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Synthesis and properties of Ti–O based nanowires

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ABSTRACT

$Ti_6Na_2O_{13}\cdot nH_2O$ and $Ti_6Na_2O_{13}$ nanowires were synthesized by a hydrothermal method. The synthesized $Ti_6Na_2O_{13}$ nanowires were used as anode materials for Li-ion cells to examine Li-storage property. The preliminary result shows that this material exhibited a discharge capacity of 1635 mAh/g at first cycle and >1050 mAh/g after second cycle. The $Ti_6Na_2O_{13}$ nanowire electrode also showed good property retention upon cycling.

1. Introduction

Titanium oxide based nanostructure materials such as TiO_2 nanomaterials are important transition metal oxides for many potential applications in a semiconductor photocatalyst, a catalyst support, sensors, materials for solar energy conversion, etc. In particular, one-dimensional (1-D) nano-sized materials can have novel properties for many applications due to their high specific surface area and unique structures. They have interesting properties which are not expected in conventional microcrystalline powders or bulk nanocrystalline materials [1–5]. Various methods have been reported to synthesize 1-D nanomaterials [6–9]. Among them, solution-based methods such as hydrothermal or solvothermal synthesis are advantageous over other vapour- or solid-based methods due to its ability of scaled-up to produce large quantities with high quality nanowires [10–12]. In particular, some of the alkali titanate nanowires are considered as promising materials for energy-storage such as hydrogen or Li-ion storage.

In the present work, we examined the electrochemical properties of $Ti_6Na_2O_{13}\cdot nH_2O$ and $Ti_6Na_2O_{13}$ nanowires which were prepared by a hydrothermal method. The synthesized nanowires were used as anode materials for Li-ion cells to examine Li-storage property.

2. Experimental procedure

Ti–Na–O nanowires were produced by a hydrothermal process which is similar to previously reported method by Zhao et al. [12]. Ti powders (99.9%, 40 μm) were put into an aqueous solution of 10 M NaOH and H_2O_2 (10:1). The solution was put into a Teflon-sealed mini-autoclave. The hydrothermal reaction was carried out by heating the autoclave at 200 °C for 24 h. The resulting solid products were isolated by centrifugal separation, and washed with de-ionized water and ethanol for three times, followed by drying at 100 °C for an hour. A portion of the synthesized products was further heat-treated at 500 °C for an hour in air.

The electrochemical evaluation of the synthesized nanowires was examined by assembling CR2032 coin cells. The electrodes were made by dispersing 80 wt.% nanowires, 15 wt.% carbon black and 7 wt.% polyvinylidene fluoride (PVDF) binder in *n*-methyl pyrrolidone (NMP) solvent to form the slurry. The slurry was then spread onto a Cu foil. The coated electrodes were dried in a vacuum oven under a vacuum pressure of 30 Torr at 120 °C for 12 h. The electrodes were then pressed at a pressure of 1200 kg/cm^2. The cells were assembled in an argon filled glove-box using lithium metal foil as the counter electrode. The electrolyte was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK, Germany). The cells were galvanostatically charged and discharged over a voltage range of 0–3.0 V. Cyclic voltammetry (CV) measurements were performed using an EG&G Scanning Potentiostat (Model 362) at a scanning rate of 0.1 mV/s.

3. Results and discussion

Fig. 1a shows field-emission SEM images of products which were formed after hydrothermal reaction at 200 °C for 24 h. Straight nanowires with a diameter of 20–50 nm formed during the hydrothermal reaction. The length of the nanowires was several hundred micrometers with high aspect ratio. A subsequent heat-treatment at 500 °C for an hour in air did not alter the morphology of the nanowires (Fig. 1b). TEM examination shows that the products are nanowires rather than nanotubes with internal hollow. The

