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Abstract
The polyanion cathodes for Li-ion batteries, namely LiFePO$_4$, Li$_2$FeP$_2$O$_7$ and Li$_2$FeSiO$_4$, were synthesized by very short high-temperature treatment (approximately several minutes) and subsequent quenching. Methylcellulose—a polymer with thermally driven water solubility—was used as the medium in which the
precursor solutions were dispersed prior to high temperature treatment. The methylcellulose pyrolytically decomposes to carbon, thus producing the polyanion material/carbon composites of LiFePO$_4$/C, Li$_2$FeP$_2$O$_7$/C and Li$_2$FeSiO$_4$/C. The obtained powders have reduced crystallinity and significant microstructural characteristics: low crystallite size and notable microstrain. They exhibit stable electrochemical performances in both aqueous and organic electrolyte. The broadening of existing peaks in cyclic voltammetry and/or the emergence of new broad peaks was attributed to the presence of the amorphous phase in the samples. In galvanostatic charge–discharge tests, the materials provided high capacities at low current densities, while the highest rate performance was demonstrated by olivine-phosphate when compared to the other two materials.

**Graphical abstract:**

**MO1:**

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**Keywords (separated by ' - '):**

Li-ion battery - polyanion cathodes - LiFePO$_4$ - Li$_2$FeP$_2$O$_7$ - Li$_2$FeSiO$_4$ - methylcellulose - quenching

**Supplementary Information**

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Graphical abstract:

MO1:
Towards a green and cost-effective synthesis of polyanionic cathodes: comparative electrochemical behaviour of LiFePO$_4$/C, Li$_2$FeP$_2$O$_7$/C and Li$_2$FeSiO$_4$/C synthesized using methylcellulose matrix

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Abstract. The polyanion cathodes for Li-ion batteries, namely LiFePO$_4$, Li$_2$FeP$_2$O$_7$ and Li$_2$FeSiO$_4$, were synthesized by very short high-temperature treatment (approximately several minutes) and subsequent quenching. Methylcellulose—a polymer with thermally driven water solubility—was used as the medium in which the precursor solutions were dispersed prior to high temperature treatment. The methylcellulose pyrolytically decomposes to carbon, thus producing the polyanion material/carbon composites of LiFePO$_4$/C, Li$_2$FeP$_2$O$_7$/C and Li$_2$FeSiO$_4$/C. The obtained powders have reduced crystallinity and significant microstructural characteristics: low crystallite size and notable microstrain. They exhibit stable electrochemical performances in both aqueous and organic electrolyte. The broadening of existing peaks in cyclic voltammetry and/or the emergence of new broad peaks was attributed to the presence of the amorphous phase in the samples. In galvanostatic charge–discharge tests, the materials provided high capacities at low current densities, while the highest rate performance was demonstrated by olivine-phosphate when compared to the other two materials.

Keywords. Li-ion battery; polyanion cathodes; LiFePO$_4$; Li$_2$FeP$_2$O$_7$; Li$_2$FeSiO$_4$; methylcellulose; quenching.

1. Introduction

Polyanion cathode materials for Li-ion batteries offer the advantage of higher safety and higher voltage values in comparison to the oxide cathodes with the same $M^{x+}/(x+1)^+$ redox pair [1]. Both higher voltage and higher stability come from strong covalent bonding within the polyanion units and these inherent characteristics have promoted investigation of different polyanion compounds: phosphates (PO$_4^{3−}$), pyrophosphates (P$_2$O$_7^{4−}$), silicates (SiO$_4^{4−}$) and others. Among them, the iron-based compounds appear attractive, as Fe is abundant, inexpensive and less toxic than Co, Ni or Mn. LiFePO$_4$ has gained worldwide fame, thanks to its outstanding electrochemical features [2], and become the most widely studied cathode material for Li rechargeable batteries. On the other hand, Li$_2$FeP$_2$O$_7$ and Li$_2$FeSiO$_4$ attracted interest due to the possibility of extraction/insertion of two lithium ions per formula unit, which would lead eventually to higher storage capacities [3, 4].

