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Research Article

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Synthesis of Co_3O_4-Al_2O_3 composites using microemulsion chemical method and their electrochemical properties

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ABSTRACT

Crystalline Co_3O_4-Al_2O_3 composite oxide was prepared by microemulsion chemical method and the electrochemical properties as anode material for lithium ion batteries were studied. The results show that the particle sizes of Co_3O_4 can be changed by amorphous Al_2O_3, but the crystal form of Co_3O_4 can't be changed. The electrochemical properties of $Co_3O_4 \cdot xAl_2O_3$ as anode material for lithium ion batteries are sensitive to its particle sizes and the $Co_3O_4 \cdot 0.1Al_2O_3$sample exhibits excellent electrochemical performance with the average particle size of about 30 nm: from the 1st cycle to the 20th cycle, the discharge capacity decreases from 929 mAh/g to 910 mAh/g, and the average decay of charge capacity is 0.01% per cycle.

Keywords: Co_3O_4-Al_2O_3 composite, Microemulsion chemical method, Anode material, lithium ion batteries, electrochemical performance.

INTRODUCTION

Lithium ion secondary battery anode material has gone research process from lithium metal to lithium alloy, carbon materials, transition metal oxides. There are some security risks for lithium metal, although the higher storage capacity of carbon materials lithium (the theoretical lithium storage capacity of 372mAh/g), the absence of high temperature treatment and defect structure of the residual carbon material, making capacity with cycling are attenuated. Thus, while further improvements in carbon materials, looking for more new reliable and higher lithium storage capacity lithium-ion battery cathode materials [1-2] become a research direction, in order to develop high-quality lithium-ion battery, many new high lithium storage and high-capacity lithium-ion battery cathode materials become a research hot [3-5].These materials have a much higher theoretical lithium storage capacity than graphite materials, but during charge and discharge, alloyed aggregates [6] or the passivation film to generate [7] easily happen, and in the process of the continuous embedding and extrusion of lithium, easy chalking or phase change causing the large volume expansion and contraction, increasing the contact resistance between the particles, resulting in the collapse of the electrode material, thus affecting the cell loss performance. According to the literature [8], controlling the particle size of lithium storage material and reducing the reunion grains can improve the electrochemical performance of the battery. Transition metal oxide material Co_3O_4 has high lithium storage characteristics, due to low prices, environmental friendliness, and excellent electrochemical properties, becoming a research hot of high lithium storage materials. Its research focuses on looking for a suitable preparation methods [9,10] and developing various types of carbon-containing metal oxide composite electrode materials. In recent years, Gupta et al [11-15] found that the transition metal composite oxidel has superior electrochemical performance to the single metal oxides. However, using Co_3O_4-Al_2O_3 composite as anode material for lithium ion secondary battery isn't reported. Author prepared uniform $Co_3O_4 \cdot xAl_2O_3$ composites by microemulsion method and studied their physical properties and electrochemical properties.

EXPERIMENTAL SECTION

Preparation of samples $Co_3O_4 \cdot xAl_2O_3$

The aluminum nitrate dissolved in nitric acid, cobalt nitrate dissolved in the secondary water, constant volume of 50 mL, respectively, mixing, adding 50 mL toluene and 50 mL 0.023mol / L dibenzosuberyl(DBS), In the mixing process, slowly adding 20mL ammonia and forming microemulsion, still stratification, taking the upper organic phase and drying at 120℃, roasting at different temperatures for 2h in Ma fluorine furnace. By changing the amount of aluminum nitrate added, $Co_3O_4 \cdot xAl_2O_3$ samples of different amount Al-doped prepared.

