Recycled Waste Paper- An Inexpensive Carbon Material for Supercapacitor Applications

On Job Training/Project Report

Submitted to

Department of Chemistry

Mahatma Gandhi Chitrakoot

Gramodaya Vishwavidyalaya, Chitrakoot (M.P.)

In partial fulfillment for the award of the Degree of

Master of Science

in

Industrial Chemistry

By

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Carried out at

Central Electrochemical Research Institute

(Council of Scientific & Industrial Research)
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No.14-03-03-2005-ICP 19 June 2006

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This is to certify that Mr. Rohit Misra, M.Sc., [Industrial Chemistry] student of M.G. Chitrakoot Gramoday Vishwa Vidyalaya, Chitrakoot carried out his project work at this institute on **RECYCLED WASTE PAPER - AN INEXPENSIVE MATERIAL FOR SUPER CAPACITOR APPLICATIONS** under the guidance of our Scientist Dr. D. Kalpana during MAR- JUN 2006.

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I hereby certify that the thesis entitled, **"Recycled Waste Paper- An Inexpensive Carbon Material for Supercapacitor Applications"** is the bonafied record of work done by **Mr. Rohit Misra,** in partial fulfillment of the award of the degree of **Master of Science in Industrial Chemistry,** Mahatma Gandhi Chitrakoot Gramodaya Vishwavidyalaya, Chitrakoot (M.P.), under my guidance during the period 20th March 2006- 20th June 2006.

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STATEMENT

The report entitled, "**Recycled Waste Paper- An Inexpensive Carbon Material for Supercapacitor Applications**" under the classification of Industrial Chemistry submitted for the degree of Master of Science by **Mr. Rohit Misra** is the record of the original and independent work carried out by him in Central Electrochemical Research Institute, Karaikudi- 630 006, India under the supervision of **Dr. D. Kalpana** during the period from 20th March 2006 to 20th June 2006.

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DECLARATION

I hereby declare that the work has been done by myself and no portion of the work contained in this report has been submitted in support of any application for any other degree or qualification of this or any other university or institute of higher learning.

(Rohit Misra)

ACKNOWLEDGEMENT

I am extremely grateful to my supervisor **Dr. D. Kalpana** for her guidance and encouragement during the progress of the work.

I thank **Dr. A.K. Shukla**, Director CECRI for extending the necessary facilities and encouragement. I express my sincere thanks to **Dr. V. Yegnaraman**, Head of Department, EEC Division for their kind encouragement.

I am extremely grateful to **Dr. N.G. Renganathan**, Head of Department, Battery Section for his help and encouragement throughout this study and I also thank **Dr. V.V. Giridhar** for his valuable suggestions and encouragement.

I wish to express my sense of gratitude to **Mr. Vivekanandan**, ICP Section, for helping me in administrative work.

I also thank **Ms. B.V. Bhuvanesvari, Mr. Rajendran** and other friends at CECRI for their timely help. I also thank **Dr. I.P. Tripathi**, Course Co-ordinator, Industrial Chemistry, Dept. of Chemistry, MGCGV, Chitrakoot for giving permission to carryout this project work at CECRI.

(Rohit Misra)

CONTENTS

CHAPTER.1 Introduction

A modern technological society demands the use and storage of energy on a major scale, employing large and small systems for that purpose. The discovery that electric charges could be stored on the plate of so called condenser, now referred to as a capacitor, was made in the mid eighteenth century during the period when phenomena associated with 'static electricity' were being revealed.

1.1.History

The storage of electrical charge in the interface between a metal and an electrolytic solution has been studied by chemists since the nineteenth century, but the practical use of double-layer capacitors only began in 1957, when a patent was placed by General Electric for an electrolytic capacitor using porous carbon electrodes. It was noted that the capacitor exhibited an "exceptionally high capacitance". In 1966, The Standard Oil Company, Cleveland, Ohio (SOHIO) patented a device that stored energy in the double layer interface. At this time SOHIO acknowledged that "the double-layer at the interface behaves like a capacitor of relatively high specific capacity". SOHIO went on to patent a disc-shaped capacitor in 1970 utilizing a carbon paste soaked in an electrolyte. By 1971, however, a subsequent lack of sales led SOHIO to abandon further development and license the technology to NEC. NEC went on the produce the ***first commercially successful double-layer capacitors*** under the name "Supercapacitor." These low voltage devices had a high internal resistance and were thus primarily designed for memory backup applications, finding their way into various consumer

appliances. Since then, a number of companies started producing electrochemical capacitors. Panasonic developed the “Gold capacitor” in 1978. Like those produced by NEC, these devices were also intended for use in memory backup applications. By 1987, ELNA had begun producing their own double-layer capacitor under the name “Dynacap”. The first high-power double-layer capacitors were developed by PRI. The “PRI Ultracapacitor,” developed from 1982, incorporated metal-oxide electrodes and was designed for military applications such as laser weaponry and missile guidance systems. News of these devices triggered a study by the US Department of Energy in the context of hybrid electric vehicles, and by 1992 its Ultracapacitor Development Program was underway at Maxwell Laboratories.

A number of companies around the world currently manufacture EDLCs in a commercial capacity. NEC and Panasonic in Japan have been producing EDLC components since the 1980’s. In the U.S.A, Epcos, ELNA, AVX, and Cooper produce components, while Evans and Maxwell produce integrated modules that include voltage balancing circuitry. Kold Ban International markets a Supercapacitor module designed specifically for starting internal combustion engines in cold weather. Cap-XX in Australia offers a range of components, as does Ness Capacitor Co. in Korea. In Canada, Tavrima manufactures a range of modules. ESMA in Russia sells a wide variety of EDLC modules for applications in power quality, electric vehicles, and for starting internal combustion engines.

1.2. Advantages over batteries

Supercapacitors are well suited to replace batteries in many applications. This is because at the moment their scale is comparable to that of batteries, from small ones used in cellular phones to large ones that can be found in cars. Even though supercapacitors have a lower energy density compared to batteries, they avoid many of the battery's disadvantages. Batteries have a limited number of charge/discharge cycles and take time to charge and discharge because the process involves chemical reactions with non-instantaneous rates. These chemical reactions have parasitic thermal release that causes the battery to heat up. Batteries have a limited life cycle with a degrading performance and acidic batteries are hazardous to the environment.

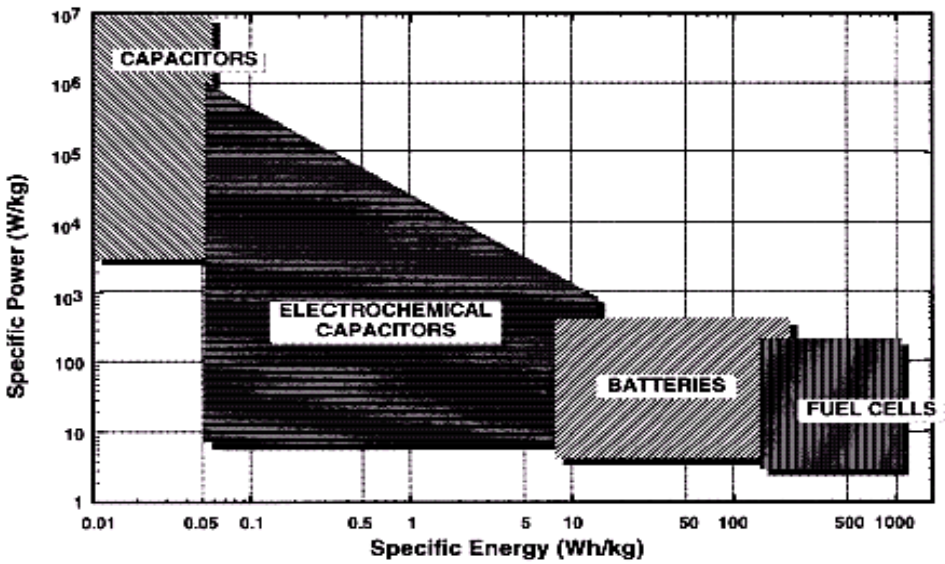


Fig. 1. Sketch of Ragone plot for various energy storage and conversion devices. The indicated areas are rough guidelines.

