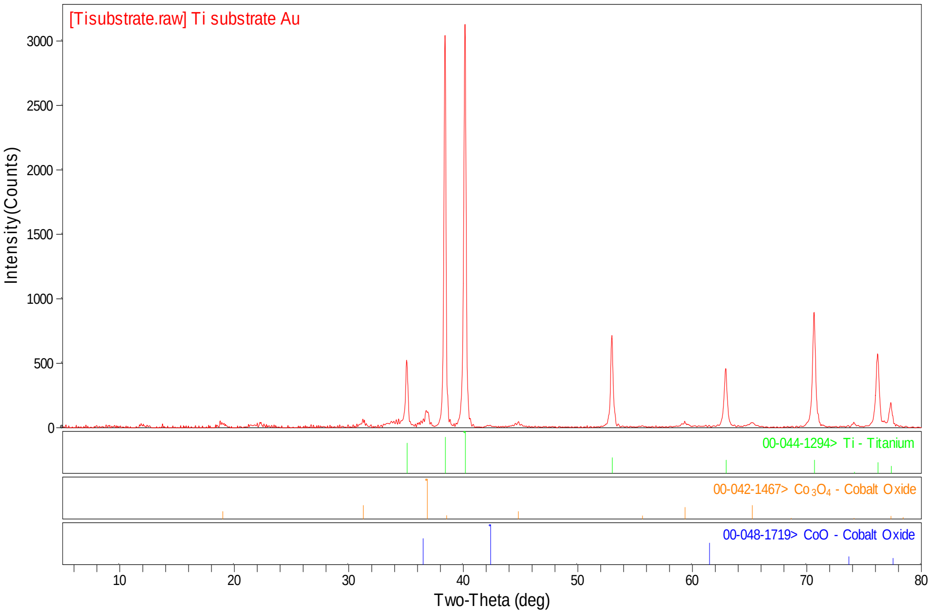

Fig.1 XRD of Co_3O_4 thin film on Ti substrate

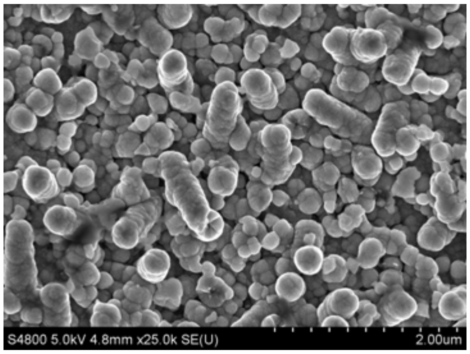

Fig.2(a) Hollow NRs of Co_3O_4 Ti substrate (x10,000)

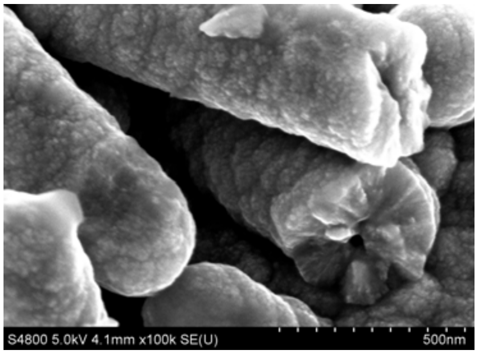

Fig.2(b) Hollow NRs of Co_3O_4 on Ti substrate (x100,000)

The first three discharge- charge cycles of Co_3O_4 NRs anode are shown in Fig.3. The Co_3O_4 NRs anode demonstrated 2484 mAh/g of discharge capacity from 2.7 V to 0.01 V and was recharged to 3 V with 1433 mAh/g capacity in the first cycle. The reversible capacity of Co_3O_4 NRs was five times higher than the carbon anode (372 mAh/g). Although it shows some of promises, the capacity gradually decreased in the following cycles (Fig.4). After 50 cycles, the capacity was reduced to 60 mAh/g (Fig.5). SEM observation shows that the most hollow nanorods were destructed to the fragments and lost electric contact with current collectors after 50 cycles (Fig,6). It is clear that to sustain high capacity, the metal oxides have to maintain their structural integrity during cyclic conversion and recovery.

