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An improvement in the ionic conductivity and electrochemical characteristics of $LiFePO_4$ by heterogeneous doping with NASICON-type phosphate

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Composite materials based on $LiFePO_4$ with olivine structure and $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ with NASICON structure have been synthesized and characterized by the XRD analysis, scanning electron microscopy and impedance spectroscopy. The investigation of electrochemical behavior of obtained composites additionally coated with a thin carbon layer demonstrated that the $LiFePO_4$-based materials doped by phosphate with the NASICON structure exhibit higher electrochemical capacity in comparison with the initial $LiFePO_4$.

Lithium iron phosphate with the olivine structure is a promising cathode material for lithium-ion batteries (LIBs). This material is characterized by a low cost, high stability, safety and a theoretical capacity of 169 mAh g^{-1}.[1,2] The drawbacks of $LiFePO_4$ include its low electron and ionic conductivity, which limits its application in devices requiring a high peak power.[3,4] Its properties can be improved by decreasing the size of material particles[5,6] and applying carbon coatings.[7] The charge and discharge of carbon-coated $LiFePO_4$ ($LiFePO_4$/C) are limited by the transfer of lithium cations.[8–10] Partial replacement of iron ions with other cations[11–13] and heterogeneous doping by the incorporation of a second phase[14–16] were performed to increase the ion component of conductivity. In the latter case, the modification was mainly performed by the addition of oxides, and the conductivity increased due to the formation of a double electric layer on the interface of a phosphate with the olivine structure and a nonconductive additive. Tan *et al.*[17] modified $LiFePO_4$ with a Li_3PO_4 film possessing a small ionic conductivity.[18] However, there are no studies on the use of materials with high ionic conductivity, for example, with the NASICON structure for $LiFePO_4$ modification.

In this work, composite materials based on $LiFePO_4$ with an olivine structure and an ion-conducting phosphate additive with the NASICON structure were synthesized. We selected $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ as the ion-conducting additive, which is characterized by high ionic conductivity (6.3×10^{-5} Ω^{-1} cm^{-1} at 298 K) owing to a 3D network of conductive channels.[19,20]

The composites were formed upon mechanical treatment in a planetary mill of a mixture of a precursor obtained after the first stage of $LiFePO_4$ sol–gel synthesis[21] and a phosphate with the NASICON structure (2–10 wt%) pre-synthesized by a reported procedure[20] followed by keeping at 600 °C in an inert atmosphere.

The XRD patterns of the composite materials $LiFePO_4$/$Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$/C showed that all of the materials are presented predominantly by $LiFePO_4$ with the olivine structure indexed in the orthorhombic syngony. A peak near $2\theta = 24.9°$, which corresponds to the most intense signal of the $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ phase, is observed. Its intensity increases with the concentration of this compound in the composite material. According to SEM data, the average particle size of the initial $LiFePO_4$/C is 50 nm. The addition of pre-synthesized $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ to the reaction mixture before the final stage of $LiFePO_4$ synthesis results in the average particle size increase to 100 nm (Figure 1). This fact is apparently caused by an increase in the rate of diffusion during the final annealing due to an increase in the concentration of defects in the samples or preferential nucleation on the surface of $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ particles. The acceleration of diffusion processes during the crystallites formation indicates that the ionic conductivity of the cathode materials can be raised.

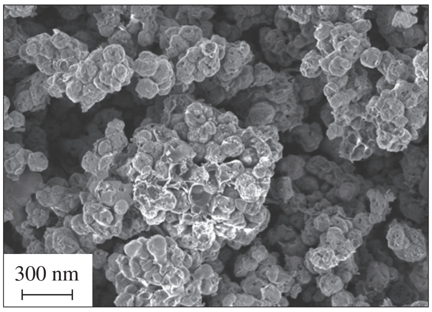

Figure 1 SEM micrograph of 95% $LiFePO_4$ + 5% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$/C.

The ionic conductivity of the composites $LiFePO_4$/*x* wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$/C was studied by impedance spectroscopy. The ionic conductivity of $LiFePO_4$ grows almost linearly with the concentration of a highly conductive phosphate with the NASICON structure in the composite from 6×10^{-12} Ω^{-1} cm^{-1} for $LiFePO_4$ to 2×10^{-10}, 5×10^{-10} and 9.8×10^{-10} Ω^{-1} cm^{-1} for samples containing 2, 5 and 10 wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$, respectively. This is explained both by a higher ionic conductivity of $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ and formation of zones with a higher ionic conductivity in the composite. In this case, the increase in the overall material conductivity occurs due to an increase in the surface component of conductivity.

