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Facile preparation of nano-micro structure $PbSbO_2Cl$ as a novel anode material for lithium-ion batteries

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We report the development of $PbSbO_2Cl$ as a new anode material for lithium-ion batteries. It is prepared by a simple hydrothermal method from $Pb(NO_3)_2$ and $SbCl_3$. The as-prepared $PbSbO_2Cl$ shows a well-dispersed nano-micro structure with particle sizes of 200–500 nm. The initial discharge capacity of $PbSbO_2Cl$ is 1011.0 mAh g^{-1} corresponding to 14.6 Li per formula storage in the structure. In the inverse charge process, a reversible capacity of 731.8 mAh g^{-1} can be delivered. This suggests that $PbSbO_2Cl$ may be a promising high-capacity anode material for lithium-ion batteries.

1. Introduction

Due to their high capacity characteristics, metal oxides have been used worldwide as lithium storage materials since lithium-ion batteries were developed. In the past twenty years, Co, Cu, Mn, and Ni-based transition metal oxides have received more attention than other metal oxides due to their superior lithium storage capabilities.[1–5] However, high prices inhibit the practical application of these materials in the commercial field of energy storage and conversion. As a result, some cheap lithium storage materials, such as Pb, Sb, Cr, and Fe-based oxides,[6–14] have been prepared to satisfy the development of lithium-ion batteries. PbO samples, which are prepared by solution techniques, show a reversible capacity of 100 mAh g^{-1} after 50 cycles.[6,7] After carbon coating, PbO@C core–shell nanocomposites show improved electrochemical properties with a reversible capacity of 170 mAh g^{-1} after 50 cycles.[8] This indicates that the present techniques are unsuitable for the development of high capacity Pb-based anode materials.

In recent years, composite oxides, such as $CaSnO_3$, $CuCrO_2$ and $CoFe_2O_4$,[15–17] have caught the attention of researchers worldwide as a result of their superior cycling ability and high capacity characteristics. In the composite oxides, the different active components react with lithium at different potentials during the charge and discharge processes. As a result, the other components can act as buffers to relieve the volume change of the sample when one component is reacting with lithium. Most recently, transition metal chlorides, such as $CoCl_2$, AgCl and $CuCl_2$,[18,19] have been used as lithium storage materials for lithium-ion batteries. They show excellent cycling capability and high reversible capacity. It has also been found that there are quite different electrochemical working plateaus between chlorides and oxides. Therefore, it can be expected that metal oxide chlorides will exhibit superior electrochemical performance due to their composite structures.

In this paper, a novel lithium storage material ($PbSbO_2Cl$) is reported. It is prepared by a simple hydrothermal method. The structure and morphology are described by XRD, FTIR, SEM and HRTEM. The electrochemical results show that $PbSbO_2Cl$ is a potential anode candidate for lithium-ion batteries.

2. Experimental section

$PbSbO_2Cl$ is obtained by using $Pb(NO_3)_2$ and $SbCl_3$ as the starting materials. Firstly, $Pb(NO_3)_2$ and $SbCl_3$ are dissolved in distilled water. Then, the Pb^{2+} and Sb^{2+} in the solution are totally deposited by the $NH_3{\cdot}H_2O$. After that, the mixed solution including the obtained white intermediate are put into a Teflon-lined stainless steel autoclave and maintained at 160 °C for 24 h. Finally, the resulting product is filtered and washed by distilled water and ethanol, then dried at 100 °C for 24 h. All chemical reagents in the experiment were purchased from Sinopharm Chemical Reagent Shanghai Co. Ltd in China.

The X-ray diffraction (XRD) phase patterns for the intermediate and resulting samples were recorded by a Bruker D8 Focus diffractometer using nickel-filtered Cu-Kα radiation. Fourier transform infrared (FTIR) spectra were collected by a Shimadzu infrared spectrophotometer at wavenumbers between 400 and 1000 cm^{-1}. The surface morphology of as-prepared samples was characterized by a Hitachi scanning electron microscope (SEM). The fine grain structure of $PbSbO_2Cl$ was observed with a JEOL high resolution transmission electron microscope (HRTEM).

