Abstract

The growing renewable energy requirement demands for the development of efficient, affordable and sustainable energy sources. This preeminent necessity encourages the researchers to pay immense attention on next generation low-cost energy dense electrochemical energy storage devices such as rechargeable batteries and supercapacitors. Supercapacitor is a subject of extensive study since the last two decades owing to their instant power delivery in comparison to rechargeable batteries and ability to sustain millions of fast charge-discharge cycles. Supercapacitors are categorized in three different groups based on their charge storage mechanisms: (i) EDL capacitors, (ii) pseudocapacitors, and (iii) hybrid supercapacitors. Pseudocapacitors possess much higher specific capacitance (10-100 times more) when compared to EDLC, but their self-life is relatively lower. Cycle life is the crucial parameter to work on for pseudocapacitive materials. Hybrid supercapacitor comprises of both EDLC and pseudocapacitive charge storage mechanisms to mitigate the drawback of each other. Energy storage devices with high energy and high power density are therefore desired. More specifically, specific energy is the parameter for supercapacitors to work on for its implementations in practical applications. On the other hand, batteries can store relatively large amount of charges but power density is lower than that of capacitors. One of the primary objectives in the research field of rechargeable batteries is to develop electrode materials which can offer high energy and power density at an affordable rate. In this effort, aluminum-ion batteries attracted significant attention in last couple of years. The reason behind the present-day grip of Al-ion batteries is such as easy handling at ambient atmosphere, less expensive aluminum resources, three electron electrochemistry of Al^{3+} ion and highest volumetric capacity (8056 mAhcm^{-3}) and better gravimetric capacity (2981 mAhg^{-1}) than that of Na, Mg, K, Zn and Ca.

The present thesis investigates nanocomposites of conducting polymers and 2D materials such as graphene, MoS$_2$ for supercapacitor applications. It also discusses the complex Al^{3+} ion electrochemistry in exfoliated phase of Ti$_3$AlC$_2$ MAX phase and LiFePO$_4$.

Chapter 1 briefly discusses the need for energy storage systems focusing on supercapacitors and batteries. Different energy storage mechanisms for charge storage of supercapacitors and batteries have been described. The importance of Al-ion batteries

has also narrated. This chapter also discusses the different electrode materials of the thesis work for electrochemical evaluation.

Chapter 2 investigates the fabrication of ternary nanocomposites of Poly(3,4-ethylenedioxythiophene) nanoparticles (PEDOTNPs) with MoS$_2$-rGO layer-by-layer structures. Ternary MoS$_2$-rGO/PEDOTNPs nanohybrids were synthesized with PEDOTNPs and MoS$_2$-rGO layer-by-layer structures exploiting one-step hydrothermal reduction process. Mesoporous and hydrophilic ternary MoS$_2$-rGO/PEDOTNPs electrode exhibits specific capacitance of 1143.7 Fg^{-1} at 1-fold of current density and 97.7% of cycling stability for 3000 GCD cycles. MoS$_2$-rGO/PEDOTNPs // MoS$_2$-rGO/PEDOTNPs symmetric supercapacitor (SSC) delivers specific capacitance of 289.25 Fg^{-1} at 1-fold of current density, 49% of rate capability at 20-fold of current density, and excellent cycling stability of 93.17% after 10,000 GCD cycles at 20-fold of current density. Moreover, MoS$_2$-rGO/PEDOTNPs // MoS$_2$-rGO/PEDOTNPs SSC exhibits specific energy of 33.56 Whkg^{-1} at specific power of 450.03 Wkg^{-1} based on the total mass at 1-fold of current density.

Chapter 3 discusses the development of ternary MoS$_2$-rGO/PPyNTs nanocomposites by combining pre-synthesized polypyrrole nanotubes (PPyNTs) with layered MoS$_2$-GO structures followed by *in-situ* hydrothermal reduction of GO. The porous layered structure of MOS$_2$-rGO nanocomposites provides enormous surface area and additional electro-active sites. The synergetic effect of layer-by-layer assembly of MoS$_2$ and rGO nanosheets with PPyNTs imparts immense electrochemical activity with specific capacitance of 1561 Fg^{-1} at the current density of 1 Ag^{-1}. MoS$_2$-rGO/PPyNTs // MoS$_2$-rGO/PPyNTs symmetric supercapacitor (SSC) delivers specific capacitance of 330 Fg^{-1} at 1-fold of current density, 28% of rate capability at 20-fold of current density, and cycling stability of 53% after 10,000 GCD cycles at 20-fold of current density. Also, MoS$_2$-rGO/PPyNTs // MoS$_2$-rGO/PPyNTs SSC exhibits specific energy of 67 Whkg^{-1} at specific power of 1167 Wkg^{-1} at the current density of 1 Ag^{-1}.

Chapter 4 re-explored the electrochemistry of modified MoS$_2$-rGO/PPyNTs ternary electrode with swift heavy ion irradiation technique as only 53% of cycling stability was obtained for MoS$_2$-rGO/PPyNTs // MoS$_2$-rGO/PPyNTs symmetric supercapacitor. The electronic properties of synthesized supercapacitor electrodes were tuned with 100 MeV O^{7+} swift heavy ions at four different fluences of 3.3x10^{11}, 1x10^{12}, 3.3x10^{12} and 1x10^{13}

ions cm^{-2}. Upon SHI irradiation, the desired properties such as specific capacitance, internal resistance of the electrode, cycling stability, rate capability and coulombic efficiency have been improved up to the fluence 3.3×10^{12} ions cm^{-2} and degraded at the highest fluence of 1×10^{13} ions cm^{-2}, employed in this work. The increased capacitive response can be attributed to enhanced crystallinity, enhanced electro-active surface area and improved electrode kinetics upon SHI irradiation. The irradiated electrodes were found to more stable with 92% cycling stability than the pristine electrodes (71% cycling stability).

Chapter 5 explains an electrochemical procedure to exfoliated MAX phase (Ti_3AlC_2) using a hybrid electrolyte. The exfoliation process avoids the harmful HF acid which is often used for the processing of MXenes. The electrolyte is an aqueous mixture of $AlCl_3$ and NaOH (1:10 v/v). The formation of exfoliated MAX phase has been confirmed from XRD, FESEM and Raman. The exfoliated MAX phase exhibits unusual electrochemical behavior in 1 M $AlCl_3$ electrolyte. It was revealed that kinetics is governed by a diffusion-controlled process. The exfoliated MAX phase possesses 82% of cycling stability in 1 M $AlCl_3$ electrolyte after 1000 repeated GCD cycles.

Chapter 6 illustrates an investigation on the electrochemical behavior of $LiFePO_4$ in Al^{3+} ion conducting aqueous electrolyte for the first time. It is inferred from the electrochemical measurements that Al^{3+} ion together with the structural Li^+ ion could take part in the reversible oxidation-reduction process of $LiFePO_4$. This is also supported by the *ex-situ* XRD and XPS investigations. It is also found that leaching of iron species from $LiFePO_4$ in the electrolyte results in low cycling stability. This could be mitigated to an appreciable degree by tweaking the electrolyte composition with a low fraction of iron species in the electrolyte.

Chapter 7 summarizes the major findings of the each chapter.