Study of the electrochemical properties of high voltage $LiCoPO_4$ cathodes via solution combustion synthesis

Semih Engün[1], E. Beyda Kamacı[2], M.Ali Arslan[2], Ezgi Yılmaz[3], Tayfun Koçak[3], Redouan El Khalfaouy[4], and Servet Turan[2]

[1]Dept. of Metallurgical and Materials Engineering, Zonguldak Bülent Ecevit University, Zonguldak, Turkey
[2]Dept. of Materials Science and Engineering, Eskişehir Technical University, Eskişehir, Turkey
[3]Tayko Battery Company, Eskisehir, Turkey
[4]Polydisciplinary Faculty of Taza, Sidi Mohamed Ben Abdellah University, Taza, Morocco

Olivine-type cathode materials are preferred due to the advantages of their orthorhombic (Pnma) crystal structures. Among these, $LiFePO_4$ (LFP) is an example that is widely used commercially. In addition to its good electrochemical properties, LFP is a cyclically stable, safe, economical, and environmentally friendly material [1]. However, since LFP's voltage potential is limited to 3.2 V, it has limitations in competing with oxide-based cathode materials in a layered structure in high energy density areas such as electric vehicle technology. For this reason, there have been searches for alternative olivine-type cathodes having high energy density. Cathode materials in an olivine structure have been produced using different transition metals instead of Fe. For example, when elements such as Mn^{2+}, Co^{2+} and Ni^{2+} are used instead of Fe^{2+} transition metal, the redox potential of the $LiMPO_4$ (LMP) compound was observed to increase to 4.1 V, 4.8 V, and 5.1 V, respectively [2]. The increase in the cut-off voltages of LMP compounds to these values has made them suitable for use in applications requiring higher energy.

However, phospho-olivine-type components have poor electronic and ionic conductivity because of their crystal nature, which results in limited reversible electrochemical performance. In particular, various approaches are used to solve the electrical conductivity problem encountered in olivine-type cathode materials, such as doping, grain size reduction, and coating of particle surfaces with various carbon sources [3].

Combustion synthesis is an effective technique widely used in synthesizing olivine-type LMP cathode materials to combine the approaches mentioned above to improve electronic conductivity. The fuel type and ratio are essential considerations in combustion synthesis, as they affect reaction conditions, stoichiometry, impurity formation, and ultimately the quality and properties of the synthesized LMP material [4].

In this study, we conducted preliminary experiments on synthesizing the $LiCoPO_4$ (LCP) cathode using combustion synthesis to achieve an olivine-type structure, smaller grain size, and desired electronic conductivity. Various fuels such as citric acid, glycine, and urea and their combinations were used to obtain the desired surface coating of the cathode with carbon. The crystal structure of the synthesized active materials of the LCP cathode was investigated using XRD, and the results are shown in Figure 1. The fuel choice affects the phase composition and impurities in the LCP synthesis process. Although using citric acid promotes the formation of a pure LCP phase, a sufficient capacity could not be obtained in electrochemical tests because the desired carbon coating did not occur on the cathode surface. When glycine was used instead of citric acid, the formation of the Co_2P and $LiCoO_2$ phases was observed. Subsequently, citric acid, glycine and urea were mixed in appropriate amounts, and the peak intensity of Co_2P and $LiCoO_2$ was observed to be reduced.

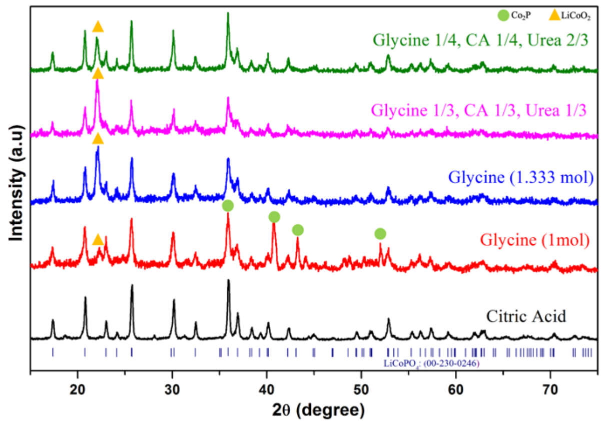

Figure 1: XRD analysis of the $LiCoPO_4$ synthesized using different fuel ratios.

Acknowledgements
The authors acknowledge that this study was supported by the TÜBİTAK 2209-A Research Project Support Programme for Undergraduate Students, No. 1139B412201083.

References

[1] Padhi et al., J. Electrochem. Soc. 144, 1188 (1997)
[2] Wolfenstine et al., J. Power Sources. 142 389–390 (2005)
[3] Julien et al., Batteries, 4, 39 (2018)
[4] R. El Khalfaouy et al., Journal of Rare Earths 38 (2020)

Dr. Semih Engün is a Research Assistant of Metallurgical and Materials Engineering at the Zonguldak Bülent Ecevit University. He received B.Sc. in 2012 and M.Sc in 2016 and Ph.D in 2022 in the Department of Materials Science and Engineering from Eskisehir Technical University. His recent works focus on synthesis and modification of cathode materials, solid electrolytes for Lithium-ion and solid-state batteries.

Semih Engün, e-mail: semihengun@beun.edu.tr Tel: +90 372 291 19 73