

Short communication

## $\text{Li}_2\text{MnSiO}_4$ as a potential Li-battery cathode material

R. Dominko<sup>a,\*</sup>, M. Bele<sup>a</sup>, A. Kokalj<sup>b</sup>, M. Gaberscek<sup>a</sup>, J. Jamnik<sup>a</sup>

<sup>a</sup> National Institute of Chemistry, P.O.B. 660, SI-1001 Ljubljana, Slovenia

<sup>b</sup> Institute Jožef Stefan, Jamova 39, SI-1000 Ljubljana, Slovenia

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### Abstract

Recently we synthesized and preliminary characterized a new material for potential use in Li-battery cathodes:  $\text{Li}_2\text{MnSiO}_4$ . Although its theoretical capacity is about  $330 \text{ mAh g}^{-1}$ , the actual measurements showed a much smaller value (about  $120 \text{ mAh g}^{-1}$ ). One of the reasons for the poor performance could be the poor electronic conductivity ( $<10^{-14} \text{ S cm}^{-1}$  at RT) causing a huge polarization during charge–discharge. However, in the present paper we show that reducing the particle size down to the range of 20–50 nm and additional particle embedment into a carbon phase does not significantly improve the electrochemistry of  $\text{Li}_2\text{MnSiO}_4$ . Observations of structural changes during the first charge shows a complete loss of peaks when reaching the nominal composition of ca.  $\text{Li}_1\text{MnSiO}_4$ . The peaks are not recovered during subsequent cycling. It is supposed that extraction of Li causes significant structural changes so that the resulting material is only able to reversibly exchange a limited amount of Li. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Lithium-ion battery; Cathode material; Orthosilicate; Manganese silicate

### 1. Introduction

The need for large-scale commercialization of Li batteries with advanced properties is a motivation for continuous research and innovations in this field [1]. Large-scale batteries should fulfil a variety of safety, environmental, price and energy density demands. In this context, several materials discovered by Goode-nough's group [2–4] and later on extensively researched by other groups, have opened a completely new range of cathode materials for Li-ion batteries. In particular,  $\text{LiFePO}_4$  has gained a lot of attention and, although it possesses a very low intrinsic conductivity, different preparation techniques have enabled the use of this material at extremely high C-rates [5–8]. Later on, several other interesting Fe-based cathode materials have been proposed [9–11]. Most recently, Nyten et al. [12,13] have reported preparation and basic characterization of the first member of silicate branch of Fe-based materials:  $\text{Li}_2\text{FeSiO}_4$ . Basically, this cathode material possesses the same benefits as  $\text{LiFePO}_4$ , with one major difference: namely  $\text{Li}_2\text{FeSiO}_4$  has two lithium ions in the structure and, at least theoretically, enables exchange of two electrons per transition metal with a theoretical capacity of approximately  $320 \text{ mAh g}^{-1}$ . However, the electrochemical tests have shown

that, within the electrolyte stability potential window, only up to 1 mol of lithium can be reversibly exchanged [12,14]. The exchange of Fe with Mn leads to an iso-structural material with a higher expected working voltage and with a possibility to obtain a cathode material where two-electron reaction (exploiting the  $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}$  and  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$  redox pairs) becomes feasible [14,15].

The synthesis and first electrochemical characterization of  $\text{Li}_2\text{MnSiO}_4$  was recently reported by our group. Although it was clearly shown that the material could be cycled, the amount of reversibly exchanged lithium was relatively small (0.7 Li per formula unit at most), while the irreversible losses, especially in the first cycles, were very large. Additionally, serious reversible capacity fading was observed.

In that preliminary study we were not able to conclude whether the observed properties were due to inherent thermodynamic properties of  $\text{Li}_2\text{MnSiO}_4$  or due to kinetic problems (caused by the low conductivity of silicates). It is well known from the extensive work on olivines that the kinetic problems can be overcome by preparing very small active particles (a few tenths of nanometers) and embedding them into an electron conducting phase, such as a carbon coating or carbon network [5–8]. In the present contribution we check if a similar strategy (particle size reduction, carbon coating) can lead to improvement of performance also in the case of  $\text{Li}_2\text{MnSiO}_4$ .

