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High field phase transition of cathode material Li$_2$MnSiO$_4$ for lithium-ion battery

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Abstract

The magnetic properties of the candidate lithium-ion battery cathode materials Li$_2$MnSiO$_4$ have been studied experimentally using static and pulsed high magnetic fields. A field-induced magnetic transition is observed in low temperature region, in which a saturation magnetization is observed above 27 T which confirms that the Mn-ion has a dominant low spin state with a saturated magnetic moment of $\sim$3.1 $\mu_B$/Mn. With the change of temperature and magnetic field, the Li$_2$MnSiO$_4$ shows a complex magnetic phase transition. Considering to the coupling between spin, charge and orbital, the field-induced magnetic transition may affect the charge-discharge behavior of the cathode material, thus, the study is expected to explore the possibility and stability of the candidate lithium-ion battery cathode materials used in the low temperature and high magnetic field circumstance and its performance degradation.

1. Introduction

The early cathode materials inevitably hold some limitations in terms of cost, environmental toxicity, inherent chemical and thermal stability such as LiCoO$_2$, LiNiO$_2$, LiMn$_2$O$_4$, LiMnO$_2$, etc. In recent years, in the field of phosphate (LiMPO$_4$), Li$_2$M$_2$(PO$_4$)$_3$, LiM$_2$P$_2$O$_7$, $M = $ Mn, Fe, Co, Ni, ... same below) [1, 2], silicate (Li$_2$MSiO$_4$, Li$_2$VOSiO$_4$) [3–5] and other polyanion materials, the research has become more and more extensive, mainly focusing on the development of suitable cathode materials. The need for better large-scale batteries has driven the development of cathode materials for lithium-ion batteries. A new class of polyyxanion cathodes Li$_2$MSiO$_4$ (where $M = $ Mn, Fe, and Co) based on the orthosilicates has aroused increasing interest [6]. The orthosilicate Li$_2$MSiO$_4$ is a competitive cathode material for the next generation of large-capacity (~330 mA h g$^{-1}$ with a possible two Li$^+$ extraction per formula unit) rechargeable lithium-ion batteries [6, 7]. It is an alternative to other polyanion compounds, because it has abundant raw materials containing iron, manganese oxide and silica, low cost, high safety, environmental friendliness and good cycling performance. Moreover, its Si–O bond is at least stable as other polyyxanion groups. Recent advance in the determination of the polymorphic structure of Li$_2$MnSiO$_4$ paves the way for a detailed study of the mechanism by which Li extracts/inserts (from/into) as a function of local and/or long-term cations from these silicates. In Li$_2$MSiO$_4$ ($M = $ Fe, Mn, Co) half the tetrahedral positions are occupied by cations and the cation site ordering can be varied, in addition the tetrahedra can be distorted giving rich and complex polymorphism.

Despite widespread interest in orthosilicates, data on basic physical properties of orthosilicates such as magnetic properties, are scarce, especially under extreme conditions: high magnetic fields and low temperatures. Furthermore, although the Fe and Mn compounds are shown to order magnetically [8], the magnetic structure has never been resolved. The understanding of the ordered magnetic ground state of these candidate lithium-ion...
battery cathode materials will be beneficial to the quantitative prediction of electronic and electrochemical properties. Numerous examples have shown that ignoring magnetic order in these materials results in large errors of both crystal structural parameters and predicted intercalation voltages (up to 30% for the latter, e.g.,)[9, 10].

The achievements in the synthesis of electrochemically active Li$_2$MnSiO$_4$ (small particles) prompt us to study their magnetic properties in detail [7]. This paper mainly studied the magnetization behavior of lithium manganese oxide manganese (Li$_2$MnSiO$_4$) in a wide range of temperature and magnetic field and discussed the possibility and stability of the application of lithium-ion battery cathode material in low temperature and high magnetic field environment, which may affect the electrochemistry properties of Li$_2$MnSiO$_4$.

