Synthesis and Investigation of Glass-ceramic $Na_4M_{3-x}M'_x(PO_4)_2P_2O_7$ (*M*, *M'* - Co, Ni, Mn) for Na^+-Ion Batteries

Ie.V. Odynets, I.V. Zatovsky, and N.I. Klyui

College of Physics, Jilin University, 2699 Qianjin Str., 130012 Changchun, P.R. China

Currently, research and development efforts on sodium-ion batteries (SIBs) those is considered as an alternative to lithium-ion batteries (LIBs) due to their lower cost, environmental friendliness and abundance of sodium in comparison with lithium [1]. As a result, in the last few years the publications of results devoted to various types of Na^+-ion electrodes and conducting electrolytes dramatically increases. In particular, compounds with general formula $Na_4M_3(PO_4)_2P_2O_7$ (*M* - Co, Ni, Mn) have considerable prospects of practical use as a positive electrode in SIBs, due to significant cyclic stability, providing extended lifetime. The successful technological implementation of such materials is possible if the cost of their fabrication will be lowered. Glass-ceramic technology fully satisfies this requirement to manufacture successfully electrode materials [2]. In this work, we obtained and investigate glass-ceramics based on solid solutions $Na_4M_{3-x}M'_x(PO_4)_2P_2O_7$ (M, M' - Co, Ni, Mn) to optimize technology of SIB production.

Glasses based on $Na_4M_{3-x}M'_x(PO_4)_2P_2O_7$ (*M*, *M'* - Co, Ni, Mn) were synthesised by a conventional melt-quenching method. Starting reagents $NaPO_3$, Co_3O_4, NiO and MnO_2 in appropriate stoichiometric ratios were melted in a platinum crucible at 1000-1200 °C for 30-120 min. The melts were quickly poured onto a copper plate. Obtained glasses were subsequently annealed at 300-600 °C, this procedure led to formation of crystalline phases in bulk material. The glass transition and crystallization temperatures were determined by differential thermal analysis (DTA). Further, samples were ground by mechanical milling in a planetary ball mill. In order to confirm glass formation and to characterize crystallized phase, all samples were investigated experimentally by FTIR spectroscopy, X-ray powder diffraction, SEM and TEM analysis. Electrical conductivities of glasses and glass-ceramics were measured by impedance spectroscopy method. Few composites for positive electrode were produced from mixture of glass-ceramic powder with conductive carbon black and conducted electrochemical tests for capacity retention and cyclability.

It was shown that the glass-ceramic technique exhibits good applicability in fabrication of solid solutions of $Na_4M_{3-x}M'_x(PO_4)_2P_2O_7$ (*M*, *M'* - Co, Ni, Mn) for subsequent use as cathode active materials for SIBs.

Acknowledgements. Funding: This work was supported by the national long-term project [no. WQ20142200205] of “Thousand Talents Plan of Bureau of Foreign Experts Affairs” of People’s Republic of China.

[1] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research Development on Sodium-Ion Batteries, *Chem. Rev.* **114** (2014) 11636-11682.

[2] S. Nakata, T. Togashi, T. Honma, T. Komatsu, Cathode properties of sodium iron phosphate glass for sodium ion batteries, *J. Non-Crystall. Solids* **450** (2016) 109-115.