The rigid structure of polyanion compounds provides cycle stability on the one side but deteriorates ionic diffusion on the other; also, the insertion of polyanion units between Fe$_n$O$_n$ polyhedrons impedes electron transfer among Fe centres in the lattice [5]. As a result, unlike oxide-based cathodes, polyanion cathodes suffer considerably from the low conductivity (both ionic and electronic), which significantly limits their rate performance and therefore application in high power devices. To overcome this, some researchers, it seemed tempting to induce a structural degradation of the polyanionic framework, to produce a disordered or defective phase and to investigate the electrochemical response. Zhang et al [6] offered the strategy of disorder/order engineering to improve the Li-ion battery anode performances. Xiong et al [7] reported the enhanced cathode storage performance of NaFePO$_4$ by mechanochemically induced disorder. Similarly, the activation of $\beta$-LiFePO$_4$ was achieved by optimized disordering via ball milling route [8]. The defective phase of olivine LiFePO$_4$ prepared at low temperature [9] or under oxidizing conditions 

Supplementary Information: The online version contains supplementary material available at https://doi.org/10.1007/s12034-021-02397-3.
conditions [10] can result in a completely new electrochemical signature (monophase behaviour). Density functional theory calculations suggest that tailoring native defects through a defect-controlled synthesis or post-synthetic treatment can enhance the electrical conductivity of LiFePO$_4$ [11]. The most common defect for LiFePO$_4$ is an anti-site defect, where Li and Fe ions exchange their positions. While its presence hinders the performances of LiFePO$_4$ through the obstruction of Li channel [12], high concentration of anti-sites in Li$_2$FeSiO$_4$ or Li$_2$FeP$_2$O$_7$ may provide the additional transfer between Li layers [13, 14] and also reduce stress during cycling [15].

This study aimed to synthesize polyanion powders of LiFePO$_4$, Li$_2$FeP$_2$O$_7$ and Li$_2$FeSiO$_4$ with reduced crystallinity. Inspired by the previous work on the subject, we utilized a method that consists of short high-temperature treatment of the precursors dispersed in a methylcellulose matrix and subsequent quenching. The interval of high temperature treatment—which usually takes several hours to obtain the above-mentioned polyanion phases [2–4, 13, 14, 16]—is reduced to several minutes. The usage of methylcellulose (or other cellulose ethers) is known in the literature for the structure control during ceramic processing [17, 18], but seldom for the synthesis of polyanion cathodes [19]. Being water-soluble, non-toxic and inexpensive (note that cellulose is the most abundant polymer on Earth), the methylcellulose proved its worth as a carbon source in our previous investigations on electrical properties of the composites [20, 21]. The method that was originally developed for Li$_2$FeSiO$_4$ [21] is now re-optimized for the group of polyanion cathode materials. The details of the chemical and technical procedures, as well as structural/microstructural examination and a comparison of their electrochemical properties, are given in the following text.