Electrochemical cycling was carried out in a voltage range of 2.6–4.0 V. The carbon content of the composites was ~4 wt%. The capacity of the initial $LiFePO_4$/C at a discharge current of 15 mA g^{-1} (0.1 C) is about 140 mAh g^{-1} (Figure 2, curve *1*). The charge–discharge curves for both the initial and doped samples have almost the same shapes typical of $LiFePO_4$-based cathode materials (Figure 2). The curves contain a plateau at ~3.45 V corresponding to the $Fe^{2+} \leftrightarrow Fe^{3+}$ transition. Notably, lithium–

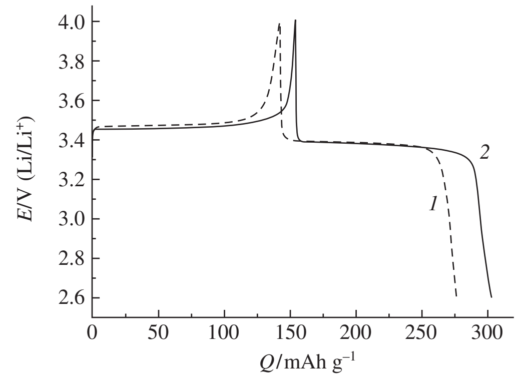

Figure 2 First cycle charge–discharge curves at a current of 15 mA g^{-1} for the samples: (*1*) $LiFePO_4/C$ and (*2*) $LiFePO_4$ + 5 wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3/C$.

titanium phosphate with the NASICON structure contained in the composite shows no electrochemical activity in the working range of potentials, where lithium–iron phosphate with an olivine structure was tested (2.6–4.0 V). This is an expected result since the transition $Ti^{4+} \leftrightarrow Ti^{3+}$ at a voltage of ~2.47 V with the $Li_3Ti_2(PO_4)_3$ phase formation[22,23] or the transition in a low-potential region of 0.2–1.5 V typical of anodic materials with incorporation of more than two lithium cations[22,24] are characteristic of $LiTi_2(PO_4)_3$.

Composites with a minimum dopant amount are preferred for the preparation of cathode materials with high capacity since the heterogeneous additive is not electrochemically active in our case. On the other hand, the more ion-conducting additive a material contains, the higher its ionic conductivity becomes. In order to determine the optimum content of phosphate with the NASICON structure, we performed the electrochemical testing of composites with various additive concentrations (2–10 wt%). The best characteristics correspond to the material containing 5 wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ with the NASICON structure. On the one hand, it is characterized by a significant increase in ionic conductivity; on the other hand, it retains a high capacity.

The capacity of $LiFePO_4$ + 5 wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3/C$ is 154 mAh g^{-1} at a discharge current of 15 mA g^{-1} (Figure 2, curve *2*).

The increase in the rate of transfer of charge carriers in $LiFePO_4/Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$ composite materials allows us to expect an improvement in the electrochemical characteristics of the cathode material at high current densities; this is extremely important for enhancing the power of LIBs. Figure 3 shows the plots of discharge capacity *versus* current density for initial $LiFePO_4/C$ and a material doped with 5% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3$. It can be seen that the composite is characterized by a higher discharge capacity compared to that of unmodified material with current density increase. Thus, the discharge capacity of the initial $LiFePO_4/C$ at 1000 mA g^{-1} is 58 mAh g^{-1}, whereas that of $LiFePO_4$/5 wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3/C$ is 75 mAh g^{-1}. The discharge capacity of $LiFePO_4$/5 wt% $Li_{1.3}Ti_{1.7}Fe_{0.3}(PO_4)_3/C$ is as high as 60 mAh g^{-1} even at a discharge current of 1900 mA g^{-1}.

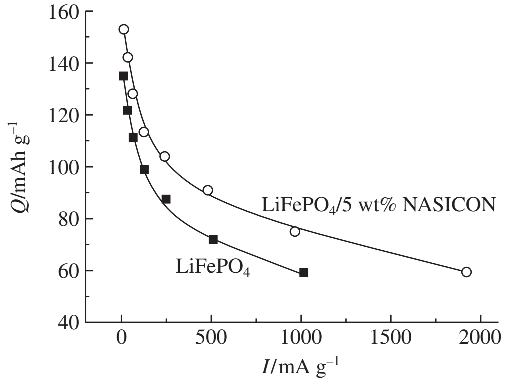

Figure 3 Plots of discharge capacity *vs.* current density.

In conclusion, $LiFePO_4$ modification with NASICON phosphates is an effective approach to improve $LiFePO_4$ ionic conductivity and high-rate capability. The composite materials obtained can be promising cathodes for devices operating at high current densities.

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