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A novel approach to employ Li_2MnSiO_4 as anode active material for lithium batteries

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Abstract In the present paper, we describe utilization of cathode active material as anode active material, for example, Li_2MnSiO_4. The lithium manganese silicate has been successfully synthesized by solid-state reaction method. The X-ray diffraction pattern confirms the orthorhombic structure with $Pmn2_1$ space group. The Li/Li_2MnSiO_4 cell delivered the initial discharge capacity of 420 $mAhg^{-1}$, which is 110 $mAhg^{-1}$ higher than graphitic anodes. The electrochemical reversibility and solid electrolyte interface formation of the Li_2MnSiO_4 electrode was emphasized by cyclic voltammetry.

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Introduction

Carbonaceous materials have dominated as anodes for lithium ion batteries since commercialization in early 1990s by Sony, although such materials offered lower theoretical capacities (for example, graphite 372 $mAhg^{-1}$) [1]. Transition metal oxides and their alloys were most widely investigated as possible alternative for the place of carbonaceous anodes. In addition, the transition metal elements afforded a high theoretical capacity, which are many folds higher than carbonaceous anodes. However, high irreversible capacity loss (ICL) during the conversion reaction and higher operating voltage restricts the possibility of using them in practical cells. In the case of alloy-based anodes, a large volume variation during alloying/dealloying process which severely affects the cycling stability, further cracking, and crumbling also possible during such process [2, 3]. Thus, it is necessary to search for new anode candidates for lithium ion batteries that are environmental friendly.

Utilization of cathode active materials into negative electrodes is the hot topic of research today. In the case of cathodes, the material should act as reservoir for the Li^+ ions; however, it acts as a buffer medium during the anodic process. For example, in $LiFePO_4$, more than 90% of the theoretical capacity (170 $mAhg^{-1}$) has been achieved when used as cathode. The insertion/extraction of lithium ions, i.e., oxidation/reduction, takes place around 3.4–3.6 V and provides the higher operating voltage. At the same time, $LiFePO_4$ exhibited the initial discharge capacity of 620 $mAhg^{-1}$ while testing its anodic performance with coulumbic efficiency around 100% [4]. In the same line, for the first of its kind, lithium orthosilicate material (e.g., Li_2MnSiO_4) has been subjected to investigate as an anode material for lithium batteries. The advantage of using such

silicate groups are low cost, high theoretical capacity, environmental benignity, and ease to prepare [5–9].

Experimental

Solid-state reaction was employed to prepare the Li_2MnSiO_4 powders. High-purity analytical grades of $LiOH \cdot H_2O$ (Junsei 95%), $MnCO_3$ (Aldrich, USA, 99.9%), and SiO_2 (Aldrich, 99.9%) were used as the starting materials. In order to prevent the agglomeration of the particles during the synthesis, an adipic acid (Aldrich, 99%) has been chosen as a chelating agent, which was fixed at 0.2 mol against the total metal ion present in the compound. The stoichiometric amounts of starting materials with gelating agent were fine ground and heat treated at 400 °C for 4 h under air atmosphere. The resultant product was fine ground using mortar and pestle and placed in the tubular furnace at 900 °C for 12 h under Ar atmosphere for the final calcination process to yield the Li_2MnSiO_4 powder.

The structural properties of Li_2MnSiO_4 were studied by using X-ray diffractometer (Rigaku, Rint 1000, Japan) with Cu-Kα as a radiation source. Morphological features were investigated by scanning electron microscope (Hitachi, S-4700, Japan). Electrochemical profiles of Li_2MnSiO_4 were performed by CR 2032 coin cell at ambient temperature. The negative electrode composed the accurately weighed 20 mg of active materials (Li_2MnSiO_4), 3 mg of conductive additive (ketjen black), and 3 mg of binder (teflonized acetylene black). The mixture was pressed on a 200 mm^2 stainless steel mesh, serving as the current collector under a pressure of 300 kg/cm^2, and dried at 130 °C for 5 h in an oven. The metallic lithium served as both reference and counter-electrodes. The cell was separated by a porous polypropylene film (Celgard 3401) filled with the conventional electrolyte solution (1.0 M $LiPF_6$ in EC/DMC (1:1 v/v, Techno Semichem, Korea). The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were performed using SP-150, Bio-Logic, France electrochemical work station. The cycling studies were carried out between 0.0 and 3.0 V in galvanostatic mode at ambient temperature using WBCS 3000, Won-A-Tech, Korea.