$PbSbO_2Cl$ working electrode was fabricated by using the resulting powder (80 wt.%), carbon black (10 wt.%) and

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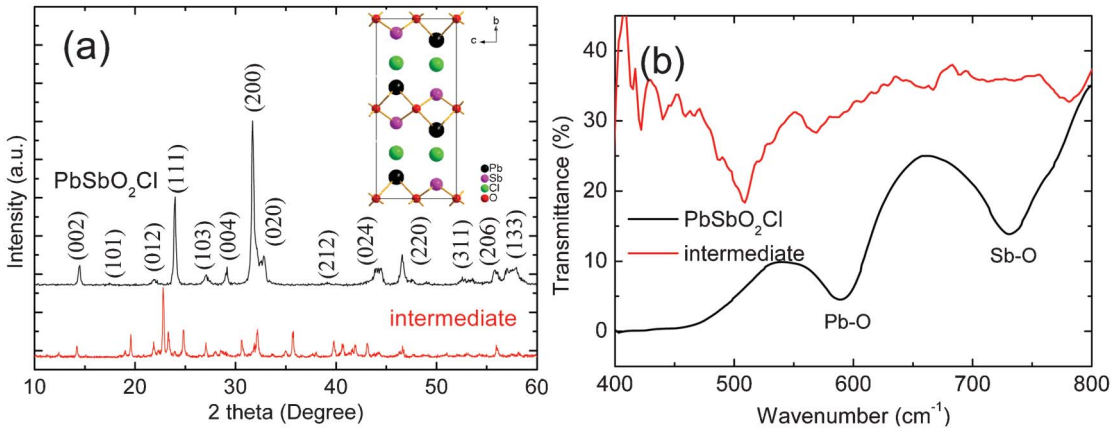

Fig. 1 XRD (a) and FTIR (b) patterns of $PbSbO_2Cl$ and its intermediate.

polyvinylidene fluoride (10 wt.%) as starting materials. A homogeneous slurry can be formed by adding *N*-methylpyrrolidine into the mixture. The testing electrode was prepared by casting the slurry on a copper foil and drying at 120 °C for 12 h in a vacuum oven, then cut into discs with a diameter of 15 mm.

$PbSbO_2Cl$/Li battery was assembled by using $PbSbO_2Cl$ film as cathode, Whatman glass fiber filter as separator, metal lithium disc as anode and 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1 : 1, v/v) as the electrolyte in an Etelux Ar-filled glove box. All the charge/discharge cycles were recorded on a multi-channel Land battery testing system in a constant temperature cabinet (25 °C). Cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) of the $PbSbO_2Cl$/Li battery were collected on a CHI 660D electrochemical working station in the frequency range between 100 000 and 0.01 Hz with an amplitude of 5 mV.

3. Results and discussion

Fig. 1a and 1b show the XRD and FTIR patterns of the intermediate and resulting samples. Based on the JCPDS cards, the intermediate obtained from the deposition of $Pb(NO_3)_2$ and $SbCl_3$ mixed solution is a mixed material composed of unknown and known compounds, such as $Pb(OH)_2$. After hydrothermal

