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Layered $Bi_2Ca_3Co_2O_9$ composite as anode material for lithium-ion battery

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Abstract Polycrystalline and single crystalline composites of $Bi_2Ca_3Co_2O_9$ have been prepared by the conventional solid-state reaction and flux method, respectively. X-ray powder diffraction exhibits single pure phase and characterization of c-axis orientation. Plate-like grains parallel to the hot-forging direction are observed using scanning electronic microscopy. Electrochemical measurement shows that lithium ions can be intercalated/deintercalated $Bi_2Ca_3Co_2O_9$ with relatively large capacity, which displays its potential as a candidate of anode material for a lithium-ion battery.

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1 Introduction

In recent years, large-scale attempts have been made to develop or design new electrode materials for batteries with high energy density and prominent cycle characteristics. In the field of lithium-ion batteries, the initiator, Goodenough [1, 2], first pointed out that the quasi-compact oxygen lattice could exhibit a high enough ionic conductivity to allow for the usage of lithium layered oxides as intercalation electrode materials. Recently, the research and commercialization of the anode materials mainly had its focus on the layered compounds with close-packed lattice in which alternate layers between sheets are occupied by oxychalcogenide and oxypnictides [3]. Lithium then inserts itself into the essentially empty remaining layers [4, 5]. Actually, layered oxides have been studied by many groups [6–10]. These layered oxides are common ternary or higher compounds in which different metal ions with different sizes and chemical requirements are incorporated. The bismuth calcium cobalt oxide $[Bi_nCaO_2]_x[CoO_2]_y$ has been extensively investigated due to its outstanding thermoelectric properties and commercialized as heat sensitive materials. This is attributed to the crystal structure characterized by CoO_2 slabs and Bi_2O_2 layers stacking between each other [10]. In fact, the ratio of x to y, which determines the distribution of oxygen-vacancies, plays a dramatic role on the properties of $[Bi_nCaO_2]_x[CoO_2]_y$ [11–17]. The existence of oxygen-vacancy provides the possibility of the intercalation for lithium. Another way for lithium intercalation is the partial replacement of Co ions by lithium, which is testified by Clarke et al. [3].

After the initial preparation of $Bi_2Ca_3Co_2O_9$ compound [6], much attention has been given to the relationship between physical properties and the microstructure of $Bi_2Ca_3Co_2O_9$. Muguerra et al. [11] have revealed that $[Bi_{0.84}CaO_2]_2[CoO_2]_{1.69}$ possesses a misfit layered structure with two subsystems: rock-salt-type layers and CoO_2 layers. The most remarkable property of this material is the large thermoelectric value along the b-axis of the crystalline [12], which makes it promising as a good electronically conductive material. Benedek and Thackeray [14] have observed the coupling effect between the block-layer structure of $Bi_2Ca_3Co_2O_9$ and the transport properties by intercalating the iodine ions into the layers. Although the transport properties of $Bi_2Ca_3Co_2O_9$ ceramics have been investigated, studies involving the electrochemical properties have

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not yet been reported. In the present paper, we examine the possibility of the ceramic $Bi_2Ca_3Co_2O_9$ as a high-capacity anode material for lithium-ion batteries.

2 Experimental section

Polycrystalline $Bi_2Ca_3Co_2O_9$ composite was prepared by solid-state reaction of a stoichiometric mixture of Co_3O_4 (99.9%), Bi_2O_3 (99.9%) and $CaCO_3$ (99.5%). The mixture was sintered twice in air at 1223 K for 20 h, pressed into a pellet, and then sintered at 1223 K for 20 h in air. The powder X-ray diffraction analysis showed that the sintered pellets consisted of $Bi_2Ca_3Co_2O_9$ only. Single crystalline $Bi_2Ca_3Co_2O_9$ composites were grown by NaCl/KCl flux reaction [18, 19].

