Preface

The global energy consumption is increasing in an alarming rate together with remarkable development and use of electronics, smart grids and electric vehicles. Therefore, the demand for energy storage devices with high energy and power densities, excellent safety, and long cycling lives is increasing. Electrochemical energy storage (EES) systems possess widespread implications in medical, electronics, and smart gadgets. Further, the alternative avenues for energy generation from wind, solar power and other renewable resources are not good enough to cope up the ever-increasing energy demand as most of these energy generation/conversion routes are intermittent, and therefore to become an alternative to fossil fuels they require proper energy storage systems. This has triggered intensive research efforts to develop superior energy stirage system then convention Li-ion batteries and supercaapcitors. A hybrid supercapacitor is the one such device that combines different energy storage mechanisms at the same time in order to utilize their individual advantages as well as to overcome their individual limitations.

The asymmetric arrangement is envisaged to attain high energy and power density at the same time. The advantages one may get are long cycle life, free of maintenance, higher power density, charging capacity at higher rates, and safer workability. The main aim of the battery-type hybrid supercapacitors is to improve both power and energy density, thus, rising along the diagonal direction of the Ragone plot. Aqueous hybrid supercapacitors (AHSCs) constitute an alternative form of supercapacitors replacing the use of flammable toxic organic electrolytes with aqueous electrolytes, potentially able to deliver an improved electrochemical energy density without influencing its power density. AHSCs supply a higher specific capacitance compared to conventional electrical double-layer SCs. AHSCs are also potentially safe and environmentally benign after replacement of the organic electrolytes, with a superior power and energy density with respect to SC or batteries, respectively. However, the electrochemical performance of AHSC faces challenges in achieving an unconventional high rate and longer life energy storage due to its poor cycle stability and difficulty in finding well-matched SC-type and battery-type, i.e., negative and positive, electrode materials with satisfactory ion/electron diffusion and sufficient structural stability.

This thesis investigates the development of a high energy and high power redox-mediated intercalating pseudocapacitive aimed to develop AHSC for large-scale energy storage solutions. Pseudocapacitance is characterized by a logarithmic relationship between electrode potential and the degree of reactions, involving charge transfer across the double layer. Intercalative pseudocapacitance also relies on redox reactions coupled with ions intercalation into the tunnels or layers of active materials, facilitating faradic charge transfer without inducing crystallographic phase changes. This process engages redox reactions within a three-dimensional structure of the electrode, contrasting with the surface interactions seen in redox-mediated pseudocapacitance. Transition metal ion-containing phosphate-based electrode materials containing those Ni, Co, and Mn, are synthesized using solution-based low-temperature chemical precipitation methods and their eelctrochemcial charge storage performance were examined to develop AHSC for large scale enrgy srtorage applications.

Hexagonal Fluffy Carbonized $KCoPO_4$ was prepared by modified sol-gel route followed by calcination of precipitate by raising the temperatute to get the crystalline material by using maleic acide as chelating agent. Materials was characterized by Powder-XRD, TGA, FT-IR, SEM, TEM, BET and XPS and electrodes were fabricated and electrochemical perofarmance of the electrode studied. $KCoPO_4$ based electrode ascribed to a dominating intercalative pseudocapacitive mechanism for charge storage, and characterized to have a specific capacitance of 725 F/g with a current density of 0.5 A/g with excellent cyclic stability. $KCoPO_4$ material with the activated carbon (negative electrode) in Aqueous Asymmetric Supercapacitor (AASc) mode offered remarkable electrochemical performance, resulted a maximum energy density of 121.1 Wh/kg and a high power density value of 6945 W/kg with a 86.3% of capacity retention.

$KCo_{1-x}Ni_xPO_4$ with x = 0, 0.1, 0.3, and 0.5 powders were synthesized through the sol-gel auto-combustion method followed by high temperature calcination at 600°C among of these, $KCo_{0.5}Ni_{0.5}PO_4$ proved to have a superior electrochemical properties, the charge storage mechanism in $KCo_{0.5}Ni_{0.5}PO_4$ predominantly observed was intercalative pseudocapacitive behavior rather than storage based on the surface, in a detailed analysis $KCo_{0.5}Ni_{0.5}PO_4$ material showed that the charge storage contributions came about 58% from intercalative (bulk) charge storage and 42% from capacitive (surface) storage. The material resulted with a specific capacity of 173 mAh/g and a capacitance of 1038 F/g at a current density of 0.5 A/g with excellent cyclic stability. In a full-cell hybrid supercapacitor (HSCs) mode with using activated carbon as the negative electrode, material exhibit exceptional energy density of 183.7 Wh/kg with a power density of 414 W/kg in a 2M KOH aqueous electrolyte at a current rate of 0.5 A/g and at 10 A/g it showed a power density of 7952 W/kg and managed to store energy density up to 36.4 Wh/kg with excellent cyclic stability.

Mn doped $KCo_{1-x}Ni_xPO_4$; $KCo_{0.5}Ni_{0.4}Mn_{0.1}PO_4$ material prepared by the sol-gel auto combustion method followed by high-temperature calcination, and uses maleic acid as chelating agent. Substituion of Mn was explored to realize high redox stability of the host framework lattice. $KCo_{0.5}Ni_{0.4}Mn_{0.1}PO_4$ characterized by powder X-ray diffraction (XRD) for structural identification and further crystal structure refinement was carried out using Rietveld refinement with FullProf Suite software, SEM for surafece morphology and XPS for the chemical composition and valence state. Further electrodes were fabricated and electrochemical perofarmance of the electrode studied, the $KCo_{0.5}Ni_{0.4}Mn_{0.1}PO_4$ based electrode offered a charge capacity of 177 mAh/g that is equivalent to 1062 F/g capacitance, at 1 A/g current density within a 2M KOH aqueous electrolyte, with a excellent cyclic stability. In a full-cell hybrid supercapacitor (HSCs) mode with using activated carbon as the negative electrode, material resulted with a specific capacity of 231 mAh/g and a capacitance of 521 F/g at a current density of 1 A/g, and exceptional energy density of 202.7 Wh/kg and power density of 9642 W/kg in 2M aqueous KOH electrolyte. These results indicate the potential of $KCo_{0.5}Ni_{0.4}Mn_{0.1}PO_4$ as a robust and high-performance positive electrode material for advanced HSCs development.

In this thesis, I conclude that framework structure material containing transition metal ions can be an excellent host to develop novel electrodes that can enable fast charge-discharge to develop high energy high power delivering battery type capacitors. Ni/Co/Mn Phosphate framework was shown to have redox-mediated charge storage capability that can dissipate power or current at fast rates to power electronic and electrical appliances and to be applied as grid-scale energy storage solutions. I found that the transition metal phosphate electrodes in full cell asymmetric supercapacitor (ASC) and hybrid supercapacitor (HSC) mode where activated carbon is utilized as a negative electrode can deliver power performance and rate capabilities comparable to lead acid batteries and further studies can bring superior aqueous redox-mediated battery type capacitor that can be employed for grid-scale energy storage solution and can also be utilized as an alternate to lead acid batteries to power inverters.