HETEROATOM CONTAINING POROUS CARBON MATERIALS FOR ELECTROCHEMICAL ENERGY STORAGE APPLICATIONS

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By

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ABSTRACT

Over the past two decades, there has been an intense focus on the electrochemical energy storage devices viz. batteries and supercapacitors (SCs). Lithium-sulphur batteries (LSBs) received more attention in the energy storage sector owing to their high theoretical capacity of 1675 mA h g^{-1} and high theoretical energy density. In this doctoral work carbon with different morphology is successfully prepared and was used for the fabrication of electrodes in the SCs and LSB cathodes. The activated carbon is prepared by $ZnCl_2$ activation followed by carbonization. Its electrochemical evaluation was carried out by using CV, GCD and EIS studies. Detailed investigations on the prepared electrode materials for LSB and SC applications were carried out and the descriptions of the results were presented in seven chapters.

In the first chapter, a general introduction on LSBs and SCs including its principle, limitations and state of art of the present scenario are mentioned. More emphasis is given to aspects which are currently focused on the thesis.

In the second chapter, Multiwalled carbon nanotube/sulphur/polyindole (MWCNT/S/PIN) nanocomposite was developed as cathode material for LSBs to alleviate capacity decay. It was synthesized by chemical precipitation of sulphur onto functionalized MWCNT followed by in-situ polymerization of indole. MWCNT/S/PIN nanocomposite exhibited 1490 mA h g^{-1} as initial specific capacity and enhanced cycling stability compared to the binary nanocomposite (MWCNT/S). The MWCNT/S/PIN composite cathode displayed 1043 mA h g^{-1} after 100 cycles at a 0.1C rate with 70% capacity retention. The better electrochemical performance of ternary nanocomposite cathode material was attributed to the synergistic effect of functionalized MWCNT and polyindole which provides improved conductivity and effective fencing of intermediate polysulphides (PSs).

In the third chapter, heteroatom doped microporous carbon (HMC) materials were prepared from 4, 4'-diamino-diphenyl sulphone (DDS) by pyrolyzing at 950 ºC in a single step without activation. The structural changes with the variation of carbonisation time were investigated. The heteroatom doped porous carbon-sulphur (HMCS) composite is used as LSB positive electrode material. A comparatives study was performed using materials prepared at the carbonisation time 1 & 2 h. The porous carbon matrix was used as a conductive host along with N, O functionalities to restrain the polysulphide diffusion into the electrolytes during the discharge process. HMC-2S exhibits better performance than the HMC-1S due to its higher surface area and pore volume, it can accommodate the volume changes of sulphur inside the carbon matrix than the HMC-1S during the cycling process. In addition, solid-state symmetric supercapacitor was fabricated using HMC with KOH and Na_2SO_4 gel electrolytes. The symmetric supercapacitor using Na_2SO_4 gel electrolyte gives a maximum energy

density of 35 W h kg^{-1} at a power of 529 W kg^{-1} and 91.07% capacity retention is obtained at 5000 cycles at a current density of 0.6 A g^{-1}.

To improve the performance of the LSBs further, inherently doped iron oxide nanoparticles and N, O heteroatom doped high surface area hierarchically porous carbon tubes (HPC) were prepared from vetiver roots in the fourth chapter. To analyse the impact of structural, morphological and energy storage capacities of HPC materials were prepared at the pyrolysis temperature varying from 600 ºC to 900 ºC was carried out. HPC with the high surface area (1879 m^2 g^{-1}) and pore volume (0.91 cm^3 g^{-1}) were obtained at 800 ºC. This material was investigated in detail for SC and LSB electrodes. The symmetric supercapacitor delivered 67.8 W h kg^{-1} at a power of 749 W kg^{-1} and exhibits 88% capacity retention after 10,000 cycles at a current density of 0.5A g^{-1}. In addition, the HPC-800 °C was used to incorporate sulphur (HPCS) and supported as cathode material for lithium-sulphur batteries. The HPCS exhibited an initial discharge capacity of 1584 mA h g^{-1} and reversible capacity of 1069 mA h g^{-1} after 200 cycles at a 0.1C rate with 67% capacity retention. The better electrochemical performance was attributed to the tubular morphology, high surface area, pore volume, N, O and iron functionalities of the porous architecture of HPC.

The fifth chapter discusses on N, O heteroatom doped hierarchical porous activated carbon, prepared from pinecone by $ZnCl_2$ activation and followed by carbonization. The carbon material has a high surface area of 2065 m^2 g^{-1} and a pore volume of 1.5 cm^3 g^{-1}. Three different combinations of sulphur loading 54, 68 & 73% were studied as cathode material for LSBs. In this chapter, the sulphur loading and distribution in this matrix is correlated with the electrochemical performance of the cell. Carbon with 54% sulphur displayed better electrochemical performance than carbon with 68 and 73% of sulphur. The initial discharge capacity was 1606 mA h g^{-1} and obtained a reversible capacity of 1269 mA h g^{-1} after 100 cycles with 79% capacity retention at the 0.1C rate. The better electrochemical performance of the 54% sulphur loaded carbon was due to the better dispersion of sulphur in the porous carbon network.

The sixth chapter elaborates on another strategy to alleviate PS shuttling. Heteroatom doped microporous carbon (HMC-1) with a surface area of 969 m^2 g^{-1} and a pore volume of 0.43 cm^3 g^{-1} was used to modify the separator. Orange peel derived carbon-sulphur composite (OPCSC) was prepared to host sulphur. Capacity degradation in the OPCSC cathode films was improved by separator modification. The modified separator was acted as a polysulphide inhibitor and accountable for the excellent electrochemical performance when compared with the MWCNT coated separator. The cell with HMC-1 coated separator exhibited 85% capacity retention while MWCNT coated displayed 74.8% capacity retention (100 cycles). The thin layer coating of HMC on separator effectively block the migration of polysulphides towards the anode, thereby decreasing the capacity loss and improving the rate performance.

The seventh chapter concerns on a better host material for sulphur, N and O co-doped honeycomb derived hierarchically porous carbon (HC) along with SiO_2. HCS

(80%) displayed a high stable capacity of 1101 mA h g^{-1} after 200 cycles at a 0.1C rate and 82% capacity retention. The HCS (80%) cathode was coated with a thin layer of HC, exhibited 92% capacity retention at 0.1C rate after 200 cycles. The role of the interlayer (HC coating) to improve the electrochemical performance of the cell was investigated in detail. The HCS (80%)-HC exhibited 1009 mA h g^{-1} at the 2C rate. It is a potential positive electrode material for LSBs.

Finally, in the conclusion, a comparison of the developed materials, summary of the complete work and the future perspectives are brought out.