UNIVERSITI TEKNOLOGI MARA

PREPARATION AND CHARACTERIZATION OF $Li_2FeP_2O_7$ AND ITS SOLID SOLUTIONS AS A POTENTIAL CATHODE MATERIAL FOR LITHIUM-ION BATTERY

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ABSTRACT

Lithium ion battery (LIB) has been one of the most studied energy storage system due to its high energy efficiency, long life cycle, high capacity, and relatively high energy density. The need to investigate on a potential improvised LIB is motivated by the depleting fossil fuel and the concerning global warming caused by burning of fossil fuel. However, the mechanism of a LIB involves the chemistry between the LIB components, namely the anode, which is lithium metal for a half-cell, the electrolyte and the cathode. The cathode material of a LIB contributes to the cost effectiveness and performance of these LIBs. Since the introduction of $LiCoO_2$ layered oxide in 1996, researchers dedicated efforts into finding a structurally, electronically and electrochemically improved cathode materials including spinel $LiMnO_4$, olivine $LiFePO_4$ and other polyanionic cathodes. Lithium iron pyrophosphate, $Li_2FeP_2O_7$ has been reported to have a high theoretical capacity of up 220 mAh/g, while the experimental value was reported to be around 110 mAh/g, without any carbon coating or particle downsizing needed making it an interesting subject to explore deeper. However, synthesizing a pure phase $Li_2FeP_2O_7$ is a challenge, as many reports the existence of secondary phases in the end-product. Low electronic conductivity and high polarization hinders researchers to obtain the optimum capacity of the fabricated LIB. In this work, $Li_2FeP_2O_7$ was synthesized by using wet ball-milling assisted solid state reaction technique, and the transition metal Fe was then doped by divalent and tetravalent elements to help improve the characteristic and performance of the parent $Li_2FeP_2O_7$ material. The modification of the structure was done by introducing 2% of divalent and tetravalent solid soluble elements which are Ge^{4+}, Mn^{4+}, Ni^{2+}, Zn^{2+} and Zr^{4+}. To lower the possibility of secondary phase existence, the optimum heat treatment temperature was obtained by thermal gravimetric analysis (TGA), all samples showed the same final decomposition temperatures, thus the heat treatment temperature were finalized to 300°C and 600°C. From X-ray diffraction (XRD) analysis, it was found that all samples except for LFZnPP and LFZrPP contained a $LiFePO_4$ secondary phase, and the structure of each prepared sample were simulated using VESTA software, verified their monoclinic structure. The surface morphology of each sample was identified by using scanning electron microscopy (SEM), all samples showed a smaller average particle size (APS) compared to the parent LFPP, whereby LFGePP has an APS of 2.59 μm which is more desirable as smaller APS helps improve a battery's performance. The Fourier transform infrared spectroscopies for all prepared samples verified the structural peculiarities of all the prepared samples are based on the pyrophosphate $(P_2O_7)^{-4}$ polyanion, proved that all samples are built in the desired pyrophosphate crystal lattice. The polarization due to electrochemical effect were significantly lowered with the partial substitution of tetravalent Ge^{4+}, Mn^{4+} and Zr^{4+}, which leads to an outstanding increase in capacity value up to 59.71 mAh/g, 59.40 mAh/g and 47.98 mAh/g, respectively, compared to only 25.19 mAh/g for the parent LFPP. Whereas partial substation of Ni^{2+} was able to improve 1.8% in capacity value compared to LFPP, while Zn^{2+} reduced the value down to 6.54 mAh/g, due to possible structural collapsing during electrochemical process.

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