Supercapacitors can be charged and discharged almost an unlimited number of times. They can discharge in matters of milliseconds and are capable of producing enormous currents. Hence they are very useful in load leveling applications and fields where a sudden boost of power is needed in a fraction of a second. They do not release any thermal heat during discharge. Supercapacitors have a very long lifetime, which reduces maintenance costs. They do not release any hazardous substances that can damage the environment. Their performance does not degrade with time. Supercapacitors are extremely safe for storage as they are easily discharged. They have low internal resistances, even if many of them are coupled together. Even though they have a lower energy density, are bulkier and heavier than an equivalent battery, they have already replaced batteries in many applications due to their readiness in releasing power.

1.3. Principle of energy storage

Electrochemical capacitors store the electric energy in an electrochemical double layer (Helmholtz Layer) formed at a solid/electrolyte interface. Positive and negative ionic charges within the electrolyte accumulate at the surface of the solid electrode and compensate for the electronic charge at the electrode surface. The thickness of the double layer depends on the concentration of the electrolyte and on the size of the ions and is in the order of 5–10 A, for concentrated electrolytes. The double layer capacitance is about 10–20 mF/cm^2 for a smooth electrode in concentrated electrolyte solution and can be estimated according to equation Eq. (1)

$$C/A = \in_0 * \in_r / d \qquad (1)$$

Assuming a relative dielectric constant or of 10 for water in the double layer. *d* being the thickness of the double-layer with surface area *A*. The corresponding electric field in the electrochemical double layer is very high and assumes values of up to 106 V/cm easily. Compared to conventional capacitors where a total capacitance of pF and mF is typical, the capacitance of and the energy density stored in the electrochemical double layer is rather high per se and the idea to build a capacitor based on this effect is tempting. In order to achieve a higher capacitance the electrode surface area is additionally increased by using porous electrodes with an extremely large internal effective surface. Combination of two such electrodes gives an electrochemical capacitor of rather high capacitance. Fig. 2 shows a schematic diagram of an electrochemical double-layer capacitor consisting of a single cell with a high surface-area electrode material, which is loaded with electrolyte. The electrodes are separated by a porous separator, containing the same electrolyte as the active material. The potential drop across the cell is also shown in Fig. 2

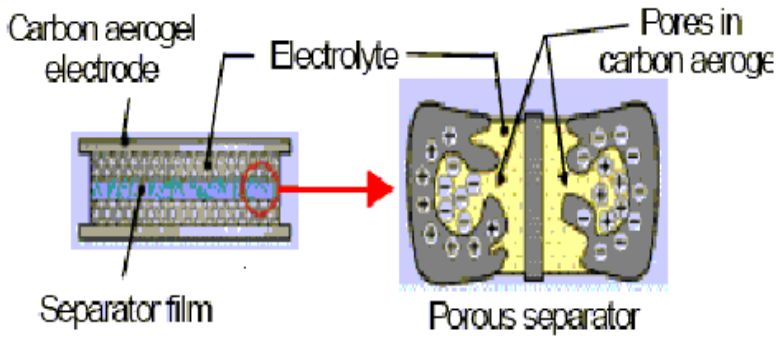


Fig. 2. Principal of a single-cell double-layer capacitor and illustration of the potential drop at the electrode: electrolyte interface

The capacitance of a single electrode can be estimated by assuming a high surface area carbon with 1000 m^2/g and a double layer capacitance of 10 mF/cm^2. This leads to a specific capacitance of 100 F/g for one electrode. For a capacitor two electrodes are needed with doubled weight and half the total capacitance ($1/C=1/C1+1/C2$) resulting in 25 F/g of active capacitor mass for this example. The difference between single electrode values and specifications given for the complete capacitor is of significant importance. Whenever specifications of an EC are given, one should indicate whether the values correspond to single electrode measurement or are calculated for a complete capacitor. The difference between these two situations is a factor of four and therefore of significant importance. The maximum energy stored in such a capacitor is given by

$$W=1/2\ C\ U_0^2 \quad (2)$$

With a cell voltage U_0 of 1 V (aqueous electrolyte) one obtains a specific energy of about 3.5 Wh/kg of active mass. Using an organic electrolyte with a typical cell voltage of 2.3 V one obtains about 18 Wh/kg of active mass. These values are considerably lower than those obtained for available batteries but much higher than for conventional capacitors. It should be mentioned that the above values depend on the double layer capacitance, the specific surface area of the respective electrode material, the wetting behavior of the pores, and on the nominal cell voltage.

1.4.Applications

Electrochemical supercapacitors are still relatively new devices that have yet to experience widespread use. This has originally been due to their limited power and energy capabilities, and they therefore only saw use in low-power, low-energy

applications such as for memory backup. Recently, however, significant advances have been made in improving both energy and power density, and new applications for EDLCs are being developed at an increasing rate. The following are a number of possible applications for the EDLC as an energy storage element.

1.4.1.Memory Backup

Computer memories, electric clocks and other electronic devices needs back up of their control functions when the source power is interrupted. Supercapacitors are more reliable and faster working back-up power sources than batteries. Low voltage supercapacitors are used in variety of products.

1.4.2.Electric vehicles

A combination of a high energy density device such as a fuel cell to provide the average load requirements and a high-power device such as a Supercapacitor bank to meet the peak load requirements that result from accelerating or climbing up hills. The utilization of supercaps also makes regenerative braking possible. Because the supercap bank can be recharged, it is possible to store some of the energy of an already moving vehicle, and therefore increase the fuel efficiency of the EV. Power flows in an EV test drive for fuel cell, super cap, and inverter.

1.4.3.Power quality

The Supercapacitor is still a young technology that has yet to experience widespread implementation. It does, however, enjoy a great amount of attention with regards to its potential application in a number of areas. A traditionally high ESR has

previously limited EDLCs to memory backup applications, and they have been used in such settings for many years. Recent reductions in ESR have improved the power capabilities of supercapacitors, however, and they are now well suited to pulsed-current applications such as mobile phones and electrical actuators. They can also perform a load-leveling function when used in combination with batteries, providing peak power in devices such as laptops, reducing power demands on the battery and therefore extending battery lifetime. EDLCs can be used in a similar manner in EVs, providing power for acceleration and allowing a primary power source such as a fuel cell to supply the average power. When used in EVs supercapacitors also allow for energy to be recuperated during braking, improving the efficiency of the vehicle. Supercapacitors can also be used on their own to provide the energy needed by power quality systems that ensure reliable and disturbance free power distribution. EDLCs then supply the energy needed to inject power into the distribution line and thus compensate for any voltage fluctuations. They can also be used to design systems that grant adjustable-speed drives the ability to ride-through temporary power supply disturbances. Such applications are vital in industrial settings, and can prevent material and financial losses that could occur due to machine downtime.

1.4.4.Other

Many applications are demanding local storage or local generation of electric energy. This may be required since they are in portable or remote equipment, since the supply of power may be interrupted or since the main power supply is not able to deliver the peak power. Local generation of energy (Diesel generator, fuel cell, gas turbine, photovoltaics, etc.) normally means a more complex system than a storage system, but it

is most adequate if a large amount of energy is needed for a long time. Storage of electric energy can be done in electric fields (capacitors), by means of chemical reactions (batteries), in magnetic fields (SMES: superconducting magnetic energy storage) or by transferring the electric energy to mechanical (flywheel) or potential (pumped hydro) energy or to pressure. The choice of the energy storage device should be adequate for the application. Similarities and differences between batteries and electrochemical capacitors were discussed by Conway et al.. The ideal applications for ECs are all those demanding energy for a duration in the time range 10^{-2} s $\leq t \leq 10^{2}$ s. For those applications, as well for batteries as for conventional capacitors, the ratio of stored energy to available power is unfavorable and the devices have to be over-dimensioned due to either the power or energy demands.

