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Free Standing Nanostructures for Anode of Li-Ion Rechargeable Batteries

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The free standing nanorods of aluminum and cobalt oxides were grown on electrode and tested as the anodes directly in the half-cell. The average diameter and length of the nanorods are 80 nm and 200 nm respectively. The aligned nanorods demonstrated high initial capacity from 1200-1400 mAh/g at rate of 0.5C. The gradually decrease of initial capacity was observed. The preliminary characterization shows that the changes of the crystalline structure and morphology during cycling may be responsible for the capacity decay.

Introduction

The capacity of carbon intercalation anodes used in Li-ion rechargeable batteries currently is limited to 372 mAh/g [1]. Ever growing demand on lighter, cheaper and safer Li-ion batteries with high energy density that can power electric vehicles and portable electronics pushes researchers to find new anode materials. A number of metals and metal oxides have been investigated for next generation of high capacity anodes [2-10]. However, the large volume expansion (300-400%) during metal-Li alloying or oxide-Li conversion cause pulverization of active materials of anodes and result in rapid decrease of initial high capacity. Furthermore, these powdery metals and metal oxides have to be mixed with conductive additives, binders and solvent and pasted on current collectors. This conventional fabrication process is not only complicated and costly, but also limits the electron conductivity during to lack of direct contact of active materials and current collectors. To grown aligned nanostructure of active materials on the electrodes may be the solution for above problem. The inter-rods vacant space may accommodate the volume expansion of the rods and provide more access site for Li ions shuttling that reduce the stress resulting longer cyclic life. Secondly, the direct contact of the nanorods and electrode improve electronic conductivity in great deal that will bring high power density to the batteries. Finally, the direct growing of active materials on electrodes eliminates multi-stepped mixing-pasting-pressing –baking process and reduces fabrication cost considerably. In this paper, we report the initial results of our investigation and discuss several interesting issues

Materials Development and Characterization

Aligned Aluminum Nanorods

Al nanorods were synthesized using glancing angle deposition. The details were reported in the previous publication [11]. A glass slide was coated with a homogenous Ti thin film

as the substrate in a sputtering chamber. Then, a thin film of aligned Al nanorods was grown on the substrate using glancing angle deposition.

SEM (Scanning Electron Microscope) conformed that the thin film consists of aligned Al nanorods (Fig.1-2). The average diameter and length of the rods are 100 nm and 0.5 μm . The EDS (Electron Dispersion Spectroscopy) analysis confirms the nanorods are pure aluminum (Fig.3-4).

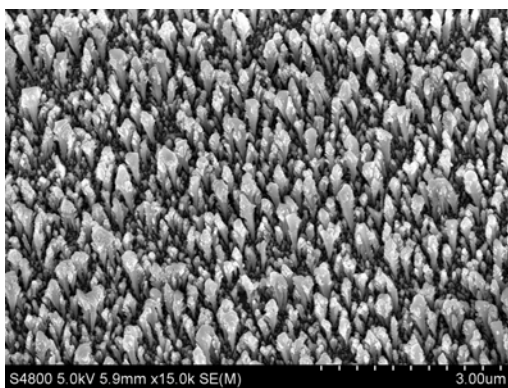


Fig. 1 Aligned aluminum nanorods (x15,000)

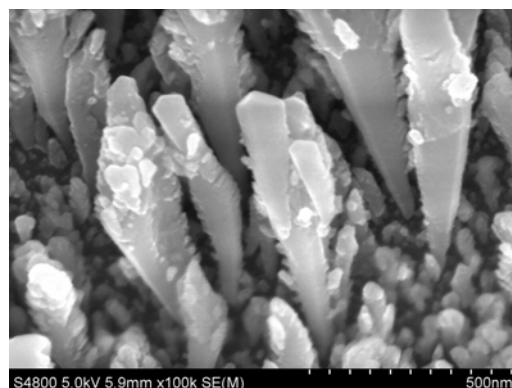


Fig. 2 Aligned aluminum nanorods (x100,000)

