Chapter 3

Silver Nanoparticle Based Flexible Electrodes for Supercapacitors

3.1 Introduction

Non-renewable energy sources are depleting for the sake of energy production. Need of alternative sustainable and renewable energy resources became essential in the present situation of energy crisis, climate change and less availability of fossil fuels and these are also the serious issues [1]. Recent research mainly concentrated on energy production from solar cells, hydro power plants and wind mills [1]. Seasonal limitations of these resources make to store the generated energy in efficient energy storage devices. The energy storage devices/systems such as batteries and electrochemical capacitors (EC’s) took crucial role in storage of energy that can be used in all utilities [2]. The performances of these devices have been increased by using nanostructured materials, these materials ultimately increase the surface area of electrodes. This can lead to the enhancement of ion transportation on the surface of electrode [3]. Commercially Sony introduced batteries which are made up of Li-ion, showed excellent performance for the new generation of energy storage device applications [3]. Similarly great efforts were done to improve the performance of batteries/ECs by using nanomaterials/organic redox couples [4-6]. EC’s are promising candidates for faster and higher power energy storage in future energy storage device applications.
Electrochemical capacitors are differentiated based on the charge storage mechanism firstly electrochemical double layer capacitor (EDLC) where electrical energy storage is by electrostatic accumulation of charges. These EDLC’s can produce high power, excellent cycle life due to the fast and nondegradation process between active materials on electrodes and the electrolytes [2, 3]. Secondly, as pseudocapacitor in which electrical energy is stored by fast and reversible redox reactions [1]. Typically EDLC’s are made from carbon based materials, transition metal oxides and electrically conducting polymers are used to make pseudocapacitors [7]. ECs are having good sets of features like charging in short time and discharging for longer duration of time [8], cyclic stability and safe operation. Carbon and metal oxides based materials for electrodes are not highly conducting in nature, this property prevents the ion transportation between the electrode surface and electrode [9-10]. It is necessary to modify the electrodes of supercapacitors, these modifications leads to flexible and stretchable electrodes and hence flexible energy storage devices [11-14].

On the other side, the flexible and stretchable electronics has already reached to the doors of commercial market. At the same time a large area flexible sensors and actuators [15-18] are now emerging frontier. Hence, in order to make a complete gadget the integration of all these devices is essential [19-22].

The work presented in this chapter has been directed to design and fabricate flexible and highly conducting electrodes for supercapacitors. In the present work the silver nanoparticles has been taken as a conducting medium and polymer foams and cellulose paper as supporting materials to produce highly conducting, flexible, low cost electrodes for supercapacitor applications.
The commercially available foam is used as a substrate to coat silver nanoparticles. These foams are made from polyurethane and polyester fibres. These are having macroscopic significant internal surface area and widely used in our daily life as a cleaning tools. Foam has more uniform size of macropores, having pore size in the range of 100-500 μm. In textile or cellulose paper or foam, fibres are interconnected virtually. Therefore, continuous coating of conducting nanostructured materials becomes easier since there are no junctions to cross [23]. These types of electrodes are promising candidates in energy storage devices with properties like high conductivity, mechanical durability and good flexibility. The porous surface allows the free accessibility of the ions, also interconnected network provides continuous channels for electron transport. This incorporates the mechanical robustness and electronic performance of supercapacitors. Carbon nanotubes with good conductivity, mechanical flexibility and stable electrochemical behaviour are attracted towards EDLC electrode material [24-28].

Cellulose is lightweight and flexible material made up of micropores and these micropores provide high surface area. The functional groups of cellulose fibres provide strong interactive sites to bind nanoparticles. This helps nanoparticles to cover the cellulose fibres and allocate throughout the structure of cellulose fibre network. The cellulose composite combines the microporous texture, high strength of cellulose paper, the good electrical conductivity, facilitates easy ion transportation and the electroactivity of nanoparticles. Hence these composites promises to overcome the low strength and low porosity of graphene or graphene oxide paper based materials [29-32].
In the present work we have tried to make high performance supercapacitor electrodes using silver nanoparticles on polyurethane foam and cellulose (filter paper). First silver nanoparticles on polyurethane foam are discussed in detail. Second silver nanoparticles on cellulose paper are taken up.

3.2 Present Investigations

3.2.1 Synthesis of Silver Nanoparticles-Polyurethane Foam Electrodes

In all the synthesis analytical grade chemicals were used as received without further purification. Silver nitrate (AgNO$_3$), tetraethylammonium tetrafluoroborate 99% (TEABF$_4$) ((C$_2$H$_5$)$_4$NBF$_4$), propylene carbonate (PC) (C$_4$H$_6$O$_3$) were procured from Sigma-Aldrich. Sodium hydroxide (NaOH) and tri-sodium citrate (Na$_3$C$_6$H$_5$O$_7$) were obtained from SD-fine Chemicals, India, and the commercially available polyurethane foam (\(-\mathrm{NH-}(\mathrm{C=O})-\mathrm{O}\)-) is used to make the flexible electrode.