The needs for long lifetime, for many charge-discharge cycles (e.g., in combination with photovoltaic) or for fast recharging rates may increase the time range to days and weeks. The poor energy density of low voltage capacitors makes ECs also attractive for pulse power applications in the ms range. The basic technology of ECs with carbon electrodes is independent of polarity. Nevertheless, present Ecs are not suitable for AC applications and for applications involving a high ripple current. Their internal resistance is higher than the one of conventional capacitors and thermal degradation may occur. In addition, some manufacturers use asymmetric electrode systems or have special treatments of one of the two electrodes causing a polarity of the devices. Most ECs are short circuit proven. On one hand, the larger internal resistance in comparison to conventional capacitors limits the peak power. On the other hand, the smaller amount of energy stored in comparison to batteries allows only a limited heating of the ECs, so that

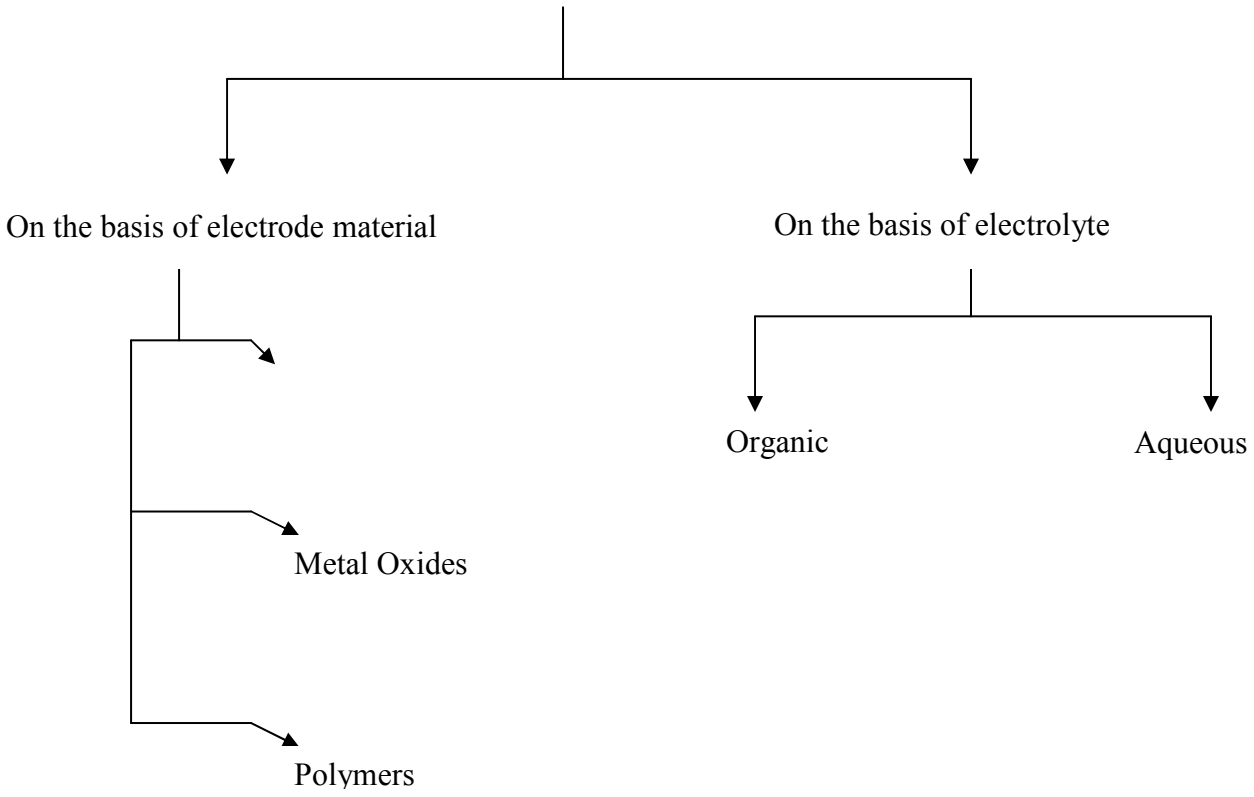
self-ignition does not occur. Another important advantage of ECs is that in general, they do not contain hazardous or toxic materials and that they are easy to dispose. They do not need any servicing during their life and can withstand a huge number of charge-discharge cycles. In a properly designed system, cycling efficiency is 95% and higher.

They are applicable in a large temperature range. Particularly at low temperature, they substantially outperform conventional batteries. Short-term (ms–s) over-voltage is in general not critical to the devices. If the applied voltage exceeds the nominal voltage for longer duration, the lifetime of the EC will be shorted. Gas may be produced which can cause leakage or rupture of the device. The characteristic time for self-discharge is in the order of days to months. The low voltage of the unit cells allows an easy adoption to the desired voltage level by connecting cells into series and a modular construction of large banks.

1.5. Classification of electrochemical capacitors

Electrochemical capacitors may be distinguished by several criteria such as the electrode material utilized, the electrolyte, or the cell design. With respect to electrode materials there are three main categories: carbon based, metal oxides and polymeric materials. A comprehensive review of possible electrode materials suitable for Electrochemical capacitors are given below.

Electrochemical Capacitors



Carbon

Carbon in various modifications is the electrode material used most frequently for electrodes of electrochemical capacitors. Reasons for using carbon are manifold such as (i) low cost, (ii) high surface area, (iii) availability, and last but not least (iv) established electrode production technologies. Carbons are available with a specific surface area of up to 2500 m^2/g as powders, woven cloths, felts, or fibers. Charge storage on carbon electrodes is predominantly capacitive in the electrochemical double layer. Carbon based

electrochemical capacitors come close to what one would call an electrochemical double layer capacitor. There are however contributions from surface functional groups which are in general present on activated carbons and which can be charged and discharged giving rise to pseudocapacitance. This corresponding pseudocapacitance is significantly reduced in organic electrolyte because protons are not available. The effect of surface functional groups containing oxygen on the stability of carbon electrodes in EC using organic electrolyte was investigated by Nakamura et al. These are found that the stability of the activated carbon increases with the oxygen content when the carbon is used for the anode and decreases when used for the cathode. In general one can observe that both the stability and conductivity of the activated high surface area carbon decrease with increasing surface area.

Metal oxides

The cyclic voltammogram of RuO_2 (and also IrO_2) electrodes have an almost rectangular shape and exhibit good capacitor behavior [11,12]. However, the shape of the CV is not a consequence of pure double layer charging, but of a sequence of redox reactions occurring in the metallic oxide. The valence state of Ru may change from III to VI within a potential window of slightly >1 V. The ratio of surface charging to bulk processes was nicely separated by Trasatti [11]. In aqueous acid electrolytes the fundamental charge storage process is proton insertion into the bulk material. Very high specific capacitance of up to 750 F/g was reported for RuO_2 prepared at relatively low temperatures [13]. Conducting metal oxides like RuO_2 or IrO_2 were the favored electrode materials in early EC s used for space or military applications [14]. The high specific capacitance in combination with low resistance resulted in very high specific powers.

These capacitors, however, turned out to be too expensive. A rough calculation of the capacitor cost showed that 90% of the cost resides in the electrode material. In addition, these capacitor materials are only suitable for aqueous electrolytes, thus limiting the nominal cell voltage to 1 V. Several attempts were undertaken to keep the advantage of the material properties of such metal oxides at reduced cost. The dilution of the costly noble metal by forming perovskites was investigated by Guther et al. [15]. Other forms of metal compounds such as nitrides were investigated by Liu et al. [16]. However, these materials are far from being commercially used in ECs.

Polymers

Polymeric materials, such as *p*- and *n*-dopable poly(3-arylthiopene), *p*-doped poly(pyrrole), poly(3-methylthiophene), or poly(1,5-diaminoanthraquinone)have been suggested by several authors [17–19] as electrodes for electrochemical capacitors. The typical cyclic voltammogram of a polymer however is in general not of rectangular shape, as is expected for a typical capacitor, but exhibits a current peak at the respective redox potential of the polymer. In order to be able to use one and the same electrode material on both capacitor electrodes polymers with a cathodic and an anodic redox process were utilized recently [19]. Using a polymeric material for electrochemical capacitor electrodes gives rise to a debate as to whether such devices should still be called capacitors or whether they are better described as batteries. In terms of the voltage transient during charge and discharge and with respect to the CV they are batteries. Compared to metallic oxides, however, the term capacitor is justified. The difference being only that the metallic oxides exhibit a series of redox potentials giving rise to an

almost rectangular CV while the polymer typically has only one redox peak. For such capacitors rather high energy density and power density have been reported [19]. The long-term stability during cycling, however, may be a problem. Swelling and shrinking of electroactive polymers is well known and may lead to degradation during cycling.

