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Effects of Co_3O_4 on Different Particle Size of Al Anode Material for Lithium Ion Battery

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A series of Co_3O_4-Al composites with different Al particle size and different Co_3O_4 contents were syntheszied and characterized by X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy and galvanostatic cycling. It is found that the composites exist in the form of core-shell structure. The formation of Co_3O_4 shell improves the discharge capacities and the cycle performance of Al anode. The influence of Co_3O_4 content on the electrochemical properties of different particle size of bare Al is basicly accordant. The composites display the optimized electrochemical performance when the Co_3O_4 content reaches 3 wt.%. Thereinto, the 3 wt.% Co_3O_4-Al composite with Al particle size of 15μm shows the best cycle performance.

Keywords: Lithium ion battery, aluminum, anode, composites, core-shell structure

1. INTRODUCTION

In recent years, lithium ion batteries are widely used in daily lives. From the small mobile telephone, laptop and digital cameras to the large electric vehicles, lithium ion batteries play more and more important roles[1-6]. The popularization of lithium ion batteries put higher demands on its performance. For anode materials, the commercial carbon with low theoretical capacity of 372 mAh/g seems can not meet the evolutive demands. Thus it is necessary to find high capacity materials as substitutes for commercial carbon[7-11].

Aluminum is regarded to be one of the promising candidates as anode material for lithium ion batteries for its many virtues: (i) High theoretical capacities. Al can form three kinds of alloys with metal lithium: AlLi, Al_2Li_3 and Al_4Li_9. Among these, Al_4Li_9 possesses the highest capacity of 2234 mAh/g. Even for LiAl alloy, the theoretical capacity is 993 mAh/g, which is much higher than that of carbon [12]. (ii) Flat and wide voltage plateaus. The charge-discharge curves of Al show flat and wide plateaus in the deintercalation and intercalation process, which is a very attractive feature for high performance anode materials [13]. (iii) Cheap price. If the cost of electrode materials could be reduced, the prospect of lithium ion batteries will be more attractive.

Currently, the prominent problem of Al anode is fast fading of capacity caused by huge volume change during cycling[14]. Many attempts have been done to solve this problem, such as the preparation of Al-based intermetallic materials, particulate-reinforced composites or mixtures, and so on[15-18].

In this paper, we tried to improve the cycle performance of Al anode through coating Co_3O_4 on the surface of Al particles. Three different particle sizes of aluminum spherules were chosen as matrix, which were coated by different content of Co_3O_4 to form Co_3O_4-Al composites with a core-shell structure. The effects of Co_3O_4 content on the electrochemical properties of different particle size of Al anode were investigated.

2. EXPERIMENTAL

2.1. Preparation of precursor

Cobaltous hydroxide carbonate and oxalic acid (AR grade) were mixed in the mole ratio of Co:$H_2C_2O_4$ = 1:1. After sufficient grinding, a proper amount of distilled water was added to form a rheological body. The rheological body was reacted at 80°C for 4 h in a Teflon-lined stainless steel vessel, and then was dried at 100 °C in an oven. Thus the cobaltous oxalate precursor was obtained.

2.2. Preparation of Co_3O_4-Al composites

The average particle sizes of aluminum spherules are 15μm, 23μm and 37μm respectively, which were used as received. Bare Al spherules and cobaltous oxalate precursor were dispersed in a proper amount of 50% ethanol and ultrasonicated for 30 min to achieve homogeneously dispersion. After drying in vacuum oven at 120°C, the mixture was heat-treated at 600°C for 30 min in muffle furnace，thus the Al-Co_3O_4 composites were synthesized.

The contents of Co_3O_4 were 1 wt.%, 3 wt.% and 5 wt.% respectively, which were calculated by strict molar ratio.

2.3. Characterization

The particle size of Al spherules was measured by Malvern Mastersizer 2000. The X-ray powder diffraction measurements were carried out with a Shimadzu XRD6000 diffractometer with Cu $K\alpha_1$ radiation (λ = 0.154056 nm). The scanning electron microscope images were observed by means of Hitachi SEM X650 performed at 25 kV. The energy dispersive X-ray spectroscopy analyses (EDS) were obtained through INCA 300.