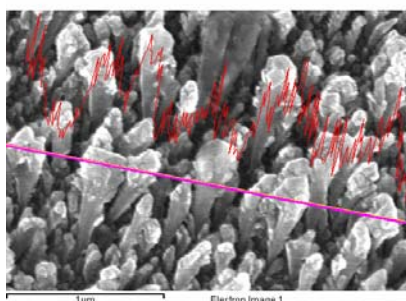


Fig. 3 EDS Al-line scan of aligned Al nanorods (x50,000)

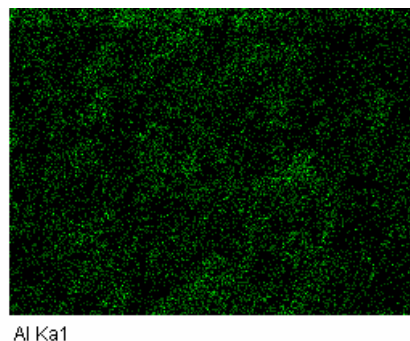


Fig. 4 EDS Al- map of aligned Al nanorods (x50,000)

XRD (X-Ray Diffraction) shows that the aluminum nanorods are well aligned with high textured orientation.

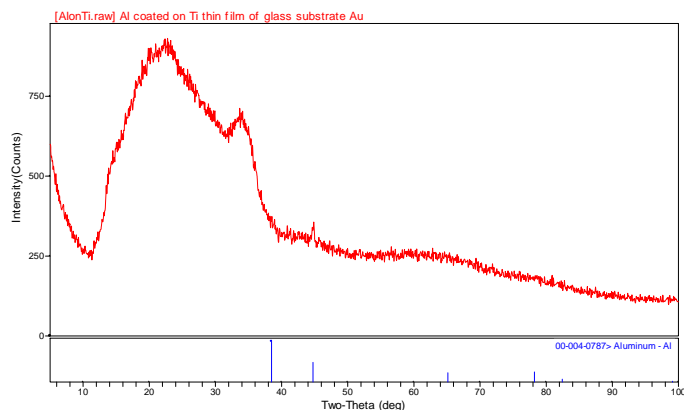


Fig.5 XRD of aligned Aluminum nanorods

Aligned Cobalt Oxide Nanorods

The thin film of Co_3O_4 nanorods were grown on a titanium substrate (10 x 40 x 1 mm) through the hydrothermal process. XRD confirmed the formation of Co_3O_4 on Ti substrate (Fig.6). SEM shows that the Co_3O_4 thin film consists of hollow nanorods with average diameter of 70 nm and length of 200 nm (Fig.7). Most of nanorods were perpendicularly grown from Ti substrate with hollow channels open to outside. This morphologic feature may facilitate motion of Li ions.

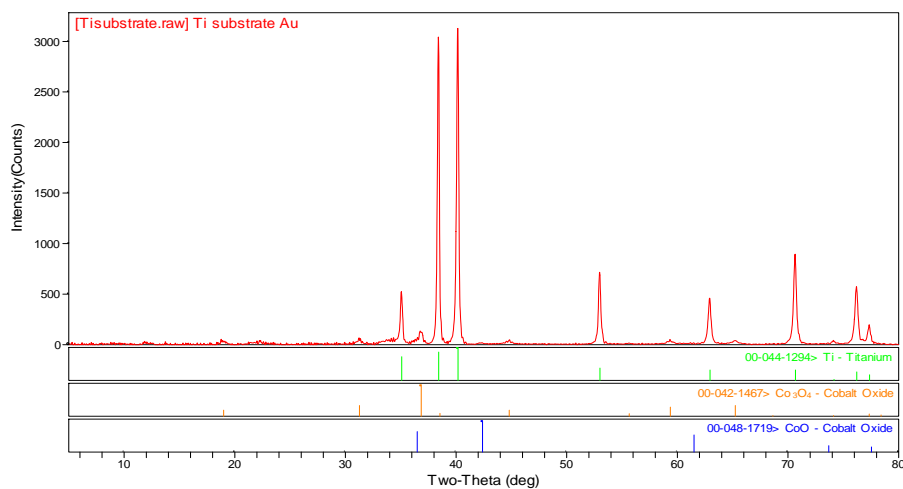
Fig.6 XRD of Co_3O_4 thin film on Ti substrate



