Short communication

Improved cycling performance of bismuth-modified amorphous manganese oxides as cathodes for rechargeable lithium batteries

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Abstract

Bismuth-modified amorphous manganese oxides were synthesized via a room temperature aqueous route. They were galvanostatically tested as intercalation cathodes for rechargeable lithium batteries at $1\,\text{mA}\,\text{cm}^{-2}$ between 1.5 and 4.3 V. In sharp contrast to severe capacity fading of unmodified amorphous manganese oxide synthesized by the same route, a stable cycling performance of the bismuth-modified amorphous manganese oxide was observed. After an initial drop from 185 to 145 mAh g^{-1} in around 10 cycles, the capacity of the bismuth-modified amorphous manganese oxide remains essentially unchanged for another 40 cycles. Based on results from X-ray diffraction and cyclic voltammetry (CV) characterization, it is suggested that an electrochemically active and stable local structure evolves inside the bismuth-modified amorphous manganese oxide upon initial cycling, leading to the stabilized cycling performance for subsequent cycles.
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1. Introduction

Manganese oxides are promising cathode materials for rechargeable lithium and lithium ion batteries owing to their natural abundance, low cost and environmental benignity. In recent years, manganese oxides in amorphous forms have attracted increasing attention [1–10]. They exhibit very high intercalation capacities over a wide voltage range corresponding to more than one electron reduction of the Mn(IV) ions, i.e. a redox reaction involving both the Mn^{4+}/Mn^{3+} and Mn^{3+}/Mn^{2+} couples. These high specific capacities offer the amorphous manganese oxides a significant advantage in applications such as in portable electronic devices where a long discharge time is desired. However, for most amorphous manganese oxides synthesized via low temperature aqueous routes, unsatisfactory cycling performance becomes a limiting factor for them. In our previous work, improved cycling performance of amorphous manganese oxides doped with

other cations such as Na^{+}, Cu^{2+} have been reported [2,3], which points to the possibility of achieving improved cycling performance by stabilizing the local structure through structural modification by incorporation of different cations.

The more than one electron transfer in the amorphous manganese oxides where at least some of the Mn^{4+} ions are reduced to Mn^{2+} during the lithium intercalation process resembles what occurs in aqueous alkaline batteries where manganese oxides function as cathodes. In alkaline batteries with manganese oxides as cathodes, a high capacity could be achieved due to the reaction involving two electrons, which corresponds to the reduction of Mn^{4+} to Mn^{2+}. The discharge of manganese dioxide in alkaline batteries is generally divided into two processes [11–16]. The first can be considered as a homogeneous solid-state proton intercalation reaction which yields a capacity of one electron per manganese and the product of MnOOH. Compared with the homogeneity of the first discharge process, the second discharge step where Mn^{3+} is reduced to Mn^{2+} is considered a heterogeneous one where the discharge products could be mainly $Mn(OH)_2$. Although the two-electron transfer can provide a high capacity

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for the manganese dioxide in alkaline batteries, difficulties are encountered when trying to make it rechargeable because of the poor irreversibility of MnO_2.

A breakthrough in developing rechargeable alkaline batteries based on MnO_2 was made by Wroblawa and coworkers [17,18] through modifying MnO_2 with Bi^{3+} either chemically or physically. The bismuth-modified manganese oxide could be cycled hundreds of times with high discharge depth. In the initial work of Wroblowa and coworkers [17], the bismuth-modified manganese oxide was obtained by co-precipitation in a mixture of dissolved Mn(II) and Bi(III) salts. The reversibility of this material was explained by the stabilization of the open layered structure by the bismuth ions during the discharge/charge process. Later Wroblowa et al. [18] found that similar reversibility can be achieved even for manganese oxides physically mixed with Bi_2O_3 and the reversibility has no direct relation with what kind of manganese oxide is used. After that, extensive research work has been conducted and many suggestions have been given with regard to the role that the bismuth ions play [19–26]. So far, it is widely accepted that the presence of bismuth prevents the formation of the poorly electroactive spinel structure, which is the main cause of irreversibility of MnO_2 in alkaline batteries. However, a very clear mechanism has not yet been established.

