Prabhu Megharaj, hereby submit this original work as part of the requirements for
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Electrochemical Study of Ceramic (BaTiO3 based)/ Polymer Composite
electrodes for Supercapacitor applications

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Electrochemical Study of Ceramic (BaTiO$_3$ based)/ Polymer Composite electrodes for Supercapacitor applications

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Abstract

Electrochemical Supercapacitors are high energy storage devices compared to the conventional capacitors. Supercapacitors work on the simple phenomena of electrostatics and electrochemistry helping to harvest energy in a greener way. This research explores supercapacitive properties of the BaTiO$_3$ system as it already is a good dielectric material. Being a non-conductive system, calcination treatments were done on Nd doped BaTiO$_3$ to make it conductive enough to be a supercapacitive electrode. The effect of calcination and graphite inclusion into the BaTiO$_3$ system (CBTG) as a composite was studied. The polymer – ceramic three way composite system was studied at varying polymer and the ceramic mixture composition. A novel sandwich type electrochemical cell setup was developed to study the supercapacitor cell. The Nd doped BaTiO$_3$ material was synthesized by ball milling and spray drying. The composites were prepared by partial solution mixing. A novel technique called partial solution mixing method, which incorporates physical milling in a selected liquid medium, was successfully developed to prepare the composite electrode specimens. The performance of the two polymers (acrylonitrile butadiene styrene and polyaniline) was studied in the BaTiO$_3$ system, exploiting respective nonconductive and conductive nature of the polymers. The supercapacitor electrode composites were characterized through cyclic voltammetry, electrochemical impedance spectroscopy and chronopotentiometry, for performance, and also through XRD, SEM and EDS for structure – property correlations. The effect of electrolyte, separator membrane and cycle life were also studied for the composite systems. Energy and power density calculations were used to assess the practical applications of the system.
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LIST OF ABBREVIATIONS

1. ABS – Acrylonitrile butadiene styrene
2. PANI – Polyaniline
3. EIS – Electrochemical impedance spectroscopy
4. CV – Cyclic voltammetry
5. H\textsubscript{2}SO\textsubscript{4} – Sulfuric acid
6. KOH – Potassium hydroxide
7. SEM – Scanning electron microscope
8. XRD – X-ray diffraction
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CHAPTER 1

1. INTRODUCTION:

1.1. Global Energy Crisis:

Energy crisis is the issue of the hour all around the world. There are a number of reasons for this, which starts with the decline of the oil reserves and the increase in the price of oil. As a result, there is a direct impact on the world’s overall economic growth. The main cause for all the above is the depletion of oil deposits. So, the world has almost come to a stage to explore other fuels that can be harnessed easily at low cost, which will last a long time, for the future generations. The immediate attractive option has been natural gas and also coal, the sources of which will not come into check for three or four decades. But again the problem is the need for greener energy, which is not entirely possible in case of coal and natural gas. Using coal gives out emissions of CO, CO$_2$ and other carbon based residues, forcing us to contemplate alternative sources of energy, renewable or non-renewable sources [1].

1.2. Alternative Sources of Energy:

The search for alternate sources of energy has elevated the energy research and development era to a higher level. Solar, wind, geothermal, tidal, and Bio- Energy are the most productive forms of renewable energy sources. Nuclear, fossil fuels, natural gas, hydrogen energy are non – renewable forms of energy. The issues faced by a source like a nuclear reactor is its cost, availability of the nuclear fuel sources like uranium, thorium, plutonium and also the risk of controlling it without any adverse reactions. Fossil fuels, apart from problems of source decline, also affect the earth’s climate change by its harmful emissions. Other natural sources are difficult
to harness, like ocean tides and light from sun. They even tend to be expensive and its efficiency is low compared to the fossil fuels. Bio fuels are another option that is extracted from micro – organisms like algae, bacteria and also from plant extracts [1] [2] [3]. There are many small and large scale energy storage and harvesting devices that are based on chemical energy, including batteries, fuel cells, supercapacitors and so on. These devices have their own advantages and disadvantages, but on balance have proved to be quite effective. They work in tandem with the other major energy systems, but they can assist in driving a whole system.

1.3. Electrochemical Supercapacitors:

1.3.1. Background:

Electrochemical supercapacitors are also called electrochemical double layer capacitors (EDLCs), ultracapacitors and also hybrid capacitors in certain cases. They are basically high energy storage devices that can be used as a replacement for batteries. The mechanism of charge storage is by electrostatic charge separation or by reversible redox reactions (as in a battery) (pseudocapcitance) or a combination of both. The supercapacitors are either used separately or in a combination with batteries to produce a hybrid system. The EDLCs charging is similar to that happening in a common capacitor. But the amount of charge storage ability is higher compared to the electrolytic capacitors. This property is due to the high surface area of the electrode materials where the charges move towards the surface of the electrode and stay at the interface of the electrode and electrolyte. The charge storage mechanism is so fast that charging and discharging is rapid. Supercapacitors tend to have high power density and nominal energy density, which contrasts with the batteries and fuel cells [4].
Shown in figure 1, is a Ragone plot of specific energy and specific power for some charge storage devices. The electrochemical supercapacitors are seen to bridge a gap between batteries and conventional capacitors. Supercapacitors cover a wide range of specific power and density values which depend on the materials selected for the electrode and electrolyte. Carbon based materials were used as supercapacitor electrodes for a long time due to their high electrical conductivity and ability to develop high surface area. Apart from carbon based materials many other materials such as conductive polymers, pure and doped metal oxides, aerogels and nanopowders of metals are being used as supercapacitor electrodes.

**Figure 1** Ragone Plot of Specific energy and Specific power of energy storage devices [4].
1.4. Electrochemical Phenomenon:

1.4.1. Electrochemical Double layer:

Double layer theory is basically an electrostatic and electrochemical phenomenon. Capacitors generally work on this double layer phenomenon (non-faradaic) apart from certain ones that work on faradaic reactions (pseudocapacitors). The capacitive properties can be studied with a single electrode interface but there is always a need for a second electrode to understand electrical circuit behavior of the system. The study of an electrochemical double layer occurs at the electrode – electrolyte interface. In a charged state, there is a drop in the potential at the interface between electrode and electrolyte. During discharge, there is an IR (ohmic) drop inside the solution and the vice versa on recharge. The double layer formation at the electrode – electrolyte interface depends on the electrode material, surface area, porosity (size and volume), and type of electrolyte. Figure 2 (a), explains the charge separation at the electrode – electrolyte interface in a capacitive medium. Figure 2 (b), explains the potential changes across the setup from electrode to the electrolyte medium during the discharging process.

Figure 2 (a). Configuration of electrochemical capacitor setup with two electrodes and two double layers.
Several models have been proposed on double layer theory and its structure. All the newly developed models are reformations of the former ones. The three important models are:

- Helmholtz double layer model
- Gouy – Chapman model
- Stern model

Von Helmholtz was the first to propose a double layer model. That double layer was a quasi-two dimensional model that consisted of two arrays of opposite charges, separated by an atomic size distance. It was first proposed for the interface of colloidal particles, where the charges originate from ionization, electrolytes, or adsorption, in case of non-aqueous colloids. The Helmholtz model does not hold for complex cases, because ions on the solution side are not static, but subject to thermal fluctuations which will depend on electrostatic forces between the ions and the charged metal. Figure 3 (a), (b), (c) depicts the double layer models proposed by Helmholtz, Gouy and Stern, respectively.

![Figure 3. Double Layer models (a) Helmholtz model (b) Gouy point charge model (c) Stern model][6]

So another theory was advanced by Gouy and Chapman with some extra details on the counterions. It was stated that the counterions will become conjugated with the metal surface’s
electron charge in a three dimensional structure, looking like a densely distributed cation and anion stream. The issue with this model is an incorrect local field around the electrode surface and also the prediction of too much capacitance. This later is defined as the rate of change of net ionic charge on the electrolyte side of the metal – electrolyte interface, which charges support the potential difference across the interface.

The overestimation of the double layer capacitance in Gouy – Chapman theory was overcome by Stern. In this model the ion distribution on the inner layer (i.e right on the surface of the electrode) was considered due to the adsorption of the ions by Langmuir’s adsorption isotherm. The region between the inner layer and the solution was called as the diffuse layer of the distributed ionic charges [6], [7], [8], and [9].

Figure 4. General representation of a double layer structure showing the adsorption of cations and anions at different layers [6]

It was also proposed, that if the ions are of a finite size, then the thickness of the inner layer can be deduced, and made to correspond with the Helmholtz compact double layer having a capacitance of $C_H$ [9]. The remaining outer layer region, which is the diffuse region, has a capacitance of $C_{diff}$, which corresponds to the capacitance of double layer in the diffuse region.
The overall capacitance is termed $C_{dl}$, which equals the capacitance of $C_H$ and $C_{diff}$ in series. Here $C_{dl}$ will be deduced from two smaller components giving a greater value due to its reciprocal form. So, the electrode potential and the ionic concentration of the solution act as an important factor in deducing the double layer capacitance.

The equivalent circuit for an electric double layer capacitor was simply considered to be a solution resistance $R_S$ in series with the double layer capacitance $C_{dl}$. But later it was found that a resistance called a charge-transfer resistance, or faradaic resistance, $R_f$ exist in parallel with $C_{dl}$, as shown in figure 5.

![Figure 5. Equivalent circuit of a double layer capacitances (a) ideal polarisable capacitor (b) Interface with a series resistance (c) capacitor in series with a resistance $R_s$ and potential dependant faradaic resistance $R_f$ [10]](image)

1.4.2. Pseudocapacitance:

Along with the earlier discussed double layer capacitance, there is another phenomenon by which charges are stored in an electrochemical capacitor. Pseudocapacitance ($C_\Phi$) comes from
the faradaic charge transfer process. Pseudocapacity was first introduced by Grahame in 1947 but was referred to as a reversible discharge of ions. Pseudocapacitance is basically the movement of ions across the double layer, like a battery working during charging and discharging. An electron transfer process occurs between the oxidized and reduced species. The types of processes in which pseudocapacitance comes up are

i. In a redox system where the electron process occurs between solid or liquid solutions, as a function of electrode potential.

ii. Chemisorption of anions at the interface of the electrode, as a partial charge transfer of an electronic charge which is potential dependent.

The electrochemical reactions take place between the electrode and the electrolyte. The two types of reactions are oxidation and reduction. Oxidation occurs at the anode and the reduction reaction occurs at the cathode. The main components in an electrochemical reaction are anode, cathode, electrolyte and the return path. Oxidation is referred to as a loss of electrons which occurs at the anode. Reduction is the gain of the electrons which take place on the cathode.

1. Oxidation reaction at the anode is represented as:

\[ M \rightarrow M^{n+} + n e^- \]  \hspace{1cm} (1)

This results in an anodic current \( i_a \) at particular a potential where the reaction occurs.

2. In order to maintain charge neutrality, these electrons released at the anode are taken by the ions in the solution and become reduced. The reduction reaction differs in case of acidic, neutral and a basic medium.

\[ 2H^+ + 2e^- \rightarrow H_2 \quad \text{(hydrogen reduction)} \]  \hspace{1cm} (2)

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(Dissolved oxygen reduction in acidic medium)} \]  \hspace{1cm} (3)

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{(Dissolved oxygen reduction in basic medium)} \]  \hspace{1cm} (4)
M^{n+} + ne^{-} \rightarrow M \quad \text{(Metal Reduction)} \quad (5)

All reduction reactions take place at the cathodic side and the reduction current is referred as $i_c$.

So these reactions and the charges produced account for the pseudocapacitance of the system. The reactions are identified with the increase in the anodic and cathodic currents at particular potential values. Each oxidation and reduction reaction has its own characteristic potential.

Now considering a Ni – NiO system with a Ni core and NiO shell, the capacitance arises from redox reactions. The pseudocapacitive behavior Ni – NiO electrodes in KOH electrolyte is indentified from the cyclic voltammetry (CV). The redox reactions are depicted by the high current density in CV plot. Figure 6, shows the CV plot of Ni – NiO system with redox reactions.

![Figure 6. CV plot of Ni – NiO system with redox peaks](image)

The reaction associated with the redox peak is:

$$\text{NiO} + \text{OH}^- \rightleftharpoons \text{NiOOH} + e^- \quad (6)$$
In figure 6, the forward scan is the oxidation cycle and the reverse is the reduction cycle, and the resulting currents are anodic and cathodic currents, respectively. The above reaction can be separately split into oxidation and reduction reactions. In the forward scan of cyclic voltammetry:

\[
\text{Oxidation: } \text{Ni}^{2+} \rightarrow \text{Ni}^{3+} + e^- \quad (7)
\]

and the hydroxide ion from the solution form Nickel oxy hydroxide. The oxidation occurs approximately at 0.45 V.

