

Activation of NaFePO₄ with maricite structure for application as a cathode material in sodium-ion batteries

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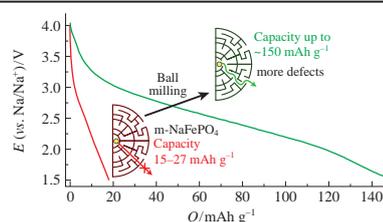
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A facile approach to a scalable synthesis of nanosized composites of maricite-type sodium iron phosphate NaFePO₄ with carbon has been proposed. Initially low capacity of the nanocomposites (15–27 mAh g⁻¹) was augmented up to ~150 mAh g⁻¹ after planetary ball-milling.



Over the last two decades, lithium-ion batteries have found a wide application owing to their outstanding capacity, efficiency, and operational reliability.^{1–4} However, low lithium content in the Earth crust limits the use of lithium-ion batteries in energy storage devices. Sodium-ion batteries (SIB) are considered as one of the best candidates for their replacement.^{5,6} The capacity of SIBs is limited mainly by the cathode materials.⁷ Phosphates of transition metals are usually characterized by better cycling and thermal stability in comparison with the oxide-based systems.^{8,9} NaFePO₄ is one of the most promising candidates due to its high theoretical capacity (154 mAh g⁻¹) and low cost. The olivine-type modification, which is isomorphic to the thoroughly studied LiFePO₄,^{10,11} is thermodynamically unstable and can be obtained only from LiFePO₄ by ion exchange, which hinders its application. Until recently, the thermodynamically stable maricite-type polymorph (m-NFP) has been considered electrochemically inactive due to its ‘closed’ framework lacking Na⁺ diffusion pathways.^{12,13} Kang *et al.* reported that m-NFP synthesized *via* a simple solid-state method had a capacity of 142 mAh g⁻¹ (92% of the theoretical value).¹⁴ However, no successful implementation of maricite-type NaFePO₄ as a cathode material for SIBs has been reported afterwards.

In this work, a modified Pechini approach to the synthesis of nanosized m-NFP was proposed. Mechanochemical activation allowed us to obtain high electrochemical capacity.

Maricite-type NaFePO₄ and its composites with carbon were synthesized *via* Pechini and solid-state methods. For the Pechini synthesis, Fe(NO₃)₃·9H₂O, NaH₂PO₄·2H₂O and citric acid were dissolved in ethylene glycol in the molar ratio of 1 : 1 : 2 and subsequently heated, which led to the formation of a polymer matrix that prevents the particle growth.^{15–17} X-ray diffraction (XRD) data showed that obtained m-NFP samples contained a single phase with maricite structure, the composition of the synthesized samples corresponded to NaFePO₄.

The Pechini method yielded agglomerated particles of 20–30 nm in diameter (sample denoted as NFP-PE@C). Thermal treatment of carbon containing precursors resulted in the formation of carbon coatings. The Raman spectra of obtained samples exhibited two bands at ~1600 and ~1350 cm⁻¹, usually referred to as the G- and D-band, respectively. The G-bands were strong and narrow, indicating a high content of sp²-carbon in the coating.¹⁸ In the case of solid-state synthesis (sample denoted as NFP-SS@C), the size of agglomerates was 50–200 nm.

