Preparation of MnSi alloy by direct electro-deoxidation from SiO_2-MnO_2 in molten salt for potential applications in lithium batteries

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It was found that Mn-Si alloys can be used as anodes for lithium ion batteries with high specific capacity and cycle efficiency. A new friendly environmental and simple method for preparation of Mn-Si alloys was promoted. MnSi powder with high purity were successfully prepared by electro-deoxidation from solid SiO_2-MnO_2 pellets in $CaCl_2$-NaCl (molar ratio=1:1) melts at 850 °C. The influence of electrolytic time and mechanism on formation of Mn-Si alloys were discussed. The compositions of the samples were analyzed by X-ray diffraction (XRD).

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Keywords: Molten salt electrolysis, Preparation, MnSi, Alloy, Deoxidation

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1. Introduction

Currently, Li-ion batteries are the most commonly commercial rechargeable batteries due to the high-specific capacity and excellent cycle performance. They have been widely used in the fields of electrical vehicles, energy-efficient cargo ships and locomotives, aerospace and power-grid applications [1-4]. It is well known that the properties of Li-ion batteries strongly depend on anode materials [5-8]. Therefore, development and fabrication of new anode materials with improved the enhancement of the rate capacity and cycle performance of these anode materials could be considered as a necessary and pressing research objective in field of batteries [9].

In recent years, the Si based materials with active–inactive matrix such as Ni-Si, Fe-Si [10] and Si-Mn [11] alloys have received more attention because of the high theoretical capacity and cycle performance. Fleischauer [12] prepared the Si-Al-Mn thin film with high discharge specific capacity and improved cycle performance by combinatorial sputtering methods. Song [8] used melt spinning prepared $Al_{55}Si_{40}Mn_5$ and $Al_{53}Si_{40}Mn_7$ alloys with specific capacity of more than 500 $mAh\cdot g^{-1}$ and the cycle efficiency of 90% after 10 cycles. Zuo [11] obtained Si-Mn composites after 60 h ball milling and annealed at 300 °C for 2 h and found that the reversible capacity and cycle efficiency are 455 mAh g^{-1} and 52%, respectively. Yin [13] found that the Si-Mn-C composites electrodes after annealing at 200 °C has an initial reversible capacity of 463 $mAh\cdot g^{-1}$.

Electro-deoxidation of solid oxides to prepare metals and alloys in molten salts described by Chen [14] exhibits advantages such as low energy consumption, simple operation and more economic.

In this work, Mn-Si alloys were prepared from SiO_2 and MnO_2 powders. The electrolytic reduction of SiO_2-MnO_2 mixture into electrode materials of Mn-Si alloys was proceeded in $CaCl_2$-NaCl at 850 °C. The samples were analyzed by X-ray diffraction (XRD) and the mechanisms of the reduction reaction were discussed.

2. Experimental

2.1 Reagents and materials

The SiO_2 and MnO_2 were provided as raw materials, NaCl and $CaCl_2$ were used as molten salt. High purity argon (99.999%) was used as protection gas during the high temperature experiments. The experimental device is shown in Fig. 1. All the reagents used in this paper were analytic grade reagents.

2.2 Pellet preparation and electrolysis

MnO_2 and SiO_2 (molar ratio of 1:1) powders were weighed and thoroughly milled in a ball mill container for 3 h (1000 r/min) mixed with high purity alcohol. After drying, 1 g MnO_2-SiO_2 powders were added into the raw materials, and pressed into small pellets (20 mm in diameter and 2.5 mm in thickness) at 20 MPa. Then the pellets were sintered at 850 °C for 6 hours in the muffle furnace to use as electrolysis cathode pellets.

The electrolysis processed in the stainless steel tube reactor, as shown in Fig. 1, an alumina crucible was used as cell, the graphite rod used as an anode, electrolysis processed in the $CaCl_2$-NaCl melts (molar ratio of 1:1) with the high purity argon gas as preparation atmosphere. Before the electrolysis process, physical combined water and metal ion impurities were further removed by per-electrolysis at 2.60 V for 2 h. Afterwards, MnO_2-SiO_2 connected with nickel wire as cathode was replaced in molten salt and electrolyzed. After electrolysis, the sample was cooled, washed with distilled water and dried.

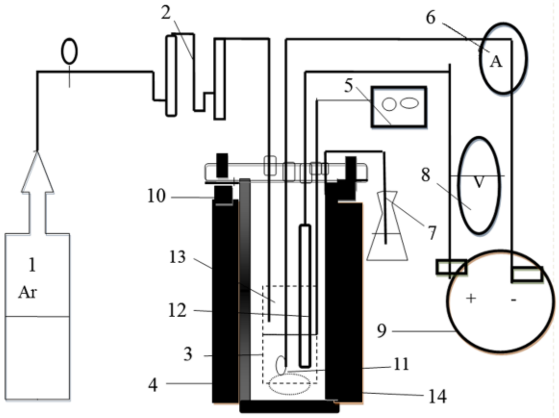

Fig. 1. Sketch map of electrolysis equipment (1-Ar cylinder; 2-spray drying tower; 3-alumina crucible; 4-stainless steel tube reactor; 5-thermocouple; 6-ammeter; 7-tail gas absorption bottle; 8-ammeter; 9-DC voltage stabilizer; 10-cooling water; 11-SiO_2-MnO_2 pellet. 12-graphite rod; 13-$CaCl_2$-NaCl melts; 14-heating furnace).