In the reverse scan:

\[
\text{Reduction: } \text{Ni}^{3+} + e^- \rightarrow \text{Ni}^{2+} \quad (8)
\]

and the hydroxide ions go into the solution, which occurs at 0.25V. This is the mode through which the charges become accumulated onto the electrode surface through the oxidation and reduction reactions [10].

For a typical double layer type capacitor, 1 – 5% charge storage is due to pseudocapacitance. Also a pseudocapacitor has about 5 – 10% double layer mode of charge storage, which is proportional to the electrochemically accessible interfacial areas. So, always there will be the presence of double layer charge storage in a pseudocapacitive model. The equivalent circuit representation for a pseudocapacitor with double layer charge storage presence is somewhat different from that of the normal double layer capacitor. For charge storage through pseudocapcitance, \( C_\phi \), there is a faradaic resistance \( R_f \), plus another resistance \( R_d \) which accounts for the discharge. In this circuit, a combination of \( C_\phi \), \( R_d \), and \( R_f \) are in parallel with \( C_{dl} \) which is the double layer capacity [6], [11]. The equivalent circuit is shown in figure 7.
1.4.3. Electrochemical Cell Design:

The electrochemical cell can be either a three electrode system or a two electrode setup. The two electrode system has two working electrodes immersed in an electrolyte with an ion permeable membrane between the two electrodes. In this type each electrode – electrolyte interface acts a separate capacitor by itself. So the whole cell by itself is made of capacitors in series [4],

\[
\frac{1}{C_{\text{cell}}} = \frac{1}{C_1} + \frac{1}{C_2} \tag{9}
\]

\(C_{\text{cell}}\) – Cell Capacitance, \(C_1\) – Capacitance of electrode 1, \(C_2\) – Capacitance of electrode 2

As per the figure 2, the two-electrode setup has a current collector, onto which the electrode material is mounted, and in between the electrodes lays the separator with electrolyte [12]. The three-electrode setup consists of a working electrode, counter electrode and reference electrode. The capacitance from this setup gives the value of one electrode which mostly corresponds to the value of the one electrode of the two electrode setup, approximately.
Figure 8. A two electrode based electrochemical capacitor setup which depicts two capacitances in series with its interfacial resistances. [4]

 Basically the current collector can be a conductive metal like silver, nickel, stainless steel, etc. The electrode materials are made to be in contact with the current collector by several methods like pressing as a pellet, coating on the metal and also by pressing it along with the metal foam, which can be used as a current collector.

 The selection of the current collector and the method of making the electrode material in contact with the former is a very important aspect in the electrochemical cell design. The resistance should be very low (i.e high conductivity) and the interfacial resistance between the current collector and the electrode should be low so as to achieve very low loss.
1.5. Material Requirements and Properties:

1.5.1. Electrode Materials:

For a device to work, its materials need to have its own unique properties. In case of supercapacitors the electrode materials need certain specified properties. The two most important properties are high surface area and high conductivity. These are the main properties that determine whether a material is a potential supercapacitor electrode component. The other properties that need to be complemented are pore structure, pore size and pore size distribution; wear resistance; corrosion resistance; processability and low cost. Electrode materials that reflect these properties include:

i. Carbon and carbon based materials [4], [13], [14],

ii. Conducting polymers (polyaniline, polypyrrole, polythiophene) [15], [16]

iii. Metal oxides and such other ceramic materials as (RuO$_2$, NiO, Co$_2$O$_3$, VN etc) [17], [18], [19]

iv. Composite systems of the above three [20 – 26].

Carbon based materials, such as graphite and carbon nanotubes, are highly preferred electrode materials due to their high conductivity and surface area. Yan Wang et al. have reported on grapheme materials with a capacitance of 205 F/g in KOH electrolyte medium, with energy and power density as 10kW/kg and 28.5 Wh/kg, respectively [12]. The ceramic – carbon composite system and polymer – carbon conductive systems have been extensively explored in the literature. Polyaniline and mesoporous carbon composite have shown a specific capacitance of 470 F/g with an energy density of 76.4 Wh/kg [24].
1.5.2. Electrolyte:

The electrolyte is the source of the positive and negative charges which provide the basis for capacitive charge storage. Electrolytes can be ionic, organic or solid state type. Ionic electrolytes can be classified into acidic, basic and salt types, with examples H₂SO₄, NaOH, and NaCl respectively. The charge storage mechanism is basically the migration of the ions toward the oppositely charged electrode to form a double layer. Each type of electrolyte has its own voltage range in which it can work. Ionic electrolytes tend to dissociate at 1.1 V over which the reversibility is not possible. Organic electrolytes like tetraethyl ammonium tetrafluoro borate can work until 3V. The voltage range for different types of organic electrolytes depends on the electrolyte material. So electrolytes are selected to be compatible with the electrode and also in accordance in the working voltage [13].

1.5.3. Advantages of Supercapacitors:

Supercapacitors are novel energy storage devices compared to batteries. These devices have a number of advantages compared to batteries and other energy storage devices. Supercapacitors are high power storage devices, have high cyclic life, very good reversibility, and high stability. Supercapacitors charge faster than batteries. The charge / discharge efficiency is around 85 – 98%. As it mostly a surface phenomenon, less material is required making the smaller device. The charge storage capacity is several hundred times more than that of the conventional batteries. One other major advantage of the hybrid capacitors is that they use benefits of both double layer and faradaic reversible charge transfer mechanisms, leading to very high charge storage ability.
1.5.4. Disadvantages of Supercapacitors:

Although they exhibit high power density and efficiency, supercapacitors have their own problems. Its low energy density is one the reasons they are used with batteries in series. The problem with the electrolyte is its aqueous nature and the voltage range in which the electrolyte can perform without decomposition. This limitation can be covered up by introducing solid state electrolytes but the cost effectiveness reduces considerably [27].

![Graph showing energy density and power density relationship](image)

Figure 9. Relationship between energy density and power density of supercapacitor and lead – acid battery hybrid system [27]

Figure 9 above illustrates the low specific energy property of supercapacitors and the reason for the use of the hybrid system.

1.5.5. Applications:

As already specified, supercapacitors are mostly being used with batteries due to their low specific energy. The major applications of supercapacitors alongside batteries are in
Regenerative – Braking systems. They have also been suggested for pulse power and bridge power applications, such as military systems, automotive subsystems and memory protection. They are also being used for low voltage and high flux photovoltaic panel charging. Electrochemical capacitors, by themselves, are being tested for use in hybrid electric vehicles, and also power tools [27], [28].

1.6. Ceramic – Carbon Composites:

Graphite is known as a very good supercapacitor material, as it exhibits large double layer formation ability, proportional to its surface area. Yan Wang et al. have reported a capacitance of 205 F/g for chemically reduced graphene oxide. Supercapacitor electrodes have been prepared using high surface area carbon black with a capacitance of 250 F/g by F. Beck et al [29]. Even carbon based materials like carbon fibers and CNT’s have been used as supercapacitor materials.

Ceramic particles are also being employed as supercapacitor electrodes. The only difference here is that they work in a pseudocapacitive manner, with redox reactions occurring at particular range of voltages. Materials such as RuO$_2$, Co$_3$O$_4$, VN, and NiO have been widely employed as supercapacitors. Xiaoping Zhou et al. showed that VN was a promising electrode material, with a capacitance of 161 F/g. Co$_3$O$_4$ was also found to be suitable for supercapacitive electrodes, with a capacitance of 456 F/g by Li Cui et al. There has been different works where the RuO$_2$ – carbon composite system was employed as an electrode material, providing very high capacitance. So a system where partially conductive ceramic and graphite material can be blended into a composite, and its performance as a supercapacitor electrode material studied, is attractive. The main reason for combining ceramic and graphite together is to bring in both
double layer and pseudo capacitive character together into a single system, and to study the behavior in an electrochemical medium in different electrolytes.

1.7. Current Work:

BaTiO$_3$ has been employed in electrostatic capacitors as dielectric medium. Even doped BaTiO$_3$ has been used to good effect. New developments like doped BaTiO$_3$ core shell structure have improved the dielectric performance of the constituent medium. The current work is aimed at studying the performance of BaTiO$_3$ as a supercapacitive electrode material. As it is not conductive, it has to be made conductive enough to make it a potential supercapacitive electrode. Processing treatments, such as doping and calcining by different available methods, can be employed to improve its conductive character and also its supercapacitive properties, by preparing it as a composite with graphite of suitable surface area. The intent was to enhance the suitable hybrid capacitive properties, with both double layer and pseudo capacitive properties character. There is also suggestion of a third system which is either acrylonitrile butadiene styrene (ABS) or polyaniline (emeraldine salt) (PANI) mixed at different compositions with the ceramic – graphite system. The reason for separately choosing ABS and PANI is because the former is a non – conductive material and the latter is conductive polymer. The idea was to test a three level composite system, one as a non – conductive system and the other as a highly conductive system.

1.8. Objectives:

The main aim of this work was to develop a novel hybrid supercapacitor electrode material and characterize its electrochemical properties. The novel part here is the use of BaTiO$_3$. So, the emphasis has been to enhance its conductivity. The main issues are the particle size and doping
so that it forms an n-type semiconductor material. Calcining the powder in a reducing atmosphere like forming gas (N₂/H₂) will make the BaTiO₃ react with H₂ and produce oxygen vacancies [29], as below:

\[
\text{BaTiO}_3 + x\text{H}_2 \rightarrow \text{BaTiO}_{(3-x)} + x\text{H}_2\text{O} \quad (10)
\]

\[
[V_o] \rightarrow [V_o]^\cdot + 2e \quad (11)
\]

This process decreases the resistance of the material by up to 10 orders magnitude. If this process works out it would be expected to be good supercapacitor electrode. Then incorporating graphite and later polymer constituents should make it an even more effective electrode material. The study was done in different electrolyte media to check the effect of electrolyte. Also the cycle life of the electrode was studied. The goal was for the electrode system to reach an optimum value of power and energy density.

**ELECTRO–ANALYTICAL TECHNIQUES**

2. **CHARACTERIZATION:**

Supercapacitors are mainly characterized by electrochemical methods for performance in an external environment. The electrochemical data are typically complemented by structural, optical and electrical characterization techniques. The three important electrochemical methods needed to characterize a supercapacitor system are: electrochemical impedance spectroscopy, cyclic voltammetry and chronopotentiometry. These tests can be performed in either two or a three electrode system. A three-electrode system simulates the characteristics of a supercapacitor
electrode, and the two electrode system helps to develop information about the electrode’s performance as a capacitor.

2.1. Electro – analytical Techniques:

Electro – analytical techniques record potential and current in an electrochemical cell containing the analyte. The three main categories are potentiometry, voltammetry and coulometry. The categories needed to study a supercapacitor are potentiometry and voltammetry.

2.1.1. Electrochemical Impedance Spectroscopy:

Investigation of electrode kinetics in any electrochemical system can be done by non-steady state techniques. A shift occurs to a new steady state due to the agitation in the system. The new state depends on parameters like double layer capacitance, charge transfer resistance, and diffusion effects. Electrochemical Impedance Spectroscopy (EIS) works in by a method where a monochromatic alternating voltage is applied to the electrode which results in a current with a phase difference of $\nu$.

\[
U(t) = U_m \sin(\omega t) \quad (12)
\]

\[
I(t) = I_m \sin(\omega t + \nu) \quad (13)
\]

$I(t)$ is the resulting current from the given alternating voltage $U(t)$, with a phase difference of $\nu$. Impedance is given by:

\[
Z = \frac{U(t)}{I(t)} = Z' + iZ'' \quad (14)
\]

where $Z'$ and $Z''$ are the real and imaginary parts of impedance, $Z$ respectively.
Impedance spectroscopy mainly gives two kinds of plots, which are the Nyquist Plot and Bode Plots. The Nyquist plots provide the impedance data at different frequencies, which is between $Z''$ and $Z'$ at different frequencies. The Bode plot gives the data of modulus of impedance against frequency.

The Nyquist Plot is the mostly used to determine the electrochemical reaction’s external circuitry by its impedance data. The electrode with a particular electrolyte forms a semicircle in the high frequency region and continues to trace a more or less straight line at an angle to the $Z'$ axis as in Figure 10. The whole plot by itself can be designed into an external circuit with resistances, capacitance and diffusion coefficients. The circuit is analogous to a design called the Randles circuit as shown in figure 11. If the straight line is sloped more towards the $Z''$ axis, the system is more capacitive in nature. If it tilts more towards the $Z'$ axis, the system is more resistive in nature. If the straight line is inclined at an angle 45° then the sample looks to be more of an ideal capacitor with both resistive and capacitive nature [6], [12]. [Fig 10 must precede Fig 11 in your discussion above]

![Figure 10. Nyquist plot of a system with Randles circuit behavior, explaining the separate components in the system. [31]](image-url)
where Rs or $R_\Omega$ – Equivalent series resistance (ESR)

$R_{ct}$ – Charge transfer resistance

$W$ – Warburg diffusion coefficient

$C_{dl}$ – Double layer capacitance

All the parameters mentioned above can be explained in the figure 10. Rs or $R_\Omega$ is defined as the equivalent series resistance (ESR) which comes from the electrolyte, electrode and the current collector together. It is the $X$ – intercept of the plot at the highest frequency. ESR is very important during the charge – discharge studies where the IR drop can be correlated to the ESR value. ESR also affects the maximum power density value $P_{max}$.

$$P_{max} = \frac{V^2}{4mR}$$  \hspace{1cm} (15)

where, $P_{max}$ – Maximum power density

$V$ – Applied Voltage

$m$ – Mass of the electrode

$R$ - Equivalent series resistance
The resistance $R_{ct}$ is defined as the charge transfer resistance which is defined as the resistance to the movement of ions during the redox reaction process. The value of $R_{ct}$ is deduced from the X – intercept of the end of the semicircle is equal to $R_\Omega + R_{ct}$ from which $R_{ct}$ can be calculated. In some cases the semicircle will not be complete. $C_{dl}$ is calculated from the formula:

$$C_{dl} = \frac{1}{\omega Z''}$$  \hspace{1cm} (16)

$C_{dl}$ – Double layer capacitance

$\omega$ – Angular frequency

$Z''$ – Imaginary part of impedance

Also the shape of the Nyquist plot depends on the type of electrode and the diffusion length. There are three other main categories by which Nyquist plots can be put into

i. Diffusion of ions in finite length region with a transmissive boundary

ii. Diffusion of ions in finite length region with a reflective boundary

iii. Plot of porous electrodes

The first category of the diffusion of the ions in finite length works mainly for diffusion phenomenon. The thickness of the diffusion layer and of the electrode plays an important role. The $45^\circ$ straight line moves downward toward the $Z'$ axis when the diffusion length approaches the thickness of the electrode at decreasing frequencies. Such a structure gives out a parallel combination of capacity, $C$ and diffusion resistance $R_d$ at low frequencies. This occurs in case of transmissive boundary conditions.
In another condition where there is barrier to the diffusion at the far end of the electrode which is a reflective boundary condition, there occurs a vertical line at low frequencies where the capacitance $C$ is in series with the negligible resistance $R_d$ resulting in a vertical straight line parallel to the $Z''$ axis.

In case of a porous electrode, factors like the pore length might be smaller than the diffusion length, which defines a finite diffusion length. The resistance in this case is offered by the pore diameter and length. At high frequencies a straight line is followed by a 45° line at low frequencies.
Thus a Nyquist plot helps in explaining the external circuit behavior of an electrochemical system. In this case, Nyquist plot aids in defining the presence of any resistances and its combination with the different capacitances, by its origin [12].

2.1.2. Cyclic Voltammetry:

Cyclic Voltammetry is an analytical technique that is used to study the kinetics and the thermodynamics of an electrochemical system. Here a current response to recorded to a stepwise change in voltage as in figure 15. The voltage applied is in the form of a triangular pulse, the current response of which is studied (figure 15a). The cyclic voltammetry depends mainly on the applied voltage, electrode material, electrolyte, and scan rate. The behavior of the material can be deduced from the cyclic voltammetry plot whether, capacitive or resistive in nature. If it’s capacitive in nature the type of capacitance can also be determined by whether it is a double layer capacitance or pseudocapacitance. For an electrode material that is capacitive the curve must be flat or rectangular in nature with a large area inside the loop. The area inside the loop accounts for the charge stored from which the capacitance can be calculated.

The capacitive CV plot for a double layer capacitor differs from that of a pseudocapacitor. The double layer CV plot looks like a rectangular loop without any peaks (figure 15 b), with a large area inside the loop which corresponds towards the capacitance of the system.

Figure 15. (a) Voltage pulse form in Cyclic Voltammetry. (b) CV Plot for a truly double layer capacitance
The CV plot of a pseudocapacitor looks to be flat with reduction and oxidation peaks at particular voltage ranges. Before a potential is applied to the electrode (t=0), the solution has the uniform bulk concentration. As the potential is applied, the concentration of the oxidized species is depleted at the surface. This effect lowers the oxidized charge concentration at the surface. According to Fick's law, the diffusion equation, there will be more flux to the surface and hence a higher cathodic current. As the potential becomes more negative, the concentration of the oxidized species at the surface will eventually go to zero. Simultaneously, the volume in the solution that is depleted of the oxidized species will increase and the concentration gradient will begin to decrease.

![CV Plot of a pseudocapacitive electrode system with cathodic and anodic peaks](image)

Figure 16. CV Plot of a pseudocapacitive electrode system with cathodic and anodic peaks

As the concentration gradient decreases, there will be less flux to the surface and current will begins to decrease. As the voltage scan is reversed, there still occurs a layer depleted of the oxidized species, but the surface concentration begins to raise so current decreases further. Finally, a region where anodic current begins to dominate is reached. A negative current peak
will be reached and then the current will decrease in magnitude as the depletion layer for the reduced species increases.

As already mentioned, the area inside the curve is analogous to the charge stored from which the capacitance can be calculated. It's known as:

\[ C = \frac{q}{V} \]  \hspace{1cm} (17)

where:
- \( C \) – Capacitance
- \( q \) – Charge stored
- \( V \) - Applied voltage

The specific Capacitance can be calculated from

\[ C_{sp} = \frac{q}{m \Delta V} \]  \hspace{1cm} (18)

- \( C_{sp} \) - Specific Capacitance
- \( q \) – Charge storage
- \( m \) – Mass of the electrode
- \( \Delta V \) – Voltage range

2.1.3. Chronopotentiometry:

Chronopotentiometry is an electrochemical technique where a constant current is applied across the electrode for a particular amount of time and its voltage response is recorded. In case of an electrochemical capacitor setup, constant current is applied across the electrode for a particular time and its voltage response is recorded; then a reverse current of the same value is applied for a particular time and its voltage response is also recorded. One of these events is the charging cycle and the other is the discharging cycle. So the cyclic life can be studied from its charging
and discharging behavior for large number of cycles. An ideal supercapacitor should show similar behavior for a large number of cycles to prove its stability. The main quantities that can be calculated from the chronopotentiometry plot are discharge capacitance, energy and power density.

The discharge curve in figure 17 shows a sudden drop in the voltage in the first second in the discharge cycle. This is called as the ohmic (IR) drop whose value correlates with that of the series resistance from the electrode, electrolyte and current collector.

![Figure 17. Chronopotentiometry of PANI + CBTG](image)

It will be almost equal to the value of $R_s$ (equivalent series resistance) calculated from the EIS Nyquist plot.

Specific Capacitance can be calculated by:
Energy density can be calculated from:

\[ E = 0.5 \ C_{sp} (\Delta V)^2 \]  

(20)

Power density, \( P = \frac{E}{\Delta t} \)  

(21)

\( C_{sp} \) – Specific capacitance

I – Current

\( \Delta t \) – Discharge time

\( \Delta V \) – Change in voltage during discharge

m – Mass of the electrodes

E – Energy density

P – Power density

Thus the cyclic life of a supercapacitor can be determined from both chronopotentiometry and cyclic voltammetry. The energy and power density are very important parameters because they help in understanding the output and application of the supercapacitor electrode.
CHAPTER 3

3. EXPERIMENTAL:

3.1. Materials:

3.1.1. Acrylonitrile Butadiene Styrene:

Acrylonitrile Butadiene styrene (ABS – 40) has a chemical formula \((C_8H_8)_x \cdot (C_4H_6)_y \cdot (C_3H_3N)_z\) which is a thermoplastic material was bought from Sigma - Aldrich. It is a copolymer synthesized by polymerizing acrylonitrile and styrene in presence of butadiene. ABS – 40 has a composition of 40% acrylonitrile, 45% butadiene and 15% styrene.

![Figure 18. Structure of Acrylonitrile Butadiene styrene](image)

It has a glass transition temperature of 110°C and flow temperature of 80°C. The particle size of the powder that were used for the experiments were less than 150 μm.

3.1.2. Polyaniline:

Polyaniline is a conducting polymer obtained from Sigma – Aldrich. It falls under semi – flexible rod polymer family. It is present in a conductive state in emeraldine salt form. It has a particle size ranging from 3 – 100 μm and is green in color. It conductivity is 2 – 4 S/m and has an average molecular weight less than 15000. Its surface area ranges from 5 – 20 m²/g.
3.1.3. Barium Titanate (BaTiO$_3$):

Barium Titanate was bought from TAM Chemicals [Now Ferro Corp]. The Ba/Ti ratio was 0.997 making it titanium rich which might help in polaron conduction during the sintered state. The precursor for Nd dopant in BaTiO$_3$ was Nd(NO$_3$)$_3$. 6H$_2$O was obtained from Sigma – Aldrich.

3.1.4. Graphite:

Highly conductive graphite powders were obtained from Asbury Graphite Mills Inc. The graphite powders used for the experiments were very fine with a surface area 115 m$^2$/g.

3.2. Synthesis of pure and Nd doped BaTiO$_3$:

Pure and doped BaTiO$_3$ was prepared by simple ball milling method and the powders were retrieved by spray drying. The precursor used is BaTiO$_3$ with (Ba/Ti = 0.997). The BaTiO$_3$ was dispersed and mixed in a solvent named 60:40 (40% deionized water and 60% iso – propyl alcohol). Apart from solvent, additives used were deflocculant, binder and a plasticizer, which were Darvan C, polyvinyl alcohol, and polyethylene glycol respectively [32]. The use of a deflocculant was to suppress the agglomeration of the BaTiO$_3$ particles in the solvent. The binder helps in binding the powder together, if a green compact has to be formed later. The work of the plasticizer is to help the binder to be flexible and not brittle. First the mixture of BaTiO$_3$ and 60:40 with 1 wt% Darvan C is ball milled for 12 hours. After this both PVA and PEG are added.
at 1wt% each concentration into the mixture and ball milled again for 2 more hours. In case of Nd doped BaTiO$_3$, previously an amount of Nd(NO$_3$)$_3$ to get 0.15 mol% Nd, was added the mixture before the first ball mill and milled for 12 hours. The resulting mixture was spray dried at an outlet temperature of 200 °C, which resulted in very fine BaTiO$_3$ particles being obtained.

3.3. Calcining BaTiO$_3$ in reducing atmosphere:

The spray dried pure and Nd doped BaTiO$_3$ particles were calcined in reducing atmosphere in an alumina tube furnace. The reducing gas used was forming gas (a mixture of N$_2$ – 90% and H$_2$ – 10%). The pure and Nd doped as – prepared BaTiO$_3$, were calcined at 1050 °C for 2, 4 and 6 hours. The calcined BaTiO$_3$ was tested for its resistivity by first pressing the powder into a die press at 120 MPa. The other improvisation was mixing Nd doped BT with 10 Vol% graphite (115 m$^2$/g) using a mortar and pestle. The same was calcined in the reducing atmosphere for 6 hours at 1050 °C. The resulting powders were named as calcined barium titanate graphite (CBTG).

3.4. Preparation of the Polymer – Ceramic Composite:

The technique used for the composite preparation was partial solution mixing [33]. The solvent used was a mixture of 90% isopropyl alcohol and 10% acetone. The filler material is first added to the solvent which is stirred for about 5 minutes. Then upon partial mixing the matrix phase is added and again stirred for 5 minutes. The mixture is emptied into a small container and then it is horizontally milled for 10 minutes at 120 rpm. The composite mixture was then filtered by vacuum filtration technique and dried at 40 °C for 12 hours. The composite mixtures are CBTG with ABS – 40 and SBTG with polyaniline.
3.5. Electrode Preparation:

The electrode preparation was a simple technique of applying a coating over the substrate which is used as the current collector. The substrate used was silver disc. The composite was made into a slurry using isopropyl alcohol as the solvent. The paste was coated carefully onto the silver disc electrode and dried in vacuum oven for 10 minutes. The coated electrode was pressed cold pressed on a Carver Laboratory die press at 40 MPa.