Considering the resemblance between proton insertion and lithium intercalation, bismuth-modified manganese oxides might yield improved cycling performance for lithium intercalation. Atwater and coworkers [27,28] investigated the behavior of $MnO_2 \cdot Bi_2O_3$ mixture in primary and secondary lithium and lithium ion batteries. Bach et al. [29] reported the effect of Bi^{3+} ions in bismuth-doped layered MnO_2 as a lithium intercalation compound. An improved cycling performance was reported and a pillaring effect of Bi^{3+} was proposed. However, despite the fact that bismuth-modified manganese oxides have accomplished significant success in alkaline batteries, related work is still scarce on their application in lithium or lithium ion batteries. Moreover, since confusion and controversy still exist as to the role of bismuth in manganese oxides despite the extensive work that has been conducted in aqueous alkaline batteries, investigation of the behavior of bismuth-modified manganese oxides as lithium intercalation hosts in non-aqueous systems might provide complementary or additional information with which to address and ascertain the role of bismuth in manganese oxides. In the present work, bismuth-modified amorphous manganese oxides were synthesized and characterized as cathodes for rechargeable lithium batteries. Significantly improved cycling performance was observed and the mechanism for the improvement discussed.

2. Experimental

The amorphous manganese oxides were synthesized by a room temperature aqueous synthesis route. A mixed solution

of manganese(II) nitrate and bismuth(III) nitrate were prepared. A H_2O_2/LiOH mixture solution was used to oxidize the Mn(II) ions and precipitate out bismuth-modified Mn(IV) oxides. Specifically, 1000 ml 0.2 M manganese(II) nitrate solution was prepared. A desired amount of bismuth(III) nitrate was dissolved into this solution where the bismuth to manganese molar ratio (Bi/Mn) was controlled. Nitric acid was added to adjust the pH to help dissolution of the bismuth salt. Then this solution mixture reacted with a 15 ml H_2O_2/LiOH solution mixture where the concentration of both solutes was 15 wt.%. The reaction occurred rapidly and bismuth-modified manganese oxides precipitated out instantly. Unmodified amorphous manganese oxide was prepared in the same way without using any bismuth salt. After dialysis to remove undesired ions, these precipitates were freeze-dried and bismuth-modified or unmodified amorphous manganese oxides obtained.

X-ray powder diffraction was performed with a Siemens Diffraktometer® using Cu Kα radiation, with a 2θ step size of 0.05° and a dwelling time of 20 s at each step. A graphite monochromator was mounted between the sample and the detector to filter noise signals from possible fluorescence induced by the incident X-ray.

For electrochemical characterization, all materials were stirred with Ketjen black carbon powders and a polytetrafluoroethylene (PTFE) binder in a weight ratio of 60:30:10 (active material:carbon:binder) in cyclohexane overnight. After vacuum drying to remove the cyclohexane, the mixture was rolled, punched and pressed into 1/4 in. diameter pellets with a thickness around 150–200 μm. These pellets were dried at 80 °C under vacuum for 24 h in a vacuum oven that serves as the antechamber of an argon-circulating glovebox. After drying, they were directly transferred into a glovebox without involving any intermediate transfer procedure or exposure to air. They were tested inside the glovebox in laboratory glass cells with lithium metal foils as the counter and reference electrodes and 1 M $LiClO_4$ in 1:1 propylene carbonate/ethylene carbonate as the electrolyte. Cyclic voltammetry (CV) of these cathodes was conducted before and after cycling in the same electrochemical cell using a Solartron 1280B potentiostat/galvanostat with a scanning rate of 0.1 mV s^{-1}.

3. Results and discussion

In synthesizing the manganese oxides, the bismuth to manganese molar ratio in the aqueous solutions were preset to be Bi/Mn = 0 and 0.2. During the reaction, the supernatant solution was sampled and titrated and the results indicated that all manganese and bismuth ions were precipitated. Therefore, the preset bismuth to manganese ratio was retained in the as-prepared powders. The X-ray diffraction patterns of the bismuth-modified and unmodified manganese oxides are shown in Fig. 1. The positions of these diffuse peaks are very similar to those of amorphous manganese oxides reported
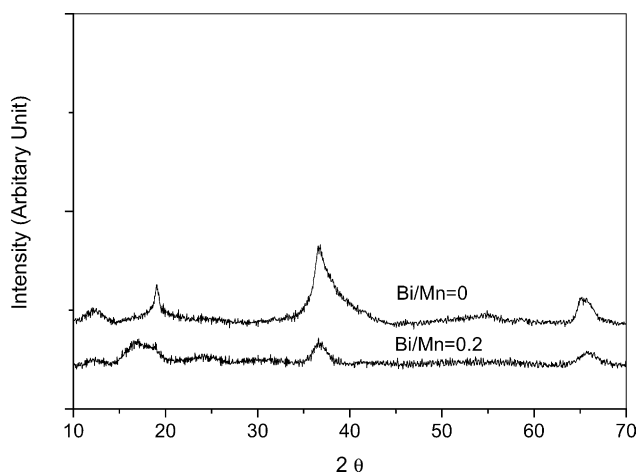
Fig. 1. XRD spectra of unmodified and bismuth-modified amorphous manganese oxides.