### 2. Experimental

The synthetic procedure consists of two basic steps: (1) precursor preparation in a methylcellulose polymer matrix and (2) short dwell at high temperature. All technical information regarding the chemicals and synthetic conditions that were used are given in Table 1. In the first step, stoichiometric amounts of precursor compounds were dissolved in water and mixed with the previously prepared methylcellulose solution. The methylcellulose to inorganic precursor components mass ratio was kept the same (≈ 0.2) for all the three samples (the ratio value corresponds to the value from the sample with the highest content of carbon in [21]). The solution was stirred at ≈ 70 °C until gel was formed. The methylcellulose is a derivative of cellulose with the superb solubility properties in aqueous media. Unlike cellulose, the methylcellulose is a water-soluble polymer with an ability to gel upon heating and reversibly liquefy upon cooling [22], due to the hydrophobic interaction between molecules containing methoxyl groups (figure 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Starting compounds</th>
<th>Thermal treatment</th>
<th>Pre-treatment</th>
</tr>
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<tbody>
<tr>
<td>LiFePO$_4$/C</td>
<td>FeSO$_4$·7H$_2$O (Sigma-Aldrich, ≥ 99.0%), LiH$_2$PO$_4$·H$_2$O (Sigma-Aldrich, ≥ 99.0%), Methylcellulose (Dow, Methocel A4C)</td>
<td>700°C, dwell time: 10 min; flowing Ar + 5% H$_2$ (flow rate ~ 0.1 dm$^3$ min$^{-1}$)</td>
<td>As above evaporated</td>
</tr>
<tr>
<td>Li$_2$FeP$_2$O$_7$</td>
<td>Li$_2$Fe(NO$_3$)$_3$·(Alfa Aesar, 99.0%), LiH$_2$PO$_4$·H$_2$O (Sigma-Aldrich, ≥ 99.0%), Methylcellulose (Dow, Methocel A4C)</td>
<td>650°C, dwell time: 30 min; flowing Ar + 10% H$_2$ (flow rate ~ 0.1 dm$^3$ min$^{-1}$)</td>
<td>As above evaporated</td>
</tr>
<tr>
<td>Li$_2$FeSiO$_4$</td>
<td>Fe(NO$_3$)$_3$·9H$_2$O·Alfa Aesar ≥ 98.0%, Li$_2$O (Alfa Aesar ≥ 99.0%), SiOC(OC$_2$H$_5$)$_3$·TEOS (Alfa Aesar, 99.9%), Methylcellulose (Dow, Methocel A4C)</td>
<td>750°C, dwell time: 10 min; flowing Ar + 5% H$_2$ (flow rate ~ 0.1 dm$^3$ min$^{-1}$)</td>
<td>As above evaporated</td>
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</table>
Thanks to this ability of methylcellulose, we were able to
homogeneously mix the precursor compounds on a molec-
ular level and uniformly disperse them inside a methylcel-
lulose matrix. The methylcellulose thus serves as an
excellent gelating agent, which later on, in the second step,
pyrolytically degrades to carbon. The second step consists of
the following: the dried gel was grounded and then intro-
duced to a furnace at high temperature, later was kept for a
short duration of time in a flowing, slightly reducing atmo-
sphere (Ar + H₂) and then subsequently quenched to room
temperature. Duration of the heating step for Li₂FeSiO₄ and
LiFePO₄ samples was approximately 10 min. For Li₂FeP₂O₇
sample, the high-temperature dwell time had to be prolonged
to 30 min due to the substantial amount of impurities that
were obtained for the shorter periods of high-temperature
treatment (see supplementary data for more information).

The X-ray powder diffraction measurement was per-
formed on a Philips PW 1050 X-ray powder diffractometer
using Ni-filtered Cu Kα radiation and Bragg-Brentano
focusing geometry. The diffraction intensity was recorded
in the 2θ range of 10°–70° with a step size of 0.02° and a
counting time of 3 s per step. Powder Cell Software was
used for determination of the constants of the lattice. The
microstructural parameters, namely the crystallite size and
the microstrain, were calculated based on the fundamental
parameters convolution approach to generate line profiles
[23] by using the XFIT-Koalariet software. Fityk program
was used for the deconvolution of X-ray diffraction (XRD)
profile to crystalline and amorphous part. The carbon con-
tent was determined thermogravimetrically. The morphol-
ogy of the synthesized powders was analysed by a field-
emission scanning electron microscope (FESEM, TESCAN,
MIRA3 XMU) at 20 kV. The particle size distributions
were determined by a laser-diffraction-based particle size
analyzer, Mastersizer 2000 (Malvern Instruments Ltd., UK).

The electrochemical measurements were conducted by
using Vertex. One potentiostat/galvanostat with an impe-
dance analyzer ( Ivium Technologies). Cyclic voltammetry
(CV) measurements were performed in a three-electrode
cell with platinum as a counter and SCE (saturated calomel
electrode, SI Analytics) as a reference electrode; 6 M
solution of LiNO₃ (Alfa Aesar 99%) in H₂O was used as an
electrolyte. Chronopotentiometric (CP) measurements were
conducted on a closed, argon-filled two-electrode cell with
metallic Li as a counter electrode and 1 M solution of
LiClO₄ (Fluka, p.a.) in PC (propylene carbonate, Sigma-
Aldrich 99.7%) as an electrolyte. Working electrode for
both CP and CV measurements consisted of the active
material, carbon black and poly-vinylidenefluoride (PVDF,
Sigma-Aldrich) mixed in 85:10:5 weight ratio and depos-
ted on a platinum foil from the slurry prepared in
N-methyl-2-pyrrolidone (Sigma-Aldrich, 99%). Electro-
chemical impedance spectroscopy (EIS) was performed in
the frequency range from 10⁵ to 10⁻² Hz with an amplitude
of 5 mV and at open-circuit conditions of two-electrode cell
with the same setup as in CP measurements.

