Synthesis of cathode composite powders from methylcellulose matrix: Li₂FeSiO₄/C, Li₂FeP₂O₇/C and LiFePO₄/C

<u>Miloš Milović</u>¹, Dragana Jugović ¹, Miodrag Mitrić ², Maja Kuzmanović ¹, Milica Vujković ³ and Dragan Uskoković ¹

¹ Institute of Technical Sciences of SASA, Belgrade, Serbia

² Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia

³ Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

Since Padhi et al. reported the electrochemical properties of LiFePO4 in 1997 [1], polyanion cathode materials for lithium-ion batteries attract interest of researchers because of the added safety and higher voltage values in comparison to the oxide analogues with the same $M^{2+/3+}$ redox pair. The higher safety and higher voltage come from strong covalent bonding within the polyanion units and, over the years, these inherent characteristics have promoted the investigation of different polyanion compounds. Among them, lithium transition-metal silicates, Li2MSiO4, and pyrophosphates, Li₂MP₂O₇, additionally offer the possibility of extraction/ insertion two lithium ions per formula unit thus increasing theoretical capacity. However, unlike their oxide counterparts, polyanion cathodes suffer considerably from low conductivity (both ionic and electronic) which significantly limits their rate performance and therefore application in high power devices. To overcome this obstacle various strategies were developed like minimization of particle size, addition of conductive additives and/or ion doping.

In this study, the approach that was used includes preparation of Li2FeSiO4/C, LiFePO4/C and Li2FeP2O7/C composites where carbon is obtained by pyrolytical degradation of methylcellulose and in situ during formation of polyanion active material on high temperatures. Methylcellulose, or methyl cellulose ether, is a water-soluble derivative of cellulose with an ability to gel upon heating and reversibly liquefy upon cooling due to the hydrophobic interaction between molecules containing methoxyl groups [2]. Thanks to this outstanding ability, the methylcellulose acts not only as a carbon source, but also as a dispersing agent that enables both the homogeneous deployment of the precursor compounds and the control of active material' particle growth from the earliest stages of crystallization. This further allowed a significant shortening of high temperature treatment (to several minutes long) with additional decreases of particle agglomeration. Being both simple and inexpensive, the described method is also beneficial for commercial purposes.

The electrochemical and microstructural properties of the obtained powders were examined and compared. Also, the

opportunity is taken to discuss potential of a redox couple Fe^{2+}/Fe^{3+} (Figure 1) in a relation to the crystal structure of a given polyanion cathode.

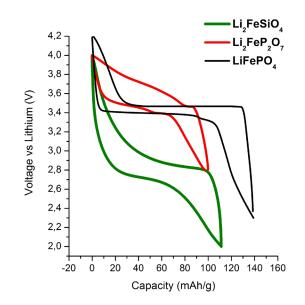


Figure 1. The electrochemical profiles of the prepared powders: Li₂FeP₂O₇/C (@ c/20), Li₂FeSiO₄/C (@ c/10) and LiFePO₄/C (@ c/3).

References

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[2] P.L. Nasatto, F. Pignon, J.L.M. Silveira, M.E.R. Duarte, M.D. Noseda, M. Rinaudo, Methylcellulose, a Cellulose Derivative with Original Physical Properties and Extended Applications, Polymers. 7 (2015) 777–803.



Miloš Milović was born in 1987 in Priština, Serbia. He studied at the Faculty of Physical Chemistry, University of Belgrade. Currently, he is working as a research associate at the Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Serbia. He holds a PhD in Physical Chemistry since 2016 and his field of interest covers chemical power sources with a focus on cathode materials for lithium ion batteries. The results of his research activities have been published in a number of peer-reviewed papers and presented at numerous scientific conferences.

Presentating author: Miloš Milović, e-mail: milos.milovic@itn.sanu.ac.rs tel: +381 11 2636 994