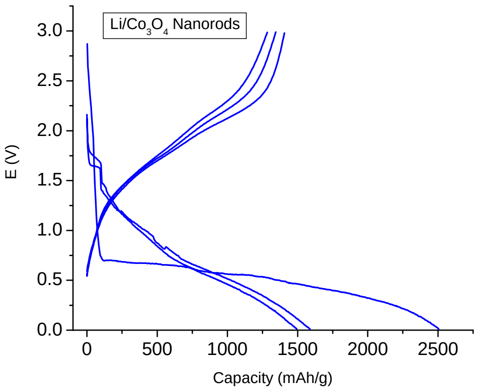

Fig.3 The galvanic discharge-charge cycles of Li/ Co_3O_4 NR cell

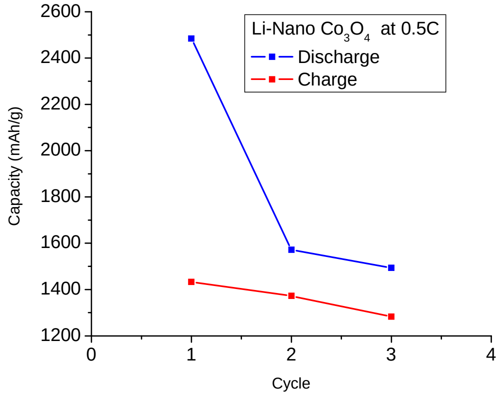

Fig.4 The capacity decrease of Li/Co_3O_4 NR cell Co_3O_4 NR cell

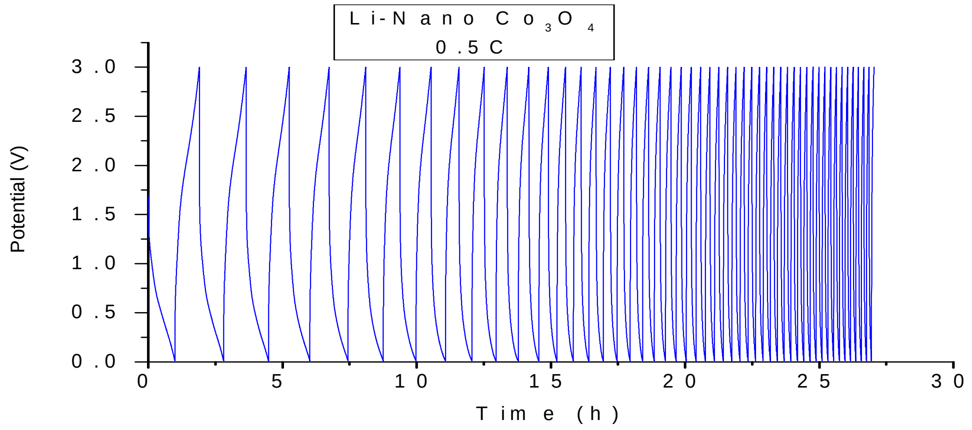

Fig.5 Fifty cycles of charge-discharge of Li/Co_3O_4 NR cell

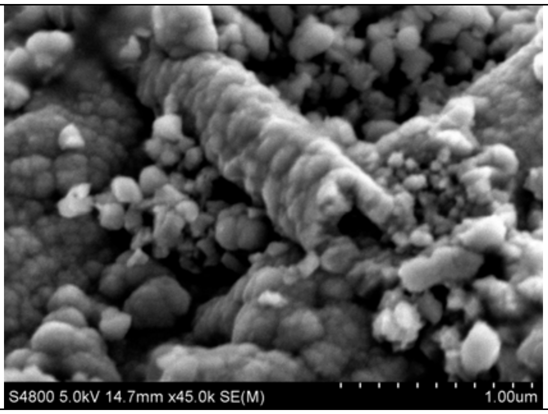

Fig.6 The destruction of Co_3O_4 NR after 50 cycles

3.2 SnO_2 nanoporous multilayered hollow spheres (NMHS)

From capacity fading of Co_3O_4 NR, it is recognizes that the microspheres may be robust in terms of maintaining structural integrity. The microspheres of SnO_2 were produced by hydrothermal processes. XRD confirmed the formation of SnO_2 (Fig.7). SEM show that SnO_2 spheres were constructed by great number of nanoparticles (80-100 nm). They have multilayered porous walls and hollow cores (Fig.8). The average diameter and wall thickness are 3 μm and 300 nm respectively. BET measured the average pore size is 25 nm.