\* Corresponding author. Tel.: +386 14760362; fax: +386 14760422.  
E-mail address: [Robert.Dominko@ki.si](mailto:Robert.Dominko@ki.si) (R. Dominko).

## 2. Experimental

$\text{Li}_2\text{MnSiO}_4$  was synthesized using a modified Pechini sol–gel process, as described elsewhere [14]. The starting precursors were lithium acetate dihydrate (Aldrich), manganese acetate tetrahydrate (Aldrich) and  $\text{SiO}_2$  particles Cab-osil M5 (Riedel-de Haën). Citric acid (Aldrich) and ethylene glycol (Riedel-de Haën) in a molar ratio 1:3 were used as complexation agents for  $\text{SiO}_2$  particles. A mixture of the solutions containing Li, Mn and  $\text{SiO}_2$  in molar ratio 2:1:1 was stirred for an hour and maintained during the night to enable formation of sol. The sol was dried at  $60^\circ\text{C}$  for at least 24 h. After thorough grinding with a mortar and pestle, the obtained xerogel was heat-treated in a gas-tight quartz tube with a moderate but constant flow of Ar 5.0. The initial heating rate was  $10^\circ\text{C min}^{-1}$ . After reaching  $700^\circ\text{C}$ , the samples were maintained at that temperature for at least 1 h and then left to cool down to room temperature.

Surfaces of samples were observed and analyzed with a field emission scanning electron microscope (FE-SEM, Supra 35 VP, Carl Zeiss, Germany) at an accelerating voltage of 1 kV. The microscope was equipped with energy dispersive spectroscopy (Oxford INCA 400, Oxford Instruments Analytical, UK). Prior to the EDX analysis, the samples were pressed into pellets and fixed on a holder with a single sided adhesive golden tape. The surface of pellets was sputtered with a thin film of gold using the Balzers SCD 050 deposition system. EDX analysis was performed at an accelerating voltage of 20 kV.

Samples for X-ray diffraction were prepared in an electrochemical cell at a current density corresponding to  $C/200$ . The experiments were stopped at points that corresponded to the removal of 0.25, 0.5, 0.75, 1, 1.5 and 2 mol lithium from  $\text{Li}_2\text{MnSiO}_4$ . X-ray powder diffraction patterns of the samples were collected on a Philips PW 1710 diffractometer using  $\text{Cu K}\alpha$  radiation =  $1.5418 \text{ \AA}$ . The data were collected in the range between  $15^\circ$  and  $70^\circ$  in steps of  $0.034^\circ$ .

The electrodes with  $\text{Li}_2\text{MnSiO}_4$  as active material were prepared by spreading either the ball-milled or manually mixed cathode slurry (80 wt.% of a prepared material + 10 wt.% of acetylene black and 10 wt.% of PVdF in NMP) onto an Al-foil current collector. Circular electrodes with a diameter of 16 mm ( $2 \text{ cm}^2$ ) were cut-out from the sheets which corresponded to an active material mass between 5 and 6 mg. The electrodes were dried overnight under vacuum at  $110^\circ\text{C}$  and stored in a glovebox. The electrochemical characteristics were measured in vacuum-sealed triplex foil (coffee bag foil) cells. The electrolyte used was a 0.8 M solution of LiBOB (Chemetal) in EC:DEC (1:1 ratio by volume) purchased from Aldrich. Solvents and salt were used as received. The working electrode and the counter electrode consisting of metallic lithium were separated with a glass wool separator. The electrochemical measurements were performed using a VMP3 potentiostat/galvanostat at a constant temperature of  $60^\circ\text{C}$  if not stated otherwise.