earlier, which were synthesized by oxidizing Mn(II) precursors with sodium hypochlorite [2,3]. The fact that no peaks other than those that belong to manganese oxides are observed would suggest that single phase materials are synthesized, although the amorphous nature of the materials renders unequivocal phase identification difficult. The diffuse peaks clearly indicate that these materials are largely amorphous. The bismuth-modified manganese oxide exhibits even more diffused peaks than the unmodified one, which might be due to the fact that the presence of bismuth ions further retarded the crystallization process of the oxide formed at room temperature.

Discharge/charge cycling tests of the unmodified and bismuth-modified amorphous manganese oxides as cathodes for rechargeable lithium cells were conducted at a current density of $1 \, \text{mA cm}^{-2}$ in the voltage range between 1.5 and 4.3 V. The specific capacities and cycling performance of

these samples are shown in Fig. 2. For the unmodified amorphous manganese oxide sample, an initial specific capacity of $230 \, \text{mAh g}^{-1}$ was obtained, and the capacity continually decreased upon cycling to $53 \, \text{mAh g}^{-1}$ in 50 cycles, an average of 1.5% drop per cycle. For the sample with the Bi/Mn molar ratio of 0.2, the initial specific capacity was $185 \, \text{mAh g}^{-1}$g. This is lower than that of the unmodified sample, likely due to a significant increase of formula weight caused by the incorporation of the heavy bismuth. Upon cycling, the capacity decreased to ca. $145 \, \text{mAh g}^{-1}$ in 10 cycles, and then stabilized at this value for the subsequent 40 cycles.

Since the bismuth-modified amorphous manganese oxide shows an interesting behavior of capacity evolution and a much stabilized cycling performance in contrast with the poor cycling performance of the unmodified sample, it is of interest to investigate the possible structure evolution upon cycling in order to address the mechanism of cycling performance stabilization by bismuth modification. Ex-situ X-ray powder diffraction analysis of the testing electrode which comprises the bismuth-modified amorphous manganese oxide, carbon and PTFE binder was conducted after 20 discharge/charge cycles. Fig. 3 shows the X-ray diffraction spectra of the bismuth-modified amorphous manganese oxide before cycling and the testing electrode after 20 cycles. The spectrum of the testing electrode is basically the same as that of the sample before cycling, with an additional peak at 18° which is from the PTFE binder. The fact that no sharp peaks appeared indicates that no long range order is developed and the material remains X-ray amorphous upon cycling. In fact, the disappearance of the diffuse peak at 67° suggests that the material becomes even more amorphous upon cycling.

Cyclic voltammetry was utilized to further investigate the cause of the cycling behaviors observed above. Since the energy level of the redox center in a material is influenced by its structure and CV reveals that energy level, it is
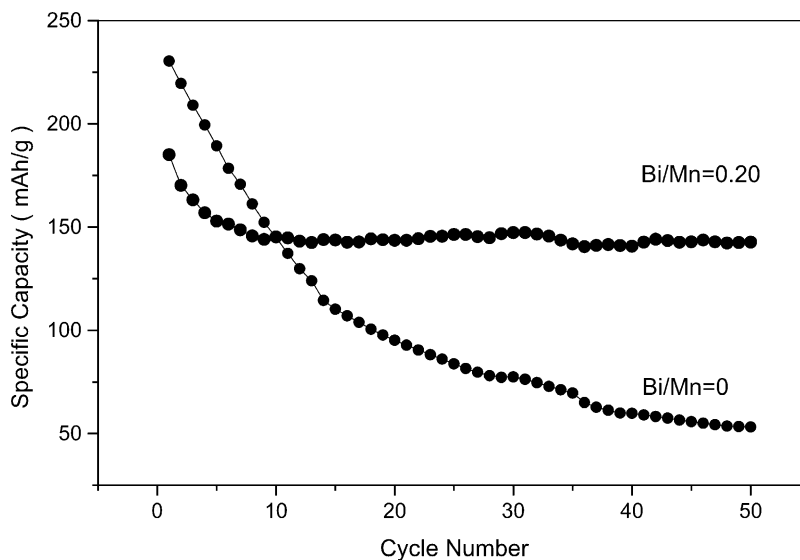