3.6. Die Pressing:

Die pressing was done to measure the resistivity of the prepared powder samples. The die pressing was done in a Carver laboratory press equipment (Model 3912). The samples were weighed to 0.5g and were cold pressed in a 1cm die at a pressure of 120 MPa for about 3 minutes. The CBTG powders, due to difficulty in pressing, were mixed with 5wt% polytertrafluoro ethylene (PTFE) and pressed at the same pressure of 120 MPa.

3.7. Electrochemical Cell Design:

An electrochemical cell is a setup in which the all the above mentioned electrochemical experiments are performed. As already stated there are two types of cells that can be used. One is a three electrode setup which has a working electrode (the electrode material to be tested), a reference electrode which is generally a Standard Calomel Electrode, and a counter electrode which could be platinum, gold, or silver, which in our case was platinum. The three-electrode setup was used for these experiments, as shown in the figure 20. The three electrode cell helps in the observation of the electrode characteristics in the particular electrolyte environment, in that the redox reactions are more prominently observed.
The two-electrode cell consisted of two electrodes composed of the same electrode material to be studied, in which it acts as a standard reference electrode by itself. An indigenous two electrode setup for experiments consisting of silver disc of 1” diameter, as a current collector [34], was developed for this purpose. The electrode material is applied as an adherent coating over the silver discs. The setup is shown in the figure 21. (a) and (b).
3.8. Electrochemical Characterization:

The entire electrochemical test is performed in either a two electrode or a three electrode using a Gamry Potentiostat 300G bought from Gamry Instruments. The embedded software, named Gamry Framework, is interfaced with the potentiostat and computer hardware, so that the experiments and data collection can be recorded directly interfaced through the computer. As indicated, the electrochemical tests for characterizing a supercapacitor setup are cyclic voltammetry, electrochemical impedance spectroscopy and chronopotentiometry.

3.8.1. Electrochemical Impedance Spectroscopy (EIS):

EIS is performed in a two electrode setup using the Gamry framework. The setup is run at 0.75 V with alternating pulses at 5 mV at different frequencies. The frequency range tested is 100 kHz to 1 Hz or 10Hz. The cell is stabilized for 15 minutes before the experiment is started. The resultant Nyquist plot is obtained
3.8.2. Cyclic Voltammetry (CV):

Cyclic Voltammetry was performed in both the two electrode cell and three electrode cells, because each of them displays different features. A three electrode cell describes the characteristics of the electrode material in a particular electrolyte medium, such as redox reactions, whereas the two electrode setup describes the characteristics of the electrodes as a whole supercapacitor cell. The CV experiments were performed over a voltage range of -0.2 V to 0.8 V, for a required number of cycles.

3.8.3. Chronopotentiometry (CP):

Chronopotentiometry is analogous to charge/discharge study in some types of potentiostats. The voltage response of a medium is recorded for a given time. It is performed at a constant current of 1mA and 5 mA. The charging and discharging time is varied depending on the electrode material. During discharge, an equal and opposite current is applied, of the same value as that of the charging cycle.

3.8.4. Echem Analyst:

Echem analyst is data analysis software that comes with the potentiostat. It is used to analyze the data recorded from all the above experiments. It also aids in calculating the capacitance, in the case of CV measurements.
3.9. Structural Characterization:

3.9.1. X – Ray Diffraction:

X – Ray diffraction is a nondestructive technique used to analyze the structural characteristics of a material, including its crystallite size, structure, phases and also lattice parameters. It works by the principle of Bragg’s law. A crystal lattice is a regular three-dimensional distribution of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. A monochromatic beam of X – ray is made to impact upon the sample at different angles and its diffraction pattern is recorded. For any crystal, planes exist in a number of different orientations - each with its own specific d-spacing. By varying the angle theta, the Bragg’s Law conditions are satisfied by different d-spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. In a sample, where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of application techniques for various material classes is available, each revealing its own specific details of the sample studied.

3.9.2. Scanning Electron Microscopy (SEM) & EDS:

The SEM is an electron microscopy technique used to study surface properties and structure at very high, but variable, magnification and resolution. The structure of the electrode materials were studied using SEM, and also the particles sizes of the BaTiO$_3$ can found from SEM studies.
Energy dispersive spectroscopy (EDS) is done along with the SEM which works on the principle of the photoelectric effect. It provides analytical data on the elemental composition of the material under study. It will also provide the distribution of the given elements in a particular area. It is done on the powders for composition analysis, and the area scan is done to study the distribution of the elements on the electrode surface, mainly to study the distribution of graphite and BaTiO$_3$ phases and distribution in the CBTG specimens.

CHAPTER 4

4. RESULTS & DISCUSSION

4. Nomenclature:

As there are a many materials present and different types of treatment being used to prepare the composite electrodes, the nomenclature and abbreviations of the materials has to be clearly delineated, as follows:

Pure BaTiO$_3$ (as prepared) (unsintered) – Pure BaTiO$_3$ or BT

0.15 mol% Nd doped BaTiO$_3$ (as prepared) (unsintered) – BaTiO$_3$ (Nd) or BT (Nd)

Calcined 0.15 mol% Nd doped BaTiO$_3$ - CBT

Calcined BaTiO$_3$ (Nd) with 5 wt% graphite – CBTG

Acrylonitrile butadiene styrene - ABS

Polyaniline – PANI
4.1. X – Ray Diffraction Analysis of different BaTiO$_3$ specimens:

The X – ray diffraction analysis of the as-prepared pure, Nd doped and calcined BaTiO$_3$ were carried, and the data is presented in Figure 22. Calculations and analyses were performed to detect the presence of BaTiO$_3$ and other impurities, dopant elements, calcination processing effects, and also the crystallite sizes. The powder X – ray diffraction analyses were performed using Cu Kα radiation at a wavelength of 0.154 nm at 2θ range of 10° - 70°.

![Figure 22. XRD Plot of Pure BT(Nd), CBT and CBTG](image-url)
The X-ray diffraction patterns of BaTiO$_3$ (Nd), CBT and CBTG were analyzed, and the results revealed the characteristic 2θ peaks of BaTiO$_3$ at 22.35°, 31.82°, 39.23°, 45.61°, 51.37°, 56.29°, and 66.49°, and allied diffracting planes (100), (101), (111), (200), (102), (211), (200), respectively. The data obtained were confirmed with the JCPDS card 01–083-1879. The peaks showed a very slight shift towards the right, indicating the lattice substitution effect of Nd doping.

The intensity of the peaks increases with the calcination time at 1050 °C, which explains the increase in the crystallinity. The CTG data shows two characteristic peaks of graphite, indicating the presence of retained graphite in the BaTiO$_3$ (Nd) system. No other impurities or secondary phases were present in the calcined system, because such excess impurities and the organic residues, become vaporized at processing temperatures over 500°C. The crystallite size was calculated from Debye – Scherer equation, which is,

$$d = \frac{n \lambda}{\beta \cos \theta}$$

where

d – crystallite size

n – shape factor (constant = 0.9)

λ – Wavelength of the X-ray source

β – Full width and half maximum of the 100% intensity peak in radians

θ – Angle between the incident ray and the scattering planes.
From the XRD pattern of the different BaTiO$_3$ specimens, the crystallite size was also calculated. Thus, the XRD data helps in the detection the material phase formation, doping and also crystallite sizes.

4.2. Conductivity of the different BaTiO$_3$:

The BaTiO$_3$ specimen samples pressed in a 1 cm die and its resistance is recorded from a Keithley multimeter. The resistivity, and in turn the conductivity, are calculated from the respective formulas.

Resistivity, $\rho = \frac{R}{\frac{l}{A}}$ \hspace{1cm} (23)

Conductivity, $\sigma = \frac{1}{\rho}$ \hspace{1cm} (24)

where, $R$ – Resistance recorded from multimeter

$l$ – Thickness of the sample

$A$ - Cross sectional area.

Table 1 displays the value of resistance, resistivity and conductivity of all the BaTiO$_3$ samples.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode Material</th>
<th>Resistance</th>
<th>Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure BT*</td>
<td>2.29 Mohm</td>
<td>0.145 Mohm/cm</td>
</tr>
<tr>
<td>2</td>
<td>BT (Nd)*</td>
<td>2.29 Mohm</td>
<td>0.145 Mohm/cm</td>
</tr>
<tr>
<td>3</td>
<td>CBT</td>
<td>73.6 ohm</td>
<td>46.22 ohm/cm</td>
</tr>
</tbody>
</table>
The value shows a high resistivity of as-prepared BT, and the BT(Nd), but shows lower resistivity in CBT due to the donor level doping of Nd$^{3+}$ ions on Ba$^{2+}$ sites, which impacts the Ti ion sublattice, causing polaron hopping between Ti$^{4+}$ and Ti$^{3+}$ states, and leading to semi-conduction in the BT-doped materials. Calcining of these powders in a reducing atmosphere at 1050˚C also aided in the creation of oxygen vacancies by the reaction given as:

$$\text{BaTiO}_3 + x\text{H}_2 \rightarrow \text{BaTiO}_{(3-x)} + x\text{H}_2\text{O}$$

(25)

$$[\text{V}_{\text{o}}] \rightarrow [\text{V}_{\text{o}}]^\cdot + 2\text{e}$$

(26)

The calcination process by addition of 5 wt% graphite to the BT(Nd) powder by balling milling gives the effect of the graphite, by lowering the resistivity. The powders CBT and CBTG exhibit very low resistivity, making them highly conductive which are one of the needed parameters for the supercapacitive electrode property.

4.3. SEM and EDS studies of the Composite electrodes:

SEM and EDS analyses were performed using a Hitachi based Scanning electron microscope. The SEM analyses were performed for CBT, CBTG, ABS – CBTG composites and also on the PANI – CBTG composites. The SEM analysis was done for CBT in the form of powders. The CBTG was separately pressed into a pellet that was subsequently polished and observed in the SEM, to try and observe the presence of a core – shell structure. The composites were evaluated
under SEM, as electrode paste over the silver discs (current collector). EDS analyses were also performed for both CBT and PANI – CBTG composite specimens.

The three images of figure 23 clearly show the nanostructure characteristics of the CBT powders. Figure 23 (a) (b) and (c) show that the structure is highly with significant clustering or agglomeration. The particles are mostly spherical in shape. One can also observe a rough
surface which might be due to the evaporation of the binders present over the surface of the BaTiO$_3$ particles.

Some CBTG powders also are pressed into a pellet, mounted in a mold and polished, to observe the structure of the CBTG. Figure 24 (a) and (b) show the cross sectional structure of the CBTG composite, which reveals the BaTiO$_3$ grains embedded into the surrounding graphite structure. Figure 25 and 26 shows the SEM images of the ABS – CBTG and PANI – CBTG composite, respectively, in the form of an electrode. Both composite electrodes show a well formed structure with highly porous surface. During the partial solution mixing process, polymer phase swells when it comes in contact with the solvent creating a porous surface, into which the over which the CBTG pigment phase gets embedded as a stable and coherent coating. The process also aids in increasing both the surface and overall porosity of the nanocomposite structure.

![Figure 24 (a) and (b) cross sectional structure of the CBTG composite as a pellet](image-url)
The SEM images of the composites were taken at low magnification, so as to show the overall structure of the composite.

EDS analyses were also carried out on the CBTG and PANI – CBTG composite. Figures 27 and 28 display the EDS plots of CBTG and PANI – CBTG composites, respectively. The EDS plots clearly show the presence of Ba, Ti, O, Nd and C (graphite) at the expected energy levels, respectively. The carbon content is high in case of the PANI – CBTG composite, due to the significant carbon content from the PANI and CBTG components.
4.4. Electrochemical Analysis:

4.4.1. EIS analysis of BaTiO$_3$s:

Figures 29. (a) & (b) show EIS plots of pure BT, BT (Nd) and CBT, CBTG, respectively. The tests were performed in the two-electrode cell at a 0.75V and in the frequency range of 100 kHz to 1 Hz. The electrolyte used was 1M H$_2$SO$_4$. Both the plots clearly indicate that the increase in the conductivity lowers the values of $R_s$, $R_f$, $Z''$ (which corresponds to a lowered capacitance). The samples CBT and CBT were all quite conductive, compared to pure BT and BT (Nd). The plots in figure 29 (a) and (b) are basically used to compare the change in series resistance of the different electrode materials and also compare the type of charging behavior whether pseudocapacitive or double layer type.

The Table 2 gives the values of $R_s$, $R_f$, $Z''$ which illustrates the effect of sample of composition and sample preparation on the electrical conductivity.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Electrode Material</th>
<th>$R_s$ (ohm)</th>
<th>$R_f$ (ohm)</th>
<th>$Z''$ (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure BT*</td>
<td>1.87</td>
<td>23.21</td>
<td>20.28</td>
</tr>
<tr>
<td>2</td>
<td>BT (Nd)*</td>
<td>2.29</td>
<td>15.66</td>
<td>12.76</td>
</tr>
<tr>
<td>3</td>
<td>CBT</td>
<td>0.56</td>
<td>4.83</td>
<td>2.25</td>
</tr>
<tr>
<td>4</td>
<td>CBTG</td>
<td>1.59</td>
<td>3.98</td>
<td>2.25</td>
</tr>
</tbody>
</table>

* Unsintered Sample

The faradaic or charge transfer resistance values $R_f$, for the different materials are given in the column 4 in Table 2. The charge transfer resistance is a very important component in the deducing type of charge storage mechanism. As explained earlier, the EIS plot for a porous
electrode with only a double layer structure, will have a straight line at the high frequency region followed by another straight line at an angle $45^\circ < \theta \leq 90^\circ$ at low frequencies. If there is an additional charge transfer quotient (pseudocapacitive behavior), the straight line turns into a curve trying to trace a semicircle. So $R_f$ is the x–intercept of the lowest frequency point [6]. All the BaTiO$_3$ electrodes exhibited some pseudocapacitive component with the curvature at low frequency region where a straight line almost tends to change into a curve in figure 29 (a). In case of figure 29 (b), which shows CBT and CBTG, the EIS plot of CBT tends to curve more due to more pseudocapacitive component in it. But there is straightening in case of CBTG which is due to the presence of the graphite, which brings in more double layer charges, compared to that of CBT. Also the lower $Z''$ value for CBT and CBTG suggests high capacitance in both compared to the as-prepared BT.

![Figure 29 EIS plot of (a) pure BT and BT(Nd) electrodes](image)
Figure 29 EIS plot of (b) CBT and CBTG

Figure 30. EIS plot of Pure BT, BT (Nd), CBT, CBTG.
4.4.2. Cyclic Voltammetry analysis of BaTiO$_3$: 

Cyclic Voltammetry was performed in the two electrode setup with 1M H$_2$SO$_4$ as the electrolyte. The cyclic voltammetry plots were recorded in between -0.2 V – 0.8 V at a scan rate of 5 mV/s for 3 cycles. Figures 31 (a) and (b) show the CV plot of all the different BaTiO$_3$ electrodes. In figure 31 (a) is shown the CV plot of the pure BT and BT (Nd) electrodes. Figure 31 (a) is plotted to compare the change in the CV curve and it’s charging behavior of pure BT to that of the BT (Nd) electrodes. The area inside the CV curve can be used to explain the capacitive nature of the two types of electrode materials. In this plot, the curve was more rectangular in form, indicating its capacitive nature, and there is no evidence of significant redox reactions. The maximum current reached on the positive side by BT (Nd) was almost 1 mA and 0.5 mA on the negative side. The area inside the curve gives the charge stored from which the capacitance can be calculated. The area inside the CV curve represents the charge stored in the electrode, so the charge is the area equivalent in the plot. The area equivalent inside the CV curve for pure BT and BT (Nd) were 0.0486 C and 0.1396 C respectively. The specific capacitance of the pure BT and BT (Nd) were calculated to be 2.43 F/g and 6.98 F/g respectively. Figure 31 (b) shows the CV plot of CBT and CBTG electrodes, respectively. The plot is used to explain the comparison between the change in charging behavior from purely pseudocapacitive (CBT) to hybrid capacitive (CBTG). The four peaks present in each curve represent the two oxidation and two reduction reactions in the forward and reverse cycle respectively. The curve also depicts the increase in the area of the curve in CBTG system. The large area (1.65F) inside the curve is due to the peaks that reach high currents of ~ 30 mA at particular voltages. The CBT plot shows two pairs of redox reactions where the forward scan is the anodic reaction (oxidation) and the reverse scan is a cathodic reaction (reduction).
In case of CBT the redox reactions arise from the conductive material formed due to the presence of the Ti ions present in the BaTiO$_3$ lattice. The curve is flat regarding its capacitive nature, but shows a large amount of pseudocapacitive behavior, which was also deduced from the EIS plot of CBT. Therefore the EIS and CV plots of the CBT confirm the pseudocapacitive behavior of the CBT electrodes. The CBTG has 5 wt% of graphite (S.A – 115m$^2$/g). This electrode data shows a large area inside the curve as a flat surface, but also redox peaks at the same voltages. This electrode material, therefore, displays both double layer and a pseudocapacitive charge storage mechanism in large amounts, which is characteristic of a hybrid supercapacitor. The area equivalent inside the CV curves for the CBT and CBTG plots were 1.65 C and 2.018C respectively. The specific capacitance of CBT and CBTG were 82.5 F/g and 100.9 F/g, respectively.
The redox reactions in CBT and CBTG system is explained in the figure 31c. Figure 31 (c) compares the CV curves of the different BaTiO$_3$ specimens with the characteristic oxidation and reduction reaction for each peak. The reduced BaTiO$_3$ is responsible for the redox reactions. In CBT and CBTG system there are two redox pairs with oxidation and reduction found at $0.12V/-0.08V$ and $0.52V/0.35V$. During the reduction of BaTiO$_3$ the oxygen vacancies are created and a number of Ti$^{4+}$, Ti$^{3+}$ and Ti$^{2+}$ ions can be present in the lattice.
The Ti ions in dilute sulphuric acid medium undergo reactions at different potentials. When Ti (IV) compounds come in contact with dilute sulphuric acid its forms $[\text{Ti(H}_2\text{O)}_6]^{3+}$ (aq) ion.

\[
\text{Ti}^{3+} \rightarrow \text{Ti}^{4+} + e^- \quad 0.12\text{V (oxidation)} \tag{27}
\]

\[
\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+} -0.08\text{V (reduction)} \rightarrow [\text{TiO}^{2+} + 2\text{H}^+ + e^- \equiv \text{Ti}^{3+} + \text{H}_2\text{O} \tag{28}
\]

\[
\text{Ti}^{2+} \rightarrow \text{Ti}^{4+} + 2e^- \quad 0.52\text{V (oxidation)} \rightarrow \text{TiO}_2(\text{s}) + 4\text{H}^+ + 2e^- \equiv \text{Ti}^{2+} + \text{H}_2\text{O} \tag{29}
\]

\[
\text{Ti}^{3+} + e^- \rightarrow \text{Ti}^{2+} \quad 0.35\text{V (reduction)} \tag{30}
\]

The dissolved oxygen is reduced on the other solution side during the oxidation reaction which is
\[ \text{O}_2(g) + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O} \]  

(31)

The reactions in case of Ti ions were found to coincide with that of reduced TiO_2. Cyclic voltammetry of reduced TiO_2 (1050°C and 6 hours) was performed and the data is presented in Figure 31d. The redox pair at 0.12V/ 0.05V, signifying oxidation and reduction respectively, is of very low current, indicating its occurrence to be low. The other oxidation and reduction reaction corresponds to 0.52V (oxidation) and 0.37 V (reduction). The above mentioned redox pairs do not perfectly coincide with the CBT but fall very close. So, it clear that the redox reaction in CBT and CBTG are due to the valence transitions of Ti ions. The second oxidation - reduction reactions will be irreversible after a number of cycles, due to the depletion of Ti^{2+} ions. Figure 31d, shows the CV plot of reduced TiO_2 with the schematic of the redox reactions.

It is clear from the plot described that the redox reactions in CBT and CBTG are due to the Ti ions present in the lattice.

Figure 31 (d) shows also the CV plot of TiO_2 reduced under the same conditions as BaTiO_3 and is used to explain the capacitive behavior of TiO_2 and compare with the behavior of CBT, which has a higher capacitance even though the redox reaction are the same. The redox reactions of TiO_2 are similar to that of reduced BaTiO_3 which would indicate that the reactions arise from the Ti ions in the BaTiO_3 lattice. The specific capacitance of reduced TiO_2 is 13.04 F/g and that of CBT is 82.5 F/g. The CV plot of the reduced TiO_2 is more pseudocapacitive, therefore, than the CBT and CBTG material. Both the CBT and CBTG material will develop capacitance charges also from the double layer charging. The presence of double layer type charging mechanisms in CBTG is a significant reason that makes the use of BaTiO_3 advantageous over TiO_2.
4.4.3. Chronopotentiometry analysis of BaTiO$_3$s:

The Chronopotentiometry study was again performed in a two electrode cell with 1M H$_2$SO$_4$ as the electrolyte. The experiments were carried out at a constant current of 1 mA and the associated voltage responses recorded. The supercapacitor was charged for 200 seconds and discharged for 75 seconds. The figures 32 (a) (b) (c) (d) show the CP plot of pure BT, BT (Nd), CBT and CBTG respectively. The chronopotentiometry plot in figure 32 is a typical charge discharge curve, with both a charging forward cycle and a discharging reverse cycle. The capacitance here is calculated from the discharge cycle. All the four curves show voltage
saturation at some point and stabilization with time, with no further charging occurring. However, this saturation behavior was less in case of CBT and CBTG, which instead displayed a small voltage increase with time, giving an arc-like profile. All the four plots show a sudden drop in voltage as the discharge cycle starts. This is called an ohmic drop, and corresponds to the resistance present inside the system. The IR drop was lowest in case of CBTG and the highest in pure BT due to its non-conductive state. The IR drop in CBT was reduced, and also in the CBTG due to the addition of graphite into the system.

![Figure 32. Chronopotentiometry plot of (a) Pure BT, (b) BT (Nd)](image)

Here again during the charging cycle there occurs a near saturation state, where there was only a very slow rise in voltage, after it had reached a particular value during the charging cycle. An ideal supercapacitor CP plot would display a triangular shape instead.
The discharge capacitance values of all the BaTiO$_3$ were calculated and are tabulated in Table 3.

Table 3. Discharge capacitance values of all the BaTiO$_3$s

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Electrode Material</th>
<th>Discharge Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure BT*</td>
<td>3.33</td>
</tr>
<tr>
<td>2</td>
<td>BT (Nd)*</td>
<td>4.31</td>
</tr>
<tr>
<td>3</td>
<td>CBT</td>
<td>28.39</td>
</tr>
<tr>
<td>4</td>
<td>CBTG</td>
<td>56.25</td>
</tr>
</tbody>
</table>

* Unsintered Sample

All the discharge capacitance values in CP tend to correspond to that of the values from the cyclic voltammetry tests. The objective was to still reduce the IR drop in the discharge cycle.

Thus, from the three experiments conducted, both the CBT and CBTG specimens showed very good capacitive properties, due to the calcination in reducing atmosphere. The addition of 5 wt% graphite before the calcination process enhanced the capacitive properties, making the CBTG to develop both pseudocapacitive and double layer enhanced charge storage capacity.
4.4.4. Electrochemical data for Graphite (115 m²/g):

The electrochemical analysis of the precursor graphite (115 m²/g) was required in order to determine the additional double layer type charge storage in the CBTG composite electrode and also to study the significance of the graphite addition in the BaTiO₃ powder. Figure 33 shows the EIS plot of graphite (115 m²/g) powders. The EIS was performed at a voltage of 0.75 V between frequencies of 100 kHz and 1 Hz. The EIS plot clearly shows a straight line at lower frequencies inclined at 45°. At higher frequencies the vertical straight line displays the pure capacitive behavior of the material. This is analogous to the EIS of a double layer type charge storage electrode. The series resistance is 230 mohm which is very low value, showing it to be highly conductive. These are the main reasons for it to be incorporated into the BaTiO₃ powder to make a composite electrode. Figures 34 and 35 show the CV and CP plots respectively, of this graphite electrode system.

Figure 33. EIS Plot of Graphite.