Material characterization

Phase analysis of samples using the Siemens X-ray diffractometer (Siemens D500, Cu Kα, λ=0.154056nm). Japan Hitachi H-600 transmission electron microscope (TEM) to observe the sample morphology and particle size distribution. Preparation of negative electrode with mixing active material $Co_3O_4 \cdot xAl_2O_3$, acetylene black and polyvinylidene difluoride(PVDF) at a mass ratio of 70:20:10 in solvent N-methyl pyrolidinone(NMP), then uniformly coated on a copper collector foil, obtaining a studing electrode. With lithium metal as the positive electrode, utilizing 1.0 mol/L $LiPF_6$ in ethylene carbonate/dimethyl carbonate (EC/DMC) (with an EC to DMC volume ratio of 1:1) as the electrolyte, the assembly was carried out in an Ar-filled glove box. All electrochemical tests were done on the electrochemical analysis system.

RESULTS AND DISCUSSION

X-ray diffraction analysis

XRD patterns of the Co_3O_4 (containing different Al_2O_3 doped contents with precursor pyrolysis at 600℃ for 4 hours in air) is shown in Fig.1. Contrasting standard pattern JCPDS (422 1467), The sample is still cubic phase of Co_3O_4, the aluminum diffraction peaks not found, show that doping Al_2O_3 does not cause a change in the crystal structure of cobalt oxide, because amorphous Al2O3 is present in the sample. And comparing to Co_3O_4 sample prepared with no Al_2O_3 in the same conditions, Co_3O_4diffraction significantly broad, shows that due to the addition of Al_2O_3, Co_3O_4 particle size smaller, the higher content of Al_2O_3, the wider diffraction peaks of Co_3O_4, the smaller particles. Estimated by the Scherrer's equation, relationship between the average particle size of the sample $Co_3O_4 \cdot xAl_2O_3$ and the ratio Co_3O_4/Al_2O_3: the average particle size of the pure sample Co_3O_4 was 35 nm; Co_3O_4/Al_2O_3 1:0.1, the average particle size of the sample 30nm; Co_3O_4/Al_2O_3 1:0.375, the average particle size of the sample 22nm; Co_3O_4/Al_2O_3 1:0.75, the average particle size of the sample 14nm. Different average particle size of the sample Co_3O_4 is bound to affect the lithium storage properties of Co_3O_4 as anode materials for lithium ion batteries. With the Al_2O_3 content increasing in the sample, the average size of Co_3O_4 crystal becomes small, but Co_3O_4/Al_2O_3 exceeds 1:0.75. With increasing the content of Al_2O_3, the average particle size of the crystals $Co_3O_4 \cdot xAl_2O_3$ is basically unchanged.

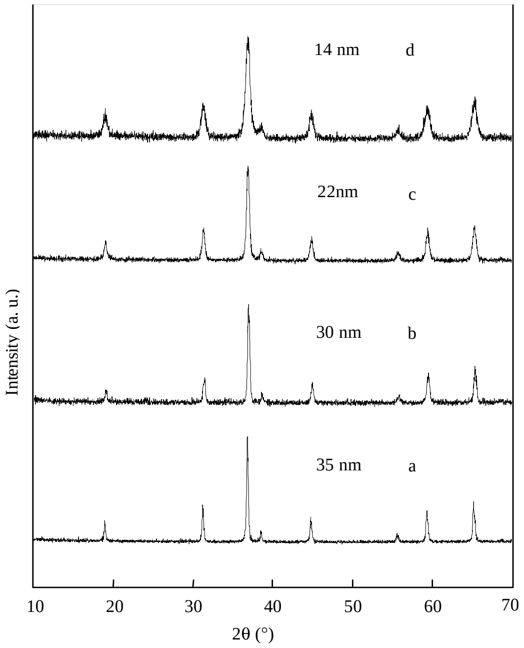

Fig . 1 XRD patterns of the Co_3O_4 containing different Al_2O_3 doped contents
a) Co_3O_4, b) Co_3O_4/Al_2O_3= 1∶ 0.1, c) 1∶ 0. 375, d) 1∶ 0.75

Impact of Al_2O_3 content on $Co_3O_4·0.01Al_2O_3$ capacity and cycle performance