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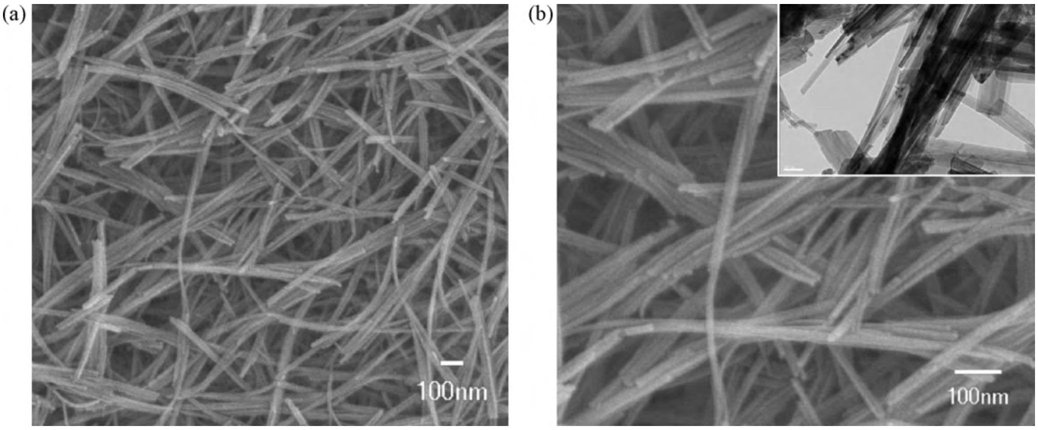

Fig. 1. SEM images of Ti–Na–O nanowires, (a) after hydrothermal process and (b) after subsequent heat-treatment at 500 °C for 1 h in air (inset: TEM image of b).

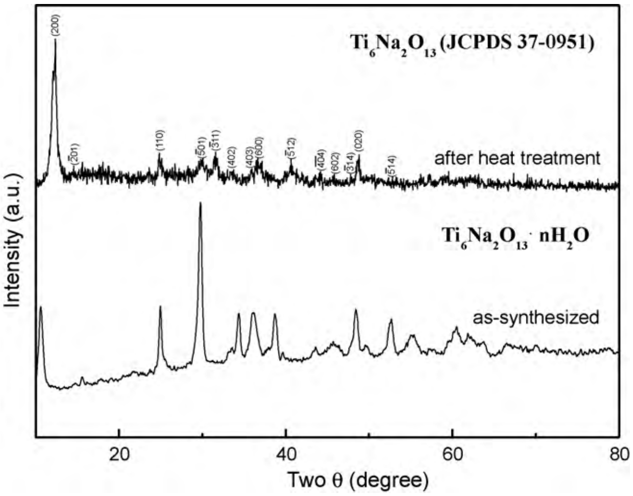

Fig. 2. X-ray diffraction patterns of Ti–Na–O nanowires, (a) after hydrothermal process and (b) after subsequent heat-treatment at 500 °C for 1 h in air.

results of X-ray diffraction indicated that the products formed after the hydrothermal reaction and the subsequent heat-treatment are $Ti_6Na_2O_{13}\cdot nH_2O$ and $Ti_6Na_2O_{13}$, respectively (Fig. 2). In the latter case, all diffracted peaks are indexed to $Ti_6Na_2O_{13}$, and no other impurity phase was detected.

The electrochemical properties of $Ti_6Na_2O_{13}$ nanowires as anodes in Li-ion cells were tested via cyclic voltammetry (CV) measurements (Fig. 3). The cycling and CV testing were conducted over the voltage range of 0.01–3.0 V versus a Li/Li$^+$ counter electrode. There exist two reduction peaks at around 0.7 and 1.4 V during the lithium insertion process, and one oxidation peaks at 1.4 V during the lithium extraction process. The first redox peaks on the CV curve for $Ti_6Na_2O_{13}$ nanowire electrode might be related to the formation of a SEI film (solid electrolyte interface) on the surface of the electrode because nanowires have a large surface area with high reactivity with organic electrolyte. During the initial lithium insertion process, a passivation film was inevitably formed due to the decomposition of the organic electrolyte. The $Ti_6Na_2O_{13}$ nanowire electrode exhibited hysteresis during the lithium intercalation and extraction process, which is similar to tin oxide anode materials [13]. However, the curves become quite stable after the second cycle.

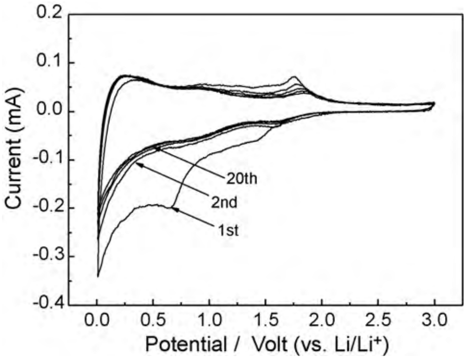

Fig. 3. Cyclic voltammograms of $Ti_6Na_2O_{13}$ nanowire electrode synthesized by a hydrothermal method. Scanning rate: 0.1 mV/s.

