PREFACE

The energy supply based on fossil fuels To fulfill the ever-increasing energy demands to sustain the continuous growth and development of society has increased the inaccessible burden on fossil fuel resources and is decisively adding to climate change concerns and global warming. Renewable energy generation (including solar energy, wind energy, geothermal energy, etc.) has drawn significant attention as an alternative to fossil fuels and a remedy of concern related to pollution, global warming, and climate change due to net carbon addition to the earth environment. However, the power supply through renewable sources is irregular or fluctuating due to the time and weather-dependent nature of renewable sources and can not be used directly in electrical and electronic appliances. Though costly, yet most efficient, Electrochemical energy storage is key to harnessing the full potential of renewable energy sources, and thus gid-scale energy storage solutions are required to reduce the burden of fossil fuel-based energy solutions and instead use renewable power sources.

In this thesis, we focus on development of high energy-high power delivering redox-mediated intercalative supercapacitor to establish grid-scale energy storage solutions. In pseudocapacitors, energy is stored by fast and reversible redox reactions at the surface of active materials. Compared to EDLCs, pseudocapacitors offer 10 to 100 times higher capacitance because charge storage is not limited to the surface only, but also to the near-surface region where ions can diffuse. Pseudocapacitance arises when electrode potential is dependent logarithmically on the extent of reactions and involves charge transfer across the double layer. The intercalative pseudocapacitance is also based on redox reactions, which arise when ions intercalate into tunnels or layers of active materials accompanied by faradic charge transfer without crystallographic phase change but involve redox reactions in a 3-

dimensional structure rather than a 2-dimensional surface in redox pseudocapacitance. Metal oxalate framework structures are employed here to develop superior electrodes for hybrid intercalative battery-type supercapacitors. Thermochemical properties especially coupling of TGA/DTA techniques with strategic precipitation schemes to develop novel highly porous nanostructures that can enable fast transport or diffusion of ions in the host structure to have large-scale charge storage capabilities are employed here to develop effective electrodes for intercalative battery type supercapacitors.

$NiC_2O_4.2H_2O$ flakes were synthesized using a single-step co-precipitation method in an aqueous medium. $NiC_2O_4.2H_2O$ -based electrode showed intercalative charge storage behavior exhibiting specific capacitance of 990 F/g at a current density of 1 A/g with excellent cyclic stability. $NiC_2O_4.2H_2O$ electrode showed superior specific capacitance equivalent to 990 F/g in the potential window of 0.45 V was observed in an aqueous KOH electrolyte and 440 F/g in 1M neutral Na_2SO_4 electrolyte in the potential window of 0.85 V.

Highly porous, anhydrous CoC_2O_4 nanorods were successfully synthesized using a two-step process, first $CoC_2O_4.2H_2O$ was synthesized by co-precipitation method in an aqueous medium followed by heating the precipitate at 210 ºC to produce porous CoC_2O_4 nanorods. Porous CoC_2O_4 nanorods showed pseudocapacitive energy/charge storage behavior with a specific capacitance of the materials reaching as high as 2116 F g^{-1} at a current density of 1Ag^{-1} with excellent cyclic stability. The predominant intercalative mechanism seems to operate behind high charge storage as intercalative (inner) and surface (outer) charges stored by porous anhydrous CoC_2O_4 were close to 75% and 25% respectively. Porous anhydrous CoC_2O_4// AC full cell resulted in maximum specific energy of 129 W h kg^{-1} and specific power of ~647 Wkg^{-1} at 0.5 A g^{-1} current density in the voltage window of 1.3 V in 2 M

KOH electrolyte.

Anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$ was successfully synthesized using a two-step process; first, $Co_{0.5}Ni_{0.5}C_2O_4 \cdot 2H_2O$ was synthesized by the co-precipitation method in an aqueous medium, and then $Co_{0.5}Ni_{0.5}C_2O_4 \cdot 2H_2O$ was heated at 230 °C for 5 h, which resulted in porous anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$. The anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$ electrode showed a highly pseudocapacitive performance with a specific capacitance of 2396 F/g at a current density of 1 A/g and excellent cyclic stability. The porous anhydrous $Co_{0.5}Ni_{0.5}C_2O_4$ //AC full cell resulted in 283 W h/kg of maximum specific energy with a specific power equivalent to 817 W/kg in the voltage window of 1.6 V in the 2 M KOH electrolyte at a 1 A/g current rate.

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. The use of TGA/TDA techniques can be an important tool to modify the synthesis schemes to develop highly porous nanostructured materials to employ as an electrode in batteries and capacitors. Ni/Co oxalate 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 oxalate electrodes in full cell asymmetric supercapacitor (ASC) 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.