The commercial foam is washed few times with tripled distilled water and ultrasonicated to remove the unwanted material. Then it was dried under table lamp for reasonable time to remove the water completely. To coat the silver nanoparticles on the skeleton of these foams, 5 mM silver nitrate solution is prepared in distilled water and solution of 1 wt% of tri-sodium citrate is also prepared in separate flask. The silver nitrate solution was heated at 90°C on a hot plate nearly for 15 minutes. When the solution starts boiling, four pieces of nicely cut polyurethane foam measuring 2 x 2 x 0.2 cm$^3$ were completely soaked and again they were left for couple of minutes in precursor solution on hot plate. At this stage tri-sodium citrate solution was added, the colorless solution of silver nitrate changed to light orange color due the precipitation of silver nanoparticles. Later these nanoparticles get deposited on the polymer foam as shiny orange material. Interestingly it is observed that the deposition of silver nanoparticles on polymer surface is deriving process and after the completion
of few minutes the entire solution appears to be colorless. At the end, these foams were thoroughly washed with distilled water for couple of times to remove the contamination and unreacted product from the foam. Finally, these foams were dried under the table lamp for the complete removal of water. In order to achieve superior electrical conductivity the solution coating of foams was carried out multiple times to deposit more amount of nanoparticles. These electrodes were used as starting materials to constitute supercapacitors. All these deposition steps are shown schematically as in Figure 3.1.

### 3.2.2 Synthesis of Silver Nanoparticles-Cellulose Electrodes

For all the chemical reactions analytical grade chemicals were used as they received without further purification. Silver nitrate (AgNO₃) obtained from Sigma-Aldrich, Germany. Other chemicals such as potassium chloride (KCl), polyvinyl alcohol (PVA) (-C₂H₄O⁻), orthophosphoric acid (OPA) (H₃PO₄) and tri-sodium citrate (Na₃C₆H₅O₇) were obtained from SD-fine chemicals, India. Whatman filter paper of 42 grade is used as a substrate to coat silver nanoparticles. Whatman filter paper is

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**Figure 3.1:** Schematic representation of deposition of silver nanoparticles on different substrates.
made from cellulose with approximate equal pore size. For all the chemical reactions Milli-Q triple distilled water is used.

The synthesis of silver nanoparticles coated cellulose paper is schematically depicted in Figure 3.1. Whatman filter paper is sized to required dimension 2 cm x 2 cm and is washed in distilled water to remove the extra unwanted material. Then it was dried under table lamp to remove the complete moisture from cellulose. Further to deposit silver nanoparticles on cellulose paper, precursor solution of 0.005 M of silver nitrate solution is prepared and 1 wt% of tri-sodium citrate solution is also prepared separately. The silver solution is heated on plate by maintaining its temperature close to 90°C, at this temperature the solution starts boiling. At that time four pieces of cellulose papers are added to the solution. After lapse of few minutes the tri sodium solution is added to the boiling silver solution. The deposition of silver nanoparticles on cellulose papers is observed and it looks like a shiny silver layer on cellulose paper. The mixed solution turns to colorless after few minutes. Then the cellulose papers were removed from the solution, rinsed in water and dried, the sheet resistance of these silver coated cellulose papers are measured and it is observed to be in the range of few kilo-ohm. For the high ion diffusion mechanism, high conducting electrodes are necessary to constitute the supercapacitors. After the repetition of the whole process for four times highly conducting silver deposited cellulose paper is achieved with measured sheet resistance of 30 Ω. It is significantly very high and it helps to transport electron from electrolyte to the electrode surface. All the silver coated cellulose papers are identical in their appearances like flexibility and electrical conductivity. This ensures that the coating of silver nanoparticles by present method is quite uniform and non-damageable. These silver coated cellulose papers are further used as an electrode material to construct supercapacitor. These composite electrodes
are characterised by various techniques to understand the electrochemical properties of supercapacitors made by these electrodes using various electrolytes are studied by cyclic voltammetry and charge/discharge measurements under different scan rates ranging from 2 mV/s to 120 mV/s.

3.3 Results and Discussion

3.3.1 Silver Nanoparticles-Polyurethane Foam Electrode

Figure 3.2(a) shows the room light photograph of a commercial foam (left corner), a foam with first time coating of silver nanoparticles (middle) and a foam with multiple time coating (fourth time) (right corner). It is clear that the initial white color foam becomes orange after the first coating. It was coated with multiple time by repeating the above producer to achieve a good electrical conductivity, the fourth time coated foam in shown in Figure 3.2(a) (right corner) that becomes dark grey (metallic) in color. The sheet resistance of final foam shows only about 14 Ω, the highly conducting foams are flexible with large internal surface areas that are essential for the electrodes of a supercapacitor. Further, the silver adhesion on foam is carried out by scotch tape peeling, the adhesion is observed to be quite good and there was no peeling of nanoparticles on repeated sticking and peeling of scotch tape, this is shown in Figure 3.2(b). The electrochemical studies were carried out on the supercapacitors constituted with these symmetrical electrodes with respect to different electrolytic solutions under the different scan rates.

