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\(_2\)FePO\(_4\)F 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\(_4\)\(_3\))] 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\(_4\)\(_3\)) compounds will be demonstrated in comparison to Pt/C system.

(iii) The bifunctional activity of various phosphate (PO\(_4^{3-}\)) and pyrophosphate (P\(_2\)O\(_7^{2-}\)) materials (e.g. NaFePO\(_4\), KFePO\(_4\), NaCoPO\(_4\), Na\(_2\)CoP\(_2\)O\(_7\), K\(_2\)CoP\(_2\)O\(_7\)) 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: