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ELECTROCHEMICAL PROPERTIES OF BiFeO₃ THIN FILMS PREPARED BY PULSED LASER DEPOSITION

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BiFeO₃ thin film is deposited on the stainless steel substrate by pulsed laser deposition (PLD). Structural characterization using X-ray diffraction indicates that the film is polycrystalline with perovskite structure. Morphology characterization by field emission scanning electron microscopy reveals that the film is composed of grains with wide size distribution with a porous structure. Charge/discharge in the potential range between 0.05 and 3 V shows that the reversible capacity of the first charge/discharge cycle at 280 mA/g current density is about 770 mAh/g with high columbic efficiency about 74%. The reversible capacity after 50 cycles remains 50% of its initial capacity. The preliminary results indicated that BiFeO₃ is a promising high capacity anode for lithium-ion batteries.

Keywords: Deposition; anode; rechargeable battery.

The demand for next generation lithium-ion batteries with high energy density and power density becomes imperative with the emergence of numerous new electronic devices such as hybrid electric vehicles and all kinds of power tools. Such new power requirements can only be satisfied by achieving breakthroughs in electrode materials. Graphite is currently the dominating anode material for lithium-ion batteries. However, the theoretical capacity of graphite electrode is only 372 mAh/g. Therefore, some lithium alloys (Si, Sn, Al and etc.) have attracted a lot of interest because their specific and volumetric capacities are potentially many times than that of graphite.1,2 However, the big volume change during Li alloying/dealloying process causes cracking and pulverization of the material, resulting in fast capacity fade. Recently, it has been found that reversible Li storage can be achieved in many transition metal oxides, which is based on heterogeneous Li uptake and extraction reactions, a novel conversion mechanism involved reversible reduction and oxidation of metal (M) nano-sized particles dispersed into a lithia matrix (Li₂O). Electrodes made of nano-particles of transition metal oxides demonstrate high reversible capacity, good capacity retention and high discharge rates, which make them promising anode materials for high-performance lithium-ion batteries. Many binary and ternary transition metal oxides (NiO, Fe₃O₄, CuO, SnO₂, NiFe₂O₄ and etc.) have also been extensively studied as potential anode materials.3–8

Ternary metal oxide BiFeO₃ (BFO) with perovskite structure has recently been studied as multiferroic material.9,10 Although there are no previous reports on its electrochemical properties as anode materials for lithium-ion batteries, it is anticipated that this material has capability to store a large amount of Li. To the reduction process, six Li are needed to reduce Bi and Fe from the BFO. Furthermore, the reduced Bi can be alloyed with another three Li.11 Totally, nine mol. Li can be stored in one mol. BFO, theoretically leading to a specific capacity of 770 mAh/g. Therefore, it is worthwhile exploring the electrochemical properties of BFO when used as anode in lithium-ion batteries.

In this work, BFO thin film is prepared on the stainless steel substrate by PLD. The electrochemical behavior of BFO thin films is investigated and the possibility of using BFO as anode material for lithium-ion batteries is discussed.
The BFO target was prepared by sintering a mixture of high-purity bismuth oxide and iron oxide in air at 500°C for 3 h and then at 800°C for 30 min. 10% excess bismuth oxide was added into the target to compensate for Bi loss during high temperature calcinations. BFO thin films were deposited on the SS substrates and SiO2/Si (SOS) substrates by PLD with a KrF excimer laser (248 nm). The laser fluence and repetition rate were controlled at 2 J/cm² and 5 Hz, respectively. Thin film deposition was carried out at a substrate temperature of 600°C at an oxygen pressure of 150 mTorr for 30 min.

Microstructure of thin films was characterized by X-ray diffraction (XRD, Shimadzu XRD-7000 X-ray diffractometer) with Cu Kα radiation. Surface morphology of thin films was characterized using field emission scanning electron microscopy (FESEM, Hitachi S-4100). Thickness of thin film was estimated from FESEM image of cross-section of the thin film deposited on the SOS substrate. The loading of thin film was obtained by measuring the weight of the substrate before and after the deposition using a microbalance with an accuracy of 0.01 mg.

Electrochemical measurements were conducted using a Solartron 1267 cell test system. The Swagelok cells consist of a Li metal foil counter electrode, a BFO thin film working electrode with an active area of approximately 0.785 cm², and 1 M LiPF6 in EC/DEC (1/1, vol%) as the electrolyte. Galvanostatic charge/discharge measurements were carried out in the potential range between 0.05 and 3 V at a constant current density (280–560 mA/g).

XRD patterns of the BFO thin film on the SS substrate and of the target are shown in Fig. 1. As shown in Fig. 1(a), the XRD pattern of the target can be attributed to a rhombohedrally distorted perovskite structure with R3c space group. Only a very small diffraction peak at about 27.5° can be attributed to excess Bi2O3. As shown in Fig. 1(b), all diffraction peaks from the film can be attributed to the perovskite phase except for peaks from the SS substrate without trace of second phases, such as Bi2O3 and Fe2O3. No preferred orientation can be observed from the thin film XRD.