3.3.1.1 Structure and Surface Morphological Studies

To study the deposition of silver nanoparticles on the internal pores of skeleton of polyurethane foam the scanning electron microscopic images were recorded. Figure 3.3(a) shows SEM image of bare foam and Figure 3.3(b) of silver nanoparticles coated foam. In both the figures it is observed that the polyurethane foam shows three
Figure 3.2: (a) Photograph of silver-foam electrodes, the samples from left to right are corresponding to bare foam, first coating of silver on foam (Orange in color), fourth time coating of silver on foam (shiny silver in color). (b) Scotch tape test of silver-foam electrode and also showing flexibility.
Figure 3.3: (a) SEM images of bare polyurethane foam. Inset image at higher resolution. (b) Silver coated polyurethane foam. Inset image at higher resolution.
dimensional hierarchical mesoporous structure with the pore size ranging between 100 and 600 \( \mu m \). The internal surface area of these foams has many advantages in depositing various nanoparticles: (i) there is reasonable size of pores having smooth internal surface area, (ii) both the internal and outside surface of foam is free from inter junctions that enhances the electrical conductivity of final composites coated with any conducting materials and (iii) there is reasonably high density of hydrophilic moieties inside and outside surfaces of these foams which makes reasonable amount of water absorption, it is observed that the bare foam takes water almost 30 times of its weight. Further, there is no significant change in the morphology of these foams after deposition of silver nanoparticles. The inset in Figure 3.3(a) is image of bare foam at higher magnification which shows that the surface is plane indicating the absence of any coating on the foam surface. Similarly, the inset in Figure 3.3(b) is the image at higher magnification for silver coated foam, the deposition of silver nanoparticles is clearly visible. Such porous nanostructure with good electrical conductivity helps electron transfer between the electrode surface atoms to electrolytic ions for electrochemical energy storage application process. From the gravimetric analysis the active mass of silver on the foam is estimated. It is observed that the first time coating gives 12 mg and fourth coating 36 mg on the dimension mentioned above. Finally, fourth time coating of silver on foam is shown in Figure 3.2(a).

The powder X-ray diffraction was recorded on bare and nanoparticles coated foams and these patterns are shown in Figure 3.4, here along with these patterns the standard peaks and their Miller indices of bulk silver from JCPDS 04-0783 is also shown for the comparison. The bare polyurethane foam shows a broad hump around \( 2\theta = 24^\circ \) that is characteristic peak of this material and the silver matches well the
patterns that are reported in the literature [27]. The silver coated foam clearly exhibits the four prominent peaks ranging from $2\theta =10^\circ$ to $80^\circ$, these peaks match well with the standard pattern having the Miller indices (111), (200), (220) and (311) of bulk silver.
These peaks indicate that there is better crystallinity of silver nanoparticles, the crystallite particle size is estimated using the Debye-Scherer’s equation 2.1 (Chapter Two). The estimated size is about 42 nm showing that the silver particles have grown up to a reasonable size. The electrical conductivity of this foam is measured by putting the foam between two electrodes of steel plate having area equal to foam’s cross sectional surface area. Current-voltage curves were recorded by sweeping the voltage between -2 to +2 V using Keithley source meter. These measurements showed reproducible curves. One of such curves is plotted in Figure 3.5 as current density versus voltage. It shows a linear behaviour and highly symmetric on the either side of the voltage, the estimated electrical resistivity using two electrode configuration is 186.67 Ohm-cm.

3.3.1.2 Electrochemical Performance

Next, the electrochemical performance of constituted supercapacitors using these foams as electrodes was studied by two-electrode configuration [28] for two different electrolytes. Stoller et al [33], others [34] and ourselves [10] have shown that the two electrode configuration for electrochemical study is quite convenient and accurate method for the determination of specific capacitance of an electrolytic capacitor. The best practices for the two electrode measurements have been very well summarized [35]. With these considerations, we have designed our two electrode setup that is quite simple, reliable and can be repeatedly used for the easy constitution of electrolytic capacitors. The details of this setup are given elsewhere [10]. In brief, the two symmetrical electrodes of silver coated foam having dimension of 2 cm x 2 cm x 0.3 cm are separated by a piece of cellulose paper of 2.2 cm x 2.2 cm (Whatman filter paper) soaked in 0.5 M tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in propylene carbonate and 1M NaOH in water as separate electrolytes. The present used
setup permits to apply a constant and uniform pressure every time a capacitor is constituted. Hence a constant separation between the two electrodes is achieved. All the measurements were carried out in ambient conditions without any inert gas atmosphere.

Cyclic voltammograms were recorded with respect to 0.5 M TEABF$_4$ propylene carbonate and 1M NaOH electrolytes for different scan rates and these are shown in Figures 3.6(a) and 3.6(b), respectively. The scan rates varied from 2, 10, 20, 50, 80, 100 to 120 mV/s for both the electrolytes. These curves show semi-rectangular shape (which is characteristic of the pseudocapacitors) that persists even at a higher scan rate 120 mV/s. These devices show a wide voltage window ranges from -800
Figure 3.6: (a) Cyclic Voltammmograms of silver treated polyurethane foam in TEABF$_4$ with propylene carbonate electrolyte. (b) Cyclic stability curves of silver treated polyurethane foam in TEABF$_4$ in propylene carbonate electrolyte.
mV and 600 mV and in both the figures the reduction/oxidations peaks are clearly observed and they shift with scan rate. In case of TEABF₄ devices the reduction/oxidation peaks occur at lower voltage as compared to NaOH devices. For a given scan rate this change is considerable, for 10 mV/sec the difference is almost 0.16 mA/cm². However, the current densities in both cases at the extreme end of potential window are almost same. To check the reproducibility of these devices, the cyclic voltammograms were repeated for more 1000 times at the scan rate 100 mV/s. The typical curves of these measurements with 100 cycles are shown in Figure 3.7(a) and 3.7(b) for TEABF₄ and NaOH electrolytes, respectively. The cyclic stability measurements clearly indicate that more than 90% of the initial capacitance retained that is reasonably a good performance. Silver foam devices operate at the high scan rate for both organic electrolytes and aqueous electrolytes [36-42].

From these curves the specific capacitance for different electrolytes is estimated using the equation 2.9 ([Chapter Two]) [40]. The numerical values of specific capacitance for two different scan rates 2 and 10 mV/s for different electrolyte are given in the Table 3.1. In case of 1M NaOH electrolyte at 2 mV/s scan rate the estimated specific capacitance is close to 3929 F/g and in case of TEABF₄ electrolyte at the same scan rate it is 3948 F/g. Further, the variation of specific capacitance for different scan rates is plotted in Figure 3.8. In both the cases the initial capacitance that is at 2 mV/s is almost same and it decreases rapidly with increase in scan rate. In case of NaOH, the initial decrease is faster as compared to TEABF₄ electrolyte device, around 50 mV/s the specific capacitance becomes minimum and thereafter it increases slightly with the scan rate. However, in case of TEABF₄ electrolyte there is continuous decrease, it goes from 3948 F/g at 2 mV/s to 363.89 F/g at 120 mV/s. As the scan rate increases the specific capacitance decreases which
Figure 3.7: (a) Cyclic Voltammograms of silver treated polyurethane foam in 1 M NaOH electrolyte. (b) Cyclic stability curves of silver treated polyurethane foam in 1 M NaOH electrolyte.
can be attributed to electrolytic ions diffusing and migrating into the active materials at low scan rates. At high scan rates, the diffusion effect, limiting the migration of the electrolytic ions, causes some active surface areas to become inaccessible for charge storage [22].

**Table 3.1:** Specific capacitance values for TEABF₄ and NaOH electrolytes at 2mV/s and 10 mV/s scan rates.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Scan Rate in mV/s</th>
<th>Specific Capacitance in F/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M NaOH</td>
<td>2</td>
<td>3929</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1058</td>
</tr>
<tr>
<td>0.5 TEABF₄+PC</td>
<td>2</td>
<td>3948</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2238</td>
</tr>
</tbody>
</table>

The galvanostatic charge/discharge curves of these silver nanoparticles based electrodes with TEABF₄ electrolyte are measured. A long time charge/discharge of 10000 cycles has been performed at the high scan rate 100 mV/s and is shown in Figure 3.9. The waveforms are highly symmetric and more stable with charging and discharging. These results clearly show that the present composites of polyurethane foam and silver nanoparticles acts as a good electrode materials in the formation of electrolytic supercapacitors that posses a high specific capacitance, a good charge/discharge stability and a better cycle stability. Further, these foams have promising features like low cost, flexible, light weight and durable.

Recent work on supercapacitors has been focused on flexible devices due to their growing demand in wearable and portable electronics [45]. For which the flexible electrodes with superior electrochemical performance is essential [46]. To achieve this 3-dimensional nanostructures are created by coating a suitable materials
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Figure 3.8: Specific capacitance versus scan rate graph: a comparison between TEABF₄ in propylene carbonate and NaOH electrolytes.