The phases of the specimens were identified using X-ray Diffraction (XRD) with Cu Kα radiation as the X-ray source. For the sintered samples, pellets were crushed into powders and then examined. The operation conditions for XRD were 40 kV (AC), 40 mA (AC) at room temperature. Scans were taken in the 2θ range of 5–70° with a step of 0.02°.

Electrodes $[Bi_nCaO_2]_x[CoO_2]_y$ were fabricated from an intimate mixture including $Bi_2Ca_3Co_2O_9$ powder: 85 wt% $Bi_2Ca_3Co_2O_9$, 8 wt% poly (vinylidene difluoride) (PVDF) polymebinder (Kynar, Elf-Atochem) and 7 wt% acetylene black (Cabot) in 1-methyl-2-pyrrolidinone (Aldrich, 99%). The electrode was then laminated onto a Cu current collector foil using a doctor–bride. The electrode mixture was dried at 120°C for 12 h. A cell was constructed inside an Ar glove box (<5 ppm). The electrolyte used was 1 M $LiPF_6$ in EC:DMC (2:1). The cell was cycled at a slow constant current (0.1C) to the preset voltage and then allowed to relax for at least 3 h for cell equilibration.

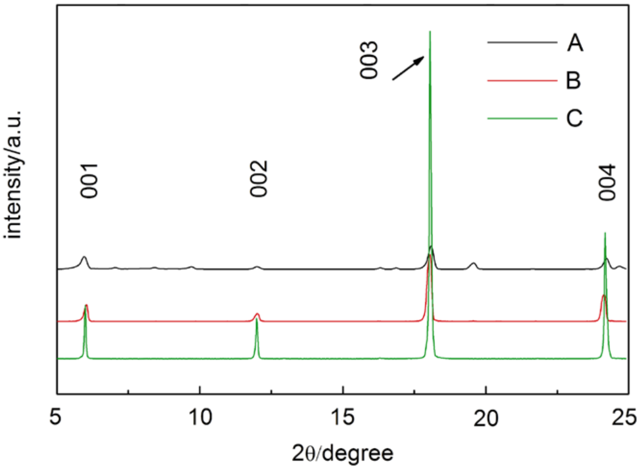

Fig. 1 XRD patterns for the $Bi_2Ca_3Co_2O_9$ samples with (*C*) single crystalline structure, (*B*) textured polycrystalline structure, (*A*) non-textured polycrystalline structure

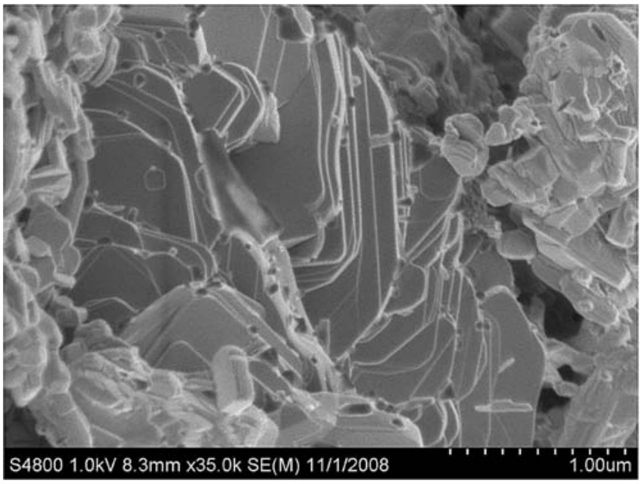

Fig. 2 SEM image of polycrystalline $Bi_2Ca_3Co_2O_9$ with texture

3 Results and discussion

From Fig. 1, it can be clearly seen that the samples are *c*-axis oriented. The (00l) plane clearly shows the usual features associated with similar misfit structures compared to the analysis of the crystal symmetry of $B_2Ca_2Co_2O_8$ [11].

