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Magnesium Sulphide as Anode Material for Lithium-Ion Batteries

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ABSTRACT

Herein, we report magnesium sulphide (MgS) as an anode for lithium ion batteries. Magnesium sulphide-carbon composite is directly synthesized by mechanically milling the elemental mixture. A possible lithiation and delithiation mechanism for MgS is proposed based on electrochemical and ex-situ XRD studies. The electrochemical reaction of MgS with lithium results in the formation of Li_2S and Mg, the as-formed Mg simultaneously reacts with lithium and forms Li_xMg alloy further contributing to the capacity. A stable reversible capacity of 530 mAh g^{-1} was achieved after 100 cycles within the voltage window of 0.001–2.5 V. The compatibility of MgS anode was tested in full cell using lithium nickel manganese cobalt oxide (LNMC) and lithium iron phosphate (LFP) as cathodes.

1. Introduction

Lithium-ion batteries are commercially successful rechargeable batteries for portable electronic devices and considered promising for applications in plug-in hybrid electric vehicles. A commercial lithium-ion battery consists of, e.g., graphite anode, lithium-ion conducting electrolyte, $LiPF_6$ in ethylene carbonate-diethylcarbonate and a prelithiated cathode, $LiCoO_2$, $LiMn_2O_4$ or $LiFePO_4$. Though metallic lithium has a theoretical specific capacity of 3,861 mAh g^{-1}, due to dendrite formation and related safety concerns alternative anodes were developed like graphite with ten times less theoretical specific capacity (372 mAh g^{-1}). Vast efforts have been made to replace graphite with high capacity anode materials [1–6]. The most promising materials are metals (Al [7,8], Sn [9–11]) and semiconductors (Si [12–14], Ge [15,16]) that can react with lithium and form alloys. In addition, a number of transition metal oxides [17–20], hydrides [21], sulphides [22,23], nitrides [24,25], and phosphides [26,27] were studied as anode for lithium-ion batteries [28]. Recently, silicon has gained much interest as it can react with more number of lithium to form a fully lithiated alloy, $Li_{4.4}Si$, with a theoretical specific capacity of 4,200 mAh g^{-1}, much higher than graphite [14]. However, it is accompanied by poor cycle life compared to graphite due to fracture and crumbling of electrode caused by large volume change (280% for Si) and due to diffusion induced stress [29]. There is a great interest for alternative high capacity, low voltage anode materials. In an attempt towards this we report the investigation of magnesium sulphide (MgS) as sustainable anode material for lithium-ion batteries.

The theoretical reaction potential of MgS with lithium is 0.5 V. It has a theoretical specific capacity of 951 mAh g^{-1} assuming the following reaction.

$$MgS + 2Li \rightarrow Li_2S + Mg$$

In addition, lithium can react with magnesium to form alloys of lithium by further increasing the theoretical capacity. The high capacity combined with low reaction potential makes MgS an interesting anode material for Li-ion batteries in principle. Hence we synthesized and evaluated MgS-carbon nanocomposites as anode material for lithium-ion batteries. Very recently, another report was published on MgS as anode for lithium-ion battery [30]. Our work is distinctive in the following aspects; 1. We report a single step preparation method of MgS carbon composite, 2. From XRD and electrochemical studies we conclude a reversible lithiation/delithiation mechanism, 3. We show that the addition of conductive carbon during electrode fabrication can significantly improve the cycling performance, 4. Further the practicality of MgS-carbon composite anode is evaluated in full cell using lithium nickel manganese cobalt oxide (LNMC) and lithium iron phosphate (LFP) as cathodes.

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2. Experimental

2.1. Synthesis

Magnesium sulphide-carbon (MgS-CB) composite was prepared from the elements by ball-milling (PM100 Retsch) stoichiometric mixture (1:1 molar ratio) of magnesium powder (Alfa-Aesar, 99.8%) and sulphur powder (Sigma-Aldrich, ≥99.5%) with carbon black (Alfa-Aesar, >99.9%) to obtain a mass fraction of MgS, 75%; carbon black, 25%. The mixture was loaded in a tungsten carbide vial with tungsten carbide balls and closed in an argon filled glove box (MBRAUN). The ball-to-powder ratio was 10:1, milling time was 20 h at 400 rpm with 10 min milling and 10 min pause to prevent excessive heating.

2.2. Structural Characterization

X-ray diffraction (XRD) patterns were obtained with a STOE STADI P diffractometer using Cu Kα radiation in transmission mode. For ex-situ XRD studies, the powders from the current collector were retrieved and characterized at different discharged and charged states. The morphology of synthesized sample was examined by scanning electron microscopy (SEM, LEO 1550 Gemini).

