Synthesis of Lithium-Manganese Orthosilicate and its Application as Cathode Material in Lithium-Ion Batteries

Maciej Boczar¹, Michal Krajewski¹, Maciej Ratynski¹, Bartosz Hamankiewicz¹,² and Andrzej Czerwinski¹,³*

¹Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
²Biological and Chemical Research Centre, University of Warsaw, Zwirki i Wigury 101, 02-089 Warsaw, Poland
³Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland
*E-mail: bhamankiewicz@chem.uw.edu.pl, aczerw@chem.uw.edu.pl

Received: 5 April 2018 / Accepted: 4 July 2018 / Published: 5 November 2018

Lithium-manganese orthosilicate powders were synthesized by a modified sol-gel method. The LMS powders were carbon coated by two different methods. The conductive cathode layer has been obtained by carbonization of organic precursor either on the grains of previously synthesized lithium-manganese orthosilicate or reduction of carbon source during active material synthesis (internal coating). Synthesized materials were analyzed by XRD, SEM, N₂ adsorption/desorption and electrochemical CP and CV methods. The internal coating approach improved the electrochemical performance of Li₂MnSiO₄ powder, increasing its specific capacity and cyclability by enhancing its electrical conductivity and enlarging its electrochemically active surface area.

Keywords: Li₂MnSiO₄, li-ion battery, sol-gel synthesis, carbon coating, lithium-manganese orthosilicate

1. INTRODUCTION

Lithium-manganese orthosilicate (Li₂MnSiO₄, LMS) is a very interesting cathode material for next generation of lithium-ion batteries and for battery industry. Due to its high theoretical capacity this compound is extensively researched as a candidate for future cathodes for Li-ion batteries. Such high capacity is related to the fact, that one mole of Li₂MnSiO₄ can intercalate/deintercalate 2 moles of lithium ions per formula unit during galvanostatic charge/discharge processes, involving Mn⁴⁺/Mn³⁺ and Mn³⁺/Mn²⁺ redox couples. In addition, low cost and high safety of the compound resulted in an increase in the attractiveness of this material [1,2].
Unfortunately, despite the mentioned advantages, Li$_2$MnSiO$_4$ is characterized by poor ionic conductivity, unstable crystallographic structure resulting in crystal amorphization during first charge/discharge cycle [2] and poor cyclability. Moreover, due to the large distances between redox centers in -Mn-O-Si-O-Mn- chain, LMS is an electric insulator, with conductivities equal to ca. 10$^{-16}$ S·cm$^{-1}$ [3]. The structure of Li$_2$MnSiO$_4$ can be linked to lithium phosphate (Li$_3$PO$_4$), which is known to crystallize in at least four different polymorphs, in $Pmn2_1$, $Pmnb$, $P2_1/n$, and $Pn$ space groups [1,4,5]. The orthorhombic forms ($Pmn2_1$ and $Pmnb$) have two-dimensional pathways for Li-ion diffusion while the monoclinic forms ($P2_1/n$ and $Pn$) are framework structures with Li-ion positions interconnected in three dimensions. Variety of structural forms of lithium-manganese orthosilicate introduces some additional challenges in preparation and evaluation of this compound. Therefore, many scientists, in order to reduce these disadvantages, began developing different ways to overcome them, including: grain size reduction by new synthetic routes (solid-state [6], sol-gel [1,2,5,7-9] hydrothermal [10-13]), surface coating [14] and the use of chemical doping [15,16]. From the synthetic point of view, the sol-gel synthesis remains one of the most used method to obtain fine powders of electrode materials used in lithium-ion technology. Dominko et. al. synthesized Li$_2$MnSiO$_4$ powder with particle size in range of 20 – 50 nm, with initial specific capacity of 74 mAh·g$^{-1}$ while discharging the cell with the current density of C/200 [2]. Deng et. al. achieved specific capacity of LMS powder as high as 140 mAh·g$^{-1}$ during first discharge while using the current density of C/30 by having an increased carbon content (10.5 wt.%) in the so-prepared powder [7]. Duncan et. al. prepared lithium-manganese orthosilicate showing good cyclability of 8% capacity loss after ten cycles, however without specifying the discharge current rate nor the carbon content present in the sample [5]. The comparison of electrochemical performance for a few previous sol-gel approaches are listed in Table 1.

<table>
<thead>
<tr>
<th>Reference</th>
<th>1st discharge capacity [mAh·g$^{-1}$]</th>
<th>10th discharge capacity [mAh·g$^{-1}$]</th>
<th>Discharge capacity retained after 10th cycle [%]</th>
<th>Primary particle size [nm]</th>
<th>Discharge current rate</th>
<th>Carbon content (wt.%, TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>95</td>
<td>53</td>
<td>56</td>
<td>20-50</td>
<td>C/10</td>
<td>7</td>
</tr>
<tr>
<td>[5]</td>
<td>105</td>
<td>97</td>
<td>92</td>
<td>20-50</td>
<td>Not given</td>
<td>Not given</td>
</tr>
<tr>
<td>[7]</td>
<td>140</td>
<td>85</td>
<td>61</td>
<td>200</td>
<td>C/30</td>
<td>10,5</td>
</tr>
<tr>
<td>[8]</td>
<td>110</td>
<td>96</td>
<td>87</td>
<td>100-200</td>
<td>C/30</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>126</td>
<td>87</td>
<td>69</td>
<td>10-20</td>
<td>C/10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>72</td>
<td>69</td>
<td>10-20</td>
<td>C/2</td>
<td></td>
</tr>
</tbody>
</table>

In this paper we examined different synthetic techniques to obtain carbon-coated Li$_2$MnSiO$_4$ powders and evaluated their influence on structure, morphology and electrochemical properties of lithium-manganese orthosilicate.
2. EXPERIMENTAL

2.1. Synthesis of Li$_2$MnSiO$_4$

All the reagents and solvents used for the synthesis were analytically pure and derived from Sigma-Aldrich. Li$_2$MnSiO$_4$ composite was synthesized by a modified sol-gel method. Firstly, 0.0188 mol Si(OC$_2$H$_5$)$_4$ (TEOS) was dissolved in 50 ml of ethyl alcohol (EtOH) and then mixed with 0.0067 mol of citric acid to create an acidic environment. Then, 0.0188 mol of ethylene glycol was added to the solution. The prepared mixture was sonificated on ultrasonic scrubber for 30 minutes to mix the reagents. Then, 0.0188 mol of Mn(C$_2$H$_3$O$_2$)$_2$·4H$_2$O dissolved in 50 ml of ethyl alcohol and 0.0465 mol of Li(C$_2$H$_3$O$_2$)·2H$_2$O dissolved in 50 ml EtOH were added dropwise to the solution. The mixed solution containing the hydrolyzed SiO$_2$ from TEOS was stirred and evaporated at 70°C to form the wet gel.

The resulting gel was subject to two forms of heat-treatment. In the first case, the gel was dried in a tube oven for 1.5 h at 250°C and then heat-treated at 700°C for 6 h in a flow of air to form pristine Li$_2$MnSiO$_4$ (LMS-P). The second mode of heat-treatment consisted of drying the gel in a tube oven at 50°C for 1 h, then at 250°C for 2 h and finally at 700°C for 6 h. In this case all the steps were carried out in a 5% H$_2$/Ar reducing atmosphere to form a carbon-coated Li$_2$MnSiO$_4$ by reducing the remaining organic compounds to elemental carbon (internal coating, LMS-C). Moreover, the pristine Li$_2$MnSiO$_4$ powder was externally carbon coated by mixing previously synthesized LMS with sucrose (10% wt.) and then wet milling with acetone in a ball mill for 8 h (500 rpm in stainless steel grinding jar with stainless steel balls). The resulting material was heat-treated at 500°C for 3 h in a flow of 5% H$_2$/Ar reducing atmosphere (LMS-C).

2.2 XRD, XRF, SEM, N$_2$ adsorption/desorption

X-ray diffraction (XRD) measurements were made in the classical Bragg-Brentano geometry. X-ray tube C was used in the optical system of the 1-degree slit and Ni filter (1:20). The Cu lamp was charged with 40 mA and 40 kV. Measurement was done in the range of 10°-120° with a step of 0.008° with extended counting time - 1 minute per step.

For SEM and EDX measurement Merlin scanning electron microscope (Zeiss) was used together with Quantax 400 energy dispersive X-ray spectroscope (Bruker). Electron beam energy used for X-ray excitation was 3-5 keV and the spectrum acquisition time was ca. 120 s. For quantitative EDX data processing a standard-less procedure was applied with the use of the software supplied by Bruker. For energy calibration X-ray signals obtained from pure Cu were utilized.

In N$_2$ adsorption/desorption experiments the procedures were conducted on Micromeritics® ASAP 2060 apparatus at 77.349 K absolute temperature in the range of 0.01 to 0.995 relative N$_2$ pressure $p/(p^0)$. Adsorption/desorption isotherm analysis was performed using ASAP 2060 software. The surface area was obtained using the BET method. Distribution and pore volume were calculated using the BJH method for desorption curves. Moreover, the average gran sizes of examined powders were also estimated by using ASAP 2060 software.
2.3 Electrochemistry

Li$_2$MnSiO$_4$ was ground in an agate mortar together with Vulcan VXC72R (Cabot) carbon for 15 min. After homogenization, 5% (wt.) PVdF solution (dissolved in N-methyl-2-pyrrolidone) was added to prepared blend and stirred for 4 h on a magnetic stirrer. The mixture was then applied on to the aluminum foil with automatic applicator, dried at 50°C for 1 h in air and then at 120°C in vacuum oven overnight. The electrodes (0.9 cm in diameter) were then cut and compressed at 200 bar on a hydraulic press for 1 min, then weighed, dried at 120°C in vacuum oven and transferred into argon-filled glove-box (MBraun Unilab MB-20-G). The electrode composition was 8:1:1 wt. ratio of LMS:PVdF:Vulcan.

The electrochemical performance of Li$_2$MnSiO$_4$ powders was tested in a Swagelok®-type, three-electrode system. Li$_2$MnSiO$_4$ electrodes were used as the working electrodes, while the counter and reference electrodes were made of metallic lithium. The separator was made of Celgard® 2325 immersed in 1M LiPF$_6$ dissolved in ethylene carbonate and dimethyl carbonate (1:1 wt./wt., BASF). Electrochemical cells were analyzed using a galvanostatic charge/discharge tests and cyclic voltammetry (CV). Chronopotentiotmetry (CP) charge/discharge experiments were made between potential of 1.5 and 4.8 V (vs. Li$^+$/Li$^0$) for 10 cycles at 0.1 C current rate (where C correspond to 333 mA·g$^{-1}$) at room temperature on a multichannel battery tester Sollich Atlas 1361. CV measurements were carried out on Solartron SI 1287 Electrochemical Interface where the working electrode was polarized between 1.5 and 4.8 V (vs. Li$^+$/Li$^0$) at a scan rate of 0.1 mV·s$^{-1}$ for 3 cycles.

3. RESULTS AND DISCUSSION

3.1 Structure and morphology

![Figure 1. XRD spectra of Li$_2$MnSiO$_4$ powders (Cu lamp charged with 40 mA and 40 kV; measurement done in the range of 10°-120° with a step of 0.008°).](image-url)
Figure 2. SEM images of LMS-P (A), LMS-S (B) and LMS-C (C) powders (beam energy – 3-5 keV; spectrum acquisition – ca. 120 s).
Fig. 1 depicts XRD patterns of LMS-P, LMS-C and LMS-S powders. Qualitative phase analysis of LMS-P shows the presence of Li$_2$MnSiO$_4$ reflections (ICSD 98-026-2720; Pnma space group) as the main phase [17]. Moreover, there are several additional reflections that are located near Li$_2$MnSiO$_4$ phase reflections identified mainly as Li$_2$SiO$_3$ and MnO phases (marked by orange and green dotted lines respectively) and suggests some degree of impurity in the synthesized powder. The Pnma phase is a modification of the Li$_2$MnSiO$_4$ Pnm2$_1$ phase, related to doubling the elemental cell and breaking some of the symmetries assumed in the Pnm2$_1$ group [18]. The LMS-C sample is distinguished from the LMS-P sample with a lower degree of crystallinity and greater MnO phase content. LMS-S sample has a small shift of peaks towards smaller angles, which may be associated with increased elemental cell size, and a small expansion of the peaks, possibly suggesting crystallite size decrease with respect to LMS-P powder.

The SEM analysis of Li$_2$MnSiO$_4$ powders is presented on Fig. 2. One can see a uniform distribution of material grains in all of the synthesized samples in a range of 20 to 50 nm. Moreover, all the characterized powders have tendency to agglomeration which can create structures up to 40 μm in diameter. Such agglomerative properties can have a negative impact on electrochemical properties of Li$_2$MnSiO$_4$ due to impossibility of transporting both the electrons and Li$^+$ ions into the center of the agglomerate. No correlation between synthetic route and the powder's morphology observed on the SEM images has been found.

Fig. 3. presents results of N$_2$ adsorption/desorption experiments on lithium-manganese orthosilicate powders. All examined powders are characterized by Brauner’s type-IV adsorption isotherms. The desorption curves do not match with adsorption isotherms due to capillary condensation phenomena inside the powders pores and suggest porous structure of synthesized compounds. BET calculations revealed the powders’ specific surface area to be 0.87 ± 0.02, 30.49 ± 0.18 and 35.55 ± 0.08 m$^2$·g$^{-1}$ for LMS-P, LMS-S and LMS-C, respectively. Both carbon-coated powders showed increased BET surface area compared to pristine Li$_2$MnSiO$_4$ sample with LMS-C revealing the highest value. The pore distribution in the examined powders is dominated by two regions, located at 3-4 and 10-12 nm in diameter, with the pore volume (between 1.7 and 300 nm) of 0.0040, 0.0940 and 0.1825 cm$^3$·g$^{-1}$ for LMS-P, LMS-S and LMS-C, respectively. One can see that the pore volume increased with carbon coating similarly to the BET surface area. Also in this case, the LMS-C sample showed the highest value of pore volume.

The analyzed compounds grain’s diameter was estimated to be 1730, 49 and 42 nm, for LMS-P, LMS-S and LMS-C, respectively. These finding are in good agreement with SEM analyses and suggest a fine and homogenous distribution of Li$_2$MnSiO$_4$ particles after carbon coating. The internal carbon coating approach showed the best morphological results, due to reduced agglomeration tendencies of powder grains by gas evolution from organic compounds during heat-treatment process. The results of N$_2$ adsorption/desorption analysis are also listed in Table 2.
Figure 3. N₂ adsorption/desorption isotherms (A, C, E) and BJH analysis (B, D, F) for LMS-P (A, B), LMS-C (C, D) and LMS-S (E, F) samples (temperature – 77.349 K; relative N₂ pressure – from 0.01 to 0.995 p·(p₀⁻¹)).

Table 2. Results of N₂ adsorption/desorption experiments of Li₂MnSiO₄ powders.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET specific surface area [m²·g⁻¹]</th>
<th>Pore diameter [nm]</th>
<th>Pore volume (1.7 – 300 nm) [cm³·g⁻¹]</th>
<th>Grain diameter [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMS-P</td>
<td>0.87 ± 0.02</td>
<td>3-4, 10-20</td>
<td>0.0040</td>
<td>1730</td>
</tr>
<tr>
<td>LMS-S</td>
<td>30.49 ± 0.18</td>
<td>3-4</td>
<td>0.094</td>
<td>49</td>
</tr>
<tr>
<td>LMS-C</td>
<td>35.55 ± 0.08</td>
<td>3-4, 20-40</td>
<td>0.1825</td>
<td>42</td>
</tr>
</tbody>
</table>
3.2 Electrochemistry

3.2.1 Chronopotentiometry

The results of galvanostatic charge/discharge experiments of Li$_2$MnSiO$_4$ powders are presented on Figs. 4 and 5 and also listed in Table 3.

**Figure 4.** Cyclability of Li$_2$MnSiO$_4$ powders during charge (A) and discharge (B) processes (charge/discharge current – C/10; potential range – from 1.5 to 4.8 V vs. Li$^+$/Li$^0$).