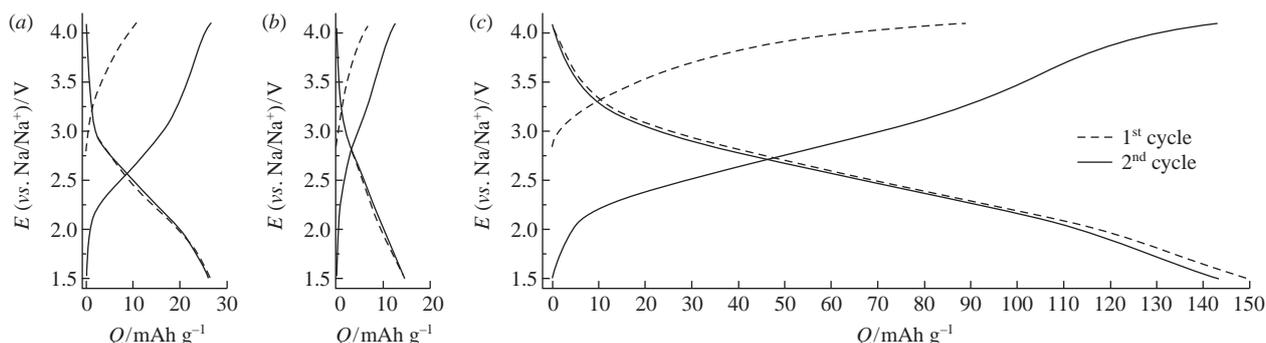


Figure 1 Charge–discharge curves for (a) NFP-SS@C and NFP-PE@C (b) before and (c) after ball-milling at 15 mA g⁻¹ (~0.1 C) charge–discharge rate.

The samples were tested as cathode materials for SIBs. In the potential range of 1.5–4.1 V vs. Na/Na⁺ all samples showed poor electrochemical capacities [Figure 1(a),(b)], which was in agreement with the previously published data.^{19–22} However, in contrast to the values reported by Kang *et al.*,¹⁴ capacity of NFP-SS@C obtained by the same method was only ~27 mAh g⁻¹ at 15 mA g⁻¹ current density.

In order to increase the m-NFP capacity, we decided to increase the defects concentration with the use of ball-milling (BM). This resulted in a dramatic increase in the m-NFP capacity up to ~150 mAh g⁻¹ for NFP-PE@C [Figure 1(c)] at 15 mA g⁻¹ charge–discharge rate (~0.1 C). The charge–discharge curve profiles of BM and non-BM samples were almost identical.

The charge curve profiles at the first cycle differed from the subsequent cycles. In addition, the charge capacity for the first cycle was much smaller in comparison with discharge capacity owing to Fe²⁺ ions partial oxidation by the oxygen during the synthesis and the ball milling. At the second cycle, they became almost equal due to the electrochemical iron reduction. The charge–discharge curve profiles for the following cycles are almost the same as in the second cycle.

It should be also mentioned that the obtained composite NFP-PE@C demonstrated high capacities after an increase in charge–discharge rate up to 150 mA g⁻¹ [103 mAh g⁻¹ (1 C)] and 1200 mA g⁻¹ [62 mAh g⁻¹ (8 C)]. This denotes good prospects for BM NFP-PE@C application in the SIBs.

Ball-milling resulted in the broadening of XRD peaks and decrease in their intensities. The mean size of the X-ray coherent scattering regions decreased from 31 to 26 nm after ball-milling. This can be attributed either to the increase in the defect concentration in m-NFP structure, or to the decrease in particle size.

The capacity increase for the obtained materials could be caused solely by the partial NaFePO₄ phase amorphization. At the same time, the XRD pattern indicates that considerable amount of the m-NFP phase remained after the ball milling. Moreover, the discharge capacity of NFP-PE@C is close to the theoretical value. This means that the activated crystalline m-NFP is also electrochemically active. The dramatic growth of its activity can be attributed to the defect formation in the m-NFP structure, the destruction of agglomerates, and partial amorphization of NFP.

In conclusion, the facile and scalable method for the synthesis of the nanosized maricite-type NaFePO₄ and its composites with carbon has been proposed. Initial particle size of 20–30 nm and the efficient carbon coating were insufficient to reach good electrochemical performance. A considerable capacity increase can be achieved using the mechanochemical activation of the material. Considerable increase in m-NFP capacity after the ball-milling

can be explained by the defect formation, the destruction of agglomerates, and partial amorphization of NFP. This leads to the acceleration in sodium ion transport within the particles.

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