2.3. Electrochemical measurements

Electrochemical studies were performed in Swagelok type cells. Electrode fabrication and assembly of electrochemical cells was done in an argon filled glove box. The electrodes were fabricated with or without additional amounts of conductive carbon. For electrodes without additional conducting carbon, the as-prepared MgS-carbon composite (75% of MgS) was mixed with the binder, polyvinylidene fluoride (PVDF) at the mass ratio of 90:10. The electrodes with conducting carbon were prepared by mixing MgS-carbon composite (75% of MgS), carbon (Super P (SP)/carbon nanofibre (CNF)/graphene (Gra)), and poly vinylidene fluoride (PVDF) in the mass ratio of 80:10:10. A slurry containing the above mixture was prepared by using N-methyl-2-pyrrolidinone as solvent, spread on a stainless steel (SS) foil (area: 1.13 cm^2), and dried in a vacuum oven at 120 °C for 12 h. Typically, each electrode contained 2–3 mg of the active material. The specific capacities were calculated based on the mass of active material in the electrode. Lithium foil (Aldrich, 99.9%) was used as the negative electrode, and a borosilicate glass fiber sheet saturated with 1 M $LiPF_6$ in 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) (LP30, BASF) was used as separator and electrolyte. The cells were placed in an incubator (Binder) to maintain a constant operation temperature of 25 ± 0.1 °C. Electrochemical studies were carried out using Arbin battery cycling unit BT2000 and Bio-logic VMP-3 potentiostat. Electrochemical impedance spectroscopy (EIS, Bio-logic VMP-3) measurements were performed with an applied AC signal amplitude of 10 mV over a frequency range of 200 kHz to 10 mHz.

3. Results and discussion

Various methods have been reported for the preparation of pure MgS which all require high temperature, long sintering time and utilizing toxic chemicals as precursors [31]. However, nanocrystalline active material (MgS) coated with carbon would be of particular interest to obtain better electrochemical performance. To achieve this, MgS-carbon composite (MgS-CB) was synthesized by mechanically milling the elemental mixture. The XRD profile of as-synthesized MgS-CB is shown in Fig. 3a. The MgS peaks are consistent with the standard JCPDS card number 35-0730 with rock salt type structure. The average crystallite size calculated by Scherrer equation was 24 nm. The microstructure of the as-prepared MgS-CB was characterized by scanning electron microscopy (SEM). Fig. 1 shows the SEM image of the as-prepared MgS-CB

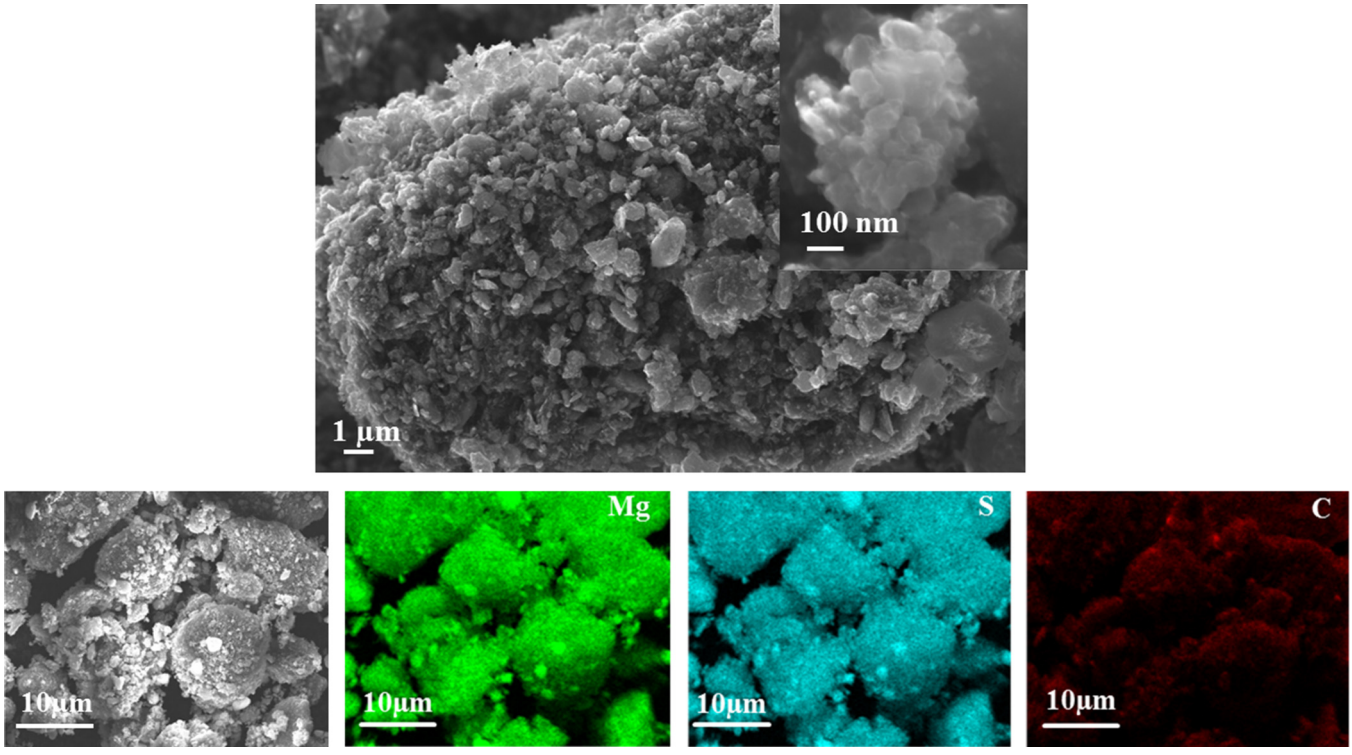

Fig. 1. SEM images of as-prepared MgS-CB and the corresponding EDS mapping of Mg, S and C.