on the macroporous architectures [47] of polymer foams [48] and metal foams [49], in latter case it is mainly the nickel. The active materials include various forms of carbon nanostructures [50], transition metal oxides [51], metal hydroxides [21, 22], conductive polymers [23] and metal sulphides [52] and also the combination of these materials [53]. The purpose is to achieve the high surface area, good electrical conductivity and active reduction/oxidation sites, superior chemical stability and low cost [54]. Some of the recent reports on polymer foam structures have given the encouraging results. Dubal et al. created hybrid electrodes with large internal surface
by depositing reduced graphite oxide and nickel/cobalt hydroxides on polymer foam to form asymmetric supercapacitors. The porous structure of these composites allows a good accessibility of electrolytic ions to surface active atoms and the observed highest capacitance is 812 F/g for 5 mV/s [55]. High performance supercapacitors are made by using graphene-polyaniline deposits and the best achieved specific is 965 F/g at 10 mV/s [56]. Wei Chen et al. coated MnO$_2$ and carbon nanotubes on kitchen foam, these authors observe a remarkable increase in specific capacitance that is 1230 F/g at 1 mV/s with specific power 63 kW/kg, specific energy 31 Wh/kg and a good cyclic stability close to 96% [52]. The significant performance in case of Ni foams are reported in recent time, Jun Pu et al. formed a uniform nanotube arrays of Co$_9$S$_8$ semiconductor by Kirkendall effect and the achieved specific capacitance is 1775 F/g [57]. Similarly, Le Yu et al. have grown hierarchical core-shell structures of

![Figure 3.9: Galvanostatic charge/ discharge curve of silver treated polyurethane foam in TEABF$_4$ in propylene carbonate electrolyte.](image)

high performance supercapacitors are made by using graphene-polyaniline deposits and the best achieved specific is 965 F/g at 10 mV/s [56]. Wei Chen et al. coated MnO$_2$ and carbon nanotubes on kitchen foam, these authors observe a remarkable increase in specific capacitance that is 1230 F/g at 1 mV/s with specific power 63 kW/kg, specific energy 31 Wh/kg and a good cyclic stability close to 96% [52]. The significant performance in case of Ni foams are reported in recent time, Jun Pu et al. formed a uniform nanotube arrays of Co$_9$S$_8$ semiconductor by Kirkendall effect and the achieved specific capacitance is 1775 F/g [57]. Similarly, Le Yu et al. have grown hierarchical core-shell structures of
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NiCo₂O₄-MnO₂ on Ni foam and these flexible devices show the capacitance value 1471 F/g [58]. Further in the direction of flexible devices, Laifa Shen et al. created binder free NiCo₂O₄/carbon textile by hydrothermal method, these result show capacitance as high as 1283 F/g [59]. The present electrodes of silver nanoparticles coated on polyurethane foam showed a significantly increase in the values of specific capacitance that is 3948 F/g and 3929 F/g with TEABF₄ and NaOH electrolytes, respectively, for the scan rate 2 mV/s in open condition.

Silver and silver oxide are a versatile material which are widely used in oxidation catalysis [60], sensors [61], fuel cells [62], photovoltaic cells [63], all-optical switching devices and optical data storage systems [64]. Ag₂O is stable below 170°C in gaseous environments in which its thermal decomposition takes place to produce O₂ and metallic silver. There is no suitable record is available about the stability of Ag₂O in aqueous conditions. Still there are clues which supports the stability of Ag₂O firstly the precipitation from aqueous silver salt and strong alkali, also considering the effect of either the Ag₂O generated by silver oxidation with O₂ dissolved in aqueous environment [65]. In this context, a simple fact that seems to have gone unnoticed for a long time: aqueous colloids of Ag₂O undergo decomposition to give silver nanoparticles at room temperature.

In the present work, we demonstrate for the first time that pristine silver and silver oxide has been used to constitute the supercapacitor in which during the charge/discharge cycle decomposition of silver to silver oxide and silver oxide to silver takes place. Here the silver nanoparticles reacts with strong alkali (NaOH which is used as electrolyte) solution in order to obtain [Ag⁺] x [OH⁻] over K_{sp} [66] and drive the silver oxide precipitation reaction according to

\[ 2Ag^{+} + 2OH^{-} \rightarrow Ag_{2}O + H_{2}O \] (charging) - - - - - - - - (3.1)
\[ \text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{Ag}^+ + 2\text{OH}^- \text{ (discharging)} \] (3.2)

The formation of the colloid in the silver/alkali composition in supercapacitor is evident since silver oxide particles exhibit a property of brown color. In two electrode configuration, during charging one electrode will be of pure silver another will be silver oxide while during reverse i.e discharging case one electrode will be silver oxide and another will be silver, or else both the electrodes turns silver oxide while charging and silver when discharging. The presence of silver oxide is confirmed by EDAX analysis, it gives the details of the elemental composition present in the silver deposited foam (measured after the reaction) as shown in the Figure 3.10. Here the high mass retention is observed even after many cycles, which leads to the high cyclic stability of supercapacitor. With these results, this material is can be a good material like other metal oxides. Among the metal oxides, hydrous ruthenium oxide (\( \text{RuO}_2 \)) is the most recognised electrode material in the field of supercapacitors with properties such as ultrahigh pseudocapacitance, low resistivity, high chemical and thermodynamic stability under electrochemical environments [67]. Due to the high cost of Ru, it is restricted for the commercial application in supercapacitors. The cost factor can be reduced by replacing \( \text{RuO}_2 \) with other metal oxides \( \text{MnO}_2 \) [68], NiO [69], ZnO [70], \( \text{SnO}_2 \) [71] and so forth. Among these \( \text{MnO}_2 \) and \( \text{SnO}_2 \) are of low cost, high electrochemical activity and more environmentally benign nature [71]. In the present study it is observed that initially the silver nanoparticles are well coated on the internal surface of polymer foam having very high electrical conductivity. Later there is selective oxidation of silver to silver oxide on the surface of silver nanoparticles. This is evident from EDAX measurements. A small fraction of silver is converted to silver oxide without losing its initial electrical conductivity. Like other metal oxide activated composite electrodes, the present electrodes are silver oxide activated silver-
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Figure 3.10: EDAX analysis of silver deposited foam (a) Silver Foam (b) silver foam after the reaction.