**Figure 5.** Charge/discharge curves of Li$_2$MnSiO$_4$ powders (solid line – 1$^{st}$ cycle; dashed line – 2$^{nd}$ cycle; shortly dashed line – 10$^{th}$ cycle; charge/discharge current – C/10; potential range – from 1.5 to 4.8 V vs. Li$^+$/Li$^0$).
Table 3. Results of CP experiments of Li$_2$MnSiO$_4$ powders.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrode loading [mg·cm$^{-2}$]</th>
<th>1$^{st}$ charge/disch. capacity [mAh·g$^{-1}$]</th>
<th>10th charge/disch. capacity [mAh·g$^{-1}$]</th>
<th>Discharge capacity retained after 10th cycle [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMS-P</td>
<td>2.26</td>
<td>54/18</td>
<td>14/13</td>
<td>71</td>
</tr>
<tr>
<td>LMS-S</td>
<td>2.06</td>
<td>159/93</td>
<td>24/23</td>
<td>25</td>
</tr>
<tr>
<td>LMS-C</td>
<td>2.53</td>
<td>194/95</td>
<td>58/53</td>
<td>56</td>
</tr>
</tbody>
</table>

The pristine Li$_2$MnSiO$_4$ showed a specific capacity of 54/18 mAh·g$^{-1}$ during first charge/discharge cycle. After 10 consecutive cycles, LMS-P capacity dropped to 14/13 mAh·g$^{-1}$, resulting in 71% capacity retained after 10 cycles of charging/discharging processes. Such substandard electrochemical performance of pristine LMS powder is a result of its poor ionic and electronic conductivity and structure instability and has been reported previously [19]. On the charge/discharge curves of LMS-P powder (Fig. 5) one can see a change in the charging behavior between first and second cycle. It was suggested that during this process an amorphization of Li$_2$MnSiO$_4$ occurs, which is a major reason of lithium-manganese orthosilicate poor cyclability [20].

The CP behavior of LMS-S differs from LMS-P sample. During the first and tenth charging/discharging processes the LMS-S sample delivered 159/93 and 24/23 mAh·g$^{-1}$ during charge/discharge processes respectively, which are greater values than in the case of pristine Li$_2$MnSiO$_4$ powder. There is also a visible change in the charging behavior of lithium-manganese orthosilicate between first two cycles caused by a structural collapse (Fig. 5). However, the charging curve is of different shape than for LMS-P sample and shows a distinctively long plateau above 4 V (vs. Li$^+/\text{Li}^0$), which is consistent with previous reports about Li$_2$MnSiO$_4$ compounds [21]. The increase in specific capacity and change in the shape of first cycle charging curve can be a result of external carbon coating which can lead to increased electronic conductivity of LMS-S powder and larger electrochemically active surface area thus providing more sites for Li$^+$ intercalation/deintercalation reactions to take place [22,23]. It can be seen, however, that after initial increase of specific capacity of LMS-S powder, its value starts diminishing quite rapidly and after ten consecutive cycles almost reaches the level of LMS-P sample specific capacity. This phenomenon results in larger capacity fade than in the case of LMS-P powder (25% of capacity retained after ten cycles for LMS-S compound). This also suggests that the carbon coating prepared externally from sucrose source is not stable during electrochemical charging/discharging processes and can lead to the coating degradation and loss of physical contact between the surface of Li$_2$MnSiO$_4$ crystals and conductive media present in the electrode. Further examination of this phenomena is required to fully understand this process.

In the case of Li$_2$MnSiO$_4$ internally coated by carbon derived from organic compounds present during sol-gel reaction, the LMS-C powder showed a specific capacity equal to 194/95 and 58/53 during the first and tenth charge/discharge cycle, retaining 56% of its initial capacity at the end of CP experiment. Once again the characteristic change in the charging behavior related to phase amorphization is present on the charge/discharge profiles of Li$_2$MnSiO$_4$ (Fig. 5.). Similar to LMS-S
powder, internal carbon coat led to a raise in Li$_2$MnSiO$_4$ specific capacities and changed the shape of the initial charging curve. The above was a result of enhanced conductivity of synthesized sample and larger electrochemically active surface area [22,23]. Moreover, the carbon coating prepared by internal reduction of organic compounds is more stable, as the specific capacity of Li$_2$MnSiO$_4$ is not diminishing as quickly as in the case of LMS-S powder, which suggests a higher stability of so prepared carbon coat and leads to higher specific capacity of LMS-C even after 10 cycles of charge/discharge reactions.

To further investigate the electrochemical behavior of synthesized Li$_2$MnSiO$_4$ powders we conducted CV analysis.