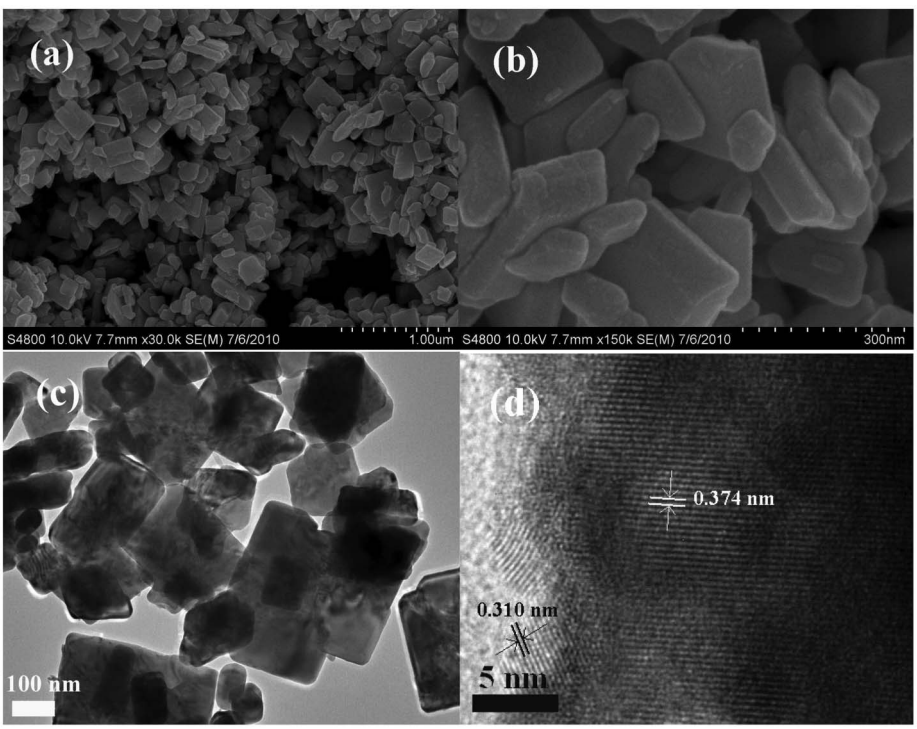

Fig. 2 SEM (a,b), TEM (c) and HRTEM (d) images of $PbSbO_2Cl$.

reaction, $PbSbO_2Cl$ phase is formed as described by the XRD pattern. The main diffraction peaks located at 14.5°, 24.0°, 31.7°, 32.9°, 44.1° and 46.6° correspond to the (002), (111), (200), (020), (204) and (220) planes. It is attributed to the JCPDS card No.17-0469, namely the $PbSbO_2Cl$ phase. As shown in Fig. 1a, the unit cell of $PbSbO_2Cl$ is orthorhombic, space group Bmmb (No. 63). The refined unit cell parameters are $a = 5.601$, $b = 5.429$ and $c = 12.189$ Å by using Fullprof software. The structure of $PbSbO_2Cl$ consists of sheets of $[PbO_{4/4}]^0$ and $[SbO_{4/4}]^+$ cations, which are separated by Cl^-. As a result of the stereoactive lone pairs, both Pb^{2+} and Sb^{3+} cations are in asymmetric coordination environments. As seen from the FTIR spectra in Fig. 1b, the featured bands for $PbSbO_2Cl$ at 589 and 732 cm^{-1} can be assigned to the stretching vibrations of Pb–O and Sb–O bonds, respectively. This is consistent with the previous results reported by Y. Porter.[20]

Fig. 2 shows the SEM, TEM and HRTEM images of $PbSbO_2Cl$. As shown in Fig. 2a and 2c, the as-prepared $PbSbO_2Cl$ powders are well-dispersed nano-micro structures with particle sizes of 200–500 nm. Therefore, they are suitable as a powder anode material for lithium-ion batteries. As the HRTEM images show in Fig. 2d, the lattice distances are measured to be 0.374 and 0.310 nm, which correspond to the featured (111) and (004) planes of the as-prepared $PbSbO_2Cl$ sample, respectively. This is consistent with the XRD result shown in Fig. 1a.

Fig. 3a shows CVs of the $PbSbO_2Cl$ lithium storage material. There are seven reduction peaks at 2.28, 1.76, 1.69, 1.13, 0.70, 0.40, 0.19 V and six oxidation peaks at 0.56, 0.67, 1.10, 1.36, 1.98, 2.34 V in the initial cycle. The appearance of so many redox peaks is attributed to the complex electrochemical lithiation process to form Li_xSb, Li_yPb, Li_2O and LiCl. The asymmetric behavior of reduction and oxidation peaks shows the irreversible reactions between $PbSbO_2Cl$ and lithium. In the subsequent scans, the shape and position of reduction and oxidation peaks are similar to each other except for the peak currents and some irreversible peaks in the high potential range (>1.5 V). This indicates that the deterioration of $PbSbO_2Cl$ as a lithium storage material in the range 0.0–3.0 V mainly results from the irreversible behavior in the initial cycles. The electrochemical cycles of $PbSbO_2Cl$ are shown in Fig. 3b. There are several lithiated and delithiated plateaus appearing in the charge/discharge cycles, which correspond to the reduction and oxidation peaks in CVs. The first discharge and charge capacities of $PbSbO_2Cl$ are 1011.0 and 731.8 mAh g^{-1}, respectively. Based on the reaction of $PbSbO_2Cl$ with Li to form $Li_{4.4}Pb$, Li_3Sb, Li_2O and LiCl, it is known that the theoretical capacity of $PbSbO_2Cl$ is 838.6 mAh g^{-1}. The extra capacity (172.4 mAh g^{-1}) is probably attributed to the irreversible electrolyte decomposition to form a solid electrolyte interphase film. At the second