The crystal lattice constants can be obtained, namely: $a = 3.670$ Å, $b = 3.556$ Å, $c = 14.707$ Å. The crystal system is monoclinic with $\beta = 102.3°$. Muguerra et al. [11] prepared single crystalline samples identified as $[Bi_{0.84}CaO_2]_2[CoO_2]_{1.69}$ with typical misfit structure and we further have structure refinement involving all possible modulated displacements related to the misfit character. As they pointed out, the CoO_2 layer was very similar to all the other corresponding layered structure in all these related thermoelectric Co oxide compounds and also that the thermoelectric power measured for these compounds were significantly different and in particular directly related to the misfit ratio. However, since we have poor quality of the single crystalline and difficulties to find a suitable model of refinement for polycrystalline, the precise atomic positions are not yet clear. Therefore, further research work is essential. We can conclude here that the samples (polycrystalline and single crystalline) are pure phase because they can be indexed. In the following part of this article, the electrochemical properties are measured on polycrystalline samples.

Figure 2 gives the SEM image of polycrystalline $Bi_2Ca_3Co_2O_9$ with texture. We can see the layered structure clearly, which is consistent with earlier reports [11].

Assuming that complete extraction and the insertion of lithium are possible, the idealized electrochemical (and

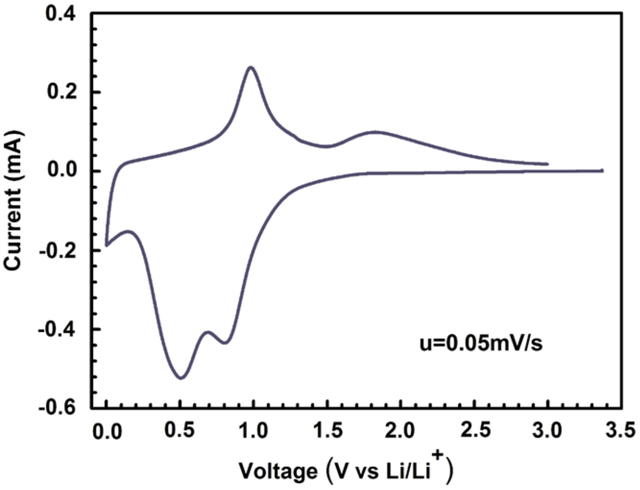

Fig. 3 The cyclic voltammetry curve of $Bi_2Ca_3Co_2O_9$ electrode

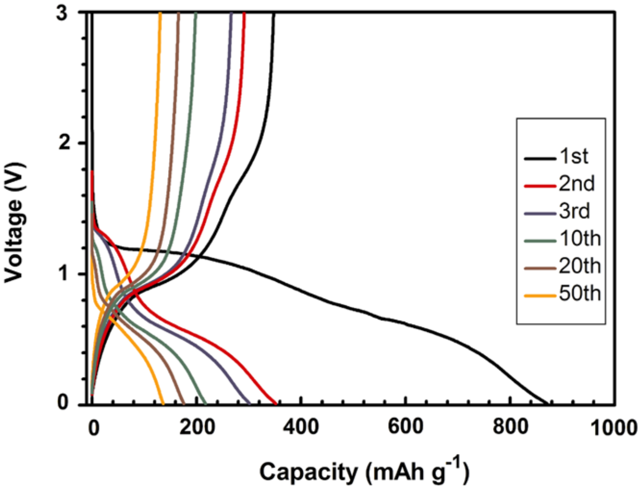

Fig. 4 Charge-discharge voltage profile of Li/$Bi_2Ca_3Co_2O_9$ operated at 50°C between 0 and 3.0 V at 0.1 mA/cm^2