## 3. Results and discussion

By merely increasing the amount of complexation agents we have managed to prepare smaller  $\text{Li}_2\text{MnSiO}_4$  particles if

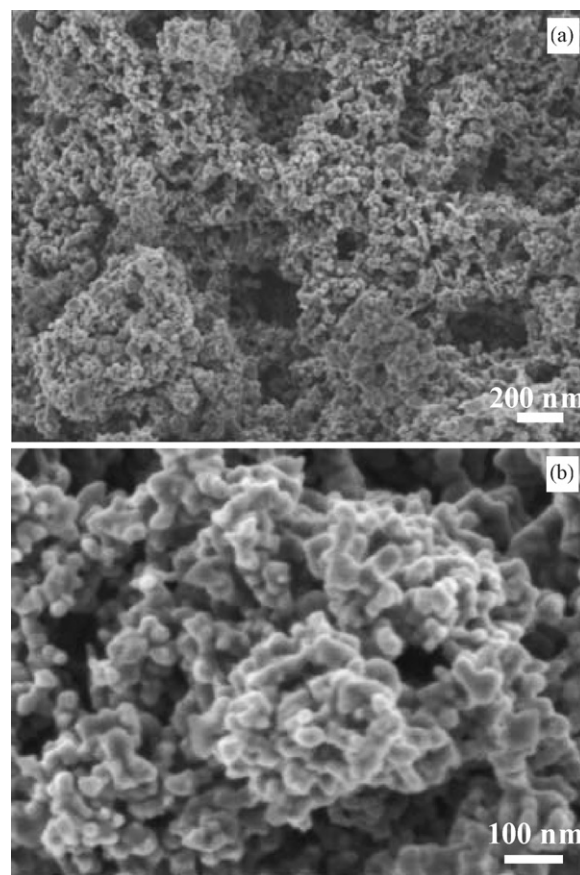


Fig. 1. SEM micrographs of (a)  $\text{Li}_2\text{MnSiO}_4$  microstructure and (b)  $\text{Li}_2\text{MnSiO}_4$  particles.

compared to our first report [14]. At the same time, this modification in preparation procedure affected the total amount and, most likely, also distribution of carbon in the final composite. The main microstructural characteristics of the modified  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composite material are shown in Fig. 1. The microstructure seems open enough to allow easy penetration of electrolyte (Fig. 1a) while the mean particle size is estimated to be in the range from 20 to 50 nm (Fig. 1b). This is at least twice smaller than in our first report [14] and comparable to the sizes that have given very good kinetics in olivines [5–8].

Although TGA showed quite a high total amount of carbon (about 5 wt.%), we cannot observe carbon as a separate phase in Fig. 1. Probably in our case the accelerating voltage was too small (1 kV). However, any increase in the voltage lead to particle instability that seriously blurred the image. For this reason we tried to find alternative ways to observe the carbon phase. Using EDX line or mapping analysis we have been able to roughly determine the distribution of carbon on the submicrometer scale. Fig. 2a presents a typical line EDX analysis of the prepared  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composite. The quantity of carbon through the whole scanned line does not change significantly, especially if we are aware that the detection quantity is also a function of sample preparation (smoothness, compactness). Similar information can be obtained from Fig. 2b which shows EDX mapping analysis of the whole area shown in Fig. 2a.

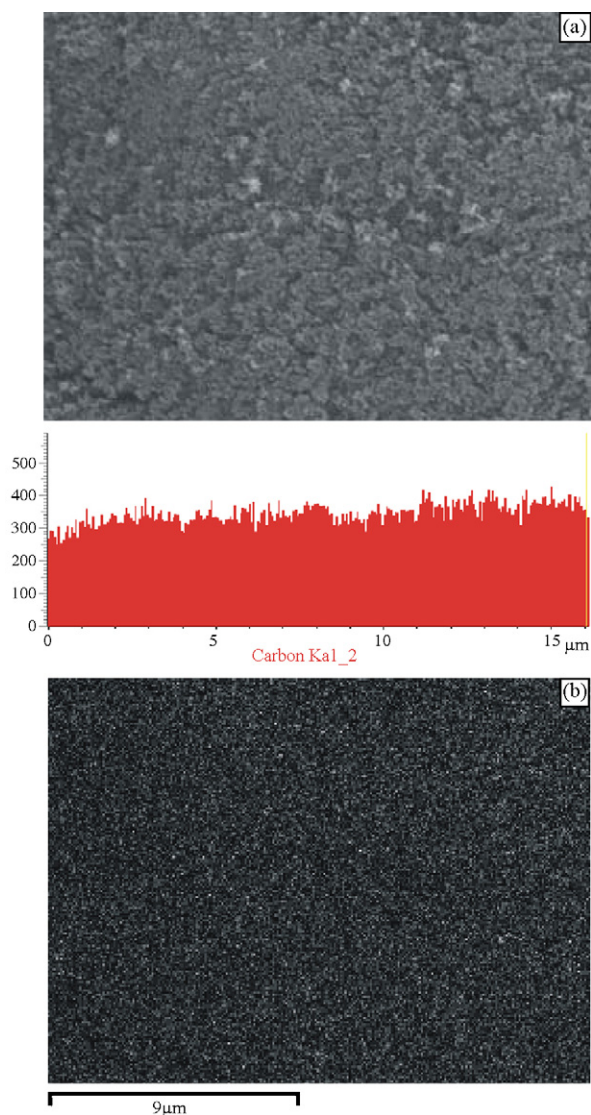


Fig. 2. EDX analysis of  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composite on carbon: (a) line analysis and (b) mapping of whole area shown in (a).

As a whole, the microstructural features of the modified  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composite (with respect to the one reported in Ref. [14]) should have a beneficial effect on the kinetics of  $\text{Li}_2\text{MnSiO}_4$ . The actual electrochemical characteristics at room temperature and at  $60^\circ\text{C}$  are shown in Fig. 3a and Fig. 3b, respectively. The cut-off voltage (4.2 V) and the salt (LiBOB) were selected in such a way to minimize the irreversible losses due to electrolyte degradation. Regardless of these careful experimental considerations and, in particular, regardless of the microstructural optimization, the RT measurements (Fig. 3a) do not show any significant improvement of reversible capacity with respect to our first report [14]. As one of our aims was to find conditions at which more than 1Li could, perhaps, be extracted from  $\text{Li}_2\text{MnSiO}_4$ , we checked the cycling behaviour also at elevated temperatures, i.e., at  $60^\circ\text{C}$  (Fig. 3b). At these conditions, the first lithium extraction proceeds smoothly through a plateau at approximately 3.9–4.0 V versus lithium reference. If we assume that all charge consumed during the first oxidation

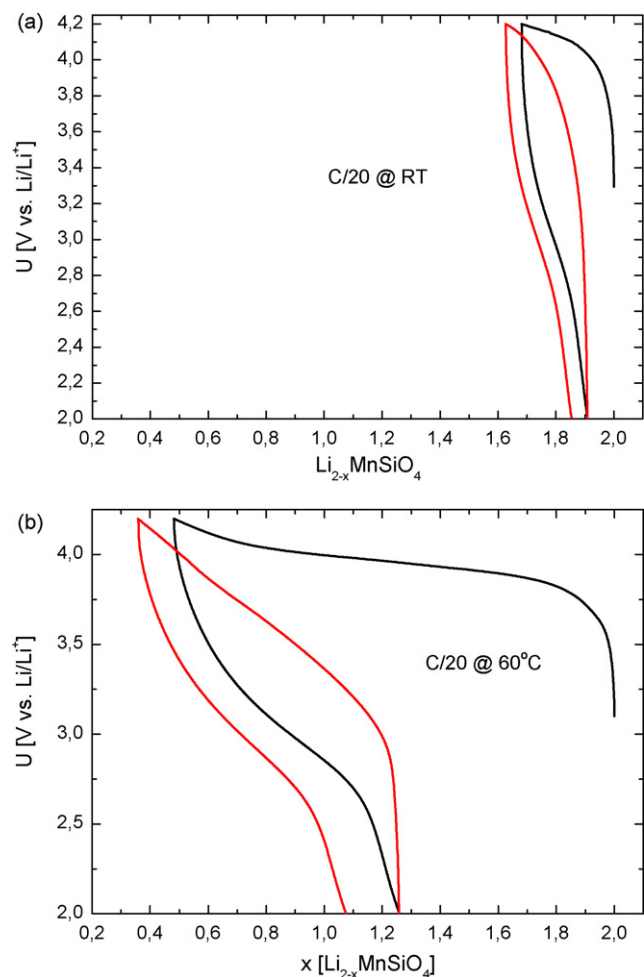


Fig. 3. First two cycles of  $\text{Li}_2\text{MnSiO}_4/\text{C}$  samples at (a) room temperature and (b) constant temperature of  $60^\circ\text{C}$ .

was due to lithium extraction, almost 1.5 mol of lithium was extracted from the structure  $\text{Li}_2\text{MnSiO}_4$ . This would mean that at least a part of the manganese had to be oxidized from Mn(II) to Mn(IV). However, the subsequent reduction half cycle and all further cycles do not exhibit any well-defined plateaux. Rather, the charge/discharge curves become inclined and the reversible capacity drops to ca. 0.7 mol Li per formula unit.

Nevertheless, the appearance of long plateau near 4 V versus lithium reference during the first oxidation process at  $60^\circ\text{C}$  seemed a good starting point, so all further testings were performed at this temperature. It is commonly known that distribution of components and the contact between them can be further improved by ball milling. Fig. 4 shows that in the case of  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites, ball milling has a rather small but measurable impact on their electrochemical behaviour. A closer inspection of the curves in Fig. 4 reveals that both ball-milled composites exhibit about 20 mV lower polarization during lithium extraction which results in a slightly higher reversible capacity.

Most importantly, this higher reversible capacity of ball-milled samples with respect to usual mixtures is retained during prolonged cycling, as shown in Fig. 5. Nevertheless, in all cases the rate of capacity fading is quite high and more than

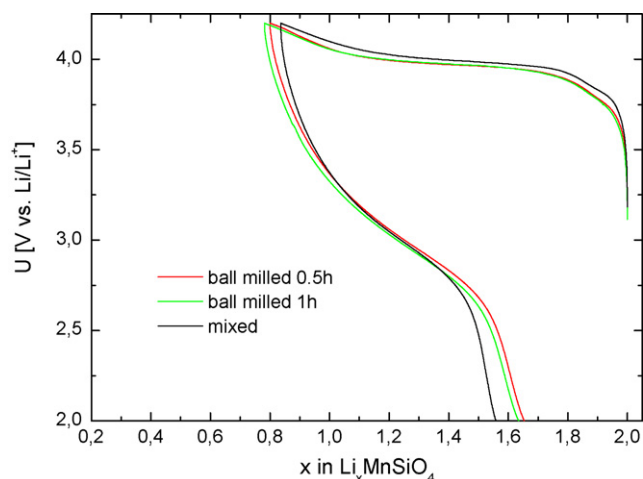


Fig. 4. First cycle of pre-treated  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites.

$40 \text{ mAh g}^{-1}$  are lost after 10 cycles. At this point we concluded that slow kinetics (due to poor conductivity) are probably not the biggest issue in  $\text{Li}_2\text{MnSiO}_4$ . We speculated that the disappearance of voltage plateau after first charge (see Fig. 3b and