1.6.Aim of the work

Paper and paper products account for more than one third of the materials discarded into India's waste stream. Today it is widely recognized that the volume of paper products we discard must be dramatically reduced soon, as the sustainability of the forest resource is also a concern. The obvious way to reduce the amount of paper waste being discarded and to conserve our forest resources is to recycle more of our waste paper. Nowadays, most supermarkets and high street stationers sell a range of recycled products such as writing paper, note books, file paper, diaries with recycled paper contents, calendars, paper table clothes and napkins, tissues, toilet rolls, kitchen paper and other items. For the first time, we have recycled the old newspaper and used as an active material for Supercapacitor applications.

1.7.Conclusion

For most of the applications described above, solutions with conventional devices, i.e. either batteries or capacitors exist. Those devices are available on the market for more then 100 years, have technically been optimized, and use elaborated manufacturing methods. Although the energy to power ratio of ECs is often more adequate, batteries or capacitors are chosen for commercial reasons. Therefore ECs have

to be cost competitive. For electronic applications, it has been shown that it is possible to produce ECs at high volume, low cost, and having high reliability.

In comparison to flywheel, SMES, and battery systems, which also have high specific energy and power, ECs offer distinct advantages. ECs have no rotating parts, are very safe devices, do not require cooling and other auxiliary installations, have a large modularity with respect to voltage and capacitance, low self-discharge, high cycle-life, can be produced at low costs, do not need any servicing, and do not contain any environmentally dangerous materials or heavy metals.

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CHAPTER.2 Experimental methods and Theory

A brief description of the various characterization techniques used in the present work has been presented in this chapter. Scanning Electron microscopy (SEM) has been used for morphological determination and phase analysis. The details of other techniques such as, TG & Differential Thermal Analyzer (DTA), Cyclic Voltammetry, Impedance analyzer and Galvanostatic Charge Discharge cycler, used for the investigations are also given.

2.1.Differential thermal analyzer (DTA)

This is a technique in which the temperature of the experimental sample is compared with the temperature of a reference sample (thermally inert materials usually Al_2O_3) and the difference of the temperature is recorded as a function of the sample temperature as the sample is heated or cooled at a uniform rate.

In Differential Thermal Analysis (DTA) two samples of similar thermal capacity are heated or cooled at the same uniform rate. Thermocouples measuring the temperatures of the two samples are connected in opposition so that the temperature difference between the samples is measured. If neither of the samples undergoes a phase change, the difference in temperature will ideally be zero throughout the entire heating range. However, if one sample is inert, while the other undergoes a phase change, say, crystallization, then the evolution or absorption of latent heat will result in a temperature difference between the samples. If the difference in temperature is recorded as a function

of temperature, for an unknown sample, any thermal effect such as crystallization or dissolution may be detected.

Dry fine powders of Al_2O_3 were used as the reference material. Temperature of DTA was calibrated using Al as the standard . PERKIN ELMER DTA 1700 system was used for the investigations. The computer communicates with the DTA instrument through the microprocessor based controller 7/4 system, which is incorporated in the instrument. The maximum furnace temperature possible with the equipment is 1773 K.

2.2.Scanning electron microscope

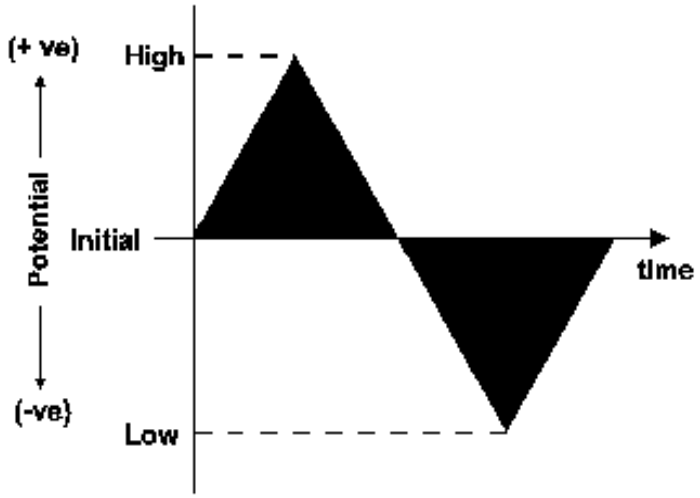
The scanning electron microscope (SEM) employs a beam of electrons directed at the specimen, which is used to study the surface structure of bulk specimens. The fine beam of electrons is scanned across the specimen by the scan coils, while a detector counts the number of low energy secondary electrons, given off from each point on the surface. The SEM produces images of high resolution, which means that closely spaced features can be examined at a high magnification. The electron beam and the cathode ray tube (CRT) spot are both scanned in a similar way to a television receiver. The scanning electron microscope normally has the facility for detecting secondary electrons and back-scattered electrons [9]. In the SEM the object itself is scanned with the electron beam and the electrons emitted from the surface are collected and amplified to form the video signal. The HITACHI, S-3000H -Scanning Electron Microscope has used for studying the morphology of the samples.

2.3.Cyclic Voltammetry

A simple potential wave form that is often used in electrochemical experiments is the linear wave form i.e., the potential is continuously changed as a linear function of time. The rate of change of potential with time is referred to as the scan rate (v).

The simplest technique that uses this wave form is ***linear sweep voltammetry***. The potential range is scanned in one direction, starting at the initial potential and finishing at the final potential. A more commonly used variation of the technique is ***cyclic voltammetry***, in which the direction of the potential is reversed at the end of the first scan. Thus, the waveform is usually of the form of an isosceles triangle. This has the advantage that the product of the electron transfer reaction that occurred in the forward scan can be probed again in the reverse scan. In addition, it is a powerful tool for the determination of formal redox potentials, detection of chemical reactions that precede or follow the electrochemical reaction and evaluation of electron transfer kinetics. An example wave form that can be used in cyclic voltammetry is shown below: In this example it is assumed that only the reduced form of the species is initially present.

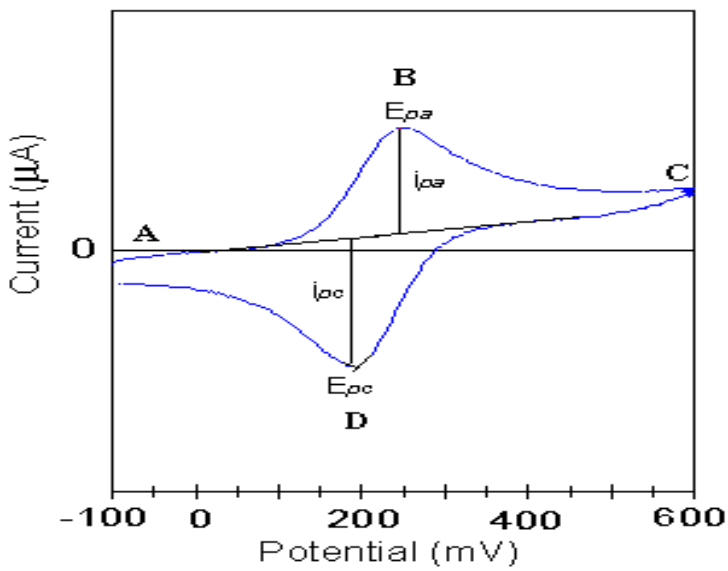
Thus, a positive potential scan is chosen for the first half cycle during which an anodic current is observed. Because the solution is quiescent, the product generated during the forward scan is available at the surface of the electrode for the reverse scan resulting in a cathodic current.