Coin cells were used for electrochemical tests. The prepared slurries consisted of 60 wt% active materials, 25 wt% acetylene black and 15 wt% PTFE binder. Lithium metal was used as a counter electrode, and 1M $LiPF_6$ solution in a 1 : 1 (V/V) mixture of EC and DMC was used as electrolyte. The cells were assembled in an Argon-filled glove box (Mikrouna-China Super 1220/750). Cells were charged and discharged galvanostatically with current density 100 mA/g in the range of 0.001 to 1.5 V at 25°C. The electrochemical properties were examined by using Neware cell test system.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of bare Al and its composites with different Co_3O_4 contents. The four strong diffraction peaks in all patterns are identified as Al, whose 2θ values are around 38.45°, 44.71°, 65.09° and 78.23° respectively, due to the (111), (200), (220) and (311) Al planes (see the JCPDS 89-4037 card). The apparent diffraction peaks appears in the patterns of composites at about 2θ values of 18.96°, 31.23°, 36.81° and 59.32°, corresponding well with the standard data of JCPDS 78-1970 card, indicating the existence of Co_3O_4.

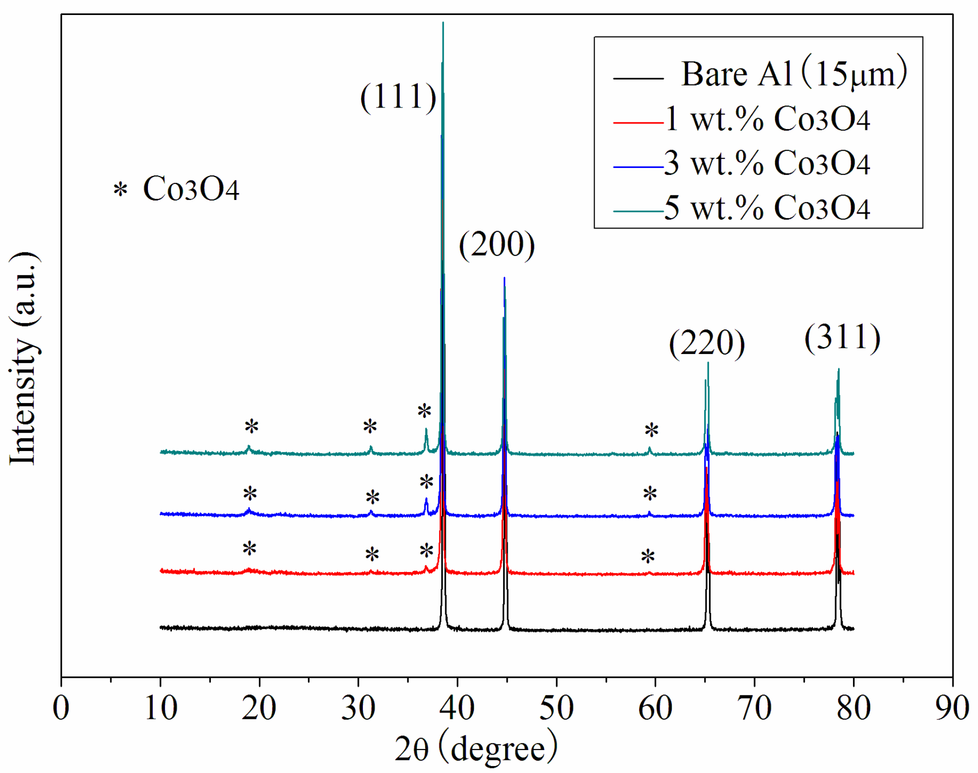

Figure1. The XRD patterns of bare Al and its composites with different Co_3O_4 contents.

Fig. 2 compares the micrographs of bare Al with different particle sizes and their 3 wt.% Co_3O_4-Al composites detected by SEM. Fig. 2(a), (c) and (e) present the morphology of bare Al with the average particle size of 15μm, 23μm and 37μm respectively. It shows that the surface of bare Al is very smooth and clear without any impurity. By comparison, Fig. 2(b), (d) and (f) depict the composites as (a), (c), (e) shows, from which it can be seen that nano-Co_3O_4 particles are deposited uniformly on the Al surface, indicating the formation of core-shell structure.