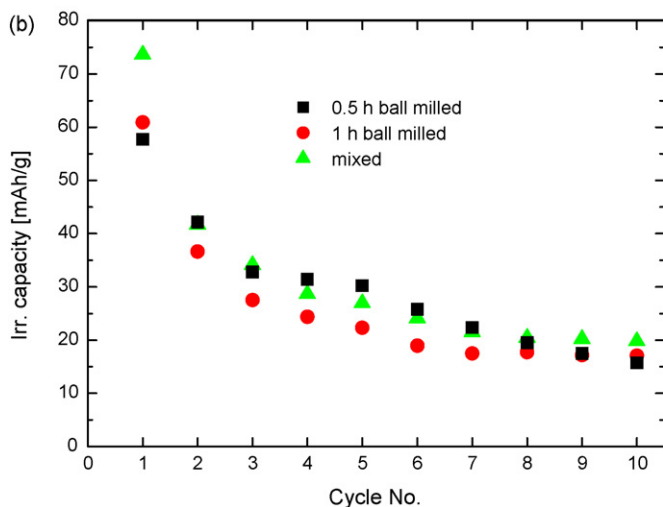
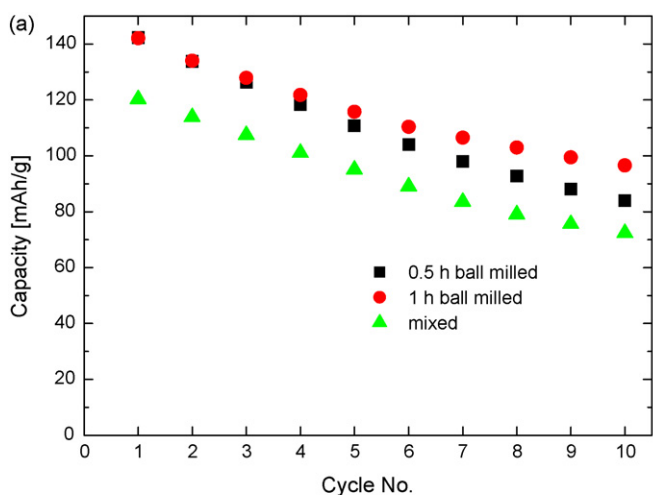


Fig. 5. (a) Cycling behaviour of pre-treated  $\text{Li}_2\text{MnSiO}_4/\text{C}$  composites. (b) Evolution of irreversible capacity with cycles as a function of pre-treatment.

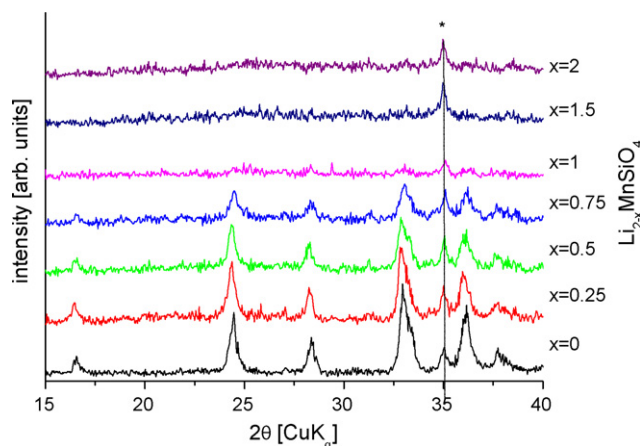


Fig. 6. X-ray diffraction patterns of compositions obtained with electrochemical oxidation of  $\text{Li}_2\text{MnSiO}_4$ -based composites. The value of  $x$  corresponds to expected chemical composition of the electrode that is based on the amount of charge passed through the cell. The remaining diffraction peak marked with asterisk denotes  $\text{MnO}$  impurity.

the corresponding text) could be due to irreversible structural changes of  $\text{Li}_2\text{MnSiO}_4$  occurring during extraction of  $\text{Li}$ .

To check this assumption, we prepared several electrochemical cells in which the initial  $\text{Li}_2\text{MnSiO}_4$  was charged to different states. If we assume that all charge that passed through the cells at the slow rate of  $C/200$  rate was consumed for lithium extraction, the prepared  $\text{Li}_{2-x}\text{MnSiO}_4$  samples had nominal compositions corresponding to  $x = 0.25, 0.5, 0.75, 1, 1.5$  and  $2$ . Fig. 6 shows X-ray diffraction patterns of these samples. For comparison, X-ray pattern of the starting  $\text{Li}_2\text{MnSiO}_4$  is added.

