Li_2CoPO_4F as cathode material for lithium secondary battery – A method to achieve two lithium ion intercalation

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Lithium ion battery is one of the fastest growing battery chemistries and it has been highly acclaimed for the high specific energy delivered. Recent developments are moving towards higher energy density electrode active materials like Li_2MSiO_4, Li_2MPO_4F, $Li_XMP_2O_7$, etc. (M=Co, Ni, Fe), that have the capability ofmore than one lithium ion intercalation.Metals like Cobalt and Nickel involved during electrochemical reaction can help in realizing high operating voltage and increases specific energy. Fluorophosphates are one of the kinds of cathode active material that have been developed for obtaining high specific capacity and high specific energy. The stabilityof phosphate ion and highly electronegative fluoride ion are capable of stabilizing the structure of the positive active material during cycling, while the metal components gets engaged in lithium intercalation and deintercalation process. Li_2CoPO_4F is one among the fluorophosphates with a calculated theoretical capacity of 283 mAh g^{-1} for two lithium intercalation reaction. [1] The specific capacity obtained has reached a maximum of 154 mAh g^{-1} with ZrO_2 coating at elevated operating potential of 5.2V.[2]Hence, more work needs to be carried out to improve the specific capacity and cycle life of Li_2CoPO_4F cathode active material.

Our work focused on maximizing the deliverable discharge capacity and to reach theoretical capacity by achieving more than one lithium intercalation. In this study, a novel approach based on altering the operating voltage has been carried out. The Li_2CoPO_4F active material was synthesized by sol-gel method. The XRD pattern in figure 1 confirmed the formation of phase pure compound that matched well with the JCPDScard 56-1493.The reflections were indexed based on orthorhombic structure with *Pnma* space group. The upper cut off voltage was fixed at 5.0V and the lower cut off potential was varied carefully to insert all the lithium ions that have been extracted and to maintain structural stability. The charge-discharge curves showed a long plateau at 4.8V during charging cycle with an additional voltage plateau at ~5.0V, which can be attributed to the two lithium intercalation reaction and has been validated using cyclic voltammetry analysis. The lower voltage limit has been extended to increase the coulombic efficiency. A high reversible discharge capacity of >210 mAh g^{-1} was achieved. The marked detrimental cycle performance observed by Wu *et al*[3]for Li_2CoPO_4F has been replaced with a stable cycle performance of >95% capacity retention (figure 2) in the present study. It is believed that the structural deformation upon cycling has been decreased, which was evident from the unaltered discharge plateaus and peak voltages observed during charge-discharge studies and in cyclic voltammograms, respectively. A detailed discussion based on the obtained results will be presented in detail.

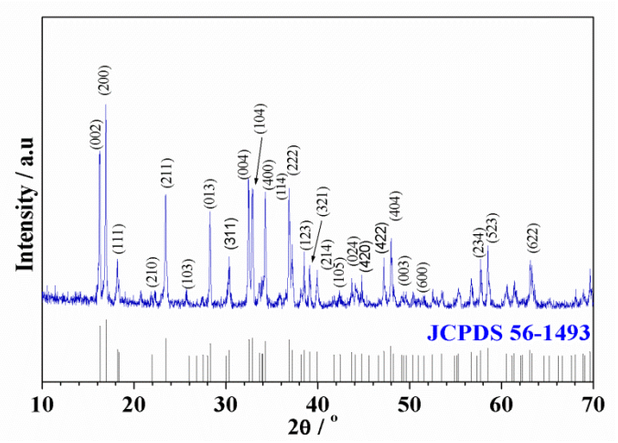

Figure 1: X-ray diffraction pattern of Li_2CoPO_4F cathode material synthesized by sol-gel method and the corresponding JCPDS card.

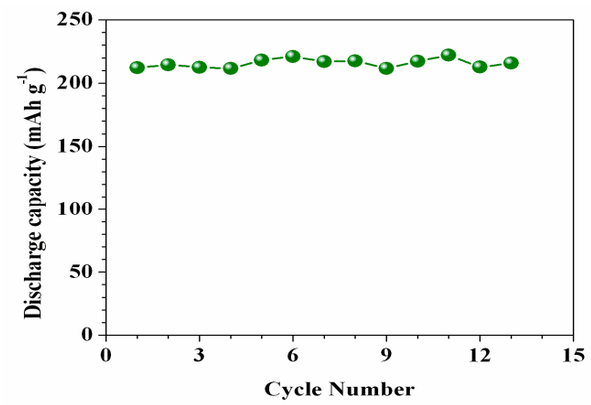

Figure 2: Cycle performance of Li_2CoPO_4F cathode material at 20 mA g^{-1}.

References:

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3) X. Wu, Z. Gong, S. Tan, Y. Yang, *J. Power Sources* 220 (2012) 122–129.