Electrochemical and Electrocatalytic Behavior of Phosphate Class of Sodium Insertion Materials: Few Case Studies

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Exploring post Li-ion battery systems, various monovalent (Na^+, K^+) and multivalent (Mg^{2+}, Ca^{2+}, Zn^{2+}, Al^{3+}) chemistry have been intensely investigated over the last decade. Among them, sodium-ion based insertion compounds have emerged as frontrunners owing to their operational similarity with Li-ion systems, low cost/ abundance and high rate kinetics [1]. Various oxides and oxyanionic compounds have been reported with great success delivering high capacity and/or redox potential leading to promising energy density. In addition, some of these systems can be exploited as electrocatalysts with bi-functional activity.

Over the past two years, our group has investigated various phosphate (PO_4^{3-}) based insertion compounds for electrochemical and electrocatalytic activity [2-9]. In the current work, we will summarize these work to give some insights on sodium intercalation properties and bifunctional (oxygen evolution/ reduction reaction) electrocatalytic activity of following PO_4 materials.

(i) Solution combustion synthesis was used to prepare phase-pure Na_2FePO_4F fluorophosphate compound involving low cost Fe(III) precursor. The target phase was obtained by annealing the intermediate complex in short duration of 1 minute. The electrochemical performance (3 V vs Na, 100 mAh/g) and one dimensional Na^+ diffusional mechanism will be demonstrated.

(ii) The electrochemical and diffusional activity of novel sodium metaphosphate [$NaM(PO_3)_3$] class of cathodes will be shown with a 2.8 V and 3.2 V (vs. Na) activity for Fe- and Co-based metaphosphate respectively. The electrocatalytic (oxygen reduction reaction) behavior of $NaM(PO_3)_3$ compounds will be demonstrated in comparison to Pt/C system.

(iii) The bifunctional activity of various phosphate (PO_4^{3-}) and pyrophosphate ($P_2O_7^{2-}$) materials (e.g. $NaFePO_4$, $KFePO_4$, $NaCoPO_4$, $Na_2CoP_2O_7$, $K_2CoP_2O_7$) will be described and compared to Pt/C system. Most of these materials were found to be bifunctional in nature with potential application in Na-air batteries.

(iv) Finally, the electrochemical and electrocatalytic performance of phosphate based alluaudite materials [$NaMFe_2(PO_4)_3$] will be reported. An overall 3 V Na (de)intercalation was noticed with reversible capacity over 70 mAh/g along with efficient oxygen reduction reaction activity.

References:

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