Complex wave form composed of two isosceles triangles. The voltage is first held at the initial potential where no electrolysis occurs and hence no faradaic current flows. As the voltage is scanned in the positive direction, so the reduced compound is oxidised at the electrode surface. At a particular set value, the scan direction is reversed and the material that was oxidised in the outward excursion is then reduced. Once the voltage is returned to the initial value, the experiment can be terminated. In this example however a further voltage excursion takes place to more negative (more reducing) values. This may be useful in probing for other species present in the sample or for investigating any electroactive products formed as a result of the first voltage excursion.

The basic shape of the current response for a cyclic voltammetry experiment is shown below. At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidised form (point A). As the redox potential is approached, there is a net anodic current which increases

exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidised to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependence is **q**t resulting in an asymmetric peak shape.Upon reversal of the scan (point C), the current continues to decay with a **q**t until the potential nears the redox potential. At this point, a net reduction of O to R occurs which causes a cathodic current which eventually produces a peak shaped response (point D).



If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be ***reversible***. In other words, equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst Equation. Under these conditions, the following parameters characterize the cyclic voltammogram of the redox process.

- The peak potential separation (Epa - Epc) is equal to 57/n mV for all scan rates where n is the number of electron equivalents transferred during the redox process.
- The peak width is equal to 28.5/n mV for all scan rates.
- The peak current ratio (ipa/ipc) is equal to 1 for all scan rates.
- The peak current function increases linearly as a function of the square root of *v*.

The situation is very different when the redox reaction is not reversible, when chemical reactions are coupled to the redox process or when adsorption of either reactants or products occurs. In fact, it is these "non-ideal" situations which are usually of greatest chemical interest and for which the diagnostic properties of cyclic voltammetry are particularly suited.

2.4.Impedance spectroscopy

Impedance spectroscopy is a technique used in materials research and development because it involves relatively simple electrical measurements, which can be readily automated, and also the results may often be correlated with many complex material properties. Impedance analyzer can be used to measure the mass transport, rates of chemical reactions, corrosion, dielectric properties, microstructure and the composition influence on the conductance of solids. This technique can also be used to predict the various aspects of the performance of chemical sensors and fuel cells, and it has been used extensively to investigate membrane behaviour in living cells. By using impedance spectroscopy the interfacial and bulk phenomena can be easily separated.

Impedance is a more general concept than the resistance because it takes phase difference into account, and it has become a fundamental branch of the tree of electrical measurements. Impedance spectroscopy or a.c.spectroscopy is the study of the dielectric properties as a function of frequency. The general approach of an impedance spectroscopy is to apply an electrical signal namely a known voltage or current to the electrodes and observe the resulting current or voltage. It is assumed that the properties of the electrode material are time invariant, and it is one of the basic purposes of the impedance spectroscopy to determine these properties and their inter relationship. The Solartron SI 1260 has used impedance/gain phase analyzer with a frequency range 0.1 μHz to 32 MHz and fully automated with a personal computer to study the electrical transport properties of the samples.

2.4.1.General a.c. circuit theory

The applied a.c. voltage and the measured current in an electrical network are given by

$$V(t) = V_0 \exp(j\omega t)$$

$$I(t) = I_0 \exp(j\omega t + \phi)$$

where ϕ is the phase angle and j = $\sqrt{-1}$.

The impedance *Z(ω)* of the circuit is given by

$$Z(\omega) = V(t)/I(t) = |Z|\exp(-j\phi) = |Z|\cos\phi - j|Z|\sin\phi$$

$$= Z_r - jZ_i$$

where *Zr* and *Zi* are the real and imaginary parts of the complex impedance. The relations that relate these two quantities are

$$|Z| = \sqrt{Z_r^2 + Z_i^2}$$

and $$\tan\phi = Z_i / Z_r$$

Admittance $Y = 1/Z(\omega) = G + jB$

Conductance $G = Z_r/(Z_r^2 + Z_i^2) = \frac{1}{R}$

Susceptance $B = Z_i/(Z_r^2 + Z_i^2) = \omega C$

The real and imaginary parts of the impedance/admittance of the samples are plotted in a complex plane and their frequency dispersion curves possess information about the effects of electrode - electrolyte interface, grain and grain boundary resistances etc. In a parallel RC combination the real and imaginary parts are

$$Z_r = R/(1 + (\omega RC)^2)$$

and $$Z_i = \omega R^2 C/(1 + (\omega RC)^2)$$

Elimination of ω from the above equations leads to,

$$\left(Z_r - \frac{R}{2}\right)^2 + Z_i^2 = (R/2)^2$$

which is the equation of a circle of radius $R/2$ with center at $(R/2,0)$.

2.5.Galvanostatic Charge-Discharge Test

One of the main advantages of the EDLC when compared to the battery is the excellent cycle stability. This parameter is determined by galvanostatically charging/discharging the cell at constant currents between defined limiting current. The specific capacitance of the carbon materials were estimated from the charge-discharge

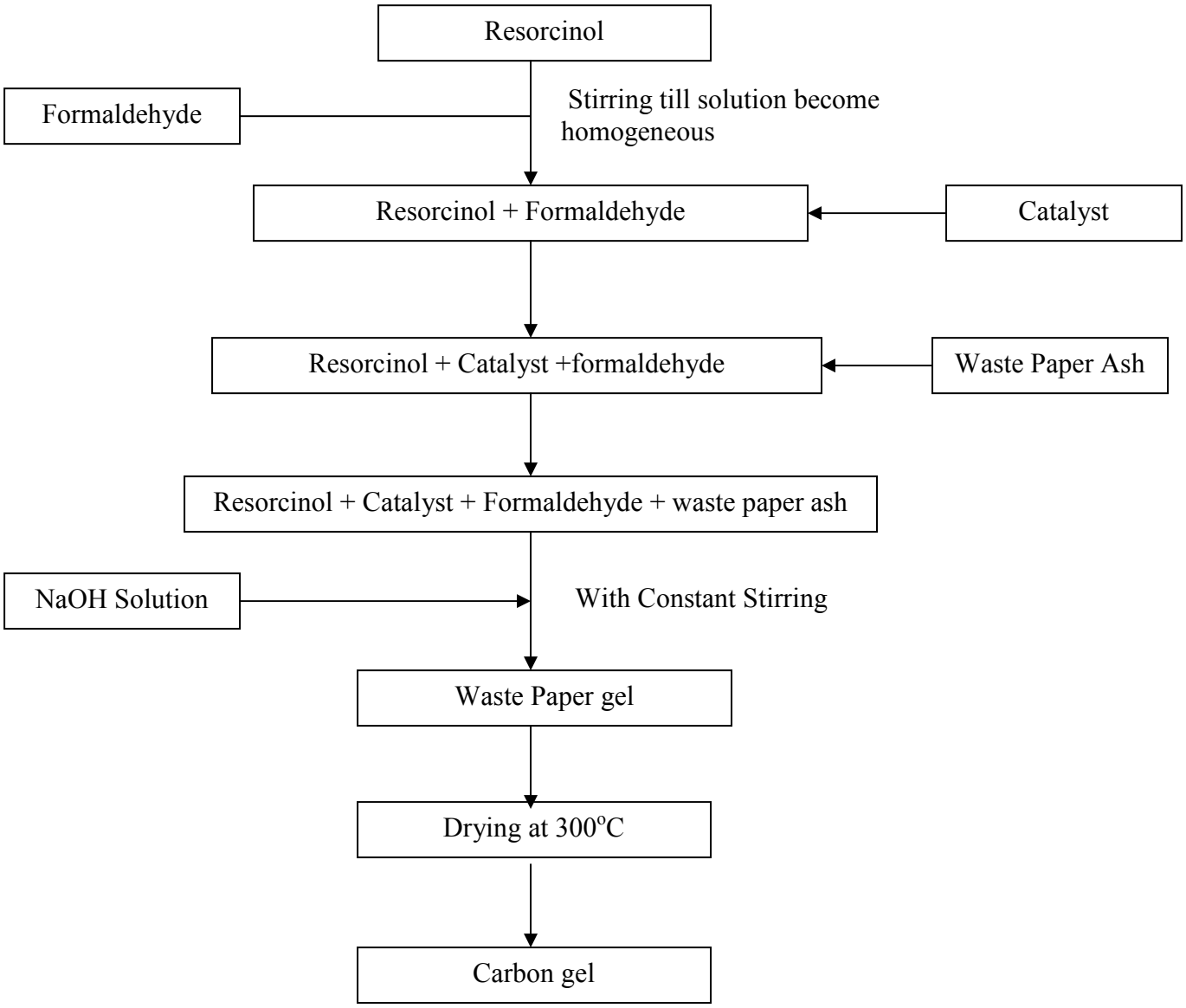
data. This set up also allows to define a series of different currents and to perform a series of different currents and to perform a series of different charge/discharge cycle which enables the calculation of the power-energy relation (Ragone plot) at various current densities.