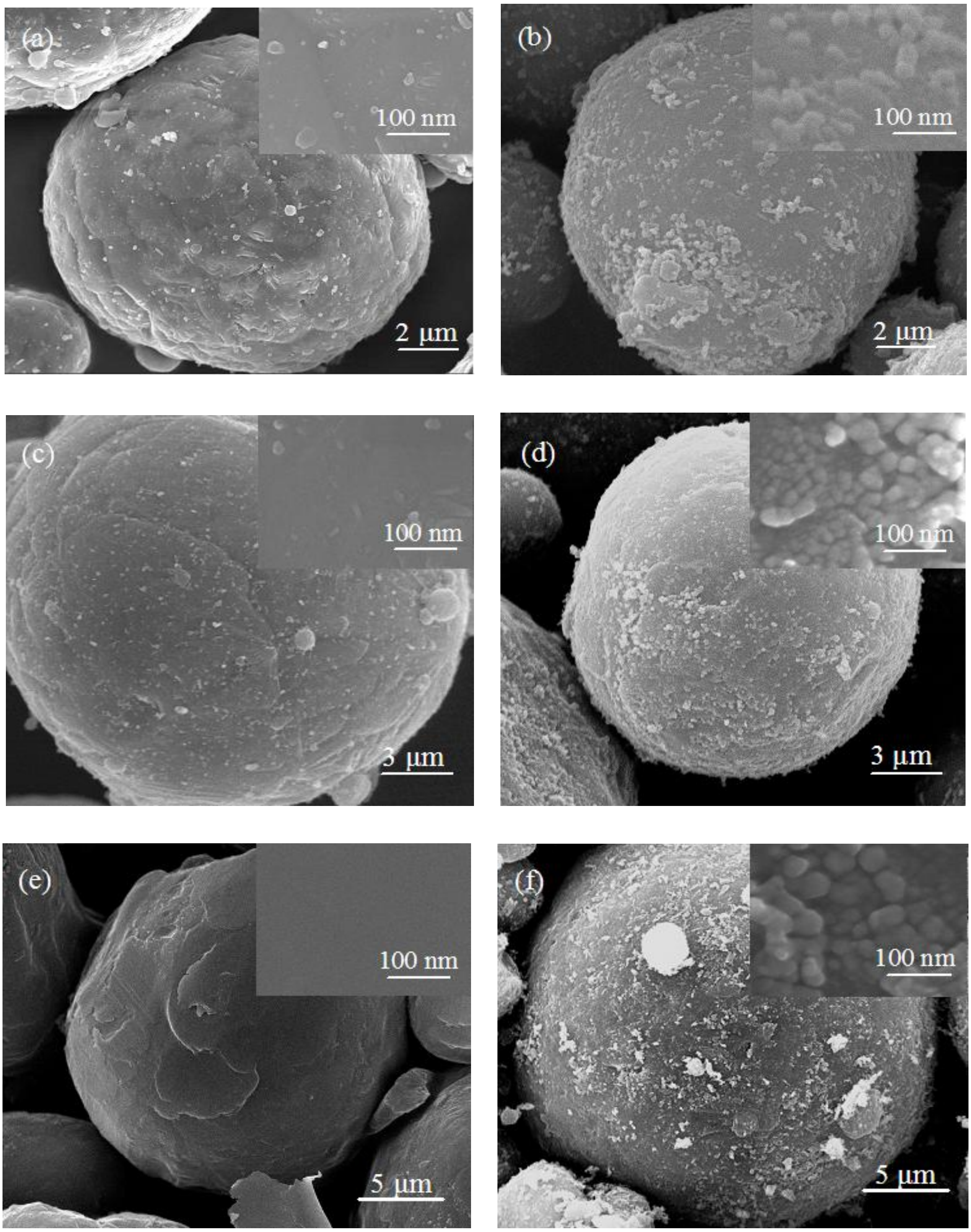

Figure 2. The SEM micrographs of bare Al and the 3 wt.% Co_3O_4-Al composites: (a) bare Al (15µm), (b) composite (15µm), (c) bare Al (23µm), (d) composite (23µm), (e) bare Al (37µm), (f) composite (37µm)

Fig. 3 shows the EDS of bare Al and 3 wt.% Co_3O_4-Al composite. In Fig.3(a), no other elements except for Al and a small amount of O were detected from the surface of bare Al. But in Fig.3(b), Co and O can be observed on the surface of composite. This result also validates the existence of Co_3O_4 coating layer on the surface of Al.