Fig.7(a) Hollow nanorods of Co_3O_4 Ti substrate (x10,000)

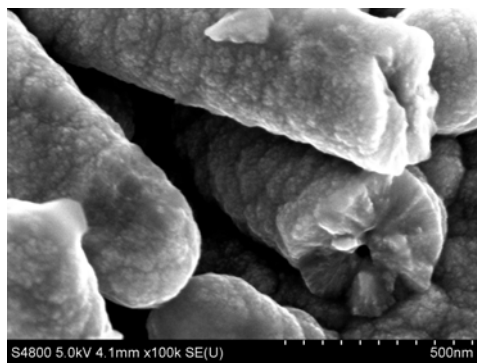


Fig.7(b) Hollow nanorods of Co_3O_4 on Ti substrate (x100,000)

Electrochemical Performance of the Anodes Made by Al and Co_3O_4 Nanorods

A half-cell was set up in the glove box. The lithium foil purchased from Aldrich was used as the cathode. The Ti substrate coated with hollow Co_3O_4 nanorods and the glass substrate coated with aligned Al nanorods were inserted in a baker cell as the anodes. The electrolyte of 1.0M LiPF_6 in propylene carbonate (PC) and dimethyl carbonate (DMC) was purchased from Ferro. Applied Physics's VersaSTAT-3 potentiostat was used for measuring of electrochemical properties of the new anodes. The charge-discharge cycling was carried out in the voltage range of 0.01V to 3.00 V at current rate of 600 mA/g (0.5C). The cyclic voltammetry (CV) were conducted in the potential region of from 0.01 V to 3.00 V (Li/Li^+) at a scanning rate of 0.1mV/s.

Performance of Al Nanorods Anode

Fig 8 shows the cyclic voltammetry of nano Al anode. Two set of similar current peaks (A_1 - A_5 and B_1 - B_5) appear in the first and second cyclic voltammetry. Following increase of the potential, the peaks of A_1 at 0.491V may correspond to lithium reduction and formation of Li-Al solid solution. After Li concentration increases and exceeds the limit of solubility ($\sim 0.5\%$), the low lithium alloy of LiAl may form resulting in appearance of the peak A_2 at 0.841V. Further charging will move more Li ions in the aluminum that transforms LiAl to high lithium alloy as Li_9Al_4 . The peak A_3 at 0.937 V may correspond to that. The proposed anode reactions could be written as:



In reverse process, the peak A_4 and A_5 may represent Li oxidation when potential was decrease gradually.

The second CV repeats similar peaks B_1 - B_5 that evidences the reversible Li redox reactions.

According to the reaction (2), aluminum anode can deliver 1411 mAh/g of capacity theoretically. In our case, the nano Al anode demonstrated 1243 mAh/g of capacity in the

first discharge (Fig.9) that is close to its theoretic maximum. It exhibits the potential of aluminum nanorods as the high capacity anodes. However, the charging capacity decreased to 440 mAh/g in the second cycle. After 10 charging-discharging cycles, the reversible capacity decreased to 100 mAh/g (Fig.10).