poly-flexible foams. The supercapacitors based on these electrodes showed the ultrahigh performance better than the various metal oxide performance. It is cost effective, environmentally benign, electrochemically stable and can be used for large scale commercial production.
3.3.2 Silver Nanoparticles-Cellulose Electrode

The mass 12.5 mg of silver nanoparticles which is deposited on cellulose papers is determined by gravimetric weight difference method by weighing the mass of the bare cellulose paper and silver deposited, using a sensitive microbalance.

3.3.2.1 Structure and Surface Morphological Studies

Surface morphology of silver nanoparticles deposited on the cellulose paper is analyzed using scanning electron microscope (SEM). SEM images of bare cellulose paper and silver coated cellulose paper were obtained. Figure 3.11(a) shows bare cellulose paper, which is having large surface area with the cellulose fibres and internal pores. As a result there is a large internal surface area of these papers and hence are suitable substrate materials in the area of supercapacitors. SEM of silver coated cellulose is shown in Figure 3.11(b), in which conformal coating of nanoparticles benefitting the electrical conductivity of the silver coated cellulose sheets, the sheet resistances reached a lowest value of 30 ohms. Due to the intermolecular forces nanoparticles formed in leaf/ petal shape, finally these petals are aligned and formed microflower on cellulose fibres, which is shown in Figure 3.12(a). The strong capillary force enables high contacting surface area between flexible cellulose fibres and the silver nanoparticles. The paper absorbs precursor solvents easily and while heating formed silver nanoparticles binds with cellulose fibres strongly, the fabrication process of conducting silver based cellulose paper is much simpler than that for flat surfaces, such as glass or plastics. In glass or plastic, the particle surface energy needs to match with that of substrates and the viscosity must be high enough to avoid surface tension-driven defects, such as rings and dewetting in the coating and drying processes. Therefore various additives are incorporated in the precursor solution to tune the rheological properties. These insulating additives
Figure 3.11: Scanning electron microscope images of (a) bare filter paper, (b) silver coated filter paper
Figure 3.1: (a) Microflower of silver nanoparticles formed of cellulose paper (b) Bending of silver-cellulose paper almost by 360°.
decrease the conductivity of the final film. In contrast, our silver solution does not need any additives to adjust the rheology, which simplifies the process and leads to high electrical conductivity. The paper does not require surfactant washing processes to achieve high film conductivity, which is necessary for other substrates.

The conductive silver based cellulose paper also has excellent mechanical properties. It is observed that bending of this conducting cellulose paper almost by 360° (as shown in Figure 3.12(b)) did not change its electrical conductivity. These mechanical behaviours are due to the combined effect of the flexibility of individual cellulose fibres, the strong binding of the silver nanoparticles with the paper fibres, and the porous morphology of the paper, which can relax the bending strain. Such flexibility could satisfy the requirement in supercapacitors and batteries.

X-ray diffraction patterns were measured and are shown in Figure 3.13. This includes XRD pattern of bare cellulose and pattern of silver coated cellulose and at the bottom the standard peaks of silver nanoparticles are shown in the figure for the comparison. In the first pattern of bare cellulose the standard peak at $2\theta = 15^\circ$ and $23^\circ$ are observed that are well reported in literature [27]. Similarly the second pattern of the silver coated cellulose paper scanned in the range of $2\theta = 10^\circ$ to $80^\circ$. A number of strong Bragg reflections can be seen which correspond to the (111), (200), (220) and (311) reflections of bulk silver. No spurious diffractions due to crystallographic impurities are found. This indicates the absence of crystallographic impurities in the silver coated cellulose paper. All the reflections correspond to pure silver metal with the face centered cubic (fcc) symmetry. The high intense peak for fcc materials is generally (111) reflection, it is observed in the present case. The sharp natures of these peaks indicate that there is a high degree of crystallinity of the silver nanoparticles. From the full width half maxima values, the size of silver crystalline is
estimated using Debye-Scherer equation 2.1 (*Chapter Two*). The estimated particle size is about 42 nm. From this silver coated cellulose current-voltage measurement is carried out using two electrodes set up. Figure 3.14 shows the current-voltage curve of silver- foam. The silver coated cellulose paper is used to measure its electrical conductivity. A two electrode configuration is adopted by putting the two flat electrode (area 2 cm x 2 cm) across the sample thickness. Current-Voltage curves