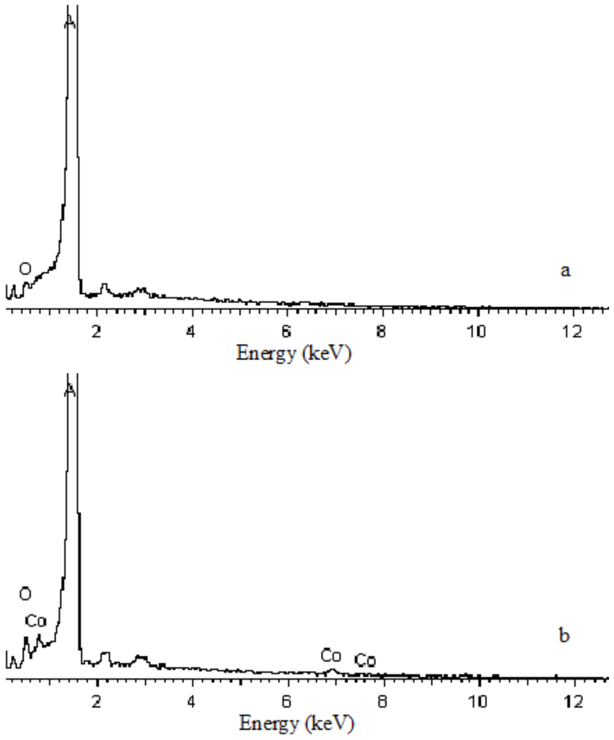

Figure 3. The EDS of bare Al (a) and 3 wt.% Co_3O_4-Al composite (b).

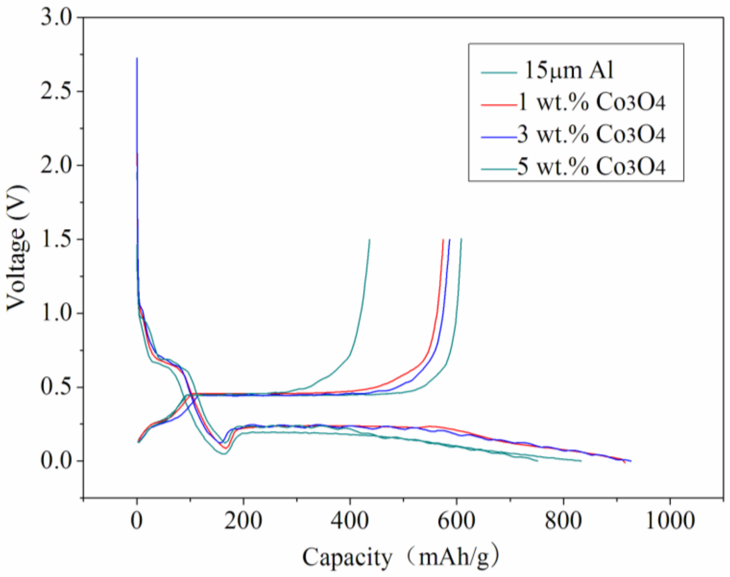

Figure 4. The initial discharge-charge curves of bare Al and its composites with different Co_3O_4 contents.

Fig. 4 displays the shape of initial discharge-charge curves of bare Al and its composites with different Co_3O_4 contents. Here the Al particle size is 15μm, profiles of other particle sizes of Al and their composites are omitted for they are similar to that of 15μm Al and its composites. In the discharge curve of bare Al, two voltage plateaus can be detected: a short plateau at about 0.8-0.65 V due to the SEI formation of the acetylene black[19], and a wide plateau at about 0.2 V owing to the formation of LiAl alloy (The corresponding dealloy plateau is around 0.44V in the charge curve). By comparison, a new short plateau at around 1.2-1.0 V can be observed in the discharge curves of composites, and this plateau becomes clearer with the increase of Co_3O_4 content. Obviously, it is concerned with the participation of Co_3O_4 in the lithium intercalation process [20, 21].

Table 1. The electrochemical data of different particle size of bare Al and their composites

Particle size	Sample	The first discharge capcities (mAh/g)	The first charge capcities (mAh/g)	The first capacity retention (%)	$R_{15/1}$
15μm	Bare Al	833	608	73	37
	1wt.% Co_3O_4-Al	915	575	63	47
	3wt.% Co_3O_4-Al	927	586	63	52
	5wt.% Co_3O_4-Al	751	436	58	42
23μm	Bare Al	845	626	74	35
	1wt.% Co_3O_4-Al	905	558	62	35
	3wt.% Co_3O_4-Al	1113	774	70	50
	5wt.% Co_3O_4-Al	1043	721	69	44
37μm	Bare Al	1029	779	76	19
	1wt.% Co_3O_4-Al	1072	731	68	27
	3wt.% Co_3O_4-Al	1103	697	63	30
	5wt.% Co_3O_4-Al	1097	656	60	30