2.6.Conclusion

The theory of cyclic voltammetry and impedance spectroscopy has been given in detail. The details of the experimental techniques such as TG/DTA, SEM and Galvanostatic charge/discharge experiments are given in this chapter.

The synthesis of carbon gel is as follows: 1:2 molar ratio of 1,3 dihydroxybenzene and formaldehyde were mixed well and after forming a homogeneous solution sodium carbonate was added as a catalyst. A fixed weight ratio of waste paper ash dissolved in acetone was added in the solution. 50% of NaOH was added and stirred well until it forms a hydro gel. After the formation of gel, it was washed by water to remove excess sodium and dried in air at 300° C for 1 hour. The temperature of pyrolysis is an important parameter in preparation of this kind of gel. The temperature was selected from TG /DTA of carbon gel. From these data it is seen that there is a gradient at 200-300° C and hence the temperature of pyrolysis was restricted to 300 ^{o}C.

The morphology and visible spectrum were investigated by scanning electron microscopy (SEM- HITACHI, S-3000H). The organic gel powder was mixed with N-N' Methyl Pyrollidene binder and the suspension was pasted on a steel substrate and dried at 80°C. The loading mass of the carbon gel was 0.02 gm/cm^2. The cell fabricated with the symmetric carbon composite electrodes separated by using a polypropylene separator. 0.1 M H_2SO_4 was used as an electrolyte. The capacitance behavior of the electrodes were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy and galvanostatic charge/discharge cycle tests. Cyclic voltammetry was measured using Electrochemical Analyzer - BAS 100 B. Galvanostatic cycling was performed using a computerized multichannel Battery Cycler Model WBCS 3000. PERKIN ELMER DTA 1700 system was used for the TG-DTA investigations .



Flow Chart for the Synthesis of Carbon Gel

The TG analysis reveals the effect of pyrolysis conditions and this indicates two major peaks of weight loss. The first peak at 100°C corresponds to the extraction of remaining solvent (acetone) or the elimination of H_2O formed by condensation of –OH groups. The second peak at 300°C may be due to desorption of adsorbed organic compounds. The elimination of carbon, oxygen and hydrogen continues at higher temperature viz. (500°C) and develops the microporosity by creation of new microporous or broadening of existing ones.

The texture of the carbon material is easily tailored in the mesoporous range by fixing the initial pH of the precursor solution. The pH is adjusted to be greater than 7. the sample is exclusively microporous after drying and becomes quasi, non porous after pyrolysis. The sample texture can be adjusted as desired between these two extremes.

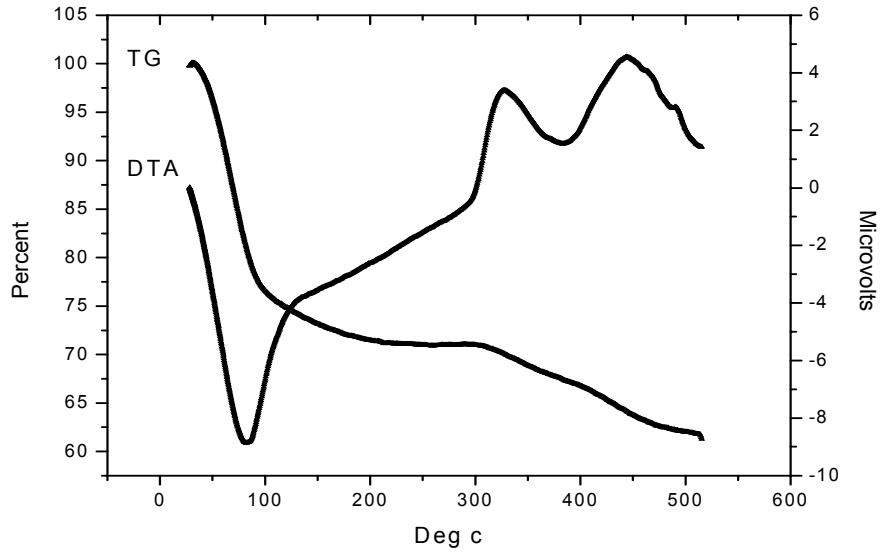


Fig.1 TG and DTA of carbon organic gel

The morphology of the gel was investigated by scanning electron microscopy (HITACHI, S-3000H). Fig.2a&b shows the SEM image of as prepared carbon gel network before cycling. The particle diameter is in the range of 20-50 μm. The pore diameters are slightly bigger than the particle diameter and the pore distribution is uniform. It is evident from the SEM that the particles are more compact and uniformly distributed and it is assumed that there is a good network of interconnected pores and these pores are in the mesoporous range. At the same time the porosity is still retained. Fig.3a,b shows SEM of the sample after 3 lakh cycles. It shows that the connectivity between the grains increases during cycling thus enhances the cyclic stability.

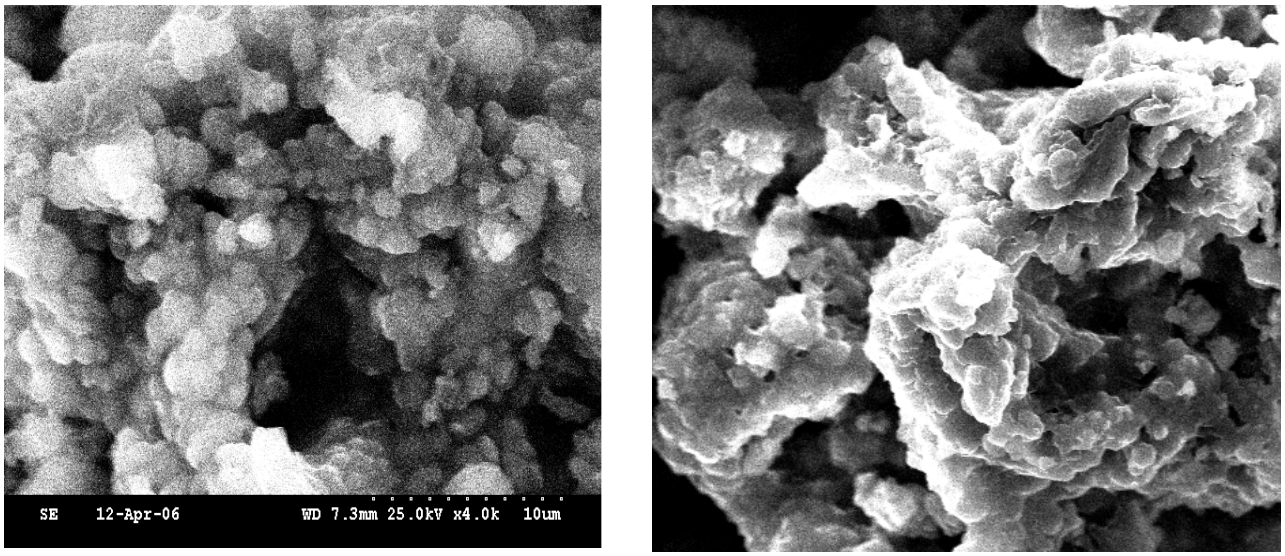


Fig. 2a&b SEM of carbon organic gel before cycling

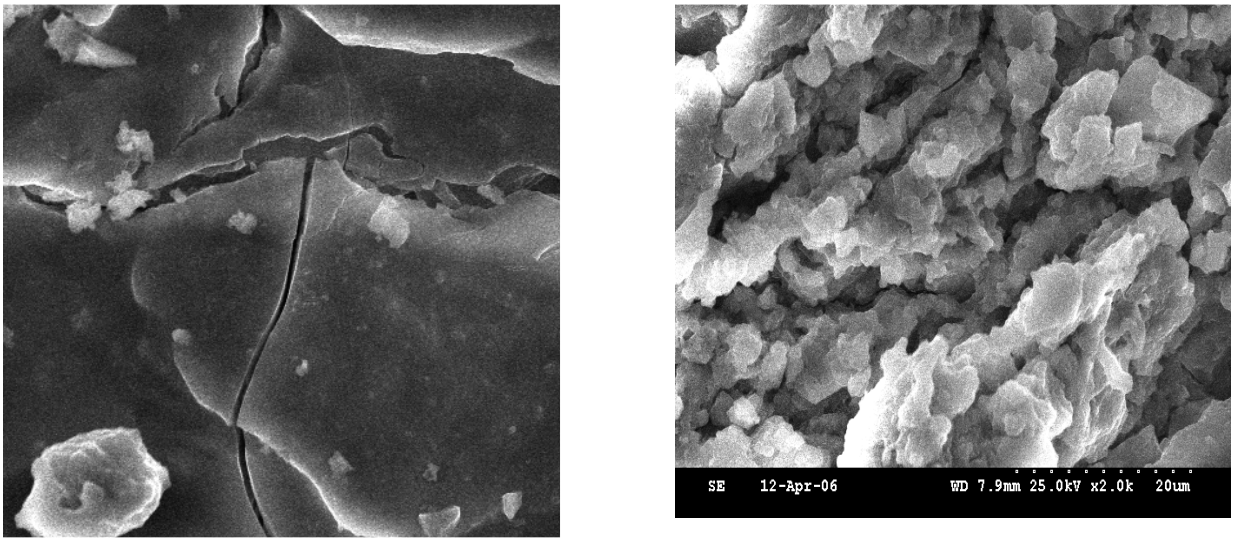


Fig. 3a&b SEM of carbon organic gel after 3 lakh cycles

The electrochemical behavior of R.F. carbon gel has been characterized by CV. Highlight of the present work is the voltage sweep done at two stages one is the usual range –1000 to +1000 mV and another –3000 to +3000 mV. In the second range this report is the first its kind reported in these gels that the potential window can be increased to ~5 V and this is highly reproducible even after 5 lakh cycles which is not reported so far. Although the specific capacitance value is comparatively low 40 F/g to the reported value of 95 F/g the voltage window has been enhanced nearly to 4 to 5 suggest that energy density of these system can be increased. This variation in capacitance can be ascribed to the different conductive percolation developed during pyrolysis stage. Doubling the specific capacitance can be done by tailor making the preparation of

supercapacitor electrode by template technique which is the future aim of the present investigation.

An apparent feature of the CV's suggests that there is simultaneous redox and capacitive behavior and these behaviors are highly reversible as indicated in both the CV's. The presence of reversible peaks -0.5 and +0.5 V can be ascribed to the oxidation of carbonyl and reduction of alcoholic groups that's are formed on the electrode surface. The nature of voltammogram does not change with increasing the number of cycles, where pyrolysis temperature of the gel impedes reversibility and this reversibility helps in getting more then 8 lakh cycles. The reversibility is still maintained even in the range –3 to +3 V. But the specific capacitance is very low ~ 80 mF/g and this is highly reproducible even after 8 lakh cycles.

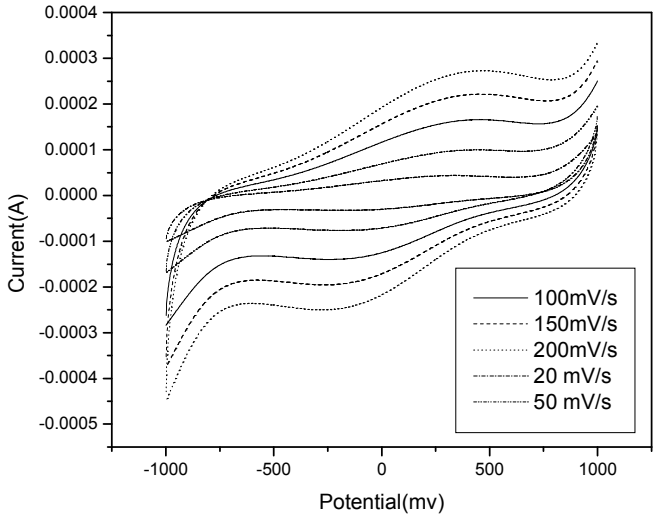


Fig.4a Cyclic Voltammetry of carbon organic gel before cycling at various scan rate

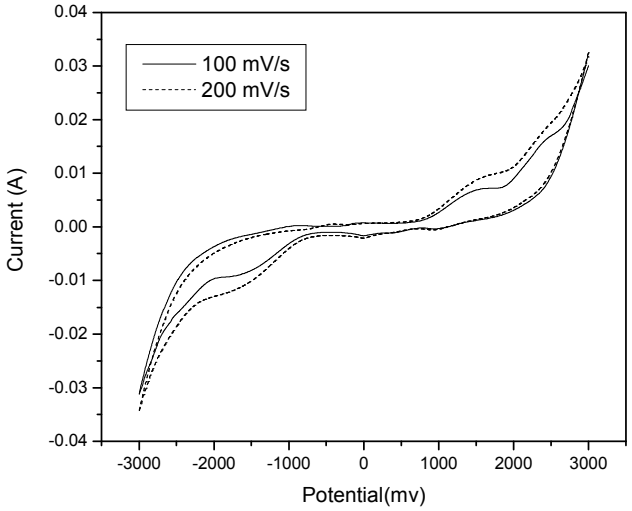


Fig.4b Cyclic Voltammetry of carbon organic gel at various scan rate after 3 lakh cycles

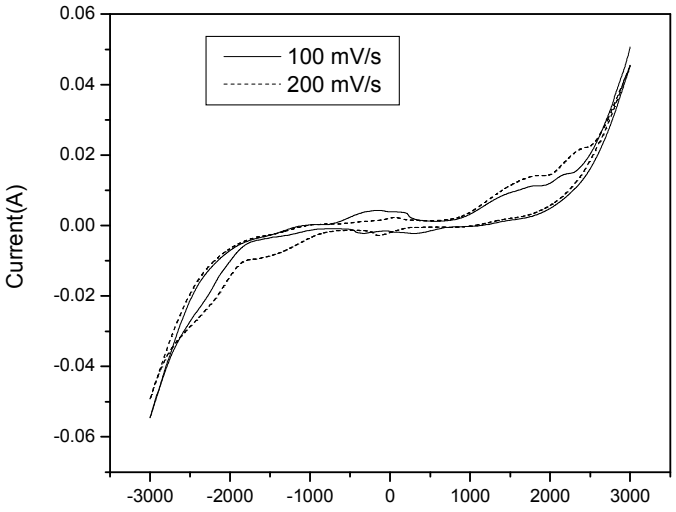


Fig.4c Cyclic Voltammetry of carbon organic gel at various scan rate after 5 lakh cycles

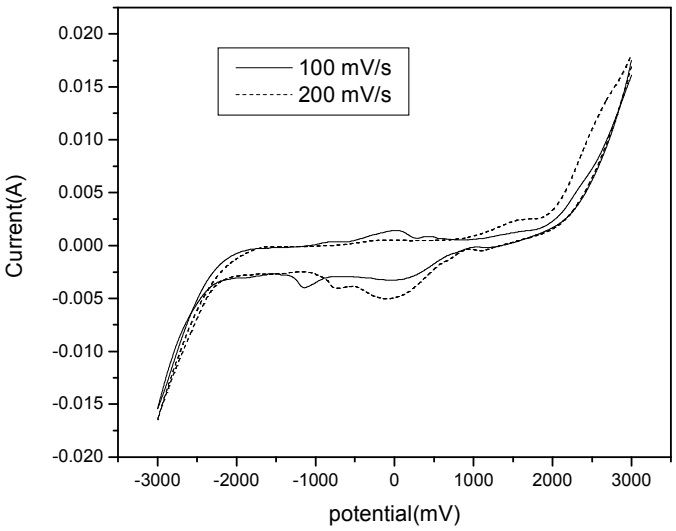


Fig.4d Cyclic Voltammetry of carbon organic gel at various scan rate after 8 lakh cycles

Fig.5.a&b shows an impedance spectrum of as prepared R.F. carbon gel, and after 3 lakh cycles. The resistance is low for the samples as prepared compound to the one which is cycled several lakh times. This is expected because during cycling the redox products formed increases resistance and double layer capacitance decreases and still it is higher 80 mF/g compare to capacitance value reported as 4.5 mF.