$Co_3O_4·xAl_2O_3$ as lithium storage materials, particle size of sample has a a great relationship with its lithium storage performance. Fig 2 shows Cycle-ability of the $Co_3O_4·xAl_2O_3$ containing different Al_2O_3 contents. For Sample A, the average particle size of 14nm, its high initial reversible capacity but poor cycling performance, after 20 weeks cycles, the capacity is less than 405 mAh/g. For Sample D（$Co_3O_4·0.01Al_2O_3$）, the average particle size of 30nm, its initial reversible capacity is low, but good cycling performance, after 20 weeks cycles, the capacity remains unchanged. When the Al_2O_3 content is further reduced, it still maintains a good cycle performance, but its lithium storage capacity has declined. Such as the sample Co_3O_4/Al_2O_3 1∶0.05 (the average size of 38nm), the reversible capacity of the first week is 881mAh/g. For $Co_3O_4·xAl_2O_3$, when the average particle size of about 30nm（Co_3O_4/Al_2O_3= 1∶0.1）, shows the best electrochemical performance.

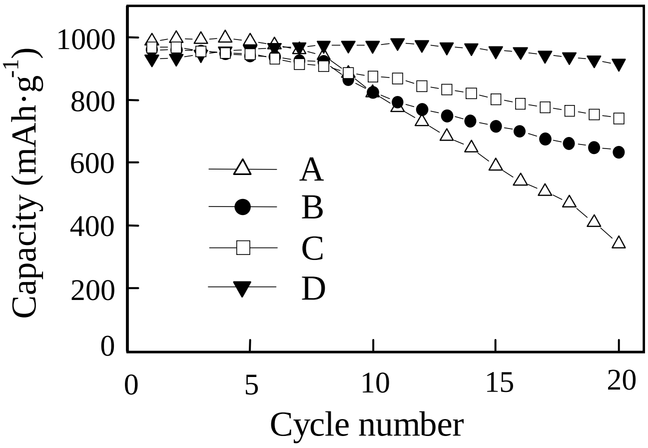

Fig. 2 Cycle-ability of the $Co_3O_4·xAl_2O_3$ containing different Al_2O_3 contents
A) Co_3O_4/Al_2O_3= 1∶0.75, B) 1∶0 .375, C) 1∶0.15, D) 1∶0.1

TEM analysis

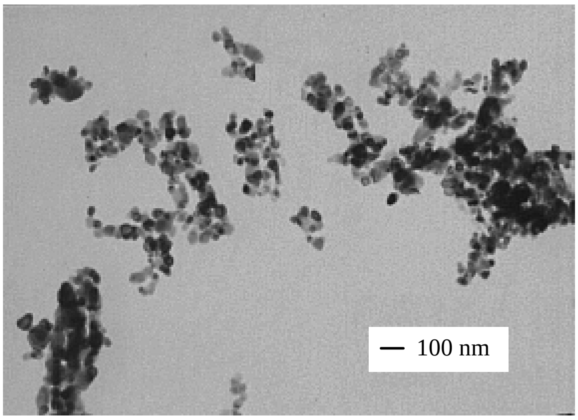

Fig. 3 TEM image of $Co_3O_4·0.1Al_2O_3$ sample

TEM image of $Co_3O_4·0.1Al_2O_3$ sample with precursor pyrolysis at 600℃ for 4 hours in air is shown in Fig.3. Its particle size distributing between 30 and 40 nanometers, uniform distribution, and slight agglomeration, this may be caused by insufficient homogeneity of dispersing the sample with ultrasonic. The particle size of the sample is substantially consistent with the calculated results by XRD analysis 。

Fig 4 is the first two discharge-charge curves of $Co_3O_4·0.1Al_2O_3$ anode. The first week discharging, the voltage rapidly decreased, A platform at 1.1 V and the second platform at 0.7 V appear, then slowly decreased to 0.01 V. the platform at 1.9 V appear when charging, from the second week, the electric potential platform of lithium storage appeares at 1.25V. The initial lithium storage capacity 1408 mAh/g, delithiated capacity of 929 mAh/g, the initial irreversible capacity loss 34%, the reversible capacity of lithium insertion and extraction more than 900 mAh/g. The sample has a high lithium storage capacity.

