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Influence of particle size and matrix in "metal" anodes for Li-ion cells

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Abstract

Electrodes of bismuth were prepared and tested as anodes for lithium ion batteries, with different particle sizes and binders, while varying the amount of active material in the mixture. Bismuth has been chosen as a "model" metal to investigate the influence of particle size on the electrochemical performance of the bismuth electrode since the potential window of Li–Bi alloys formation is relatively "high" (0.8–0.6 V) and prevents other components within the electrode from being electrochemically active versus lithium in this potential window. It appears that the use of nanosized particles with large amount of binder improves the electrode cyclability but that other problems are highlighted while using such electrodes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Metal anodes; Lithium ion batteries; Bismuth

1. Introduction

Different metals and alloys have been recently investigated as possible anodes for lithium ion batteries [1–4]. The main advantage of these compounds is the huge mass and/or volume capacity compared to standard carbonaceous anodes [5]. However, their main drawback is the impressive volume changes of the compounds upon cycling, which leads to the mechanical disintegration of the electrode [6], and subsequently to a drastic capacity fade.

In order to improve this cycling ability of metals and alloys, several studies have aimed at the improvement of both the microstructure of the materials and the matrix designed with a binder and conductive additive. In this work, we have examined the preparation of anodes by using small particle size Bi. Lithium can react with bismuth, leading to the Li_3Bi alloy with 385 mAh/g specific capacity, or a volumetric capacity of 3800 Ah/l, whereas the standard lithiated graphite has a specific capacity of 372 mAh/g or a volumetric capacity of 800 Ah/l. However, the volume expansion of carbon after reaction with lithium is only 12% while the volume of Li_3Bi is 2.15 times larger than the initial metallic bismuth. The study of such electrodes is also a good model to highlight both the microscopic and macroscopic changes that occur in "metal" anodes upon cycling.

2. Experimental

The bismuth powder was either commercially available material (Aldrich Chemicals) sieved down to 40 μm and submicronic powder prepared by arc plasma processing. In this last technique, a bismuth ingot was set in a DC arc discharge under argon atmosphere at reduced pressure (2.7×10^{-7} Pa) [7]. The ingot was set down in a conical graphite crucible at the anode. The material was vaporized and carried out by a gas flow. Finally, it was trapped on a membrane filter. The bismuth powder was collected and stored in a glove box under a high purity argon atmosphere.

Electrodes have been prepared by using a slurry technique involving a mixture of bismuth powder: graphite (SLM44, Le Carbone Lorraine): binder in *n*-metyl-2-pyrrolidinone. The binder was either PVDF (Aldrich Chemicals) or PVDF/HFP SOLEF copolymer (Solvay). The slurry were coated on Cu foil and tested on a MacPile II in simple two-electrode cells using a metallic lithium foil (Aldrich Chemicals) as both reference and counter electrode. The electrolyte was a 1 M solution of $LiPF_6$ dissolved in EC/DEC 2:1 (Merck).

3. Results and discussion

The first electrodes were prepared with standard Bi powders with an average particle size of 40 μm, but the electrochemical tests performed on these anodes lead to a

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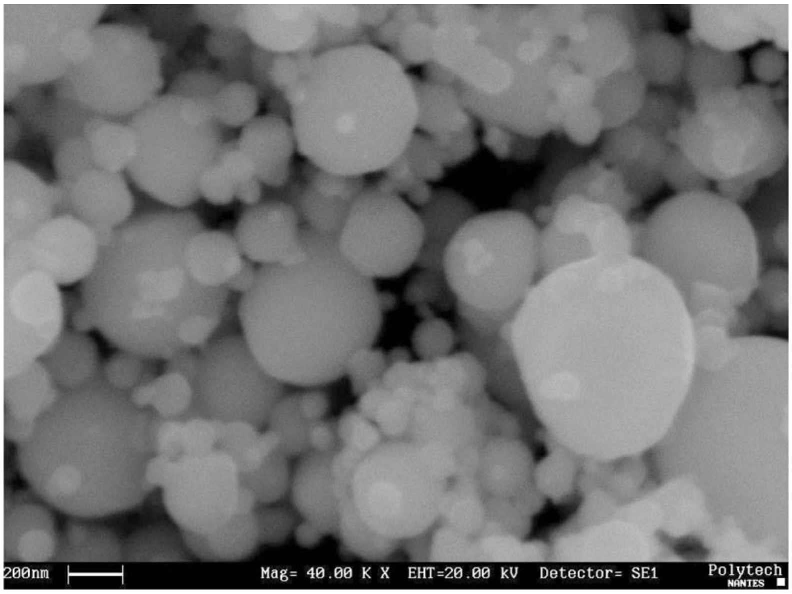

Fig. 1. SEM picture of Bi nanoparticles (×40,000).

very poor cyclability due to the large particle size. We assume that the huge volume expansion/contraction that occurs during reaction with lithium ($V[Li_3Bi] = 2.15V[Bi]$) de in capacity.

Fig. 1 shows a SEM picture of Bi powders prepared by DC arc discharge. The particles thus obtained have an average diameter of about 300 nm and have been electrochemically tested with different amounts (85, 50, 12 and 6 wt.% of bismuth, respectively) in the Bi/Graphite/PVDF system. The cells were tested in the voltage range 0.5–1.2 V versus lithium in a potentiostatic mode with 10 mV/2 min step rate. Fig. 2 shows the capacity fade of the electrodes during the first 10 cycles. The cycling behavior of nanosized Bi anodes is better compared with commercial large particle size bismuth. Moreover, we are able to observe an improvement in the cycling life of the electrodes as the amount of active material decreases, but this improvement is not dramatic, even with only 6 wt.% of bismuth in the electrode.