3. Results and discussion

Fig. 2 shows the XRD spectra of sample from electrolysis of the pellets (sintered at 850 °C for 6 h) at 3.10 V in a $CaCl_2$-NaCl melts (molar ratio of 1:1) at 850 °C for 19 h. The surface appearance of cathode piece was deep black gray, and the pellet has a certain mechanical strength before the experiment. After sintering, the surface of cathode showed a little brown color, shrank slightly and high mechanical strength. After electrolysis, the surface of sample showed steel gray with low strength and was easily grounded to a powder. The XRD showed that the product was mainly MnSi.

Fig. 3 shows the XRD spectra of MnO_2-SiO_2 pellets sintered at 850 °C for 6 h. It can be seen that the peaks are identified as Mn_2O_3 and SiO_2, the MnO_2 has no apparent effect on the phase structure of pellets. The appearance of Mn_2O_3 is due to the MnO_2 lost oxygen ions, and changed into Mn_2O_3 after sintering.

The MnO_2 lost oxygen ions and converted to Mn_2O_3, which promoted the formation of oxygen vacancies, so the cathode pellet has a certain pore to help the oxygen ions migrated and molten salt immerged after sintering.

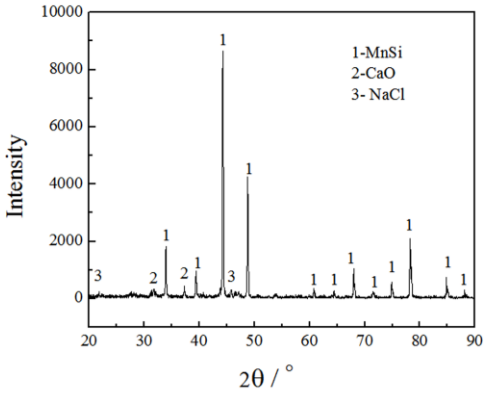

Fig. 2. XRD pattern of sintered MnO_2-SiO_2 pellets after electrolyzing (Ball-milled for 3 h, compacted at 20 MPa, sintered at 850 °C for 6 h, and electrolyzed in molten $CaCl_2$-NaCl at 850 °C for 19 h under 3.10 V).

In order to discuss the formation mechanism of Mn-Si alloys in $CaCl_2$-NaCl molten salt, the experiments were carried out at different electrolytic time. The XRD spectra of samples were shown in Fig. 4.

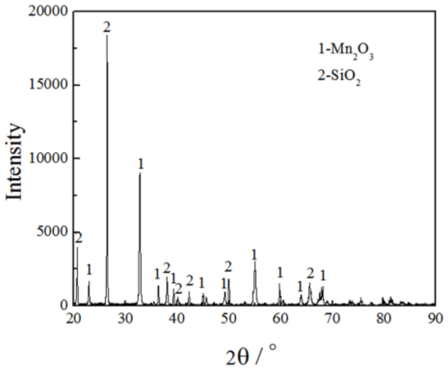

Fig. 3. XRD pattern of MnO_2-SiO_2 pellets sintered at 850 °C for 6 h.

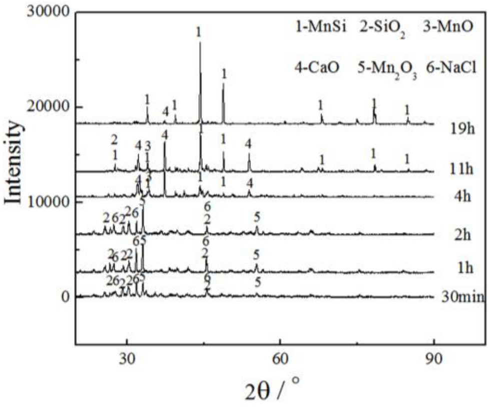

Fig. 4. XRD pattern of sintered MnO_2-SiO_2 pellets after electrolyzing at different time(30 min, 1 h, 2 h, 4 h, 11 h, and 19 h) (Ball-milled for 3 h, compacted at 20MPa, sintered at 850 °C for 6 h, and electrolyzed in molten $CaCl_2$-NaCl at 850 °C for 13 h under 3.10 V).

In the primary deoxidized stage of electrolysis, electrolysis process mainly happened in the surface of cathode, the Mn_2O_3 was reduced to MnO, because the Mn_2O_3 has lowest decomposition voltage at 850 °C.

The formation mechanism of alloys (cathode reaction) can be described as follows:

$$Ca^{2+} + 2e^- \rightarrow Ca \qquad (1)$$

$$Ca + SiO_2 \rightarrow CaO + SiO \qquad (2)$$

$$SiO + Ca^{2+} + 2e^- \rightarrow CaO + Si \qquad (3)$$

$$MnO + Si + 2e^- \rightarrow MnSi + O^{2-} \qquad (4)$$

4. Conclusions

The Mn-Si alloys were prepared from SiO_2 and MnO_2 powders in $CaCl_2$-NaCl (molar ratio is 1:1) melts at 850 °C. Mn-Si alloys were obtained at 3.10 V for 19 h with the sintering pressure of 20 MPa at 850 °C for 6 h. The phases of the samples were affected by electrolytic time. MnO and the pre-formed Si were reduced to form Mn-Si alloys. MnSi alloys obtained will have the potential applications as anodes for lithium batteries.

Acknowledgments

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