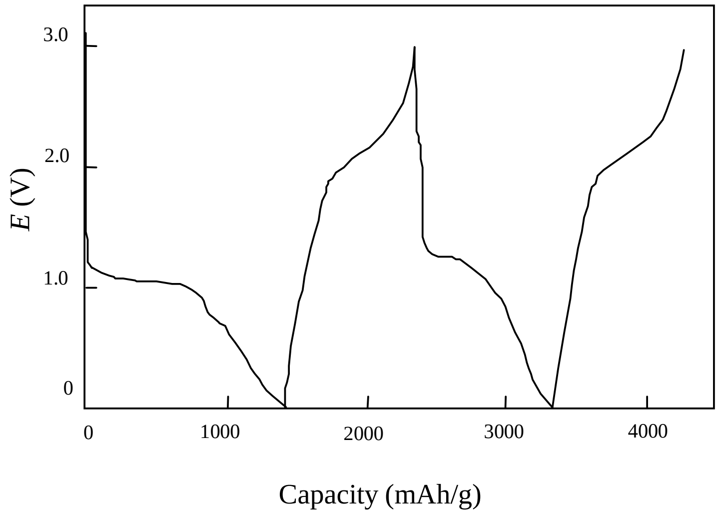

Fig. 4 The first two discharge-charge curves of Co_3O_4·$0.1Al_2O_3$ anode

Fig 5 is Cycle- ability of Co_3O_4·$0.1Al_2O_3$ anode after 20 cycles. As mentioned above, during the first week of the cycle, Irreversible capacity loss 34%. From the second week, the charge-discharge efficiency obtains more than 94%. After 10 weeks of the cycle, the charge-discharge efficiency is close to 100%, shows that the lithium can sufficiently reversibly embed and extract in the negative electrode material. This is due to non-electrochemical activity Al_2O_3 into Co_3O_4 lattice, forming crystal defects in Co_3O_4 lattice, expanded the quasi two-dimensional area of Pseudo capacitance electrochemical reaction, in favor of lithium freely into and out of Co_3O_4, thus increasing the reversibility of the electrochemical reaction and improving cycle capacity. The reversible capacity of the 20th week 910mAh/g, the average decay rate of 0.01% per cycle, the sample maintains a good cycle performance。

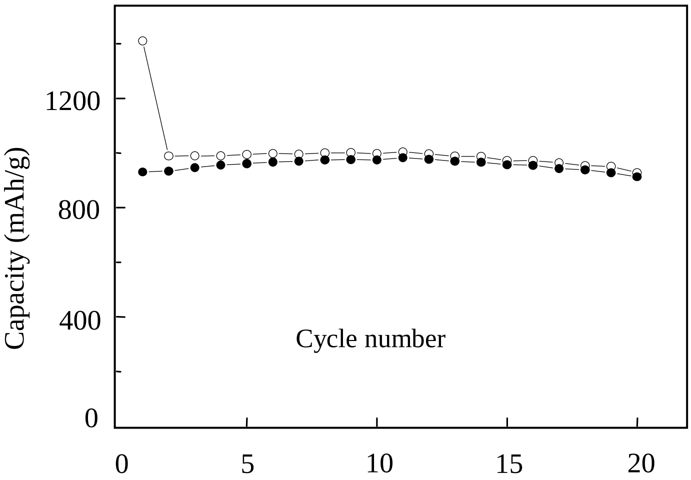

Fig. 5 Cycle- ability of Co_3O_4·$0.1Al_2O_3$ anode after 20 cycle

CONCLUSION

Introducing amorphous Co_3O_4 does not change the crystalline form of Co_3O_4, but change the particle size of Co_3O_4 crystal, its lithium storage performance has a great relationship with the particle size of Co_3O_4·xAl_2O_3 samples. Experiment shows, Co_3O_4·$0.1Al_2O_3$ (the average particle size of 30nm) has the best electrochemical performance, initial reversible capacity of 929mAh/g, after 20 cycles, the reversible capacity remains 910mAh/g, the average decay rate of 0.01% per cycle.

Acknowledgement
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