3. Results and discussion

The presented gel-combustion procedure gives rise to
similar morphologies of the obtained powders, as revealed by field emission scanning electron microscopy
(figure 2). The particles are agglomerated and irregular in
shape. Particle bonding and neck generation, indicating
inter-particle sintering, leads to a formation of irregularly
shaped pores of variable widths. The particle size distri-
butions have a lognormal shape (figure 2d) with close
span values of 1.09–1.27 (table 2). Distribution profiles
of Li₂FeSiO₄/C and LiFePO₄/C practically overlap each other,
while Li₂FeP₂O₇/C is a bit shifted in terms of particle size and span.

The crystal phases of the synthesized powders were
confirmed by X-ray powder diffraction (figure 3). In
LiFePO₄/C sample, LiFePO₄ olivine phase (orthorhombic
space group no. 62, Pnma) was revealed along with the
traces of Fe₃P₂O₇ and Li₇P₄O₁₅ (altogether less than 5 wt%).
In Li₂FeSiO₄/C sample, Li₂FeSiO₄ phase crystallized in a
monoclinic space group no. 14 (P2₁/c), which corresponds
to the γₔ polymorph of the material [24]; besides the desired
phase, traces of Li₅SiO₃ were observed (< 2 wt%). In the
last sample, Li₂FeP₂O₇ phase crystallized within the same
space group no. 14 (P2₁/c) and was accompanied by the
olivine LiFePO₄ phase in the amount of 9–10 wt%.
Extended heat treatment (from 10 to 30 min) of the Li₂,
FeP₂O₇/C sample brought reduction of impurities, but not a
complete removal of olivine phase (supplementary data).
Since both phases are capable of Li intercalation and our
plan was to synthesize powders with significant
microstructural parameters, further prolongation of the heat
treatment was avoided. The creation of significant amount
of side products during synthesis of Li₂FeP₂O₇/C indicate,
however, a higher complexity, and thus slower kinetics of
formation of pyrophosphate Li₂FeP₂O₇ phase than olivine

![Figure 1. (a) Molecular structure of methylcellulose and (b) temperature dependence of methylcellulose's aqueous solubility.](image)
LiFePO$_4$, although starting from the same precursor compounds (table 1).

The calculated unit cell parameters (table 2) are fairly consistent with earlier reports for the given phases. The obtained unit cell volumes are however slightly lower than in annealed powders (335.65 Å$^3$ for Li$_2$FeSiO$_4$ [25], 291.44 Å$^3$ for LiFePO$_4$ [16] and 1034.00 Å$^3$ for Li$_2$FeP$_2$O$_7$ [20]), which might be related to the significant quantity of strain that is observed (table 2). There was no evidence for the formation of crystalline carbon in the samples, therefore the internal non-graphitic carbon could be assumed to contribute to the background of XRD patterns. The amounts of the *in-situ*-formed carbon, established thermogravimetrically, were found to be 13, 10 and 8 wt% for Li$_2$FeSiO$_4$/C, LiFePO$_4$/C and Li$_2$FeP$_2$O$_7$/C, respectively. The crystallinity of a given sample was quantitatively estimated by resolving the diffraction intensity profile into contributions from the crystalline (sharp) diffractions and amorphous (diffuse) halo; the degree of crystallinity then equals the ratio of area of crystalline fraction to sum of areas of crystalline and amorphous fractions. The estimated values of crystallinity with regard to carbon content of the samples suggest that lattice distortions also contribute to the amorphous halo (table 2). The Li$_2$FeP$_2$O$_7$/C sample has somewhat higher degree of crystallinity, along with larger crystallite and particle size, probably due to the longer heat exposure. Because of the different chemistries involved, the comparisons from table 2 are not straightforward, but we can make some general comments: (a) fraction of amorphous phase, small crystallite size and notable microstrain confirm that the presented method yields powders with pronounced microstructural parameters; (b) in a given range of temperatures 650–750 °C, the dwell time had primary role to agglomeration and crystallite growth than temperature.

![SEM micrographs](image)

**Figure 2.** SEM micrographs of (a) Li$_2$FeSiO$_4$/C, (b) LiFePO$_4$/C, (c) Li$_2$FeP$_2$O$_7$/C and (d) their particle size distributions.
value itself (see Li$_2$FeP$_2$O$_7$/C, which has the largest crystallites/particles although obtained at the lowest temperature, or Li$_2$FeSiO$_4$/C and LiFePO$_4$/C, which are obtained at different temperatures but with the same dwell time and both with similar particle size distributions); (c) the increase of carbon amount leads to a decrease of crystallite and particle size.