2. Experimental

Li$_2$MnSiO$_4$ samples were prepared by two-step solid state method. High purity powder of LiOH $\cdot$ H$_2$O (99.99%), Mn(CH$_3$COO)$_2$ $\cdot$ 4H$_2$O (99.99%) and SiO$_2$ (99.99%) as raw materials were taken in stoichiometric proportion and magnetic stirred. The mixture was dried at 80 °C and then calcined at 350 °C, followed by calcining at 750 °C for 10 h in argon atmosphere, Li$_2$MnSiO$_4$ powder was obtained. The lattice structure of the powder sample was measured by x-ray diffractometer (XRD, Philips X'pert pro) with Cu-K$\alpha$ radiation. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi instrument with a monochromatic Al K Alpha (1486.68 eV) x-ray source, in which all samples were measured under an ultrahigh vacuum. The binding energies were calibrated using the C(1 s) carbon peak (284.8 eV). All the high-resolution spectra were obtained under CAE mode with pass energy of 30 eV and step size of 0.05 eV. The magnetization was measured using a superconducting quantum interference device with a vibrating sample magnetometer (SQUID-VSM, Quantum Design). High field magnetization measurements were performed with a 60 T pulse magnet at Wuhan National High Magnetic Field Center.

3. Results and discussion

The room temperature powder XRD pattern of the Li$_2$MnSiO$_4$ polycrystalline powder sample has been measured. The diffraction pattern of Li$_2$MnSiO$_4$ indicates the sample is with an orthorhombic Pmn2$_1$ structure, is shown in figure 1, with a little impurity of Li$_2$SiO$_3$ (red arrows) and LiMnO$_2$ (blue arrows). The lattice parameters of Li$_2$MnSiO$_4$ after Rietveld refinement are shown in table 1. The crystal structures of the orthosilicates can be understood as being based on hexagonal close-packing of oxygen atoms in which half the tetrahedral voids are filled by Li, Mn, or Si. The cation distributions over the tetrahedral positions and related structure distortions produce a large number of polymorphs with orthorhombic symmetry. All the cation tetrahedra point in the same direction perpendicular to the oxygen close-packed layers as shown in the inset. The results agree with that of Belharouak [8]. Primary sites of Li, Mn and Si are within the tetrahedral (oxygen atoms are in the corners), while alternate, partially occupied tetrahedral sites Li1, Mn1 and Si1 are shown as balls and their connectivity is indicated by thin bonds [11–13]. The tetrahedral sites occupied crystal structure induce rich

![Figure 1. The XRD pattern of Li$_2$MnSiO$_4$ measured at room temperature with orthorhombic Pmn2$_1$ structure. The inset is the schematic of crystal structure.](image-url)
polymorphism, and electrochemical properties of orthosilicates have been thoroughly investigated by various research groups and later reviewed [14].

In order to identify the oxidation state of Mn-ions, the XPS spectra of Li$_2$MnSiO$_4$ were measured. As shown in figure 2, the peaks of Mn, Li, Mn, Si and O were observed. In this study, we mainly focus our attention on the Mn-3s peaks in the XPS spectra, as shown in the inset (a) at top left. It can be seen clearly that Mn cations yield a well-defined structure that has two, multiple split components, which may result from the coupling of the 3d valence-band electron with the non-ionized 3s electron. After the calibration of binding energies by referencing adventitious C-1s peak located at 284.8 eV, split double peaks of Mn-3s via peak processing straightforwardly identify Mn chemical states with the magnitudes of peak splitting $\Delta E \sim 6.0$ eV, 5.3 eV and 4.7 eV from the 3s peak of higher binding energy located at $\sim 89$ eV, which corresponds to the splitting of the Mn$^{2+}$ (MnO), Mn$^{3+}$ (Mn$_2$O$_3$) and Mn$^{4+}$ (MnO$_2$). The Mn3s spectrum clearly evidences the presence of three chemical environments for manganese. The fitting parameters for Mn3s peak are shown in table 2. The shapes of Mn$^{2+}$ (olive line), Mn$^{3+}$ (navy line) and Mn$^{4+}$ (violet line) also signal the proportions of those cations. In addition, the Mn$^{2+}$ percentage in Li$_2$MnSiO$_4$ is estimated to be 74.4%. Therefore, we can assume that Mn$^{2+}$ dominates in Li$_2$MnSiO$_4$, and that both Mn$^{3+}$ and Mn$^{4+}$ are in the minority. According to the law of charge neutrality, lithium should have +1 or zero valence due to oxygen vacancy, which may result from sample preparation under argon environment.