Fig. 2. Cycling performance of unmodified and bismuth-modified amorphous manganese oxides. Current density = $1 \, \text{mA cm}^{-2}$.
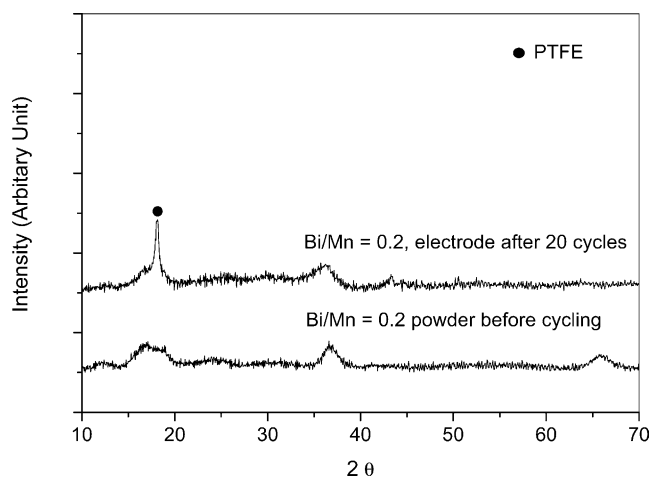
Fig. 3. XRD spectra of as-prepared bismuth-modified amorphous manganese oxide and its testing electrode after 20 cycles of galvanostatic cycling.

capable of providing information with which to address possible structural evolution. For our CV experiment, battery discharge/charge cycling tests of both the bismuth-modified and unmodified amorphous manganese oxide electrodes were performed with the same experimental conditions as used in Fig. 2, namely, at a current density of $1\,\mathrm{mA\,cm^{-2}}$ and in the voltage range of 1.5–4.3 V. The CV experiment was conducted before the cycling test and after the electrode was cycled for 10, 20 and 30 cycles, in the same electrochemical cell as used for the galvanostatic cycling test and in the voltage range between 1.5 and 4.3 V with a scan rate of $0.1\,\mathrm{mV\,s^{-1}}$. As shown in Figs. 4 and 5, both the unmodified and bismuth-modified (Bi/Mn = 0.2) amorphous manganese oxides show broad peaks in their cyclic voltammograms throughout the galvanostatic cycling tests. This is consistent with the fact that their structure remains amorphous as indicated by X-ray diffraction.
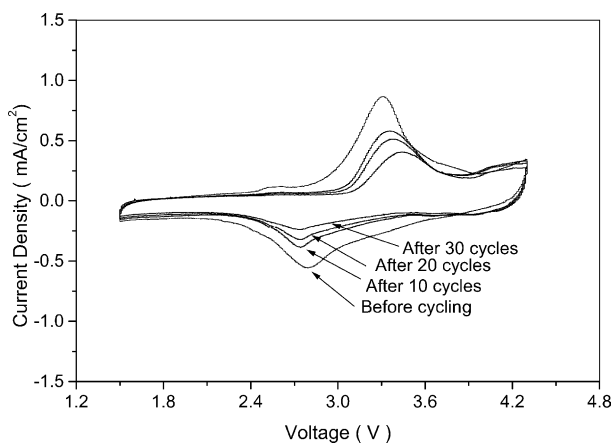

Fig. 4. Cyclic voltammograms of unmodified amorphous manganese oxide before galvanostatic cycling and after every 10 cycles of galvanostatic cycling. Scan rate = $0.1\,\mathrm{mV\,s^{-1}}$.
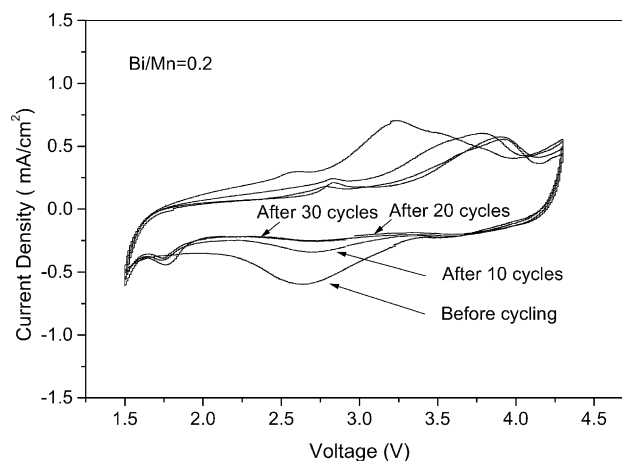

Fig. 5. Cyclic voltammograms of bismuth-modified amorphous manganese oxide before galvanostatic cycling and after every 10 cycles of galvanostatic cycling. Scan rate = $0.1\,\mathrm{mV\,s^{-1}}$.