56
Figure 34. CV plot of graphite

Figure 35. CP plot of Graphite
The cyclic voltammetry plot of graphite seems to be a rectangular curve with almost no redox reactions. The specific capacitance was calculated to be 55.86 F/g. The charge/discharge behavior shown is figure 35 is a perfect triangular shaped plot with fast charging and discharging. There is no point where the voltage saturates and become a straight line during discharging cycles. The discharge capacitance was calculated to be 36.28 F/g. All these double layer mechanism, charging/ discharging behavior, high conductivity and high surface, are among the compelling reason for the incorporation of graphite into BaTiO$_3$ matrix.

4.4.5. ABS – CBTG Composite Electrode system:

The ABS – CBTG composite electrode system was prepared by physical mixing method. The composite was tested for its electrochemical properties by varying its composition to detect how the system behaves. The ABS particles size is less than 150 μm and the CBTG particles are even finer, compared to its ABS counterpart. As there is large difference in the density of the two mixtures its volume% was used in the composition calculation.

4.4.5.1. EIS of ABS/CBTG composite:

EIS analysis was performed in a two electrode setup with 1M H$_2$SO$_4$ as the electrolyte operated at 0.75V from 100 kHz to 1 Hz. The electrode is named with the composition of ABS. The figure 36 (a) shows the EIS plot of the composite with ABS 70%. Figure 36 (b) shows the EIS plot of the composite electrode with ABS 50% and 60%. Figure 36 (c) shows the EIS plot of the composite electrode with 40%, 30%, 10% ABS. The figures 36 a,b and c are used to compare the charging behavior (from double layer to pseudocapacitive) and the resistance of the electrode with change in the ABS composition. It is used to explain the effect of the non-conductive ABS on the capacitive response of the composite. One clear conclusion that may be drawn from the
data is that for the three plots the \( R_s \) and the \( Z'' \) values decrease with decrease in the ABS content. This trend was expected because the ABS is a highly resistive material; with relatively low. All the four plots show a sudden drop in voltage as the discharge cycle starts. This is called an ohmic drop, and corresponds to the resistance present inside the system. The IR drop was lowest in case of CBTG and the highest in pure BT due to its non-conductive state. The IR drop in CBT was reduced, and also in the CBTG due to the addition of graphite into the system.

![Figure 36 (a).EIS plot of ABS – CBTG composite electrode system 70%](image)

Figure 36 (a). EIS plot of ABS – CBTG composite electrode system 70%
Figure 36 (b). EIS plot of ABS – CBTG composite electrode system ABS 50%, 60%.

Figure 36 (c). EIS plot of ABS – CBTG composite electrode system ABS 10%, 30%, 40%.
But the factor to be observed is the effect of ABS on the CBTG system. Firstly, Table 4, gives the values of $R_s$, $R_f$ and $Z''$ for each composite mixture.

**Table 4. EIS data of ABS – CBTG composite electrode system.**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Vol% ABS (in electrode)</th>
<th>$R_s$ (ohm)</th>
<th>$R_f$</th>
<th>$Z''$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>70%</td>
<td>61.4</td>
<td>45.6</td>
<td>57.03</td>
</tr>
<tr>
<td>2</td>
<td>60%</td>
<td>0.485</td>
<td>27.51</td>
<td>33.47</td>
</tr>
<tr>
<td>3</td>
<td>50%</td>
<td>1.131</td>
<td>14.45</td>
<td>13.63</td>
</tr>
<tr>
<td>4</td>
<td>40%</td>
<td>1.263</td>
<td>16.65</td>
<td>9.19</td>
</tr>
<tr>
<td>5</td>
<td>30%</td>
<td>2.419</td>
<td>16.61</td>
<td>5.82</td>
</tr>
<tr>
<td>6</td>
<td>10%</td>
<td>0.734</td>
<td>4.76</td>
<td>1.83</td>
</tr>
</tbody>
</table>

As Table 4 indicates, the 70% ABS and pure ABS do not show very good capacitive properties, as the ABS powder is highly resistive, which is in keeping with the $R_s$ and $Z''$ values obtained. As the composition of ABS decreases, the $R_s$ value falls less than 5 ohm and $R_f$, which is the faradaic or charge transfer resistance, gradually reduces also. Figure 36 (a), for the 70 vol% ABS specimen, shows a typical Randles circuit behavior. It traces a semicircle followed by a straight line at almost 45°. But as the ABS composition decreases the shape of the curve changes to be analogous with that of the CBTG’s EIS curve. Figure 36 (b), starts tracing a semicircle at lower frequencies with a straight vertical line at high frequencies. As the volume of ABS decreases further (figure 36 (c)) the semicircular curve becomes smaller with low values of $R_f$ and $Z''$, which means more pseudocapacitance and low charge transfer resistance. The ABS component did not show very high capacitive effect, although composites in the region from 60% - 90% ABS showed very similar and table values.
4.4.5.2. Cyclic Voltammetry of ABS – CBTG composite electrode:

The ABS – CBTG is a complex three-way electrode system as it has three components that can affect the electrochemical properties of the materials. So, the cyclic voltammetry was used to evaluate the three electrode system, in order to elucidate the properties of the electrode material and also explain the type of charge storage. The three-electrode system magnifies the redox reactions so that the materials’ properties and the redox reactions can be studied. In figure 37 is shown the CV plot of ABS 70%, 60% and 50%, and figure 38 shows the CV plot of 40%, 30% and 10% ABS. Figures 37 and 38 are used in explaining the effect of change in pseudocapacitive behavior with the ABS content. They can also explain the reduction in area (lowering of capacitance) with increasing ABS, and also the change in the intensity of the redox peaks with ABS content. All the CV plots looked similar, with two redox pairs. One redox pair occurs at 0.12 and -0.08 V, which are oxidation and reduction reactions respectively.

Figure 37. CV plot of ABS – CBTG composite with ABS composition 30%, 40% and 50%
The other redox pair occurs at 0.62 and 0.37V which are again oxidation and reduction reactions respectively. One region would appear to be rectangular in form, indicating the electrode’s capacitive behavior. The difference between the curves is in the intensity of the redox peaks and the areas enclosed within the curve. Comparing the curves with 70% ABS and 10% ABS, the curves from the outset look very similar, but the maximum current reached for the redox peaks is higher in the case of lower ABS composition. Also, the area inside the curve became reduced within the narrow middle region, for the lower ABS composition. The Table 5 compares the CV data for the ABS – CBTG composites, as determined from the 2 and 3 electrode system.

Cyclic voltammetry evaluations of the 30% and 10% ABS composite electrode system were carried out using the two-electrode system. These plots did not show much redox reaction, due to the lesser amounts of electrolyte used, but a pseudocapacitive condition was clearly evident.
Table 5. Capacitance data of ABS – CBTG composite

<table>
<thead>
<tr>
<th>S. No.</th>
<th>% ABS</th>
<th>Area equivalent in CV curve (C)</th>
<th>Specific Capacitance (F/g)</th>
<th>Specific Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3 electrode cell</td>
<td>3 electrode cell</td>
<td>2 electrode cell</td>
</tr>
<tr>
<td>1</td>
<td>70</td>
<td>1.871</td>
<td>93.56</td>
<td>3.38</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>2.47</td>
<td>123.5</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>2.53</td>
<td>126.5</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>2.57</td>
<td>128.5</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>3.001</td>
<td>150.05</td>
<td>36.89</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>3.405</td>
<td>170.25</td>
<td>84.28</td>
</tr>
<tr>
<td>7</td>
<td>0 (pure CBTG)</td>
<td>3.787</td>
<td>189.36</td>
<td>100.9</td>
</tr>
</tbody>
</table>

Figure 33 and 34 show the CV plots and data for the ABS 10% - CBTG and ABS 30% - CBTG. The two figures 33 and 34 depict the behavior of an ABS-CBTG composite in a two electrode setup and the difference in area inside the curve in 10% and 30% ABS which accounts for the capacitance. These two curves are a clear indication that the area inside the curve can be closely correlated with changes in capacitance.

In case of 10% ABS composite only one of the redox pairs of the CBTG takes place. The area equivalent inside the curve was 0.7464 C. The capacitance of the composite electrode is 37.32 F/g. In case of 30% ABS the current response becomes lower because of the lower conductive composite, and the capacitance was also lower. The area equivalent inside the curve was 1.8062 C.
The specific capacitance of the 10% ABS composite electrode was 90.31 F/g. The redox reactions in each case were slightly displaced, which is an outcome attributed to the higher resistance of the electrodes.

4.4.5.3. Chronopotentiometry of the composite electrodes:

Chronopotentiometry measurements were performed using the two-electrode cell at 1 mA control current, to test charge/ discharge characteristics of the electrode specimens. Figures 41
and 42 display the charging and discharging characteristics of the composite electrodes with ABS 30% and 10%, respectively. There is clear indication of the curves tracing an arc in the charging cycle in the figure 41 and 42 which is a sign of voltage saturation and a non-linear charging. The discharge capacitance of 30% ABS electrode was 41.22 F/g. The discharge characteristics were similar to that of the CBTG electrode. The discharge capacitance of 10% ABS electrode was 49.36 F/g. The sudden drop in the voltage is due to the IR drop which is connected to the high resistance of the ABS particles. The important discussion that can be brought about after the ABS – CBTG electrode system is its structure. Even though the ABS system is non – conductive, 30% ABS seems to provide a fairly high capacitance value, due in part to the unique composite structure that is formed. The capacitance is high because of the fact that the whole system is still fairly conductive. This might be due to the fact that a core – shell structure is developed with an ABS core and CBTG shell, as confirmed by SEM analysis, which makes the system conductive.

Figure 41. Chronopotentiometry plot of ABS – CBTG composite electrode with 30% ABS
Figure 42. Chronopotentiometry plot of ABS – CBTG composite electrode with 10% ABS

Considering the fact that the CBTG particles are very fine and of high surface area, as the ABS content increases the CBTG shell volume will decrease, developing in the process a lower conductive material, because of the lessened conductive shell volume

4.4.6. Polyaniline (PANI) – CBTG Composite electrode system:

The PANI – CBTG composite system was also explored and developed as an electrode material, where the ABS matrix content is replaced by PANI. Polyaniline (PANI) is a conductive material and also has very good pseudocapacitive properties. The composite was varied in its composition between PANI and the CBTG, and its electrochemical behavior observed. The PANI, being a good capacitive material, was expected to significantly enhance the overall capacitive property of the composite. The composite was prepared using physical blending and mixing of the CBTG powders. The electrode composite itself was prepared by coating and subsequent pressing methods.
4.4.6.1. Cyclic Voltammetry of PANI – CBTG composite:

In order to determine the different redox reactions in the system, the three electrode system was employed in 1M H$_2$SO$_4$ from -0.2 V to 0.8 V. Figures 43 and 44 show the CV curves of PANI – CBTG composite at different PANI composition. Both figure 43 and 44 show the change in the pseudocapacitive and the double layer behavior. One can also note the changes in the area of the curve and the redox peaks with the changes in composition. This data is compared in Table 6. The area changes and the redox peak shift are the main features evident, and were used to explain the capacitive effect on both components, at each composition. The electrode was first tested with 40 Vol% of PANI which showed little residual characteristics of the PANI. It was mostly dominated by the CBTG redox peaks. There is a small issue with the recognition of the redox peaks in this system. In case of CBTG electrode and ABS – CBTG composite electrode, one of the redox pairs occur at 0.61 V and 0.34 V, which represents oxidation and reduction reactions, respectively. In case of PANI, the physical state in which it is used is emeraldine salt. One of the redox reactions pair in PANI occurs at 0.66V and 0.30 V which are oxidation and reduction reactions respectively. At 0.66 V the emaraldine salt is oxidized to the leucoemaraldine base and vice verse at 0.29 V, which is a reduction reaction. So in this case, carefully observing the redox reaction voltage is very important.