It is reported that, despite belonging to the different structural families, these compounds share the same magnetic topology and thus adopt magnetic structures of the same type [11]. The temperature dependence of magnetization of Li$_2$MnSiO$_4$, measured from 0.005 T to 7 T with zero-field cooling (ZFC) and field cooling (FC) are shown in figure 3, and the inset illustrates the magnification of the magnetization curves of the lower temperature and lower magnetic field regions. In the ZFC mode with 0.005 T, with increase of temperature from 2 K to $T_N \sim 42$ K, the magnetization increases slightly, indicating an antiferromagnetic (AFM) behavior. At $T_N$, an AFM to paramagnetic (PM) transition is observed, followed by Curie-Weiss behavior above $T_N$ of which detailed analysis will be given below. In addition, in the FC mode, after a monotonic increase of magnetization

*Figure 2.* The XPS patterns of Li$_2$MnSiO$_4$, the insets are spectra of Mn-3s peak (a) and Li-1s peak (b).

| Table 1. The lattice parameters of Li$_2$MnSiO$_4$ after Rietveld refinement. |
|-----------------------------|---------|---------|---------|---------|---------|---------|
| a (Å) | b (Å) | c (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) | V (Å$^3$) | wRp | Rp |
| 6.309 | 5.378 | 4.977 | 90.00 | 90.00 | 90.00 | 168.870 | 0.0596 | 0.0392 |

| Table 2. Fit parameters for Mn3s peak in Li$_2$MnSiO$_4$. |
|-----------------------------|---------|---------|
| BE (eV) | FWHM (eV) | Area |
| Mn$^{2+}$ (MnO) | 83.11 | 2.715 | 452.606 | 100 |
| Mn$^{3+}$ (Mn$_2$O$_3$) | 83.81 | 2.645 | 116.413 | 94 |
| Mn$^{4+}$ (MnO$_2$) | 84.41 | 2.150 | 39.100 | 0 |