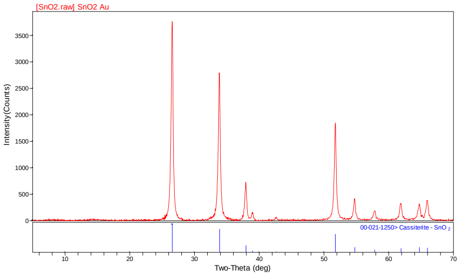

Fig.7 XRD of SnO_2 nanoporous spheres

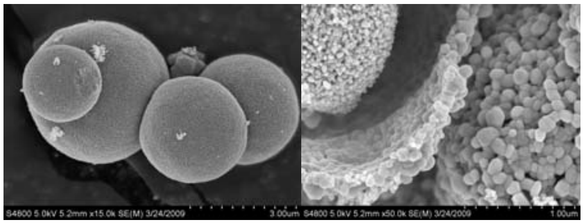

Fig.8 SEM image of SnO_2 nanoporous multilayered hollow spheres (left X15,000, right X50,000)

The 20 mm coin batteries made by Li cathodes and SnO_2 NMHS anodes were evaluated for their electrochemical properties. The voltammetry shows that the series redox reactions took place at 0.45 0.9V and 1.1 V in the respectively (Fig.9). The literature suggested the redox is the SnO_2 conversion such as $SnO_2 + 4Li + 4e^- \rightarrow 2Li_2O + Sn$ [19]. The SnO_2 anode exhibited large capacity as 745 mAh/g in the first discharge (Fig.10), which is close to theoretic capacity of 711 mAh/g. However, it is not reproducible due to irreversible SnO_2 conversion. The redox reaction occurred at 0.75V and 0.45 V in the first charge, not at 0.9V and 1.1 V as the first diacharge shown (Fig.9). It is proposed and verified that the charge is the alloying process as $xSn + Li \leftrightarrow LiSn_x$ [20,21]. The allying process produces several phases of Li-Sn alloys corresponding to the multiple redox peaks appeared in CV. After the first discharge, the reversible electrochemical reactions will be alloying and dealloying of Li and Sn as $xSn + Li \leftrightarrow LiSn_x$.

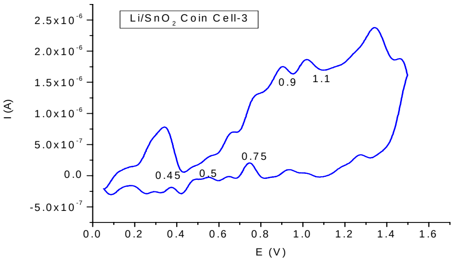

Fig. 9 The cyclic Voltammogram (CV) of Li/SnO_2 cell

The coin cell of Li/SnO_2 NMHS was evaluated in galvonastatic charge-discharge cycles. It demonstrated 745 mAh/g capacity in the first discharge and 400 mAh/g capacity in the following cycles (Fig.10). After 50 cycles, the coin cell was disassembled and the SnO_2 NMHS anode was examined under SEM. It is exiting to see the SnO_2 NMHS maintaining their integrity (Fig.11). The SnO_2 is still in sphery shape and the pores filled with Li metals (dark spots). It is prove that concept that nanopores on the wall provide pathway for Li^+ shuttling and the hollow cores of NMHS accommodate the volume expansion of SnO_2 conversion.

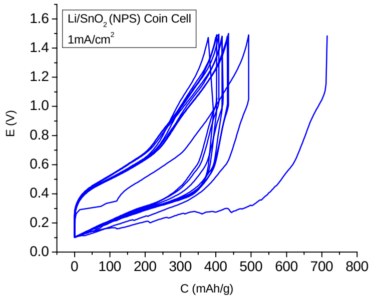

Fig.10 The charge-discharge cycles of Li-ion battery with SnO_2 anode

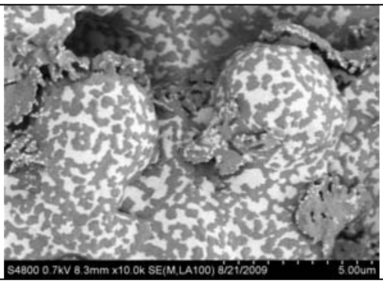

Fig.11 SEM image of SnO_2 anode after 50 cycles. SnO_2 maintains its sphery shape. The dark spots are the pores filled by lithium (X10,000)

3.3 Mn_2O_2 nanoporous hollow spheres (NHS)

The nanoporous hollow spheres of SnO_2 were produced by hydrothermal processes. XRD confirmed the formation of Mn_2O_3 with impurities of Mn_3O_4 and $Na_2Mn_5O_{10}$ (Fig.12). SEM shows that Mn_2O_3 spheres have maze-like structure with porous wall. The average diameter of the spheres and the pore size are about 2 μm and 120 nm (Fig.13).

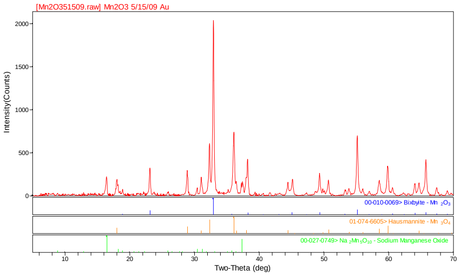

Fig.12 XRD of Mn_2O_3 NHS

Fig.13 SEM image of Mn_2O_3 NHS

The cyclic voltammogram of 20 mm coin cells made by Li cathode and Mn_2O_3 NHS anode shows the two redox reactions occurring at 0.75 v and 1.25 V respectively (Fig.14). Differing with SnO_2, the second CV is exactly same as the first one. It implies the mechanism of Li redox is not same as in Li-SnO_2 system. Since Li can not form alloys with Mn, the electrochemical process would be Mn_2O_3 conversion suggested as (1) $Mn_2O_3 + 2Li \leftrightarrow 2MnO + Li_2O$ (339 mAh/g) or (2) $Mn_2O_3 + 6Li \leftrightarrow 2Mn + 3Li_2O$ (1018 mAh/g).

The galvonastatic discharge-charge cycles show that the Li/Mn_2O_3 cell demonstrated 450 mAh/g capacity in the first discharge. After then, the cell maintained 200 mAh/g capacities in following cycles (Fig.15). The experimental data supported the hypothesis of the conversion (1). It is possible that a partial conversion (2) also took place in the first discharge resulting in the exceed capacity (450 mAh/g) than theoretic prediction (339 mAh/g). The multiple cycles and morphology observation are underway. We will report later.

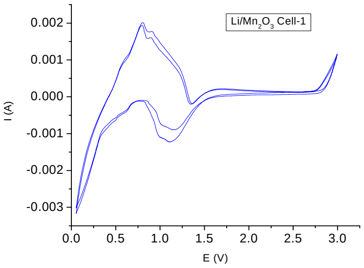

Fig.14 The cyclic voltagram of Li-ion battery with Mn_2O_3 anode

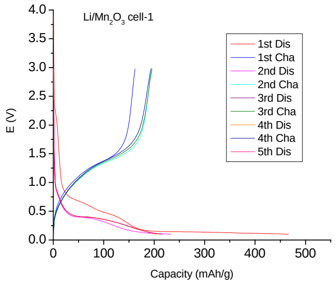

Fig.15 The charge-discharge cycles of Li-ion battery with Mn_2O_3 anode

4. Conclusions

The aligned nanorods of Co_3O_4 and nanoporous hollow spheres (NHS) of SnO_2 and Mn_2O_3 were investigated as the anodes for Li-ion rechargeable batteries. The Co_3O_4 nanorods demonstrated 1433 mAh/g capacity in first three cycles. The high capacity decreased to 60 mAh/g in 50 cycles. One of the reasons is the instability of the structure of the free-standing nanorods. The anodes made by nanoporous hollow spheres (NHS) of SnO_2 and Mn_2O_3 delivered 400 mAh/g and 250 mAh/g capacities respectively in multiple discharge-charge cycles. It was found that the sustainable high capacity of NHS of metal oxides is attributed robust material integrity during cycling. The nanostructured metal oxides exhibit great potential as the new anode materials for Li-ion rechargeable batteries with high energy density, low cost and inherent safety.

Acknowledgements

This work is financially supported by Savannah River National Laboratory LDRD program. Savannah River National Laboratory is operated by Savannah River Nuclear Solution for US Department of Energy under contract DE-AC09-08SR22470.

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