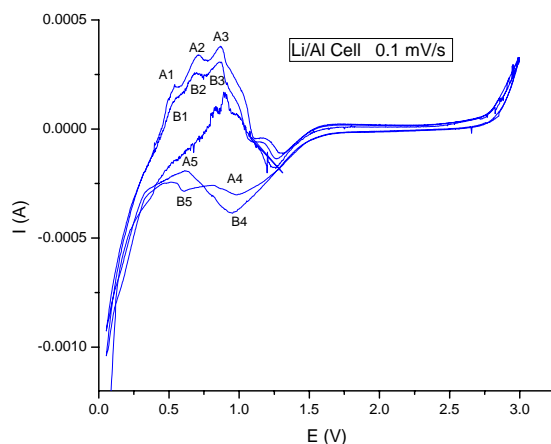
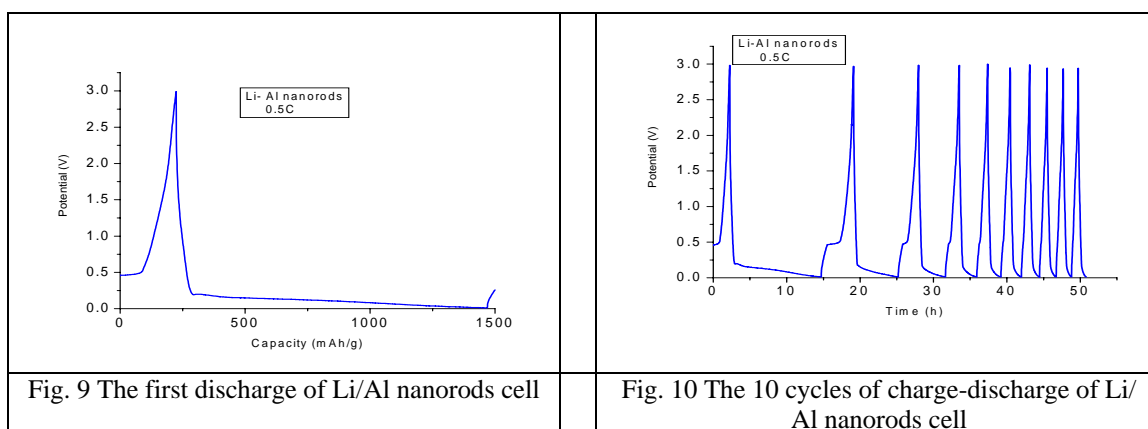


Fig. 8 Cyclic voltametry of Li/Al nanorods half cell



The SEM observation reveals some of the possible reasons of the capacity decay. After first discharge, the Al nanorods maintain their original aligned character, but the image was blur due to the static charge accumulated (Fig.11). It implies the poor electronic conductivity caused possibly by either aluminum oxidation or losing contact of aluminum nanorods with titanium substrate. After 100 cycling the original high capacity diminished (Fig.12) and SEM shows the Al nanorods networking together (Fig.13). XRD shows disappearance of texture of aligned nanorods and appearance of typical crystalline feature. The unfavorable morphology and structure change results in poor electronic contact of aluminum and electrode and reduction of surface area.

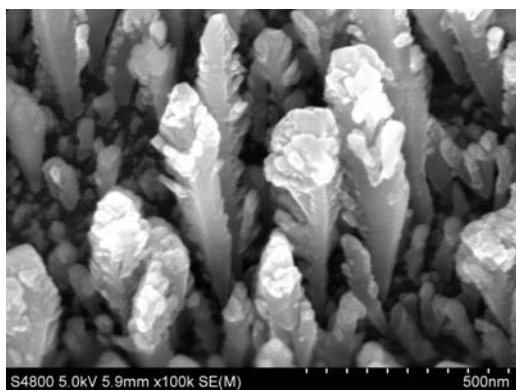


Fig.11(1) The image of fresh Al nanorods (x100K)

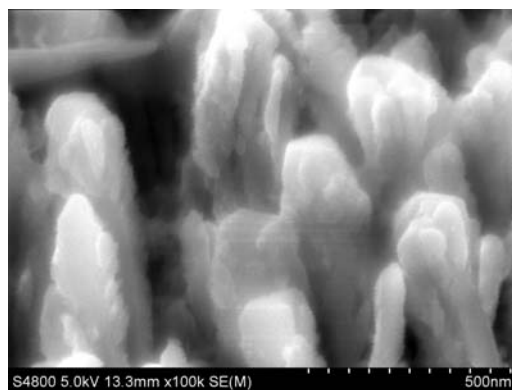


Fig.12 (2) The image of Al nanorods after first discharge (x100K)

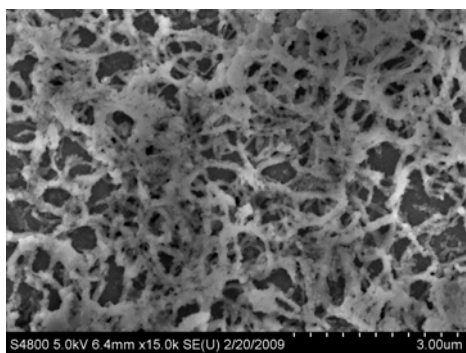


Fig.13 The image of Al nanorods after 100 cycles (x15K)