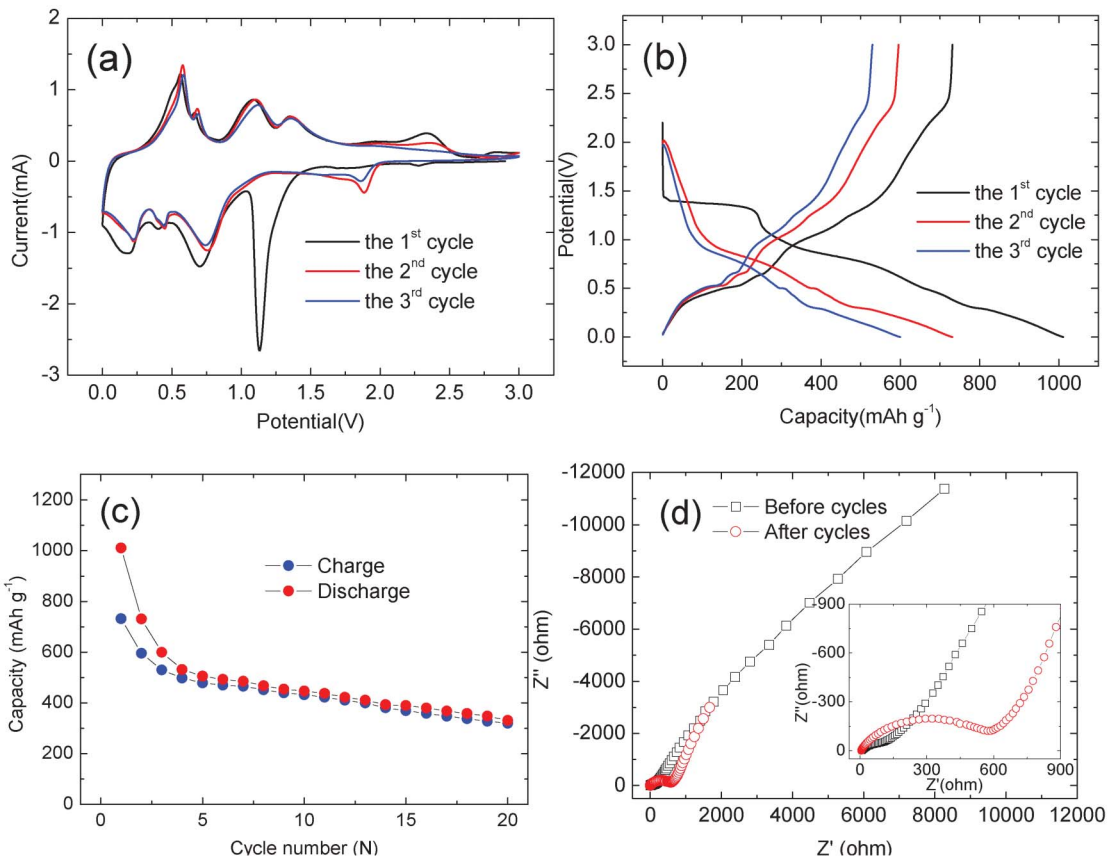

Fig. 3 CVs (a), charge/discharge curves (b), cycling properties (c) and EIS (d) spectra of $PbSbO_2Cl$.

