Summary and conclusions

Electrochemical supercapacitors are high power density device that possess much higher capacitance ($10^5$ times) than normal capacitors and can be coupled with batteries to provide peak power. The main three materials employed for electrochemical supercapacitor electrode preparation includes carbon based material, metal oxides and electrically conducting polymers. Among these the conducting polymers offers the advantages of lower cost in comparison with metal oxides and high charge density in contrast to carbon materials, they have been paid much attention as electrode materials. Polyaniline (PANI) has been studied in great detail because ease of synthesis, different oxidation states and high environmental stability. The excellent electrode required for the supercapacitor consists of good electronic conductivity, electrochemical stability and high surface area. Taking into account the above mentioned parameters influencing the performance of Electrochemical supercapacitor we attempted to improve the electronic conductivity, surface area and electrochemical stability of the PANI based electrode and hence its supercapacitive behavior.

The aim of the present study concerns with the synthesis of PANI based films using simple and economical chemical route. The PANI, Mn-PANI, Ag-PANI, AC/PANI and Ag-AC/PANI prepared by chemical polymerization via dip coating technique to examine supercapacitive properties. The work has been distributed in seven chapters.

Chapter I is introductory chapter which provides the information about need of power sources, comparison of energy storage technologies, historical background and basic terminologies in supercapacitor. The type of supercapacitor and information about the electrode materials is involved therein. It also includes the detailed explanation of conducting polymer based supercapacitor, theoretical background of conducting polymer and literature
survey on PANI based supercapacitor. The purpose of dissertation and plan of work is stated at the end of the chapter.

**Chapter-II** begins with the description of the dip coating technique. The dip coating technique and its advantages over other techniques are given in detail. The necessary theoretical background and detailed description of the structural, morphological characterization techniques, such as FT-IR, FT-Raman, FE-SEM, EDS, XPS and electrical resistivity is given. The theoretical background of cyclic voltammogram for the electrochemical measurement is described in details.

**Chapter III** describes the formation of PANI films by easy and cost effective chemical polymerization via dip coating on stainless steel substrate. The used methods are quite simple and do not need any sophisticated instrumentation. The PANI films have been prepared, confirmed from the FT-IR, FT- Raman, XPS studies. FE-SEM micrograph showed the aggregated nanofiber structure over the substrate surface. The prepared PANI films further utilized as supercapacitor electrode. The three-electrode configuration system with graphite as a counter, PANI as working and saturated calomel (SCE) as a reference electrode were used. In this study the performance of electrodes was studied in 1.0 M H₂SO₄ electrolytes using cyclic voltammetry.

The performances were studied in terms of specific capacitance, in order to check effect of film thickness. Further stability was checked for best performed films. The highest specific capacitance 285 F g⁻¹ observed for optimized sample. This optimized thickness was used for further electrodes.

**Chapter IV** focuses on the synthesis of Mn doped PANI by chemical route. Synthesis of Mn doped PANI films as electrode for supercapacitor is important to decrease the resistivity of the PANI electrode with acceptable level of specific capacitance. To study the Mn doping effect on the specific capacitance of PANI, concentration of Mn was varied from 0.4 to 1.6 weight percent. The specific capacitance value increases from 285 F g⁻¹ to 474 F g⁻¹ as the Mn concentration was increased. The highest specific capacitance of 474 F g⁻¹.
is observed at 5 mVSec\(^{-1}\) for PANI film having 1.6 weight percent Mn doping concentration in 1.0 M H\(_2\)SO\(_4\).

**Chapter V** deals with preparation of Ag doped PANI electrodes in order to increase the electronic conductivity and hence the supercapacitive properties. It was observed that synthesis of Ag doped PANI electrode is a better choice for supercapacitor as compared to previously prepared Mn doped PANI. From FESEM, it reveals that the presence of Ag particles provides the least resistance path to electron between electrode and electrolyte. The highest specific capacitance of 512 Fg\(^{-1}\) is observed at 5 mVSec\(^{-1}\) for PANI film having 0.9 weight percent Ag doping concentration in 1.0 M H\(_2\)SO\(_4\) electrolyte.

So far, the efforts were focused to enhance the electronic conductivity of the PANI electrode by incorporating metal ions (Mn and Ag) into the PANI matrix. Surface area of the electrode plays significant role in the specific capacitance. Now our attention is to improve the surface area of the electrode.

**Chapter VI** discussed synthesis and characterized of AC/PANI composite electrode by in situ polymerization method. The highest specific capacitance of 534 Fg\(^{-1}\) is observed at 5 mVSec\(^{-1}\) and AC/PANI composite electrode in 1.0 M H\(_2\)SO\(_4\) electrolyte. This enhancement into the specific capacitance is attributable to both pseudocapacitance and electric double layer capacitance arising from PANI and activated carbon respectively.

Up to now, we found that Ag doped PANI electrode shows the better results than the Mn doped PANI due to the excellent electronic, catalytic properties of Ag. On the other side, AC/PANI electrode illustrates the superior electrochemical performance than the pure PANI due to high surface area and mechanical strength. It is interesting to see combining properties of both material i.e., electronic conductivity of Ag and surface area of AC to form the promising material for electrochemical supercapacitor.

**Chapter VII** describes preparation and characterization of ternary material Ag-AC/PANI by simple chemical route. In this chapter, we compared the results with previously prepared PANI, Ag-PANI and AC/PANI. The highest
specific capacitance of 534 Fg\(^{-1}\) is observed for the Ag-AC/PANI film at 5 mVSec\(^{-1}\) scan rate.

This work demonstrates a simple strategy of improving specific capacitance of the polymer electrodes. Thus the work will open a new avenue for designing low cost high performance devices for better supercapacitors.

Finally, Chapter VIII provides the extract of all the chapters i.e., summary and conclusions.

**Conclusions**

For electrochemical supercapacitor specific capacitance and electrochemical stability are the two important parameters which are plotted in the Fig. 8.1 for all the types of supercapacitor electrode materials investigated in this work.

![Graph showing variation of specific capacitance and electrochemical stability](image)

**Fig. 8.1** Variation of specific capacitance and electrochemical stability of the different supercapacitor electrodes fabricated in this work

But it is found that both the specific capacitance and electrochemical stability values are better for Ag-AC/PANI electrodes due to-
1. The presence of Ag nanoparticles on nanofibers background of PANI provides the least resistance path to electron due to its high electronic conductivity. Hence the fast electron transport between the current collectors and the active materials.

2. Activated carbon provides large surface area leading to a high charge/discharge rate and hence the specific capacitance.

3. Contribution of both types of capacitances viz., electric double layer capacitance of AC and pseudocapacitive behavior of PANI.

4. Mechanical strength of AC improves the electrochemical stability.