Figure 43 shows the CV plot of the PANI – CBTG composite system with 40% and 50% PANI. The electrode with 40% PANI shows a very large area inside the curve, unlike the ABS composite. This characteristic is mainly due to the addition of PANI into the system. As already discussed, the one redox pair is confirmed to be from CBTG, which has an oxidation peak at 0.12 V, and reduction peak at -0.1V. The other redox pairs occur at 0.60 V and 0.35 V. This can be confirmed to be a redox pair, arising from CBTG also.
But in case of 50% PANI, the same redox peak displacements occurred towards the PANI’s side, which can be either from PANI or CBTG. Figure 44 shows the plot of the composite with 60%, 70% and 90% PANI. For this condition, the displacement of the redox pair towards the PANI side still occurred.
In 70% specimens, the redox reactions appears to be from PANI, where at 0.639 V the emeraldine salt reduces to its leucoemeraldine base, and again at 0.284 V, where the leucoemeraldine base gets re-oxidized to the emeraldine salt [24]. The center region shows a rectangular curve with a very large area, interpreted as capacitance from the double layer. On another side, the plots show that the redox pair from CBTG curve at left became progressively lower in intensity as the PANI composition increased. It is at about 70% PANI, that both the effects of PANI and CBTG are fully attained, resulting in the very high area in the CV curve, corresponding to the high capacitance condition. When the PANI composition further increased to 90%, the effect of CBTG almost disappears, with a corresponding decrease in capacitance. So the composite with PANI 70% shows very good pseudocapacitance properties from both PANI and CBTG contributions.

Table 6. Capacitance from CV analysis of PANI – CBTG composite.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>PANI (%)</th>
<th>Area equivalent in CV curve (F)</th>
<th>$C_{sp}$ (F/g) (3 electrode)</th>
<th>Oxidation peak 1 (mV)</th>
<th>Oxidation Peak 2 (mV)</th>
<th>$C_{sp}$ (F/g) (2 electrode)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure CBTG</td>
<td>3.787</td>
<td>189.36</td>
<td>310</td>
<td>580</td>
<td>100.9</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>3.369</td>
<td>168.45</td>
<td>340</td>
<td>601</td>
<td>120.65</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>3.922</td>
<td>196.10</td>
<td>328</td>
<td>616</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>4.928</td>
<td>246.4</td>
<td>282</td>
<td>638</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>5.776</td>
<td>288.8</td>
<td>284</td>
<td>639</td>
<td>189.2</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>5.504</td>
<td>275.2</td>
<td>292</td>
<td>646</td>
<td>182.78</td>
</tr>
<tr>
<td>----</td>
<td>-----</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>------</td>
<td>--------</td>
</tr>
<tr>
<td>7</td>
<td>Pure PANI</td>
<td>4.572</td>
<td>228.6</td>
<td>290</td>
<td>646</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 45 shows the CV plot of the PANI-CBTG composites, compared with that of pure PANI. There are two redox peaks that are clearly visible. In Figure, the areas inside the curve and the redox reactions can be used to check whether the redox reactions in each composition are from CBTG or PANI. One curve represents the conversion between the emeraldine salt and leucoemeraldine base at 0.63 V and 0.28 V, respectfully. The other curve represents the conversion between emeraldine salt and peringraniline salt is at 0.3 V and 0.22V. The middle region has a very large area, indicative of very high capacitive properties. These are all the reactions that are possible in the PANI composite system but the pure PANI curve also exhibits a large area in the central region corresponding to double layer charging. Both these mechanisms contribute, therefore, to the overall high capacitance of this system.

Figure 45. CV plot of Pure PANI compared with PANI – CBTG system (emeraldine salt) in a three electrode system.
Figure 46 shows the CV plot of PANI + CBTG system in a two electrode setup with PANI 40%, 70% and 90%. The plot with 40% PANI clearly shows one redox pair from the CBTG system, which is the more dominant case here. The PANI in the two electrode system did not appear to express its redox reaction to a high intensity. This is due to a lower conversion rate from one state to another, which means less production or intake of ions. As the PANI composition increases to 70% and 90%, however, the CBTG redox reactions become suppressed, showing the dominance of PANI. There is also a large area formed inside the curve, indicative of a large amount of double layer charge storage. The specific capacitance values are given in Table 6.

![CV plot PANI + CBTG electrode system in two electrode setup.](image)

When there is 40% PANI in the electrode, due to low PANI quantity, one can only observe the redox pair of the CBTG, which is assumed to be from the Ti ions present in the BaTiO₃. As the PANI composition increases to 70%, the shape of the curve shows a large difference, becoming
slightly rectangular shaped and more asymmetric. The narrow snout shaped part in that curve is due to the effect of CBTG as it shows a similar behavior to that of the 40% curve. But the large and broad redox curve of the 70% PANI composite is due to the combined reaction occurring in both CBTG and PANI. As already mentioned the shift in the voltage can also be due to the resistance factors [6]. When the 90% and 70% curves are compared, the area inside the curve is almost the same with slight higher area for the 70% curve due to the pseudocapacitance. The areas equivalents in the curves are 2.393C for 40% PANI, 3.784C for 70% PANI and 3.655C for 90% PANI. In most of the literature redox reactions are not clearly observed in the two electrode setup, so that an asymmetric curve is attributed to the presence of pseudocapacitance. The slope changes in the curve are also explained as a pseudocapacitive behavior. So, it is not necessarily the case that pseudocapacitive curves need to be attributed by redox reactions.

4.4.6.2. Chronopotentiometry of electrodes:

Chronopotentiometry measurements for PANI – CBTG composites composite electrodes were performed in the 2 electrode cell at 1 mA. Figures 41, 42, 43 show the CP plots of the PANI – CBTG composite with PANI 40%, 70%, and 90% respectively. The chronopotentiometry plots show a linear charging behavior in all the three plots without voltage saturation which is perfect for an ideal supercapacitor. These electrodes were charged for 200 seconds and were discharged for 100 seconds, making efficiency to be ~ 50%, which was assumed to be the case.
According to the capacitance value from the CV curves, the chronopotentiometry also shows a similar behavior in the discharge capacitance. The composite electrode with 70% PANI gives the best value of 84.88 F/g. These values are shown to be equal to or somewhat lower than the CBTG electrodes. This is because the efficiency of the CBTG was 25%, and this composite electrode has an efficiency of 50%.
The Table 7. shows the values of the discharge capacitance of these electrodes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>% PANI</th>
<th>Discharge Capacitance (F/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>42.73</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>84.88</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>67.47</td>
</tr>
</tbody>
</table>

The curves were analogous to a perfect supercapacitor curve with no saturation in voltage after a particular value, and they showed a triangular shaped behavior, indicating fast charging and discharging characteristics.

4.4.7. Effect of current during Chronopotentiometry:

The PANI 70% + CBTG composite electrode was found to be one of the best compositions in the composite electrode system. The system was tested for performance at a higher current in the chronopotentiometry using two electrode system with 1M H₂SO₄ as electrolyte. The electrode setup was charging and discharging for 100 seconds and 75 seconds, respectively. The efficiency
of the cell was 75%. Figure 50 shows the CP plot of the composite electrode system charged at 1 mA and 5 mA. From figure 50, it is clear that the discharge curves are very similar, except for the fact that the IR drop is increased in case of the 5mA CP plot. This was due to the higher reverse current which resulted in a higher drop. The discharge capacitance of the electrode charged at 1 mA was 61.8 F/g and the one charged at 5 mA was 173.29 F/g. The electrode charged at 1 mA shows a lower discharge capacitance, compared to the one charged at 1 mA for 50 seconds, because of the fact that the efficiency here is 75% and the 50% in the earlier case.

![Figure 50. CP plot of the composite electrode system charged at 1 mA and 5 mA.](image)

The discharge capacitance increases, therefore, with the charging current, which itself is a function of the charges stored.
4.4.8. Cyclic Life of PANI 70% + CBTG composite:

The PANI 70% + CBTG composite electrode was studied for its cyclic life and its repeatability. So again the chronopotentiometry was performed for the electrode system for 100 cycles at 1 mA and 5 mA at similar conditions as described above. Figure 51 and 52 shows the plot between cycle number and discharge capacitance for 1 mA and 5 mA respectively. The data in figures 51 and 52 can be were used to explain the life of the capacitor cell in the electrolyte present in the cell. The stable, the capacitance value for a large number of cycles, the higher is the cyclic life, as in PANI – CBTG composite. The value from both the plots clearly shows a stable value of capacitance without any deviation.

![Figure 51 Cycle vs. Capacitance of PANI 70% + CBTG composite at 1 mA](image-url)
4.4.9. Effect of electrolyte on PANI 70% + CBTG composite:

The electrolyte is a very important factor in case of pseudocapacitive electrodes. The experiments were performed in a three electrode cell. The redox reactions and its current intensity response will differ in a CV plot accounting to its capacitive behavior. Here the PANI 70% + CBTG composite were tested in 1M H$_2$SO$_4$ and 1M KOH. Figure 43, shows the CV plot of the composite in both the electrolytes in a three electrode system. The two curves show the changes in redox reaction when an electrolyte is changed. The change can be explained from the difference in the area of the curve and the different redox reactions. The area equivalent inside the CV curve of the PANI – CBTG composite with 1M H$_2$SO$_4$ and 1M KOH were 5.776 C and 1.87 C respectively. The capacitance of the PANI - CBTG with 1M H$_2$SO$_4$ and 1M KOH were 288.8 F/g and 93.5 F/g respectively. The redox reactions in 1M KOH were similar, as explained in the case of 1M H$_2$SO$_4$. Additional reactions were also observed with the KOH electrolyte, and
the redox pairs of the CBTG were also not as prominent in the KOH electrolyte system. Instead, a more intense double layer phenomenon is observed, without any redox reactions of the CBTG.

![Graph showing CV plots of PANI 70% + CBTG composite in 1M H$_2$SO$_4$ and 1M KOH system.](image)

Figure 53. CV plots of PANI 70% + CBTG composite in 1M H$_2$SO$_4$ and 1M KOH system.

The redox pairs in figure 53, were mostly from PANI. The emeraldine to leucoemaraldine oxidation occurs at 0.62 V which can also be CBTG’s reaction and its corresponding reduction at 0.275 V. The other oxidation approximately at 0.3V should be from emeraldine salt to peringranilne salt and again its oxidation to emaraldine state at -0.1V. The reaction in the KOH system is only from the PANI and the redox reactions of BaTiO$_3$ are absent which is mainly due to the fact that the Ti ions does not actively with hydroxide. Thus, only due to the presence of
the redox reactions of PANI, the capacitance of the PANI – CBTG electrode in KOH electrolyte is fairly lower compared to that of the \( \text{H}_2\text{SO}_4 \).

4.4.10. Energy & Power Density of Composite electrode system:

The energy and power density of the composites are important factors dealing with the practical application of the composite electrodes. The energy density can be calculated from

\[
E = 0.5 \ C_{sp} (\Delta V)^2
\]  

and power density can be calculated from

\[
P = \frac{E}{\Delta t}[9]
\]

Table 8 show the Energy density and Power density of the composite electrode materials.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Material</th>
<th>Energy Density (Wh/kg)</th>
<th>Power Density (W/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CBTG</td>
<td>0.373</td>
<td>26.85</td>
</tr>
<tr>
<td>2</td>
<td>PANI 70% + CBTG (1 mA)</td>
<td>0.423</td>
<td>20.32</td>
</tr>
<tr>
<td>3</td>
<td>PANI 70% + CBTG (5 mA)</td>
<td>0.777</td>
<td>37.33</td>
</tr>
</tbody>
</table>

These are calculated from the chronopotentiometry plot of the composites. The energy and power density are quite high for PANI – CBTG composite system.

4.4.11. Electrochemical data of CBTAC (Calcined BT – Activated Carbon):

The activated carbon used to prepare this electrode has a surface area, 900 m\(^2\)/g. The composite is prepared in the same way as CBTG. The electrode contains 5 wt% of activated carbon. The electrochemical tests were performed to observe the effect of activated carbon, and to compare it
with the graphite (115 m²/g). Cyclic voltammetry tests were performed in the voltage range between 0.2 V – 0.8 V in 1M H₂SO₄ electrolyte. Figures 48 (a), (b) show the cyclic voltammetry and EIS plots of the CBT-AC sample. The plot shows redox reactions similar to that of CBTG and CBT, but the peak current and potential changes are present in this case. The lowering of the peak current is basically due to the effect of activated carbon as it forms a shell over the BT structure whose surface area (900 m²/g) is very high compared to graphite (115 m²/g). The CV plot shows a large area inside the curve which is due to double layer charging associated with the activated carbon. The area equivalent inside the CV curve was 3.78 F. The specific capacitance was determined to be 183 F/g, which is high compared to CBTG, and is due to the higher double layer charging present in the activated carbon. In figure 54 (b), the EIS spectra show a similar type of behavior as in figure 33 which was the EIS of graphite. The EIS plot (figure 54(b)) showed more of a double layer type charging with Rs 726.3 mohm. The low frequency region traced a straight line as in a double layer charging, unlike the pseudocapacitive electrode.

