

SODIUM PYROPHOSPHATE CATHODE MATERIAL $\text{Na}_2\text{FeP}_2\text{O}_7$ FOR Na- AND Li-ION BATTERIES

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Sodium-based insertion materials are interested for low-cost and large-scale Na- and Li-ion batteries. In 2012, Yamada *et al.* [1] proposed a new polyanion-based $\text{Na}_2\text{FeP}_2\text{O}_7$ cathode material. The $\text{Na}_2\text{FeP}_2\text{O}_7$ pyrophosphate has a theoretical capacity of 97 mAh/g, high operating voltage (3.0 V vs. Na/Na^+), three-dimensional channels for Na^+ diffusion and good thermal stability. Adopting a triclinic symmetry (S.G. *P*-1), the crystal structure of $\text{Na}_2\text{FeP}_2\text{O}_7$ consists of the corner-sharing FeO_6 octahedra and the bridging pyrophosphate groups P_2O_7 , thereby creating large tunnels along [100], [-110] and [01-1] directions for facile and fast Na^+ ion migration [1].

In the present study, we prepared $\text{Na}_2\text{FeP}_2\text{O}_7/\text{C}$ by mechanochemically assisted solid state synthesis using $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, Li_2CO_3 and $(\text{NH}_4)_2\text{HPO}_4$ as reagents and 5 wt% of carbon as a coating agent. Mechanochemical activation was performed using a high-energy AGO-2 planetary mill. The activated mixture was subsequently heat treated at 600 °C in Ar flow. Crystal and local structure, particle size and electrochemical properties of the as-prepared $\text{Na}_2\text{FeP}_2\text{O}_7$ material were analyzed by XRD with Rietveld refinement using GSAS software package, SEM, EDX, Mössbauer, ^{23}Na and ^{31}P MAS NMR spectroscopy, and galvanostatic cycling in Na^+ and Na^+/Li^+ cells.

The refined lattice parameters ($a = 6.4163(3)$ Å, $b = 9.4077(4)$ Å, $c = 10.9786(5)$ Å, $\alpha = 64.468(2)^\circ$, $\beta = 85.693(3)^\circ$, $\gamma = 72.934(3)^\circ$, $V = 570.63(5)$ Å³, $R_{\text{wp}} = 6.69$ %) well correlate to the literature data [2]. According to Mössbauer spectroscopy, a majority of Fe^{2+} ions are in a high-spin state. The sample contains about 20% of Fe^{3+} impurities, indicating the presence of a large amount of structural distortion. The ^{23}Na MAS NMR spectrum of the $\text{Na}_2\text{FeP}_2\text{O}_7$ is presented by two components at -14 and 175 ppm overlapped with satellites, contrary to a broad line in the spectrum of $\text{Li}_2\text{FeP}_2\text{O}_7$ [3]. ^{31}P MAS NMR signal of $\text{Na}_2\text{FeP}_2\text{O}_7$ is located at ~0 ppm.

Galvanostatic cycling of $\text{Na}_2\text{FeP}_2\text{O}_7$ was performed in the 2.0–4.3 V range at C/20 rate and at room temperature starting with discharge. A sloping solid solution-like charge-discharge profile was observed. The discharge capacity was 87 mAh/g in Na-cell and 92 mAh/g in Li-cell. Electrochemical Na^+/Li^+ ion exchange was completed after the 4th cycle. Na^+/Li^+ non-oxidative chemical ion exchange was carried out in the solution of LiBr in acetonitrile for 24 h. According to EDX, only one Na^+ can be readily replaced for one Li^+ to produce the $\text{NaLiFeP}_2\text{O}_7$ composition with *P*-1 S.G.

[1] P. Barpanda, T. Ye, S. Nishimura, S. Chung, Y. Yamada, M. Okubo, H. Zhou, A. Yamada, *Electrochem. Commun.* 24 (2012) 116.

[2] T. Honma, A. Sato, N. Ito, T. Togashi, K. Shinozaki, T. Komatsu, *J. Non-Cryst. Solids* 404 (2014) 26.

[3] N.V. Kosova, A.M. Tsapina, A.B. Slobodyuk, S.A. Petrov, *Electrochim. Acta* 174 (2015) 1278.