The discharge curves of $Ti_6Na_2O_{13}$ nanowire electrodes are shown in Fig. 4. During the first discharging, the potential curve promptly drops to less than 0.9 V and then slopes down to the cut-off voltage of 0.01 V. The nanowire electrode exhibited large irreversible capacity during the first and second cycles (1635 and 1150 mAh/g) due to the formation of the SEI film.

However, after the first cycle, $Ti_6Na_2O_{13}$ nanowire electrode demonstrated a quite stable cyclability. The capacity retention with cycling is shown in Fig. 5. The $Ti_6Na_2O_{13}$ nanowire electrode retained lithium storage capacity of about ~1050 mAh/g after the second cycles. The stable cyclability until the 20th cycle is also noticed in CV curves shown in Fig. 3. For $Ti_6Na_2O_{13}$, it should react with 26 Li per formula to form Li_2O. Therefore, the theoreti-

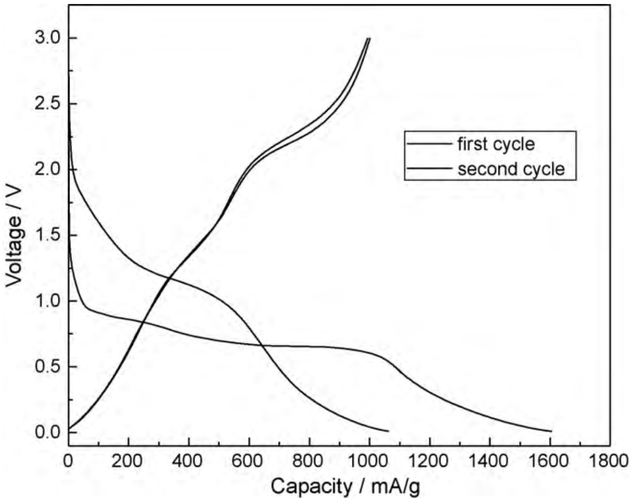

Fig. 4. Discharge profiles of $Ti_6Na_2O_{13}$ nanowire electrode in Li-ion cells.

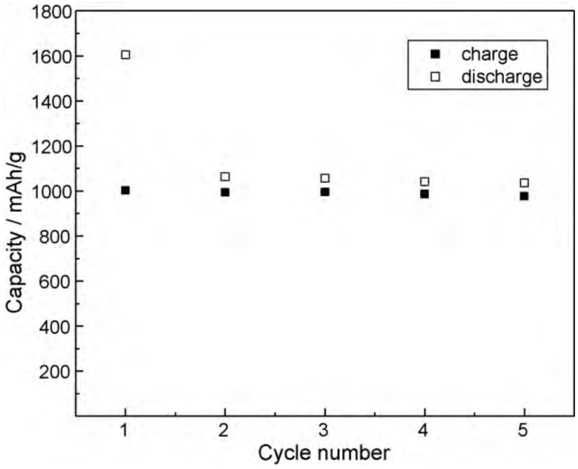

Fig. 5. Discharge capacity of $Ti_6Na_2O_{13}$ nanowire electrode versus cycle number.

cal capacity is 1287.58 mAh/g. We achieved almost the theoretical capacity for this material. Recently, a variety of candidate materials for Li-ion cell electrode has been studied to replace conventional carbon anode with the theoretical capacity of 375 mAh/g. Some of these materials exhibited higher discharge capacity values at the first cycle than carbon, but showed a quick degradation of capacity after the second cycle. The poor cyclability in these materials has been known mainly due to crystalline volume increase during lithium intercalation caused by an excess reaction with lithium. The cause of good cyclability in the present case of Ti–Na–O is thought to be related to the fact that there is no compound formation in Na–Li and Ti–Li alloy systems.

4. Conclusions

High quality $Ti_6Na_2O_{13}\cdot nH_2O$ and $Ti_6Na_2O_{13}$ nanowires were produced by a simple hydrothermal method which has many advantages such as the ability of scale-up production. Lithium storage property of the $Ti_6Na_2O_{13}$ nanowires was examined to see the possibility of this material to be used as an anode in Li-ion cells. The first result showed that the $Ti_6Na_2O_{13}$ nanowire electrode has the discharge capacity of up to 1000 mAh/g with good cycle property. This shows that hydrothermal processed $Ti_6Na_2O_{13}$ nanowires are very promising materials as anode materials, when comparing with the theoretical capacity of conventional carbon electrode, 375 mAh/g. Longer cycle property is under examination. Further study is needed to clarify the mechanism of good cyclability retention.

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