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Structure and electrochemical performance of Li_2MnSiO_4 and Li_2FeSiO_4 as potential Li-battery cathode materials

R. Dominko [a], M. Bele [a], M. Gaberšček [a,*], A. Meden [b], M. Remškar [c], J. Jamnik [a]

[a] *National Institute of Chemistry, Materials Electrochemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*
[b] *Faculty of Chemistry and Chemical Technology, Aškerceva 5, SI-1000 Ljubljana, Slovenia*
[c] *Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*

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Abstract

Recently, preparation and preliminary testing of Li_2FeSiO_4, a representative of a new class of Li storage materials, has been reported [A. Nyten, A. Abouimrane, M. Armand, T. Gustaffson, J.O. Thomas, Electrochem. Commun. 7 (2005) 156]. In the present paper, we report preparation of another material from this class: Li_2MnSiO_4. To the best of our knowledge, the existence of this compound has not been reported so far. Similarly as in the case of the $LiMPO_4$ materials family (M = Fe, Mn), the Mn analogue shows considerably poorer electrochemical performance. Quite unexpectedly, however, the Mn analogue shows a better stability, especially under harsh conditions. This property appears to be crucial for determination of detailed structural features of this class of materials. The obtained structure reveals partial occupation of alternate tetrahedral sites by Li and Mn, thus implying a high ionic conductivity of these materials. The poor electrochemical performance is most likely due to poor electron wiring.

Keywords: Lithium-ion battery; Manganese silicate; Iron silicate; Cathode material; Crystal structure

1. Introduction

Despite the successful commercialization of even three types of cathode materials for Li-ion batteries, that is, $LiMn_2O_4$, $LiCoO_2$ and $LiNiO_2$, we have been witnessing, for more than a decade, tremendous efforts to find alternatives that would be less toxic, cheaper and, particularly, more stable – and thus safer. In this context, iron-based active materials seem to be almost ideal candidates. A well-known example is $LiFePO_4$ whose stability is a consequence of a strong covalent P–O bond. The main drawback of this material is its low intrinsic electron conductivity (10^{-9} S cm^{-1} at room temperature [2]) which, however, can be minimized by sufficiently reducing the length of solid state transport paths (e.g. by preparing nanosized [3–5] or porous [5,6] particles) and decorating such a material with a thin electron conductor (in most cases carbon nanofilms have been used [3,5–7]).

A natural further step in search for iron-based materials with aforementioned qualities seems to be the replacement of phosphorus with silicon, as recently reported by Nyten et al. [1]. Indeed, a first testing of pristine Li_2FeSiO_4 [1] has shown quite good reversible capacity (84% of the theoretical value). As regards the crystal structure of Li_2FeSiO_4, the authors proposed an orthorhombic structure with refined cell parameters: $a = 6.2661(5)$, $b = 5.3295(5)$ and $c = 5.0148(4)$ Å; space group: *Pmn2*$_1$. Although, as pointed out by the authors themselves, these results agree with those of Tarte and Cahay [8], where Li_2FeSiO_4 had been proposed to be isostructural with Li_3PO_4, they are different from those proposed by Setoguchi et al. [9] for a single crystalline Li_2FeSiO_4: $a = 12.55$, $b = 10.65$ and $c = 5.021$ Å. We speculate that this disagreement is partly due to inherent difficulties in structure determination of powder samples containing a significant amount of

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[*] Corresponding author. Tel.: +386 1 4760 320; fax: +386 1 4760 300.
E-mail address: miran.gaberscek@ki.si (M. Gaberšček).

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impurities but partly also due to subtle structural differences in this family of compounds [10,11].

An obvious next step in search for further active cathode materials from the Li_2MSiO_4 family is to find a material that would allow (at least in principle) extraction of both lithium ions. As a target material we selected Li_2MnSiO_4 – a material the existence of which has not been known so far. Instead of solid state state reaction, we used a modified Pechini process. For comparison, we also prepared a Li_2FeSiO_4 material using the same procedure and, alternatively, via a hydrothermal synthesis route. As shown in Section 3 the electrochemical performance of Li_2MnSiO_4 is poorer than that of Li_2FeSiO_4. However, due to its better stability, Li_2MnSiO_4, which is isostructural with Li_2FeSiO_4, has helped us resolve several important structural details of both materials.