Clearly, the diffraction peaks are fading with increasing  $x$ . Their position, however, is not changing significantly, in agreement with prediction of *ab initio* calculations [15]. At about  $x = 1$  the intensity of peaks is already so weak that is hard to distinguish between them from the background. Most importantly, after the subsequent discharge half-cycle, the initial structure is not recovered, that is, no peaks are observed anymore after the first charge. At this point it is not clear whether the particles are powderized below or a significant structural change occurs after the first charge. The significant change in the shape of galvanostatic (disappearance of plateau) is in favour with the latter scenario. However, even if the structural changes are significant, it is obvious from Fig. 5, that also the modified structure (exhibiting no X-ray peaks) is able to reversibly exchange more than  $100 \text{ mAh g}^{-1}$  of charge.

Currently, we are performing DFT calculations in order to identify such possible structure(s). The ultimate strategy to be pursued based on these results, however, is to find ways to stabilize the initial structure of  $\text{Li}_2\text{MnSiO}_4$  (possibly by suitable heterogeneous doping). Based on the results of Fig. 3b this would mean that one could be able to exchange reversibly up to  $1.5\text{Li}$  per formula of  $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$  ( $x > 0.5$ ).

#### 4. Conclusions

Neither reduction of particle size nor increased carbon content (and optimized carbon distribution) have significantly

improved the electrochemical performance of  $\text{Li}_2\text{MnSiO}_4$ . The polarization resistance decreased by merely 20 mV and the capacity increased by ca.  $20 \text{ mAh g}^{-1}$  to reach a maximum of about  $140 \text{ mAh g}^{-1}$ . The cycling stability has remained poor (about  $4 \text{ mAh g}^{-1}$  are lost per cycle). Obviously, the strategy that has proven extremely efficient in the case of  $\text{LiFePO}_4$ , does not work in the case of  $\text{Li}_2\text{MnSiO}_4$ . Based on ex situ X-ray diffraction measurements of partially charged samples, we speculate that extraction of Li leads to a progressive collapse of the initial structure. Hence, it can be suggested that in future one should focus primarily on the structural stabilization of  $\text{Li}_2\text{MnSiO}_4$  rather than on improvement of electronic/ionic transport.

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### References

- [1] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188–1194.
- [3] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1609–1613.
- [4] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 2581–2586.
- [5] N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, *Proceedings of the 196th ECS Meeting, Hawaii, October, 1999*, pp. 17–22.
- [6] H. Huang, S.C. Yin, L.F. Nazar, *Electrochem. Solid-State Lett.* 4 (2001) A170–A172.
- [7] C. Delacourt, L. Laffont, R. Bouchet, C. Wurm, J.B. Leriche, M. Morcrette, J.M. Tarascon, C. Masquelier, *J. Electrochem. Soc.* 152 (2005) A913–A921.
- [8] R. Dominko, M. Bele, M. Gaberscek, M. Remskar, D. Hanzel, S. Pejovnik, J. Jamnik, *J. Electrochem. Soc.* 152 (2005) A607–A610.
- [9] V. Legagneur, Y. An, A. Mosbah, R. Portal, A. Le Gal La Salle, A. Verbaere, D. Guyomard, Y. Piffard, *Solid-State Ionics* 139 (2001) 37–46.
- [10] C. Wurm, M. Morcrette, G. Rousse, L. Dupont, C. Masquelier, *Chem. Mater.* 14 (2002) 2701–2710.
- [11] S. Patoux, C. Wurm, M. Morcrette, G. Rousse, C. Masquelier, *J. Power Sources* 119–121 (2003) 278–284.
- [12] A. Nyten, A. Abouimrane, M. Armand, T. Gustafsson, J.O. Thomas, *Electrochem. Commun.* 7 (2005) 156–160.
- [13] A. Nyten, S. Kamali, L. Hångstrom, T. Gustafsson, J.O. Thomas, *J. Mater. Chem.* 16 (2006) 2266–2272.
- [14] R. Dominko, M. Bele, M. Gaberscek, A. Meden, M. Remskar, J. Jamnik, *Electrochem. Commun.* 8 (2006) 217–222.
- [15] M.E. Arroyo-de Dompablo, M. Armand, J.M. Tarascon, U. Amador, *Electrochem. Commun.* 8 (2006) 1292–1298.