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**Figure 3.13:** X-ray Diffraction pattern of bare filter paper, silver coated paper and standard silver pattern.
were measured that is shown in Figure 3.14. It clearly shows that the film is highly conducting and current versus voltage curve is highly linear in behaviour. Also the films were tested for hydrophobicity (inset of Figure 3.14) by measuring the contact angle between the surface of the film and the water droplet surface by using our home built setup as discussed in *Chapter Two*. The observed contact angle is as high as 150.49°. Which indicates the film is highly hydrophobic in nature. A highly textured coating of nanoparticles on cellulose surface exhibits super hydrophobicity. In case of silver nanoparticles such behaviour has been observed [72].

![Current-Voltage curve of silver coated filter paper. Inset shows hydrophobicity of silver coated filter paper with contact angle of 150°.](image)

**Figure 3.14:** Current-Voltage curve of silver coated filter paper. Inset shows hydrophobicity of silver coated filter paper with contact angle of 150°.

### 3.3.2.2 Electrochemical Performance

Further, the silver deposited cellulose papers are used to construct supercapacitors using various electrolytes like potassium chloride (KCl), poly vinyl alcohol dissolved in orthophosphoric acid (PVA+OPA) and sodium hydroxide (NaOH). For all the
Figure 3.15: (a) Cyclic Voltammogram curves of Silver based filter paper in KCl electrolyte (b) Cyclic stability curve of silver based filter paper in KCl electrolyte.
constituted devices electrochemical properties were studied using Swagelok type two electrode configuration as discussed in Chapter Two. The cyclic voltammograms are recorded at room temperature with different scan rates ranging from 2 mV/s to 120 mV/s. The measured cyclic voltammograms for 1 M KCl electrolyte are showed in Figure 3.15(a) with different scan rates. In KCl electrolyte reversible faradaic reactions takes place between the electrode and the electrolytic ions. These faradaic reactions are responsible for the redox peaks as observed in both positive potential and the negative potential of the CV curves. Hence the pseudocapacitance charge storage mechanism is taking place in these constituted supercapacitors. Pseudocapacitance is accompanied with an electron with an electron charge-transfer between electrolyte and electrode surface from a desolvated and adsorbed ion where only one electron per charge unit is participating. This faradaic charge transfer originates by a very fast sequence of reversible redox, electroosorption or intercalation processes [73]. The adsorbed ion has no chemical reaction with the atoms of the electrode. No chemical bonds arise [74], only charge-transfer takes place. A faradaic pseudocapacitance occurs with static double-layer capacitance. This pseudocapacitance and double layer capacitance both contribute indivisible to the total capacitance of the constituted capacitor. Here the electrode is having high surface area with high conducting silver nanoparticles causes the high pseudocapacitance. High pseudocapacitance is achieved because of the reactions are very fast sequence of reversible processes with electron transfer without any phase changes of the electrode material.

Depending on the electrodes structure or surface material, pseudocapacitance can originate when specifically adsorbed cations pervade the double layer, proceeding in several one electron stages. The electrons involved in the faradaic processes are
transferred to or from valence-electron states of the redox electrode reagent. They enter the negative electrode and flow through the external circuit to the positive electrode where a second double-layer with an equal number of anions has formed. The ability of electrodes to accomplish pseudocapacitance effects by redox reactions of electroactive species, electrosorption of H or strong intercalation between the chemical affinity of electrode materials and the ions adsorbed on the electrode surface as well as on the structure and dimension of the electrode pores.

Similarly, the supercapacitor is constituted using silver deposited cellulose papers with polymer electrolyte PVA+OPA. The electrochemical properties of these devices were studied, these CV curves are shown in Figure 3.15(b) for different scan rates. Here with this polymer electrolyte the redox peaks are clearly observed in both positive potential and negative potential that shows pseudocapacitance behaviour of these devices.

Further, the devices were constructed using 1 M NaOH electrolyte. The electrochemical properties were analysed and curves are shown in Figure 3.16(a) for different scan rates. Here also the pseudocapacitance is observed. Redox peaks are clearly visible on both sides of the potential window. The peaks are not symmetric on both sides of potential window. An important observation from these CV curves of different electrolyte, there is decrease in current level as we go from KCl, PVA+OPA to NaOH electrolytes. In this case also the conversion of pure silver to silver oxide is observed. The silver cellulose papers turn black after the reaction. The same is confirmed by EDAX measurements in case of silver foams as shown and confirmed in Figure 3.10.