Similar experiments were made with nanosized bismuth and graphite but with a PVDF/HFP copolymer, with the same ratio than for the previous binder. PVDF/HFP has better mechanical properties compared with the standard PVDF (maximum elongation at yield: 15% instead of 5%; maximum elongation at break: 750% instead of 50%) and so the copolymer is expected to have much greater elasticity to absorb the volume changes of the electrode upon cycling. Moreover, tests were performed on electrodes containing

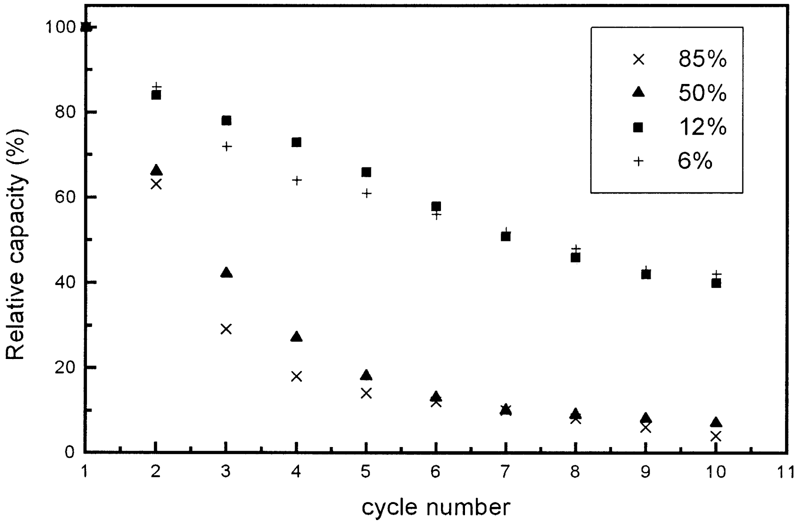

Fig. 2. Capacity fade of nanosized Bi electrodes with varying amounts of active material.

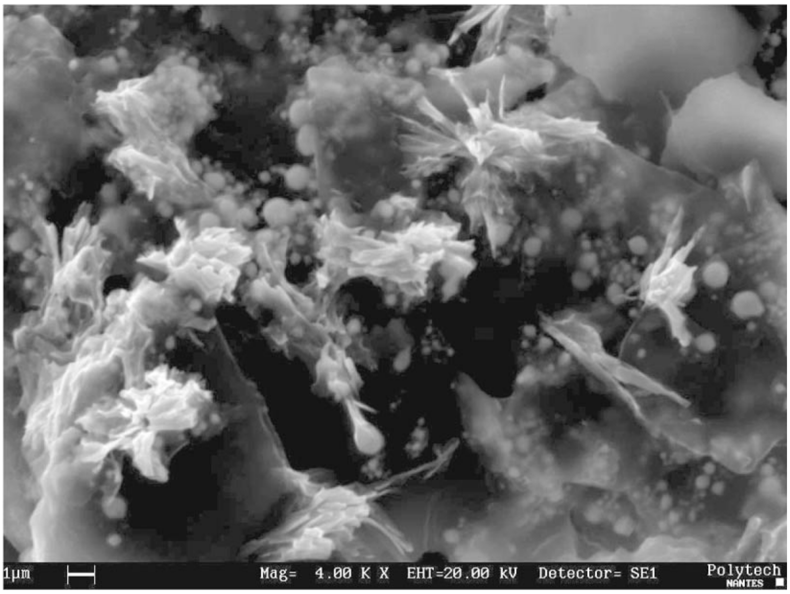

Fig. 3. SEM picture of Bi dendrites after 10 cycles (×4000).

50 wt.% nanosized bismuth with varying ratios of graphite/copolymer. It appears, as for the previous binder, that the cyclability of the anodes is substantially enhanced while the amount of bismuth decreases, and that changing the binder from pure PVDF to the copolymer substantially increases reversibility. This better behavior is not unexpected since the copolymer can better resist forces before fracture. Tests were also performed on the identical bismuth compositions (50 wt.%) where the only difference between the electrodes was the reversal of the concentrations of binder and carbon additive (40, 25, and 10%). Once again as expected the anode with the highest elastomer composition showed better reversibility. However, this experiment also indicates that the lower currents observed in the carbon lean sample are probably indicative of a relatively high and prohibitive resistance to the carbon lean electrode.

Although in changing the particle size as well as the binder and the concentration of active Bi in the electrode, an improvement was observed, there is still a quick fade in capacity. SEM micrographs were taken of several electrodes prior to and after cycling. It appears that the Bi particles are not homogeneously distributed throughout the electrode prior to cycling. Fig. 3 shows that after cycling, the bismuth agglomerates combine to make dendrite Bi which looses its electrochemical activity.

4. Conclusions

In this study, we have examined bismuth electrodes with commercial powders and nanosized particles, with different binders and different amount of active material. It appears that the better electrochemical behavior is obtained with PVDF/HFP copolymer and with very small amount of active nanosized bismuth. However, the substantial loss in the electrochemical activity of bismuth in these electrodes can be explained by an inhomogeneous electrode resulting in intimate contacts between the bismuth particles which lead to dendrite formation.

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