Redox behaviour of the synthesized polyanionic composites was first evaluated by the CV measurements in an aqueous electrolyte. All materials showed the electrochemical activity caused by the Fe$^{3+}$/Fe$^{2+}$ redox pair. It can be observed from figure 4 that the redox process is strongly influenced by the chemical environment in a polyanion-based compound. When a FeO$_n$ polyhedron is coordinated with the [SiO$_4$]$^{4-}$ polyanions, the Fe$^{3+}$/Fe$^{2+}$ redox process in Li-containing electrolyte is evidenced at $-$0.55/$-$0.32 V potentials vs. SCE at the scan rate of 10 mV s$^{-1}$ (figure 4a). The amount of lithium ($x$) that can be reversibly removed upon this redox process may vary between 0 < $x$ < 1, depending on the scan rate, since the removal of lithium above 1 occurs at higher potentials. The peak potential separation of 180 mV at 2 mV s$^{-1}$ was found to be considerably smaller than that obtained for the carbon-coated Li$_2$FeSiO$_4$ (370 mV at 0.1 m Vs$^{-1}$ in an aqueous electrolyte) prepared via citric acid-assisted method followed by 7 h thermal treatment [26]. It indicates faster charge transfer of our sample with approximately equal (13:14) carbon content, but prepared under rapid heating regime. However, the specific capacity of Li$_2$FeSiO$_4$/C sample measured galvanostatically in an organic electrolyte (see figure 6 below) was found to be comparable in the same voltage range to that obtained by the authors in [26],

Table 2. Structural and microstructural parameters of the prepared powders.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon content (wt%)</th>
<th>Lattice parameters</th>
<th>Crystallinity (%)</th>
<th>Mean crystallite size (nm)</th>
<th>Microstrain (%)</th>
<th>Mean particle size (μm)</th>
<th>Span*</th>
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<td>Li$_2$FeSiO$_4$/C</td>
<td>13</td>
<td>$P_2_1/c$</td>
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<td>LiFePO$_4$/C</td>
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<td>$Pnma$</td>
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<td>Li$_2$FeP$_2$O$_7$/C</td>
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<td>$P_2_1/c$</td>
<td>89</td>
<td>58</td>
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*Span* = (d(0.9) − d(0.1))/d(0.5).

Figure 3. X-ray diffraction patterns of the obtained powders (solid line) and corresponding profiles taken from a crystallographic database (dotted line). The most prominent peaks are indexed in $P_2_1/c$ for Li$_2$FeSiO$_4$ and Li$_2$FeP$_2$O$_7$, and $Pnma$ (LiFePO$_4$) symmetry group and observed impurity peaks are marked with a geometrically shaped signs.
which conveys that diffusion of Li\(^{+}\) in the bulk of the material is still a limiting factor for the intercalation kinetics. The peak potential separation of the other two samples is slightly higher (\(\sim 240\) mV in the given scan rate) than that of Li\(_2\)FeSiO\(_4\)/C, which suggest higher resistance of the charge transfer probably caused by the lower amount carbon and larger crystallites/particles.

Due to the higher electronegativity of P vs. Si (inductive effect), the redox potential of Fe\(^{3+}/Fe^{2+}\) is shifted towards a more positive value in phosphates than in silicates, and due to the increased electron delocalization in P\(_2\)O\(_7\) (than in PO\(_4\)) to even more positive values in pyrophosphate compound \([1]\). One can see in figure 4b, the two main redox peaks (labelled as I and II) of lithium iron pyrophosphate are positioned at 0.16/0.39 and 0.28/0.69 V vs. SCE (10 mV s\(^{-1}\)); these characteristic peaks, partially merged together into a single broad peak, originate from Fe\(^{3+}/Fe^{2+}\) pair in FeO\(_6\) octahedral and FeO\(_5\) bipyramidal coordination, respectively \([27]\). There is, however, a third peak (III) occurring at a lower potential of \(-0.55/-0.26\) V vs. SCE at 10 mV s\(^{-1}\), which is not commonly seen in the literature data of Li\(_2\)FeP\(_2\)O\(_7\) (the small peak can be seen in \([28]\), but it is not commented). Interestingly, the occurrence of a similar peak is observed for Na\(_2\)FeP\(_2\)O\(_7\) phase and is prescribed to a single-phase reaction of (de)sodiation, while the peaks at higher potentials are related to the two-phase reactions \([29]\); the whole profile, although somewhat shifted, much resembles our Li\(_2\)FeP\(_2\)O\(_7\)/C.