Table 1 lists the initial discharge-charge capacities, the first capacity retention and $R_{15/1}$ data of all samples. Here $R_{15/1}$ is the ratio of discharge capacity in the 15th cycle relative to the 1st, indicating the material cycle performance[22]. Four points can be concluded according to Table 1: (i) Almost all the discharge capacities of composites are increased compared with that of bare Al, indicating that the Co_3O_4 coating reinforces the electronic contact between Al particles and other conductive materials, which facilitates the lithium intercalation process. (ii) All the initial capacity retentions of composites are decreased compared with that of bare Al. The reason may be explained as follows. Co_3O_4 reaction mechanism acted as anode material can be written as[23]:

$$Co_3O_4 + 8Li \leftrightarrow 3Co + 4Li_2O$$

In the initial discharge process, Co_3O_4 is decomposed into a mixture of Co nanoparticles and amorphous Li_2O, then the products Co and Li_2O are changed into Co_3O_4 reversibly and Li particles are released by Li_2O simultaneously in the following charge process. This revesible process can only be finished at the voltage higher than 2.1V[24]. But in this paper the voltage range is from 0.001 to 1.5 V, that is to say, the reversible reaction can not be occured in the voltage range, which means that part of Li ions is trapped in Co_3O_4 shell in the form of Li_2O after the initial cycle. So, the initial capacity retentions of composites are decreased. (iii) All the $R_{15/1}$ data of composites are higher than that of corresponding bare Al, arguing that the cycle perfrmances of Al anode are improved by coating Co_3O_4 layer. (iv) Combined discharge-charge capacities with the data of $R_{15/1}$, it can be concluded that the influence trend of Co_3O_4 content on different particle size of bare Al is basicly accordant. The composites display the optimized electrochemical performance when the content of Co_3O_4 reaches 3 wt.%.

Fig.5 compares the cycle performance of 3 wt.% Co_3O_4-Al composites with different Al particle size in addition. It is clear that the composite displays the highest capacity when the Al particle size is 23μm, while the composite shows the best cycle performance when the Al particle size is 15μm.

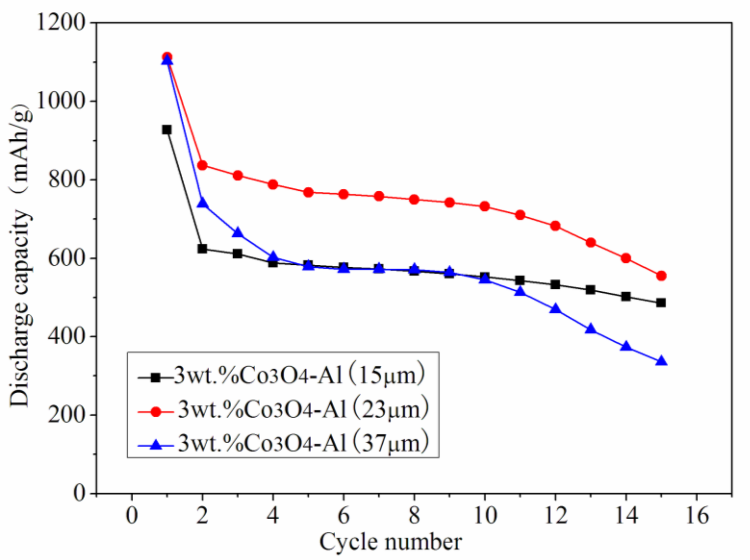

Figure 5. The cycle performance of 3 wt.% Co_3O_4-Al composites with different Al particle size.

4. CONCLUSIONS

A series of Co_3O_4-Al composites were syntheszied, and the effects of Co_3O_4 on the electrochemical properties of different particle size of bare Al anodes were investigated. The XRD, SEM and EDS results shows that the Co_3O_4 particles, which are nanosized, are dispersed uniformly on the Al surface to form a core-shell structure. The existence of Co_3O_4 shell improves the electrochemical performance of Al anode. After surface modification of Co_3O_4, the discharge capacities are increased and the cycle performances are improved in spite of the decreased first capacity retentions. The influence trend of Co_3O_4 content on different particle size of bare Al is basicly accordant. When the content of Co_3O_4 reaches 3 wt.%, the composites display the optimized electrochemical performance. Thereinto, the 3 wt.% Co_3O_4-Al composite with particle size of 15μm shows the best cycle performance.

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