3.2.2 Cyclic voltammetry

The CV curves of LMS-P, LMS-S and LMS-C powders are presented on Fig. 6. For the LMS-P powder, there are two oxidation/reduction peak couples present at 2.9/3.1 and 4-4.2/4.2 V (vs. Li$^+/\text{Li}_0$) along with a large oxidation peak at potentials higher than 4.6 V. These values correspond to the observed plateau regions in the charge/discharge profiles and may originate from the Mn$^{4+}$/Mn$^{3+}$ and Mn$^{3+}$/Mn$^{2+}$ redox couples. The large oxidation peak above 4.6 V may be due to the liquid electrolyte oxidation reaction. Of no value is the presence of a pair of oxidation/reduction peaks above 4 V for LMS-P powder which are similar to the ones observed in spinel LiMn$_2$O$_4$ powders [24,25] and may suggest contamination of LMS-P sample by this compound.

For the LMS-S sample, there is only one pair of oxidation/reduction peaks present at 2.5/3.35 V (vs. Li$^+/\text{Li}_0$) and one irreversible oxidation peak at 4.4 V (vs. Li$^+/\text{Li}_0$). Both oxidation peaks might be connected with Mn$^{3+}$/Mn$^{2+}$ and Mn$^{4+}$/Mn$^{3+}$ redox couples. A doublet above 4 V is no longer present, suggesting no LiMn$_2$O$_4$ impurity in examined compound. The oxidation peak above 4.6 V may be due to the liquid electrolyte oxidation reaction. The fact, that the peak currents are diminishing quite rapidly with each consecutive cycle, suggesting deterioration of carbon coating and LMS-S sample’s electrochemical properties is of no importance.
For the LMS-C sample, there are two pairs of oxidation/reduction peaks, present at 2.9/3.1 and 4.0/4.3 V (vs. Li⁺/Li⁰). Both of them might be connected to Mn³⁺/Mn²⁺ and Mn⁴⁺/Mn³⁺ redox couples. In this case as well, there is no LiMn₂O₄ impurity present, but a large oxidation peak observed above 4.6 V, related to liquid electrolyte decomposition on electrode's surface, is still visible. The current values are higher than in case of LMS-P and LMS-S samples, suggesting enhanced kinetics of oxidation/reduction reactions due to larger electrochemically active surface area [22,23] and more stable nature of carbon-coat prepared by internal reduction of organic substrates used in sol-gel synthesis. Moreover, as evident from CV and CP curves, the electrochemical processes in LMS-C sample are of more adsorptive nature than intercalation/deintercalation ones. It is surprising that, despite the increase in BET specific surface area for both carbon coated samples (LMS-S and LMS-C) of comparable magnitude, only LMS-C powder shows drastic increase in current values during CV measurements. It is an indication of obtaining carbon coating of better quality during internal coating process, which surrounds Li₂MnSiO₄ particles in higher degree than in the case of carbon coating acquired during external coating process. The internal coating approach provides a lot more active sites for electrochemical reactions to take place, increasing the electrochemically active surface area of the powder as a result. It also opens up a path for powders prepared with such method to be used as lithium hybrid-supercapacitors.

4. CONCLUSIONS

We successfully synthesized Li₂MnSiO₄ powders and coated them with carbon. The powders were characterized by XRD, SEM, N₂ adsorption/desorption, CP and CV methods. Coating with carbon improved LMS specific surface area, reduced the average grain size and lead to enhancement in electrochemical properties of Li₂MnSiO₄. From two different coating approaches, i.e. external coating by addition and reduction of sucrose and internal coating by reduction of organic compounds used in sol-gel synthesis the most successful was the latter. It lead to the lowest average grain sizes, highest specific surface area, improved capacities and highest cyclability. Moreover, only internal carbon coating method resulted in drastic enhancement to LMS electrochemically active surface area. The larger specific surface area and lower average particle size is a result of gas evolution from organic compounds during heat-treatment process. This property, along with presence of carbon layer increased electrical conductivity of Li₂MnSiO₄ and caused enhancement in its electrochemically active surface area, which, as a result, lead to increased specific capacity of lithium-manganese orthosilicate and its charge/discharge reaction kinetics. Our work demonstrates that internal approach to carbon-coating can improve the electrochemical properties of lithium-ion battery materials, especially those of insulating character like Li₂MnSiO₄.

ACKNOWLEDGEMENTS
This work was supported by The Polish National Centre of Science through the research grant UMO-2014/15/B/ST5/02118.
References