Result and discussion

Powder X-ray diffraction (XRD) pattern of Li_2MnSiO_4 electrode material is given in Fig. 1. The XRD pattern shows the well-defined sharp intense reflections, which indicate the highly crystalline nature of the synthesized Li_2MnSiO_4. The crystalline peaks are suggesting the orthorhombic structure with $Pmn2_1$ space group. The presence of impurity phases like MnO and less amount of
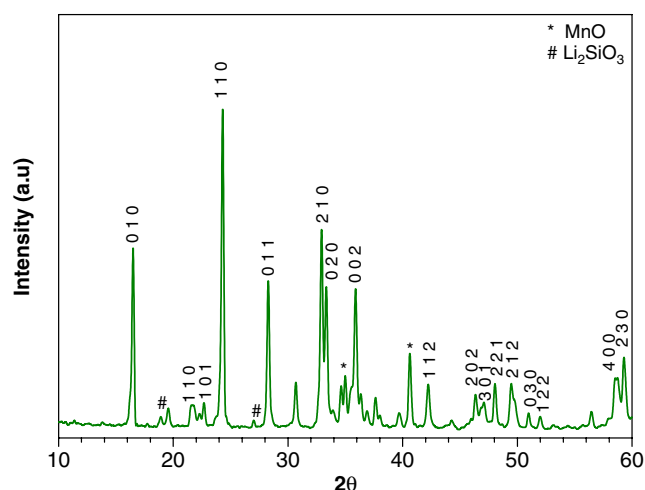

Fig. 1 X-ray diffraction pattern of Li_2MnSiO_4

Li_2SiO_3 are unavoidable during the synthesis process. A similar kind of impurity phases are noticed by the researchers during the synthesis of Li_2MnSiO_4 powders by various approaches [5–10]. Abnormal pressure conditions provides the MnO and Li_2SiO_3 free Li_2MnSiO_4 phase. However, the obvious amount of Mn_2SiO_3 phase could be inevitable under such conditions by de Dompablo et al. [11]. Moreover, the presence of Mn_2SiO_3 phase is much higher than those of MnO present in the conventional synthesis. Earlier reports and present study shows that the preparation of phase pure Li_2MnSiO_4 is a complicated one.

Morphological pictures of the synthesized Li_2MnSiO_4 are analyzed by scanning electron microscopy (SEM) as shown in Fig. 2. The SEM image results connote the uneven size (submicrometer) morphology of the Li_2MnSiO_4 particles synthesized by solid-state reaction method. Furthermore, the appearances of small-size particles are also seen along with the larger-size particles. It is well known that controlling growth of particle size/morphology by a solid-state reaction method is a very complex process.

The electrochemical performances of Li_2MnSiO_4 against lithium reference electrode at ambient temperature are represented in Fig. 3. The cycling performances were carried out between 0 and 3 V at constant current density of C/20 galvanostatically. The Li_2MnSiO_4/Li cell presents the initial discharge capacity of 420 $mAh g^{-1}$. The initial discharge capacity of Li_2MnSiO_4 electrode is 110 $mAh g^{-1}$ higher than commercially graphitic anode (372 $mAh g^{-1}$) [12]. In the second cycle, the discharge capacity drastically reduced from 420 to 181 $mAh g^{-1}$. This reduction in capacity may be believed for the formation of solid electrolyte interface (SEI) especially at lower potentials. Generally, carbonaceous materials actively involved to the formation of SEI at lower potentials. Herein, the carbonaceous additives like adipic acid (it is carbonized during the calcination) and
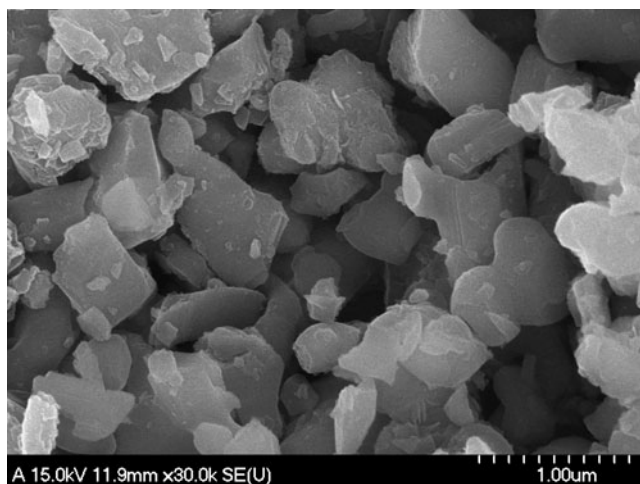
Fig. 2 Scanning electron microscopic images of Li_2MnSiO_4