Impedance measurements did reveal the real picture of capacitive behavior of the carbon composites. As prepared sample, the solution resistance is low compared to charge transfer resistance. This is understandable, that, as prepared sample is not capacitative. It requires some formation cycles since it is highly crystalline. But when it is cycled the carbon tends to become amorphous and the surface area has also been increased. The carbon is activated by the formation of edge plane activators and thus adsorption of OH groups becomes possible which is electroactive and thus redox behavior is induced and capacitance is increased with cycling.

This is reflected from the impedance diagram (after 3 lakh cycles) eventhough the second process is diffusion controlled which has got high charge transfer resistance. This is understandable; that electroactive species trapped inside the mesopores has got diffusion-limited reaction, reflecting in the increase of charge transfer resistance for the redox active species.

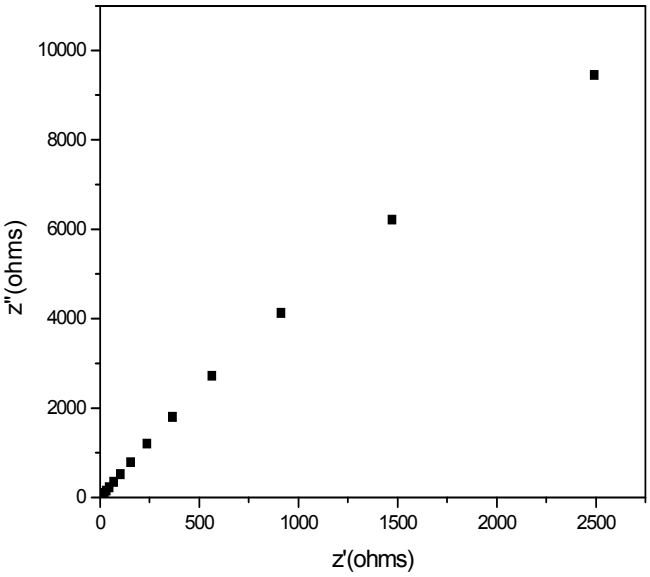


Fig.5a. Nyquist impedance spectroscopy of as prepared sample

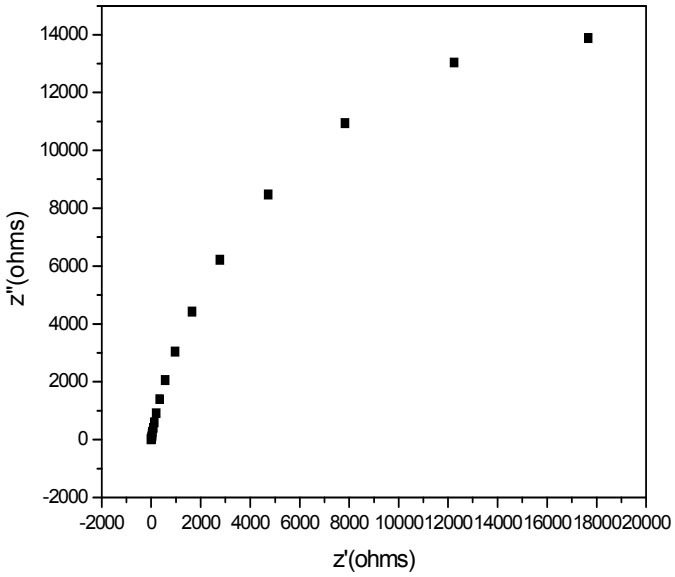


Fig.5b. Nyquist impedance spectroscopy of RF gel after 3 lakh cycles

Fig. 6 shows the galvanostatic charge-discharge curves of carbon gel based cell in 0.1 M H_2SO_4. The cell was run at various current densities like 50, 75, 100 and 150 mA/cm^2. The curves are linear indicating that the electrodes behave as a capacitor and

have good cyclic stability even after 8 lakh cycles. The cells run at 150 mA/cm^2 current density upto 8 lakh cycles with minimum IR drop.

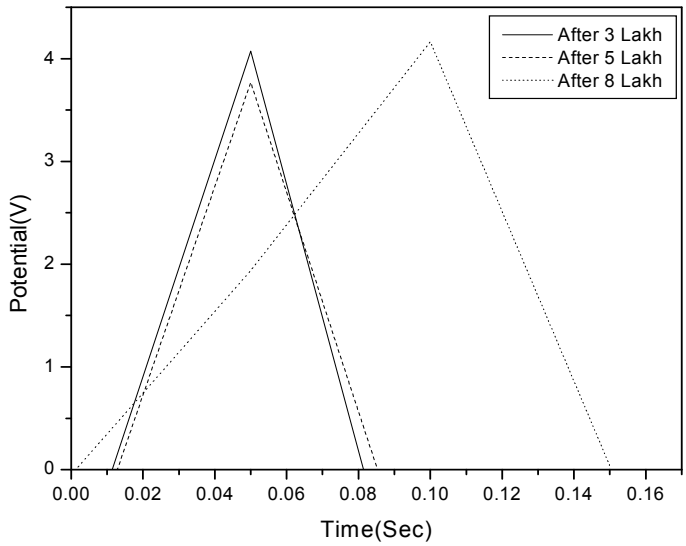


Fig.6 Galvanostatic Charge-discharge Cycles of carbon gel at 150 mA/cm^2 current density for 3 and 5 lakh cycles and at 50 mA/cm^2 current density for 8lakh cycles

The specific capacitance of the supercapacitor can be calculated by using the following equation.

$$C = (i \times \Delta t)/(W \times \Delta V) \quad (F/g)$$

Where C is the capacitance (F/g), i is discharge current, Δt is the discharging time, W is the weight of the sample and ΔV is the voltage variation in the time range measured. Based on the experimental results of Fig. 6, it can be found through the above calculation that the highest specific capacitance of the supercapacitor was 300 F/g. Higher reactant densities in the present investigation are another important feature for getting higher

capacitance and unlimited cycle life. The increase in density of the reactants in the initial solution results in decrease in the surface area. The surface area of these gels has a weak dependence in the acidic range but at a pH higher than 7 the surface area diminishes completely. However pore volume of these gels increases when increasing the pH and hence the electrochemical double layer capacitance is expected to be increased.

Summary

The present study presents the current status of research into the production of active carbons from environmental applications using waste newspaper. A number of studies have been performed to investigate the pyrolysis of waste paper ash to carbon gel.

Although several studies report the production of carbon from waste tyre, bamboo, coconut shell, this study is first of its kind that for the first time, the waste newspapers have been used as a raw material for supercapacitor electrodes. A cheap raw material, and a simple method of preparation make this carbon gel more economically attractive. By carbonizing a waste paper a new carbon-carbon composite as electrode material was prepared through RF gel. The surface morphology and electrochemical characteristics of the carbon composite were investigated by Scanning Electron Microscopy, Cyclic Voltammetry, Electrochemical impedance spectroscopy and galvanostatic charge-discharge cycle tests with various current densities. The SEM study reveals that the connectivity between the grains increases during cycling thus enhances the cyclic stasitity. The CV's suggests that there is simultaneous redox and capacitive behavior and these behaviors are highly reversible even after 8 lakh cycles. The reversibility was still maintained even in the range – 3 V to + 3 V. The charge/discharge cycle tests reveal the cycle stasitity and delivered more then 8 lakh cycles at 100 mA/cm^2. The maximum specific capacitance of 300 F/g was obtained at 150 mA/cm^2 current density. These results imply that this newspaper based carbon gel be used as potential candidate for supercapacitors.