While the cyclic voltammograms of both samples show broad peaks throughout the galvanostatic cycling tests, distinctly different evolutions of their cyclic voltammograms are observed. Before galvanostatic cycling, the cyclic voltammograms of both samples are similar. Upon galvanostatic cycling, the redox peaks in the cyclic voltammogram of the unmodified amorphous manganese oxide basically remains in the same position (Fig. 4), which indirectly suggests that the structure of this material does not evolve significantly upon cycling. However, the area covered by the peaks, namely, the charge/discharge capacity shrinks sharply upon cycling, which is consistent with the capacity fading observed in galvanostatic cycling (Fig. 2). This capacity fading might be partially due to the dissolution of manganese ions into the electrolyte since dissolution of manganese ions into the electrolyte is one of the main reasons for capacity fading observed of manganese oxides as lithium intercalation hosts, or it could be due to the generation of some inactive phases during cycling similar to what happens in alkaline batteries.

For the bismuth-modified amorphous manganese oxide, after the first 10 galvanostatic cycles, the cyclic voltammogram becomes significantly different from before the galvanostatic cycling test (Fig. 5). The positions of the peaks have shifted significantly, and the areas covered by the peaks have shrunk significantly as well. The former suggests that certain structural evolution has occurred inside this material, and the later is consistent with the significant capacity fading observed for the first 10 cycles in galvanostatic cycling (Fig. 2). Considering that no long range order is developed upon galvanostatic cycling as shown by X-ray diffraction (Fig. 3), most likely the structure evolution is confined on a local scale. After the first 10 cycles, only minor changes occur in both the positions of and the areas covered by the peaks, and the cyclic voltammograms after 20 and 30 cycles of galvanostatic cycling are essentially the same. This suggests that the structure and charge capacity of the bismuth-modified amorphous manganese oxide are essentially stabilized after

the first 10 cycles, consistent with the stabilized capacity observed in the galvanostatic cycling test after the first 10 cycles, as shown in Fig. 2. It appears likely that an electrochemically active local structure that is stable is formed in the bismuth-modified amorphous manganese oxide after initial galvanostatic cycling, leading to a stabilized intercalation capacity.

The effect of bismuth in rendering rechargeability to manganese dioxides in alkaline batteries is well known. It is believed that two kinds of mechanism may be involved. One is that the bismuth ions help stabilize the open layered structure through a pillaring effect and prevent the structure from collapsing [17]. The other is that bismuth ions play a catalytic role in either promoting formation of an electrochemically active phase such as Birnessite [19–22,25] or suppressing the formation of inactive spinel Mn_3O_4 from the dissolved Mn^{2+} and Mn^{3+} intermediates in aqueous solutions [22–24]. In our work, the bismuth-modified amorphous manganese oxide likely undergoes a structural evolution to form a locally more stabilized structure during the initial galvanostatic cycling. Therefore the role of bismuth ions might be similar to the catalytic role proposed for them in bismuth-doped manganese dioxides for alkaline batteries. Due to the difficulty associated with characterizing the local structure of amorphous materials, a detailed understanding of the mechanism for capacity stabilization in the bismuth-modified amorphous manganese oxide must await more detailed structural characterization by advanced techniques.

4. Conclusion

Unmodified and bismuth-modified amorphous manganese oxides were synthesized by an aqueous precipitation method and investigated as intercalation hosts for rechargeable lithium batteries. In contrast with continuous capacity fading of the unmodified sample, a very stable cycling performance was observed of the bismuth-modified amorphous manganese oxide after the first 10 cycles. While both samples remain X-ray amorphous upon cycling, cyclic voltammetry tests after gavalnostatic cycling suggest that an electrochemically active local structure that is stable may have evolved in the bismuth-modified sample after initial cycling, leading to stabilized intercalation capacities in subsequent cycles.

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