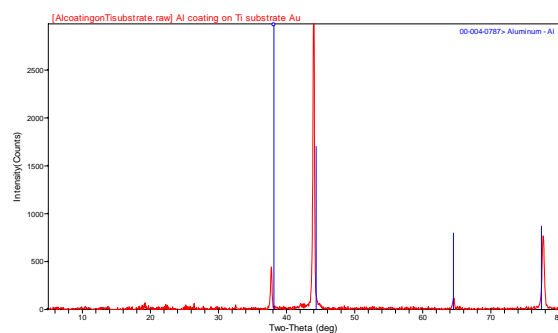


Fig.14 XRD of Al nanorods after 100 cycles

The Li/nano Co_3O_4 cell was tested for its electrochemical storage capacity. The first three cycles of discharging- charging of hollow Co_3O_4 nanorods anode are shown in Fig.15. The Co_3O_4 nanorods 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 nanorods was five time higher than carbon anode (372 mAh/g). The great potential of nanostructured metal oxide anodes was clearly demonstrated. However, the capacity gradually decreased in the following charging-discharging cycles (Fig.16). After 50 cycles, the capacity was reduced to 60 mAh/g (Fig.17). Further investigation on the capacity decay is on going. We will report in the near future.

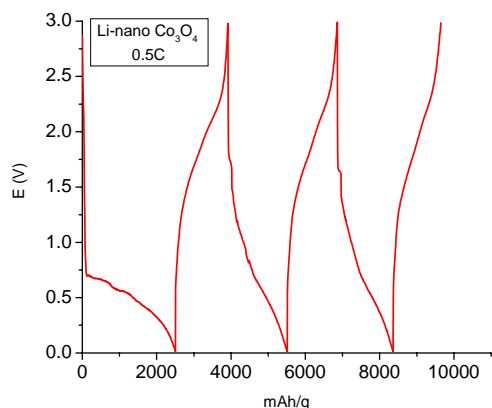


Fig.15 V~t of Li- nano Co_3O_4 cell in the first three cycles

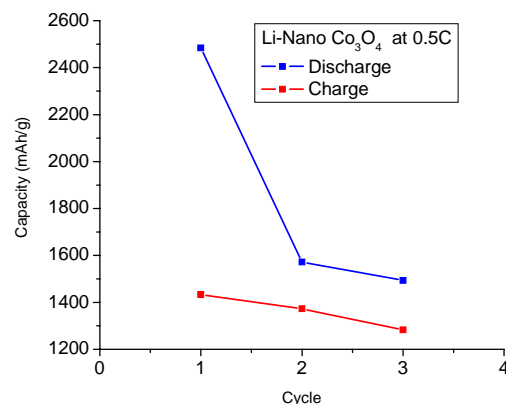


Fig.16 The capacity decrease of Li-nano Co_3O_4 cell in three cycles

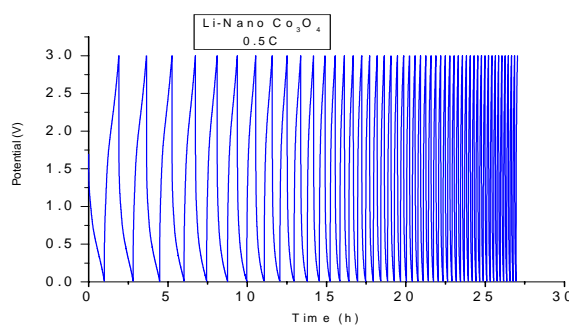


Fig. 17 Fifty cycles of charge-discharge of Li-nano Co_3O_4 cell

Conclusions

The aligned nanorods of aluminum and cobalt oxide that were directly grown on electrodes demonstrated high anode capacities as 1243 mAh/g and 2484 mAh/g respectively at the rates of 0.5 C. However, the initial high capacity decreased gradually in charge-discharge cycling. It was found that the changes of crystalline structure and morphology might be partially responsible for the capacity decay. In light of the great potential for replacement of carbon based anodes, further investigation is warranted. Future work will be focused on mechanism of capacity decay and the approaches to sustain capacity.

Acknowledgements

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