From Randles-Sevcik equation that is discussed in Chapter Two, as the scan rate increases the peak current ($i_p$) also increases in both sides of the potentials this is
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Figure 3.16: (a) CV curves of silver based supercapacitors in 1M NaOH electrolyte. (b) Randles-Sevcik plot for NaOH and PVA+OPA electrolyte based supercapacitors.
observed mainly in case of PVA+OPA and NaOH electrolytic supercapacitors. While in KCl electrolytic supercapacitors this behaviour is not observed. So considering the PVA+OPA and NaOH electrolytic supercapacitor electrochemical properties of CV curves, as the scan rates increases the peak current also increases respectively. Hence the peak current versus square root of scan rates plotted as shown in Figure 3.16(b). The plot clearly shows the linear behaviour for these two electrolytic devices. In both the cases of electrolytes the linear behaviour is observed only for five scan rates ranging from 2mV/s to 80 mV/s. For OPA+PVA, at higher scan rates of 100 mV/s and 120 mV/s peak current $i_p$ is less in order. Contrarily for NaOH electrolyte the last two high scan rates of 100 mV/s and 120 mV/s it is observed that the peak current $i_p$ is high in order.

From the CV curves of these electrodes with different electrolytes, the values of specific capacitance are calculated using equation 2.9 as discussed in Chapter Two. The variations of specific capacitance as a function of scan rate are plotted in Figure 3.17. Highest specific capacitance of 4664 F/g is attained for the KCl electrolyte at 2mV/s scan rate. Similarly for PVA+OPA electrolyte 1493 F/g specific capacitance is achieved for the 2 mV/s scan rate and the lowest specific capacitance achieved for NaOH electrolyte that is only 353 F/g at 2 mV/s scan rate. From Figure 3.17 it is clear that specific capacitance decreases rapidly with increase in scan rate. As mentioned it is common phenomenon in all supercapacitors. The diffusion limits the movement of electrolyte ions at higher scan rates because of the time constraint and only the outer active surface can be utilized for the charge storage resulting in a lower electrochemical utilization of electroactive materials.

Further charge discharge curves also recorded for all the constructed devices. As an example in Figure 3.18(a) is shown the curves for PVA+OPA electrolyte for
Figure 3.17: Specific capacitance versus scan rate curve of supercapacitors, constructed using silver based cellulose paper in KCl electrolyte, PVA+OPA electrolyte and NaOH electrolyte.

3000 seconds at the scan rate of 100 mV/s. It is observed that there is consistency after many cycles. The current order remained same till the last scan. Indicating the devices are stable for longer duration and longer cycles. The beginning curves are enlarged for 500 seconds for clarity which shown in Figure 3.18(b). The curves can be clearly seen with the current order. Beginning of the cycles the current is slight less and as the cycles increases current also increases and later becomes constant. The
Figure 3.18: (a) Charge/discharge curves of a supercapacitor using PVA+OPA electrolyte, measured for 3000 seconds at the scan rate of 100 mV/s. (b) Charge/discharge curves of a supercapacitor using PVA+OPA electrolyte, measured for 500 seconds at the scan rate of 100 mV/s.
constructed supercapacitors also tested for cyclic stability for 1000 cycles at 2 mV/s scan rate as shown in Figure 3.19. In which KCl showed the specific capacitance value retention after the 1000 cycle is 97.36 %. While the PVA +OPA showed the high specific capacitance retention of 98.67 % similarly f or the NaOH the lowest among the remaining electrolytes 95.43% specific capacitance retained after the 1000 cycle. The achieved values of specific capacitance retention directly depict the performance of constructed supercapacitors for the higher cycles.

Figure 3.19: Cyclic stability of all the constituted supercapacitors measured for 1000 cycles at 2 mV/s scan rate
3.4 Conclusions

Highly crystalline silver nanoparticles are firmly coated on ordinary polyurethane foams as an electrode material for electrochemical supercapacitors by a simple solution route. The resulting material is macroporous with large internal surface area, highly conducting, flexible, light weight, low cost and durable. The electrochemical performance of these electrodes is carried out by constituting symmetrical supercapacitors under open condition. The specific capacitance, cyclic stability and charging/discharging are studied using TEABF$_4$ and NaOH electrolytes. These devices exhibit pseudo-capacitance (faradaic) with excellent performance, a remarkable increase in specific capacitance has been observed as compared to the other electrode materials that are studied recently. At 2 mV/s scan rate these values are 3948 F/g and 3929 F/g for TEABF$_4$ and NaOH electrolytes, respectively, in open air condition. Hence, these are potential electrode materials for supercapacitor applications.

Silver coated cellulose electrodes are prepared by simple chemical precipitation technique. High porosity of these electrodes provides high internal specific surface area. The supercapacitors are constructed using simple Swagelok cell type two electrode configuration. Supercapacitors constituted using various electrolytes. Among them KCl showed ultrahigh specific capacitance of 4664 F/g. The supercapacitors also exhibited high cyclic stability with high specific capacitance. Hence these silver deposited electrodes can be used as electrodes in commercial energy storage systems. Both these methods include simple deposition technique, low cost. These electrodes are highly flexible, mechanically stable with high surface area. These unique properties of these electrodes improve the performance of supercapacitors.
References

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