conductive additive (ketjen black) effectively played a vital role for SEI formation [13, 14]. The SEI is necessary for the safe operation of the lithium cell during the prolonged cycling. Moreover, SEI prevents the unwanted side reaction with electrolyte counterparts. In the case of carbon-based materials, the coloumbic efficiency is around 100% except
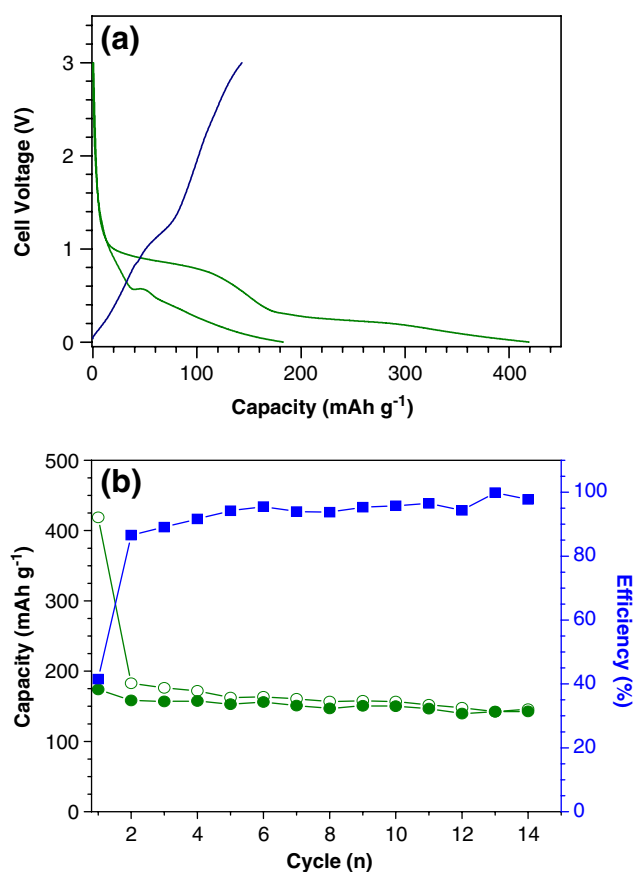
for the initial cycle, which indicates that such materials act as a buffer during intercalation/deintercalation process. However, Li_2MnSiO_4 electrodes exhibited coulumbic efficiency over 95%. This result suggests that Li_2MnSiO_4 host material, which acts as the buffer host during discharge, provides enhanced columbic efficiency.

Generally, kinetic properties of lithium insertion/deinsertion properties can be effectively studied by cyclic voltammograms (CV). A family of voltammograms is given in Fig. 4 between the potential range of 0–3.5 V Vs Li/Li^+ at ambient temperature with the scan rate of 0.1 mV/ s. The operating potential covers the irreversible interactions between the host, lithium, and the electrolyte counterparts [13]. Moreover, this potential range is representative of the process at the anode under the normal battery operating conditions. In the first sweep, the cathodic peak around 0.56 V is representing the formation electronically insulating and ionically conducting SEI. Typically, the reversible lithium insertion and deinsertion processes takes place potentials below 0.5 V (versus Li/Li^+). After the first cycle, the reduction in the intensities of the Li^+/Li potential indicates the involvement of lithium ions in the surface film formation, i.e., SEI [14]. Almost-stable voltammograms are observed from the subsequent cyclings, except for the first cycle. This confirms good reversibility of the Li_2MnSiO_4 electrodes during lithium insertion/deinsertion process and corroborates cycling studies.

Conclusion

The anodic performance of the Li_2MnSiO_4 electrodes was herein demonstrated. The cell experienced the initial discharge capacity of 420 $mAh\,g^{-1}$, which is well ahead of commercially available graphitic anodes. The formation
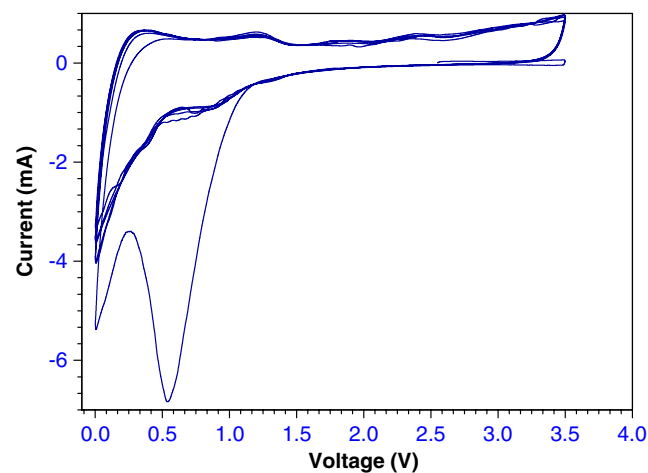

Fig. 3 Electrochemical performance of Li_2MnSiO_4/Li cell **a** charge–discharge and **b** cycling profile (*open circles* for discharge capacity, *filled circles* for charge capacity, and *squares* for efficiency)

Fig. 4 Cyclic voltammograms of Li_2MnSiO_4 electrodes, when metallic lithium serves as counter and reference electrodes with the scan rate of 0.01 mV/s

of SEI and reversibility has been confirmed by cyclic voltammetric measurements. The XRD and SEM analyses were conducted to analyze the structural and morphological features, respectively.

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