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with decreasing temperature from 300 K to 52 K, significant increases were seen in \(T_C\), indicating a PM to FM (or canted AFM) transition. Below \(T_N\), a plateau of magnetization is observed showing a saturated magnetization behavior, which leads to a spin-glass-like magnetic properties. The spin-glass-like magnetization behavior may result from the competition between the AFM and canted AFM phases. With increase of the applied magnetic field to 0.05, 0.5 and 1 T, as shown in the inset, the AFM ordering temperature \(T_N\) decreases step by step, indicating the AFM coupling is partially destroyed by the external magnetic fields. On the other hand, enhanced magnetic moments due to external magnetic fields are observed below \(T_N\) in FC mode as shown in the inset. However, the transition temperature \(T_C\) from PM to FM (or canted AFM) shifts to a higher temperature region with the ascending of magnetic field, showing some kinds of double-exchange (DE) interaction mechanism, which suggests that the transition may be related to the FM behavior of \(\text{Mn}^{2+}/\text{Mn}^{3+}\) and/or \(\text{Mn}^{3+}/\text{Mn}^{4+}\). Examination of the neutron powder diffraction data collected at 3 K reveals additional intensity due to long-range magnetic ordering. In order to investigate the spin state of Mn-ions, we measure the susceptibility at 0.005 T with FC mode shown in figure 4. An obvious PM to FM transition is observed at \(T_C \sim 52\) K, and susceptibility \(\chi\) increases sharply with the temperature decreasing below \(T_C\), which indicates an FM ordering transition. Analysis from the magnetic field dependence of magnetization measured with pulsed high magnetic fields at lower temperature region and arrows indicate the temperature sweep directions. The magnetic field field higher than 3 T, which indicates that the pinning effects of the AFM ordering is suppressed largely and only a canted AFM behavior is observed in lower temperature region. Meanwhile, the spin-glass-like magnetization is also suppressed with the higher magnetic field higher than 3 T, which indicates that the pinning effects of the AFM phases on the weak FM (canted AFM) ordering is destroyed by the higher magnetic fields. As shown in the magnetization curves measured at both 5 T and 7 T, kinks are observed at \(\sim 20\) K, showing an AFM ordering behavior of \(\text{Mn}^{2+}\). As in the case of other orthosilicates, Li/Mn anti-site disorder can be expected, which may also lead to an enhanced FM contribution. In order to investigate the spin state of Mn-ions, we measure the susceptibility at 0.005 T with FC mode shown in figure 4. An obvious PM to FM transition is observed at \(T_C \sim 52\) K, and susceptibility \(\chi\) increases sharply with the temperature decreasing below \(T_C\), which indicates an FM ordering transition. Analysis from the temperature dependence of the \(1/\chi\), a deviation is observed with temperature decreasing to \(\sim 130\) K, indicating that some kinds of FM ordering are formed below the temperature. The Curie-Weiss law gives a good fitting in the temperature region between 150 to 300 K. The Weiss temperature \(T_\theta\) and effective magnetic moment are \(-29.57\) K and \(-4.56\) \(\mu_B/\text{Mn}\), respectively, and the negative Weiss temperature indicates the AFM coupling is partially destroyed by the external magnetic fields. As shown in the inset, the magnetization curves measured at both 5 T and 7 T, kinks are observed at \(\sim 20\) K, showing an AFM ordering behavior of \(\text{Mn}^{2+}\). As in the case of other orthosilicates, Li/Mn anti-site disorder can be expected, which may also lead to an enhanced FM contribution.
to the observed magnetic hysteresis loop. For the pulsed high magnetic field magnetization data shown in the main plane of figure 5, with increase of the magnetic field, the magnetization increases linearly showing a robust AFM behavior. With the magnetic field increase to $B \sim 27$ T, an AFM to FM transition with a saturation magnetization $\sim 3.1 \mu_B/Mn$ is observed to 60 T, which is slightly bigger than the theory saturation magnetization $3 \mu_B/Mn$, indicating the Mn$^{2+}$ with the low spin state $t_{2g}^4e_g^1(\uparrow\uparrow\uparrow\downarrow)$. The high field experimental result coincides with the Curie-Weiss fitting. With increase of the temperature, the transition magnetic fields of the AFM to FM transition decreases and the transition becomes indiscernible, with the temperature above 40 K, an obvious PM magnetization behavior is observed, showing the thermal fluctuation is dominant in higher temperatures. The detailed phase diagram is shown in the bottom inset of figure 5, in which with decrease of temperature, a PM to FM transition is observed at $T_c \sim 52$ K. With magnetic field increase, complex transitions are induced: FM, AFM and weak FM (canted AFM). The different magnetic coupling assumes to show different magnetic properties and leads to different electrical properties.

Usually, the cathode materials are used in room temperature and earth magnetic field. According to the magnetic phase diagram as shown in figure 5, in the common conditions, the cathode Li$_2$MnSiO$_4$ is in a PM state, in which the spin and magnetic moments related Mn-ions are distribution randomly. However, with the temperature decrease and magnetic increase, the spin and magnetic moments of Mn-ions are tuned by the temperature and high magnetic field, the electrical properties and charge and discharge may be influenced due to the couplings of the spin-orbital and spin-lattice etc. Thus, the explore of the stability of the cathode materials and/or the Li-battery used in extremely condition is important for their widened application regime.
4. Conclusion

The magnetization behavior of Li$_2$MnSiO$_4$ has been investigated with static and pulsed high magnetic field in a widen temperature region. Experimental results show that the temperature and magnetic field have important effects on the magnetic properties, especially, below the temperature $\sim$52 K the Li$_2$MnSiO$_4$ is induced to form complex magnetic coupling phases: FM, weak FM (canted AFM), AFM. In these phases, the Mn-ions show totally different magnetic moment coupling and spin states, which may result in the properties of cathode materials Li$_2$MnSiO$_4$ degradation. The detail measurements will be carried in the next using a Li-ion battery model.

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