Figure 2 shows the top-view FESEM images of the BFO thin film deposited on the SS substrate and the cross-sectional image of the BFO thin film deposited on the SOS substrate. As shown in Fig. 2(a), the BFO film is uniform and composed of well-defined grains without any cracks. However, the grains are not closely packed showing a porous structure. High magnification image shown in Fig. 2(b) reveals that the BFO grains exhibit irregular shape and the grain size is not uniform. The big grains can reach about 100–200 nm while the small grains are only about 20–50 nm. The size of the pores between the grains ranges from 20 to 50 nm. The thickness is estimated to be about 280 nm as shown in Fig. 2(c). The porous structure of the BFO thin film may not be ideal for ferroelectric property because the porous structure may cause an increase in leakage current. However, the porous structure is advantageous for lithium-ion battery as these pores will facilitate electrolyte penetration into the film and increase the interface area between the BFO film and the electrolyte.
The first three charge/discharge curves of the BFO thin film with loading of 0.18 mg in the voltage window 0.05–3 V at a current density of 280 mA/g are shown in Fig. 3(a). The first discharge and charge capacities are 1040 mAh/g and 770 mAh/g respectively. Taking into account the accuracy of the microbalance (0.01 mg), the error in the loading of thin film is about ±5.5%. It is noted that the first discharge capacity is much larger than the theoretical capacity of BFO (∼770 mAh/g), which should be attributed to the surface-electrolyte interphase (SEI) film formation due to the electrolyte decomposition. The first reversible capacity is very close to the theoretical capacity, even considering the loading error, indicating the high electrochemical activity of the BFO film. The columbic efficiency for the first cycle charge/discharge is about 74%, which is much larger than other transition metal oxides such as SnO₂ and Co₃O₄.

Multiple voltage plateaus can be observed from both charge and discharge curves due to different redox reactions during Li insertion and extraction. These redox reactions can be better illustrated in the dQ/dV curves as shown in Fig. 3(b). For the first discharge, there is one peak at about 1.5 V followed by two peaks between 0.5 and 1 V. When Li is initially inserted into the BFO thin film, Bi and Fe metals will be first reduced with the formation of Li₂O. This mechanism is applicable for other transition metal oxides and the first reaction can be expressed as follows:

$$\text{BiFeO}_3 + 6\text{Li}^+ + 6e^- \rightarrow \text{Bi} + \text{Fe} + 3\text{Li}_2\text{O} \quad (1)$$

The well-separated two peaks between 0.5 and 1 V should correspond to the two steps of alloying processes between Li and Bi. These two step alloying processes were well studied in previous work by several groups and can be expressed as
follows:

\[ \text{Bi} + \text{Li}^+ + e^- \rightarrow \text{LiBi} \]  

(2)

\[ \text{LiBi} + 2\text{Li}^+ + 2e^- \rightarrow \text{Li}_3\text{Bi} \]  

(3)

For the first charge process, one peak at about 0.9 V and two peaks between 1 and 3 V correspond to the one step dealloying process and two oxidation processes of Bi and Fe, respectively. The perovskite structure should be destroyed after the first discharge, leading to two step oxidation processes for Bi and Fe separately.

To investigate the cycle performance of the BFO thin film, the subsequent 50 cycles of charge/discharge were performed in the voltage window between 0.05 and 3 V at a relatively high current density of 560 mA/g. As shown in Fig. 4(a), the specific capacity decreases quickly for the first 20 cycles and then the capacity fade slows down for the next 30 cycles. After 50 cycles, the capacity decreases to 370 mAh/g, which is close to the theoretical capacity of graphite. Except for the first several cycles, the columbic efficiency is always above 95% and keeps increasing with cycling. To understand the capacity loss of the BFO thin film electrode, the structure and morphology of the film after electrochemical tests were investigated and results are shown in Fig. 4(b). From the XRD pattern of the film after electrochemical test, it can be seen that the perovskite structure has been destroyed after Li insertion and extraction and the film becomes a composite of Bi$_2$O$_3$ and Fe$_2$O$_3$. The FESEM image of the film after electrochemical test clearly shows that the film becomes a highly porous structure with very small sized grains. From previous works, it is known that electrochemical lithiation into transition metal oxides typically leads to in situ formation of a M/Li$_2$O nanocomposite where nanometer-scale metal clusters are embedded in a Li$_2$O matrix, accompanied by a large volume expansion. In the BFO film, besides the metal oxidation and reduction reactions, Li-Bi alloying/dealloying reactions also induce big volume change. Such big volume change often induces huge strain in the film and, leading to cracks and pulverization, and finally to loss of active material from the substrate. This probably explains the pronounced capacity loss for the BFO thin film. The fast capacity fade can be improved by using nano-sized transition metal oxides or transition metal oxides with special nanostructures (like hollow spheres, nanotubes), which can accommodate big volume change during Li insertion/extraction. BiFeO$_3$ thin films with perovskite structure were prepared on the SS substrate by PLD. For the first time, the BFO thin film is tested as anode material in lithium-ion batteries. A high reversible capacity about 770 mAh/g and high columbic efficiency about 74% can be obtained for the first cycle charge/discharge between 0.05 and 3 V at a current density of 280 mA/g. About 50% of its initial reversible capacity can be maintained after 50 cycles. The capacity loss is due to the big volume change during Li insertion/extraction. Based on these preliminary results, BFO especially nanocrystalline BFO electrode could be a promising high capacity anode material for lithium-ion batteries.

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