Figure 54 (a) CV plot of CBTAC; (b) EIS plot of CBTAC
4.4.12. Discussion:

The results from the structural characterization and electrochemical characterization have to be correlated to understand pseudocapacitive behavior of the reduced BaTiO$_3$ system. The major part of the electrochemical data has to be explained by the structural features (using SEM) developed in the electrode material during the processing step. The Nd doped BaTiO$_3$ was prepared using a simple ball milling technique where the doping was clearly indicated by the shift in the XRD peaks created by the strains introduced due to interstitial position attained by the dopant (Nd). The (reduced BaTiO$_3$) CBT had low resistivity (43.8 ohm/cm) due to the polaron conduction of the influenced by the creation of Ti ions during the calcinations process. The introduction of the 5 wt% graphite into CBT (CBTG) reduced the resistivity (0.98 ohm/cm) of the composite. The SEM of the calcined CBT powder showed the presence of the highly porous structure with rough surface. The rough surface was formed due the evaporation of the binder which was present over the particles before calcination. The electrochemical data of the BaTiO$_3$ at different levels of synthesis which are pure BT, Nd doped BT, CBT and CBTG showed progressive increase in the capacitance from 2.43 to 100.9 F/g respectively. The capacitance change was attributed to the onset of the pseudocapacitance in the CBT and CBTG electrode. The presence of graphite in the CBTG system increased the double layer charging of the BaTiO$_3$ electrode system. The important factor in the CBT(C=82.5 F/g) ($A_{eq}$=1.65C) and CBTG (C=100.9 F/g) ($A_{eq}$=2.018C) system is to identify the redox reaction which brings the pseudocapacitance. This is accounted to the creation of the Ti ions in the system which is reactive in an acidic environment. In order to confirm that the reactions were solely from Ti ions and the intermediates, reduced TiO$_2$ electrode was characterized electrochemically using cyclic voltammetry (CV) to see if a similar cyclic
voltammetry behavior was obtained. The CV of CBT and reduced TiO$_2$ was similar indicating the redox reaction in CBT and CBTG was from the Ti ions [35]. The capacitance of reduced TiO$_2$ was 13.04 F/g with an area equivalent of 0.2608 C inside the CV curve. Comparing both TiO$_2$ and CBT, the redox reactions were same in both but the areas inside the curve and the resulting capacitance was small. There lays a major reason for BaTiO$_3$ being more capacitive than TiO$_2$ which is because BaTiO$_3$ by itself is dielectric material with a dielectric constant ranging from 2000 to 10000 which makes it an electrostatic capacitor material. The electrostatic charge storage adds to the double layer and pseudocapacitance of the electrode formulating CBTG to be supercapacitor material. The area inside the CV curve of CBTG (2.018 C) was very high compared to that of CBT (1.65 C) which was due to the graphite due to its double layer charging behavior. The area is mentioned in terms of coulombs because the area inside the CV curve is the charge stored as integration of current with respect to time gives us the charge. The structure of the CBTG composite was studied to explore the behavior provided both pseudocapacitance and double layer charging in the CBTG system. The CBTG pellet was observed for its cross-sectional structure which revealed a core – shell like structure with a BaTiO$_3$ core and graphite shell. From the CBTG structure it is evident that the graphite core was the reason for low resistivity (0.98 ohm/cm) and the hybrid capacitive behavior of CBTG electrode. Now the ABS – CBTG composite structure was developed which proved to be diminishing effect in terms of capacitance as the ABS content increased. Reduction in the capacitance with increasing ABS was due to the non – conductive nature and bigger particle size of the ABS. The higher capacitance (90.31 F/g) in case of 10% ABS composite was due to the coating of the CBTG particle over the ABS particle which increased the conductivity. The PANI – CBTG composite developed by partial solution mixing method showed a highly capacitive behavior due to inherent capacitive properties of PANI. The 70% PANI composite showed a capacitance of 189.2 F/g which was contributed by
both PANI and CBTG. The area equivalent inside the CV curve was (3.784C). The two electrode CV curves of PANI – CBTG were skewed. The slope difference and asymmetric shapes of the curves can also express pseudocapacitive behavior in a two electrode cell system [36]. The charge – discharge characteristic of the PANI – CBTG composite for 100 cycles showed a steady capacitance of 61.8 F/g and 110 F/g for electrodes charged at 1mA and 5 mA respectively. The charge – discharge curve showed high capacitive behavior (75% efficiency) with fast charging and discharging without any signs of voltage saturation. The behavior of activated carbon (S.A-900m²/g) was studied instead of graphite in the CBT system named CBTAC. The capacitance was 189 F/g with no effect on the redox reactions of the BaTiO₃. The increased capacitance in CBTAC was due to the high surface area of the activated graphite which increased the double layer charging and it was evident from the larger area equivalent (3.66C) inside the curve. So, as a whole when the capacitive behavior a the BaTiO₃ system has been studied, every step has been take from the pure BaTiO₃ to improve the capacitive properties either by improvising through a processing step or by making a composite or both together. The table 9, below shows the capacitance different electrode materials studied in this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>As prepared Nd: BaTiO₃</th>
<th>Graphite</th>
<th>TiO₂</th>
<th>CBT</th>
<th>CBTG</th>
<th>CBTAC</th>
<th>PANI + CBTG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area in CV curve (C)</td>
<td>0.1396</td>
<td>1.117</td>
<td>0.2608</td>
<td>1.65</td>
<td>2.018</td>
<td>3.66</td>
<td>3.784</td>
</tr>
<tr>
<td>Capacitance F/g</td>
<td>6.98</td>
<td>55.86</td>
<td>13.04</td>
<td>82.5</td>
<td>100.9</td>
<td>183</td>
<td>189.2</td>
</tr>
</tbody>
</table>

The capacitive characteristics of the earlier studied materials PANI, ABS, graphite, activated carbon, TiO₂, NiO were basically from the either double layer charging or pseudocapacitance. But BaTiO₃ is unique in its own in reduced state where capacitance comes from two major
contributions. One is the pseudocapacitance arising from the Ti ions present in the lattice and the other is from the inherent, electrostatically charging capacitive nature of BaTiO$_3$. When graphite comes into the system there are three components that add to the capacitance which are pseudocapacitance from the Ti ions, electrochemical double layer from graphite, electrostatic (dielectric) charging from BaTiO$_3$ itself. When high surface area activated carbon (900 m$^2$/g) is using instead of graphite the capacitance increase due to the high surface which provided increased double layer charging compared to low surface area graphite (115 m$^2$/g). So from the table 9, one can clearly indentify the difference with different modes of charging possessed by the electrode materials, from pure EDLC type in graphite to pseudocapacitance in TiO$_2$ and combined effect of EDLC, electrostatic charging and pseudocapacitance in case of CBTG, CBTAC and CBTG-PANI composite.

5. **SUMMARY**

1. A novel, two electrode sandwich cell was developed for testing the performance of the electrode material as a capacitor cell.

2. The calcination of BaTiO$_3$ (Nd) in a reducing atmosphere greatly increased on the conductivity of the material. The process of ball milling the BaTiO$_3$ (Nd) with 5 wt% graphite and calcining in a reducing atmosphere, resulted in high conductivity. The desired low resistivity was one of the supercapacitor electrodes were achieved; the resistivity achieved for CBT was 43.8 ohm/cm and 0.98 ohm/cm for CBTG specimen.

3. The capacitance of 82.5 F/g for CBT sample was recorded by cyclic voltammetry and its EIS plot was consistent with pseudocapacitive charge storage in 1M H$_2$SO$_4$. The CBTG had a capacitance of 100.9 F/g according to the CV plot but, its EIS showed a showed a slight
deviation from the semicircular trace, making it almost a straight line, consistent with the presence of double layer capacitance along with pseudocapacitance. The excess double layer capacitance was due to the addition of graphite with a surface area 115 m²/g.

4. The ABS – CBTG composite showed lower capacitance with increasing ABS content. The composite electrode with 30% ABS and 10% ABS showed capacitances of the 37.32F/g and 90.31F/g respectively in a 1M H₂SO₄. The charge/discharge curves showed a discharge capacitance of 37.67 F/g and 49.86 F/g for 30% and 10% ABS composites respectively.

5. In the PANI – CBTG composites, CBTG’s redox reactions dominated when the composition of CBTG was high and vice versa. The 70 vol% PANI electrode showed a capacitance of 189.2 F/g with the redox reactions of both PANI and CBTG. The charge discharge exhibited a triangular shaped curve typical of a supercapacitor. The discharge capacitance was 84.88 F/g.

6. The effect of current on the charge/discharge curves on PANI/CBTG composite was studied. The cell was charged at 1 mA and 5 mA for 100 second and discharges for 75 seconds at the same reverse currents. The sample charged at 1 mA had a discharge capacitance of 61.8 F/g and the one charged at 5 mA had a discharge capacitance of 110 F/g. The efficiency of this cell was 75%.

7. The energy and power density of the PANI – CBTG composite was calculated from the chronopotentiometry data. The energy density was 0.777 Wh/kg and the power density calculated was 37.33W/Kg.

8. The SEM of the CBTG composite shows that the BaTiO₃ coated with graphite material resulted in a core – shell structure with a BaTiO₃ core and a conductive graphite shell. The overall effect was a highly conducting and high surface area composite electrode.
6. CONCLUSIONS

1. A new two electrode electrochemical cell design consisting of two electrodes on a current collector sandwiching a separator membrane with electrolyte, developed during the course of the study, was successful used to measure the capacitive properties of composite electrode materials in a capacitive cell.

2. An increase in the conductivity of the BT (Nd) electrodes was observed due to the calcination under reducing atmosphere producing ample Ti ions at $3^+$ and $4^+$ oxidation states attributed to development of polaron conduction on the Ti lattice. This increased conductivity made the electrode suitable for a supercapacitor electrode.

3. The inclusion of graphite before calcination formed a core – shell type structure on calcinations, with a BaTiO$_3$ (Nd) core and a graphite shell making it a hybrid composite electrode with of both pseudocapacitive and double layer properties.

4. A new ABS – CBTG (Calcined Barium Titanate Graphite) composite system was found to be a supercapacitive electrode at high CBTG composition. This system forms a core – shell structure with a non – conductive ABS core and a highly conductive CBTG (BT – graphite composite) shell. As the ABS content increases the conductivity gradually decreases, decreasing the capacitance of the composite.

5. A new PANI – CBTG system showed high capacitance of 189.2 F/g, exploiting the pseudocapacitive and the double layer features of both CBTG and PANI.
6. The partial solution mixing technique used for the preparation of the composite provided the basis for the core – shell structure which resulted in higher and more stable capacitive properties compared to the PANI/Graphite and metal oxide electrodes studied earlier.

7. The cyclic life of PANI – CBTG composite was studied at different currents (1 and 5mA) for 100 cycles without any decay to the capacitance. The composite also shows energy and power density in the supercapacitive range.

8. A comparative study has been made to indicate progressive increase in the capacitive properties in Pure BT, CBT, CBTG, CBTAC and PANI – CBTG composite electrode with separate and combined type charging behavior.

7. **SUGGESTIONS FOR FUTURE WORK:**

1. The TEM studies of the CBTG composite structures is suggested so as to gain a better understanding of the core – shell type structure and its effect on electrochemical phenomenon.

2. The effect of other electrolytes like TEATBF$_4$, HCl, KOH and also neutral salts like KCl can be studied with the view to enhance the capacitive properties.

3. New type of electrode preparation techniques, such as spin coating, screen printing and like methods should be incorporated to study the effect in electrochemical behavior.

4. The current collector used here is silver, but substitution of nickel, stainless steel and copper can be evaluated to study its adherence and performance of the electrode material.

5. The sol-gel or solid – state preparation synthesis techniques of Nd doped BaTiO$_3$ can be studied to observe its effect on electrochemical behavior as the synthesis technique has effect on morphology, surface area, particle size, dopant distribution.
6. The stability of the electrode system can be studied for longer cycles ranging from 500-1000 cycles to the estimate the life time of the electrodes

8. REFERENCES


7. H. Von Helmholtz; Annals of Physics, (Leipzig) 89 (1853) 389.


32. Relva C. Buchanan, Eusiuk Park, Rajesh Surana, Harshani Tennakone, Kirthi Tennakone; “High piezoelectric actuation response in graded $\text{Nd}_2\text{O}_3$ and $\text{ZrO}_2$ doped $\text{BaTiO}_3$ structures”; *Journal of Electroceramics* (2011) **26**; 116 -121.