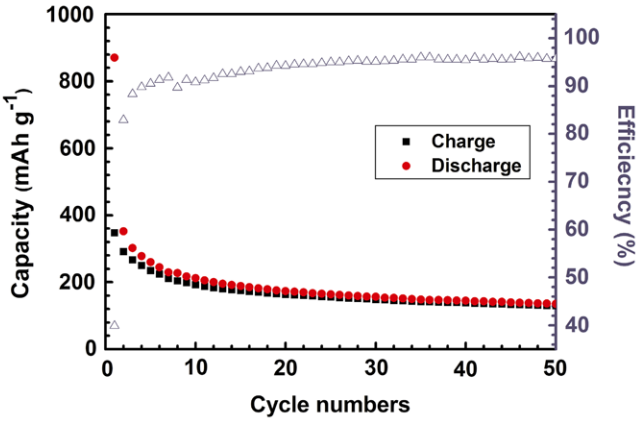

Fig. 5 Change of charge-discharge capacity of $Bi_2Ca_3Co_2O_9$ with cycle number

chemical) reaction would be

$$Bi_2Ca_3Co_2O_9 + 6(Li^+) + 6(e^-)$$
$$= 3CaO + 3Li_2O + 2Bi + 2Co.$$

According to the electrochemical reaction equation, the theoretical capacity is 214 mAh/g.

Figure 3 shows the Current-Voltage obtained from $Bi_2Ca_3Co_2O_9$ electrode in contact with 1 M $LiPF_6$ electrolyte at a sweeping potential rate of 0.05 mV/s. The CV is acquired by first sweeping from negative to positive potential. We can see from Fig. 3 that two pairs of obvious peaks exist along the curve. According to the theoretical chemical potential energy for Li–Bi alloy and Co, the peak for 0.84 V/1.79 V should be attributed to Li–Bi alloy while 0.5 V/0.98 V peak refers to the Co redox reaction. The large discrepancy between the oxidation and reduction peaks demonstrates the large polarization of the materials.

Figure 4 shows the charge-discharge curves of the Li/$Bi_2Ca_3Co_2O_9$ electrode. The averaged discharge voltage of the material is about 0.6 V deduced from the profile. The averaged charge voltage is about 0.8 V. Obviously, they deliver a significantly high initial discharge capacity (∼840 mAh/g). Unfortunately, the capacities decrease remarkably with increasing cycle numbers, to about 200 mAh/g after 50 times of cycle. It is suggested that the formation of surface layers considered as SEI (solid-electrolyte interface) can account for this phenomenon [12, 13]. Since the surface of the $Bi_2Ca_3Co_2O_9$ is composed of a layered structure as shown in Fig. 2, lithium ions can intercalate into the $Bi_2Ca_3Co_2O_9$ at the defect sites, which induces the formation of the SEI layers [20, 21]. As is reported by Broussely et al. [14], the reaction with surface oxide, a kind of extrinsic process, may be responsible for the capacity fading of the high energy batteries, which usually occurs at small insertion in the initial transient. Based on these results, we can see that the polycrystalline $Bi_2Ca_3Co_2O_9$ can be partly insertion/extraction with Li ions.

Figure 5 shows the capacity retention of the $Bi_2Ca_3Co_2O_9$ electrode. The initial cycling is even lower than the usual transition-metal oxides anode [15]. After 50 times of cycle, the charge/discharge flat voltage keeps constant which accounts for its stable configurations.

The second discharge capacity decreases remarkably compared with the first one. Then they stay on a relatively stable flat plateau nearing 300 mAh/g and also show a high efficiency from the second cycle, approaching one hundred percent. Moreover, the capacity efficiencies in both electrodes of the semi-battery are very high except for the first cycle, meaning that almost all the charged capacity can be discharged. The decreasing capacity indicates that the resistance increases with increasing cycle numbers. The possible reason may be that the catalytic $Bi_2Ca_3Co_2O_9$ is isolated by the nonconducting material such as Li_2O.

4 Conclusion

Polycrystalline and single crystal $Bi_2Ca_3Co_2O_9$ are prepared through a conventional solid-state reaction and flux method, respectively. XRD measurement confirms their phase purity. The characterization for electrochemical properties shows that they can be partly insertion/extraction with Li ions. The first discharge capacity reaches 840 mAh/g. From the second cycle, they display good reversibility, which demonstrates a relatively stable structure. However, further research is essential to improve the capacity and reversibility for practical application.

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