In figure 4c, one can notice characteristic redox peaks of LiFePO\(_4\) olivine phase, which correspond to the well-known galvanostatic plateau at \(\sim 3.4\) V vs. Li. The current response of LiFePO\(_4\)/C sample is significantly higher than that measured for Li\(_2\)FeSiO\(_4\)/C and Li\(_2\)FeP\(_2\)O\(_7\)/C samples. This indicates a significantly higher amount of stored charge in olivine compared to other two samples under a common current regime (note that a regular scan rates of several mV s\(^{-1}\) in CV correspond to high current rates in galvanostatic cycling, \(>1\)C). An additional, small and broad oxidation peak (marked with an asterisk) also appears at a...
Table 3. The fitted kinetic parameters obtained from EIS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_e$ (Ω)</th>
<th>$R_1$ ($\times 10^3$)</th>
<th>CPE1 ($s^{N_1}$ Ω$^{-1}$)</th>
<th>N1</th>
<th>$R_{ct}$ (Ω)</th>
<th>$Z_w$ ($s^{-1/2}$)</th>
<th>CPE2 ($s^{N_2}$ Ω$^{-1}$)</th>
<th>N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$FeSiO$_4$/C</td>
<td>69.12</td>
<td>1.00</td>
<td>8.824 $\times 10^{-3}$</td>
<td>0.98</td>
<td>135.5</td>
<td>34.8</td>
<td>7.919 $\times 10^{-6}$</td>
<td>0.85</td>
</tr>
<tr>
<td>LiFePO$_4$/C</td>
<td>84.27</td>
<td>9.27</td>
<td>4.596 $\times 10^{-3}$</td>
<td>0.93</td>
<td>173.9</td>
<td>15.7</td>
<td>3.592 $\times 10^{-5}$</td>
<td>0.72</td>
</tr>
<tr>
<td>Li$_2$FeP$_2$O$_7$/C</td>
<td>81.61</td>
<td>1.18</td>
<td>2.146 $\times 10^{-2}$</td>
<td>0.95</td>
<td>208.7</td>
<td>30.8</td>
<td>2.113 $\times 10^{-5}$</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Figure 6. Discharge curves of the (a) LiFePO$_4$/C, (b) Li$_2$FeP$_2$O$_7$/C, (c) Li$_2$FeSiO$_4$/C and (d) their cycling performance.
potential of \( \approx 0 \) V vs. SCE (10 mV s\(^{-1}\)), which can be attributed to the presence of the amorphous olivine phase [31]. Now, if we look back to our previous voltammogram (figure 4b) and take into consideration that amorphous olivine exhibits a single-phase reaction behaviour [10, 32], by analogy we could assume that the unknown peak (III) originates from amorphous Li$_2$FePO$_4$, which would also be consistent with the reports regarding single-phase reaction of Na$_2$FeP$_2$O$_7$ [29]. After proved electrochemically both active and stable during CV measurements in aqueous electrolyte, the materials were tested as cathodes in Li-ion cell by galvanostatic charge–discharge tests in an organic electrolyte. Prior to galvanostatic tests, the assembled cells were examined by EIS at open circuit voltages. The impedance response is shown in figure 5. Each plot is composed of a depressed semicircle in the high-to-intermediate frequency region, followed by an inclined line at the lower frequencies. The impedance data were fitted with the equivalent circuit, shown in the inset of figure 5. The equivalent circuit model includes: (1) resistor \( R_a \), which represents the sum of electrolyte resistance and the resistance of metallic contacts; (2) resistor \( R_t \) paralleled with the constant phase element CPE1, which is related to the cathode composite and metal (Pt) current collector interface and/or solid electrolyte interface (SEI) film phenomena [33, 34]; (3) resistor \( R_{ct} \) paralleled with the constant phase element CPE2 and in serial with the general Warburg impedance \( Z_w \), related to the cathode/electrolyte charge transfer resistance, double-layer capacitance and Li\(^+\) solid-phase diffusion [35]. The inclusion of the constant phase elements, instead of pure capacitors, ensured a better fitting to the experimental data, as they better describe a real electrochemical system [34]. The charge transfer resistance of the tested electrode composites decreases in order Li$_2$FePO$_4$/C > LiFePO$_4$/C > Li$_2$FePO$_4$/C (table 3), due to the reduction of crystallite/particle size and increase of conductive carbon concentration, both facilitating electron transfer. On the other hand, the lowest Warburg impedance for olivine composite indicates faster diffusion kinetics of this material. The galvanostatic tests were performed at the room temperature in 4.0–2.8 V, 4.2–2.3 V and 4.0–2.0 V voltage range for Li$_2$FePO$_4$/C, LiFePO$_4$/C and Li$_2$FePO$_4$/C composites, respectively. From the obtained chronopotentiometric curves at the given current rate, the specific capacities were calculated using the mass of the active material only (mass of carbon is subtracted from loading). The discharge curves along with the cycling performances are presented in figure 6. The current rates are given in c/n units, where c is a 1-electron theoretical capacity of the material (which is 166, 170 and 110 mAh g\(^{-1}\) for Li$_2$FePO$_4$/C, LiFePO$_4$/C and Li$_2$FePO$_4$/C, respectively) and n is a discharge time given in hours needed for a complete discharge. Discharge profile of LiFePO$_4$/C is distinguished by a flat plateau at around 3.4 V vs. Li (figure 6a), a mark of the two-phase process of lithium insertion/extraction reaction [2]. On the other side, sloping curves of Li$_2$FeSiO$_4$/C and Li$_2$FePO$_4$/C (figure 6b and c) suggest a monophasic reaction [36, 37]. Due to the presence of LiFePO$_4$ (rather than some phase transformations), the sloping curve of Li$_2$FePO$_4$/C changes to a plateau at 3.4 V vs. Li (figure 6b), which makes this electrode a hybrid one. The materials were stable and performed reasonably well in accordance with its intrinsic capabilities. At low current densities, the capacities of 160 mAh g\(^{-1}\) (at c/10) for LiFePO$_4$/C, 124 mAh g\(^{-1}\) (c/10) for Li$_2$FeSiO$_4$/C and 101 mAh g\(^{-1}\) (c/20) for Li$_2$FePO$_4$/C were obtained. Upon the increase of current rate, LiFePO$_4$/C powder exhibits the highest capacity preservation: 94% (at c/10), 80% (c/3), 65% (1c), 53% (2c) and 42% (3c). When compared to remarkable olivine, both Li$_2$FePO$_4$/C and Li$_2$FeSiO$_4$/C show significantly lower performances (figure 6d). Although low in nominal specific capacity (due to the high molar mass of Li$_2$FePO$_4$), the Li$_2$FePO$_4$/C exhibits 92% utilization of its theoretical capacity at low current density. At different current rates, both Li$_2$FePO$_4$/C and Li$_2$FeSiO$_4$/C utilize 75–77% (c/10), 60–63% (c/5) and 29–31% (1c) of its theoretical capacities. The capacity retention at the given rate was high for all the materials.

4. Conclusions

The polyanion cathode material’s composites with carbon, namely, LiFePO$_4$/C, Li$_2$FePO$_4$/C and Li$_2$FeSiO$_4$/C, were obtained by performing the experiments under extreme conditions of rapid heating, short high-temperature dwell and quenching to room temperature. A methylcellulose, water-soluble derivative of cellulose, was used as a polymer medium and a carbon source. The composites that were obtained have reduced crystallinity, with low crystallite size (20–60 nm) and significant microstrain (0.1–0.2). They provided stable electrochemical performance in both aqueous and organic electrolyte. The presence of amorphous phase induced spreading of existing peaks and/or the emergence of new broad peaks in CV. LiFePO$_4$/C powder exhibited superb electrode performance when compared to the Li$_2$FePO$_4$/C and Li$_2$FeSiO$_4$/C samples. It manifests in significantly higher currents per gram provided in CV measurements and higher both capacity and capacity vs. current retention in galvanostatic charge–discharge tests. The potential application of Li$_2$FeSiO$_4$/C and Li$_2$FePO$_4$/C composites thus may be limited to low power devices.

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