2. Experimental

The synthesis of Li_2MnSiO_4 or Li_2FeSiO_4 was carried out using a modified Pechini sol–gel process. In the case of Li_2MnSiO_4, the starting precursors were lithium acetate dihydrate (Fluka, 62393), manganese (II) acetate tetrahydrate (Fluka, 63537) and SiO_2 particles Cab-osil M5 (Riedel-de Haën, 13760). Two separate solutions were prepared by dissolving 0.075 mol of LiAc in 100 ml of water and 0.0375 mol of $MnAc_2$ in 100 ml of water. Prior to use, SiO_2 particles in a concentration of 0.1 M were sonificated in an ultrasonic bath for at least 1 h. Citric acid (Aldrich, C8,315-5) and ethylene glycol (Riedel-de Haën, 24204) in a molar ratio of 1:3 (0.0125 mol of citric acid and 0.0375 mol of EG) were added to the SiO_2 dispersion and the obtained mixture was thoroughly stirred. Finally, the separately prepared solutions of LiAc and $MnAc_2$ were added to this mixture so that the molar ratio between Li:Mn:Si was 2:1:1. The obtained mixture was stirred for an hour and maintained during the night to enable formation of sol. The sol was dried at 60 °C for at least 24 h.

The preparation procedure for Li_2FeSiO_4 was essentially the same. As a source of Fe(III) cations, iron (III) citrate (Aldrich, 22,897-4) and iron (III) nitrate nonanhydrate (Fluka, 44952) in molar ratio 1:1 were used.

After thorough grinding with a mortar and pestle, the obtained xerogels were fired in a reductive (Ar + 5 wt% H_2) atmosphere at 700 °C (Li_2MnSiO_4), or in an inert atmosphere (Ar) at 700 °C (Li_2FeSiO_4) from 1 h up to 96 h.

Alternatively, Li_2FeSiO_4 was prepared using a hydrothermal process. The starting precursors, 0.4 mol of lithium hydroxide (Aldrich, 44,241-0) and 0.1 mol of SiO_2 – Cab-osil M5 (Riedel-de Haën, 13760), were mixed together in 200 mL of water and sonificated in an ultrasonic bath. Separately 0.1 mol of iron(II) chloride tetrahydrate (Aldrich, 22,029-9) was dissolved in 100 mL of water. The prepared dispersion and solution were mixed together and transferred into a Teflon-lined stainless-steal autoclave, sealed, and maintained at 150 °C for at least 72 h. After the hydrothermal treatment had been completed, the resulted green powder was rinsed several times with a distilled water. Prior the use, the distilled water was boiled with a continuous flow of Ar through the whole volume. The whole procedure was carried out in an Ar atmosphere.

The electrodes with either Li_2FeSiO_4 or Li_2MnSiO_4 as active material were prepared by casting and pressing a mixture of 85 wt% of this material, 7 wt% of a teflon binder (ALDRICH 44,509/6) and 8 wt% of carbon black (Printex XE2, Degussa) on aluminum foil and drying in vacuum at 120 °C for 24 h. The active material loading was about 2.5 mg/cm^2 and the typical thickness of the active layer was 50 μm. The electrolyte used was a 1 M solution of LiPF6 in EC:DMC (1:1 ratio by volume), as received from Merck.

A laboratory-made three-electrode test cell was used to carry out the electrochemical tests. The working and the counter (lithium) electrodes were held apart with two separators (Celgard No. 2402) between which a thin strip of lithium serving as a reference electrode was positioned. Electrochemical testing was performed using an EG&G 283 Potentiostat/Galvanostat at room temperature.

X-ray powder diffraction pattern of Li_2MnSiO_4 was collected on a Simens D-5000 diffractometer in reflection (Bragg–Brentano) mode using Cu Kα radiation, monochromatized by a secondary graphite monochromator. The data were collected in the range between 7 and 140° 2θ in steps of 0.03° and the integration time of 17 s per step.

Powdered material spread on holey carbon coated Cu grid was investigated by high-resolution field-emission TEM Jeol 2010F. Transmission electron diffraction observation was focused on scattering of electrons by single crystallites.

3. Results and discussion

Using the modified Pechini method we were able to prepare quite pure Li_2MnSiO_4, while Li_2FeSiO_4 prepared according to the same method contained too many impurities to be used for reliable structural characterization. Much better purity of the latter was obtained via the hydrothermal synthesis route. By contrast, we have not succeeded at all to prepare Li_2MnSiO_4 using the hydrothermal route. Bearing these problems in mind, we decided for the following strategy of preliminary materials characterization: in structural investigation we compared the Li_2MnSiO_4 obtained using the Pechini method with the Li_2FeSiO_4 material prepared via the hydrothermal synthesis; for the electrochemical characterization, however, exclusively materials obtained using the Pechini method (which gave much smaller crystallites) were used.

XRD profiles of the as-prepared Li_2MnSiO_4 and Li_2FeSiO_4 are shown in Fig. 1a and b, respectively. The broad peaks indicate that in neither case the crystallinity is good. Furthermore, impurities were observed in both cases. In the case of Li_2FeSiO_4, at least two impurities can be detected of which one is Fe_3O_4. The impurities in the case of Li_2MnSiO_4 are MnO, a small amount of Li_2SiO_3 and at