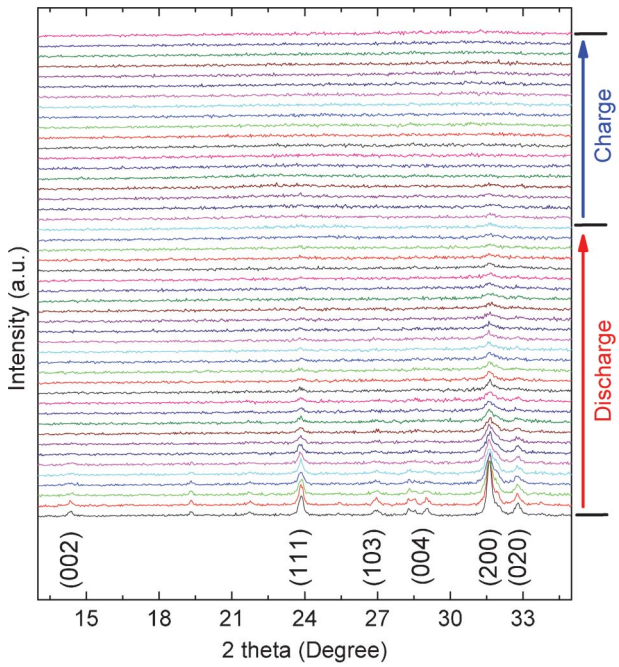

Fig. 4 *In situ* XRD patterns of $PbSbO_2Cl$ cycled in 0.0–3.0 V.

cycle, the discharge and charge capacities of $PbSbO_2Cl$ are 731.2 and 595.7 mAh g^{-1}, respectively. As shown in Fig. 3b, the decrease of reversible lithium storage capacity in the initial two cycles is mainly attributed to the disappearance of lithiated plateau at 1.38 V. After twenty cycles, the reversible discharge and charge capacities of $PbSbO_2Cl$ as shown in Fig. 3c are 330.7 and 319.4 mAh g^{-1}, respectively. Based on calculation, it is known that the capacity retention is merely 43.5%. It suggests that there is a huge irreversible capacity during the electrochemical cycles. It also indicates that pure $PbSbO_2Cl$ has some disadvantages as a lithium storage material for lithium-ion batteries. To study the capacity loss, the EIS spectra are shown in Fig. 3d before and after cycles. It is found that the impedance of the electrode increases after the electrochemical cycles. As reported,[1,21] this always comes from the structure changes of the power electrode. To investigate the effect of structural evolution on the cycling properties, *in situ* studies were performed on the initial cycle of $PbSbO_2Cl$. As the *in situ* XRD results show in Fig. 4, the featured diffraction peaks for $PbSbO_2Cl$ gradually disappear with the increase of lithium content in the structure. In the charge process, the compound maintains an amorphous state as no diffraction peak reappeared in the XRD patterns. These phenomena are similar with the structural changes of oxides or fluorides during their electrochemical cycles.[19,22] It indicates that the breakdown of structure and pulverization of nano-micro structured bulks should be responsible for the impedance increase and capacity loss of $PbSbO_2Cl$. Therefore, carbon coating may be a favorable way to maintain the crystal structure and improve the cycling properties of $PbSbO_2Cl$ in future work.

4. Conclusions

In this paper, $PbSbO_2Cl$ is studied as an anode material for lithium-ion batteries. The preparation of $PbSbO_2Cl$ is accomplished by the hydrothermal reaction of $Pb(NO_3)_2$ with $SbCl_3$ in a $NH_3{\cdot}H_2O$ saturated solution. The well-dispersed samples are light yellow nano-micro structures with particle sizes of 200–500 nm. Upon use as a lithium storage material, the initial discharge and charge capacities of $PbSbO_2Cl$ are 1011.0 and 731.8 mAh g^{-1}, respectively. After twenty cycles, the reversible discharge and charge capacities of $PbSbO_2Cl$ can be maintained at 330.7 and 319.4 mAh g^{-1}, respectively. *In situ* XRD results show that the breakdown of the structure may be responsible for the capacity loss of $PbSbO_2Cl$ during cycles.

Acknowledgements

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