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I, Dushyant Gautam, hereby submit this original work as part of the requirements for the degree of Master of Science in Materials Science.

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Electrochemical study of Barium Cuprate system for super capacitor electrode applications

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Abstract:

Super capacitors are energy storage devices capable of storing capacitive charges orders higher than the regular capacitors. Notable for supercapacitors is that the discharge rate is orders higher compared to a battery leading to high power density. This combination of high charge storage and high discharge rate gives the supercapacitor a unique utility as an adjunct power source. Modern super-capacitors employs pseudocapacitance by using transition metal oxide (NiO, RuO$_2$, MnO$_2$, CuO, Co$_3$O$_4$) and their ability to yield redox reactions [40]. These oxides are usually associated with traditional carbon material (Activated Carbon, Graphite, Carbon Nanotubes), primarily dependent on electrical double layer capacitance (EDLC) for storing energy, to enhance overall capacitance. Some oxides such as Ruthenium Oxide can produce multiple oxidation state transitions and this particular property allows them to store more energy per unit volume [40]. The commercial application of Ruthenium Oxide is limited due to scarcity and expensive nature of extraction [42]. Much attention has been accorded to the binary and ternary oxide systems since the enable multiple redox reactions originating from different oxides [35]. The study explores and establishes Barium Cuprate (BaCuO$_2$) as base binary oxide compound from the standpoint of supercapacitor electrode material. Barium Cuprate can be synthesized at lower temperature of 500°C by sintering under lower partial pressures of oxygen. Also the structure consist of planes where there is only Copper and oxygen present, which is essential for the redox transitions. Electrochemical characterization of pure Barium Cuprate exhibited Cu$^{+1}$/Cu$^{+2}$ transition. Further, a ternary oxide solution was created by doping Barium Cuprate with Bismuth (III) (5% and 10%). The electrochemical properties indicated redox reactions from Bismuth (Bi$^{3+}$/Bi$^{+1}$) and Copper (Cu$^{+1}$/Cu$^{+2}$). Addition of Bismuth to the Barium Cuprate also enhanced copper’s redox reactions. Copper’s redox reaction were also found to improve with heat treatment of Barium Cuprate in
reducing atmosphere (90% Nitrogen and 10% Hydrogen) at 500°C for 2 hours. Structural characterization and Vibrational studies indicated partial reduction of Cu$^{+2}$ to Cu$^{+1}$ due to the Bismuth (III) substitution at Barium site and Heat treatment respectively. The combined effect of both bismuth doping and heat treatment was found to be most effective in improving electrochemical properties. The powders of Barium Cuprate, Bismuth doped Barium Cuprate, heat treated Barium Cuprate and heat treated Bismuth doped Barium Cuprate were prepared and spin coated with Poly-Ethylene oxide (PEO) and Graphite onto stainless steel substrates [41, 42]. The electrochemical characterization showed that redox reactions of Copper and Bismuth were retained and maximum of charge storage was obtained at 343mC/cm$^2$ (101.5 F/g) for heat treated 5% Bismuth doped Barium Cuprate powder based films. The composite electrodes posts very high charge storage value considering the large range of operation of 1.15V (-0.70V-0.45V vs SCE). These electrode are able store charge on both side of 0V vs SCE and can serve as symmetric electrodes in a supercapacitor.
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1. Chapter 1

1.1 Introduction:
As the new sources of renewable energy emerge and gain prominence, there is a greater need for storing the energy. Batteries and Capacitor for a very long time have been the most convenient alternatives but both lie at the opposite end of the spectrum for both power density and Energy density (see Figure 1.1.). Batteries exhibit very high energy density and can supply energy at a sustained level for a very long time. Batteries find application in the Automobiles and energy sources for Digital Electronics. Capacitors have very low energy storage value but have really high power density and find applications in digital integrated circuits. Supercapacitors are midway between these ends in both categories (Energy density and Power density) [1, 42]. The Ragone plot shown in Fig.1.1 displays the Energy density vs. Power density for the different storage media. Each category has its own domain and thus demarcates each mode of energy.

Figure 1.1. Shows Ragone plot [2] - plot shows regions where the battery, capacitors and electrochemical supercapacitors lie. The diagonal lines on the plot show the charging and discharging time. Supercapacitor lie right in the region between the capacitors and a battery.
Supercapacitors are energy storage devices that possess orders higher energy density than traditional electrolytic capacitors but the release or charge the energy at much faster rate than a battery. Supercapacitors have potential application in situations where the energy storage has to occur at much greater rate such as hybrid automobiles. Such devices can be used in tandem with DC devices to provide constant power to counter the fluctuations in regular devices when used alone [1, 2].

Batteries are fundamentally different from the capacitor as they use Faradaic mechanism or Redox reactions as a mean to source energy. For capacitors, the stored energy is electrostatic in nature. To increase the energy storage in capacitor up to the level of a battery, a huge increase surface area will be required. Thus supercapacitor become very important in such a situation.

1.1.1 Cell Design of Supercapacitors:
The cell design is very similar to a battery, as shown below in the figure 1.2. Although there are two electrodes separated by an electrolyte /separator, there is no such polarity associated to any electrode, as in a battery. This is usually the case with supercapacitors when the electrodes are symmetric, i.e. they can behave both as cathodic, as anodic or as double-layer capacitors. Symmetric electrodes produce nearly equal capacitance on both electrodes. Although there are electrodes which are asymmetric, where the capacitance of electrode is different (higher or lower) from the other electrode. Such electrodes would have their polarities assigned to them, and thus charging and discharging can become directional [1, 2, 42]. The particular components are:
1) Electrode

2) Separator/Electrolyte (solid or liquid)

3) Current Collectors

Supercapacitor electrodes typically have three mechanisms for storage of energy:

1) Electrical Double Layer Capacitance

2) Pseudo Capacitance

3) Hybrid Capacitance

1.1.2 Electrical Double Layer capacitance:
Any surface in contact with an electrolyte will form a layer of ions on the interface. This is a result of the residual charge present on the surface, causes ions to form a potential profile or electric field in the vicinity of surface. This is not exactly a parallel plate capacitor but it stores energy electrostatically. The ions that get absorbed can either accelerate reactions or retard them depending on the type ions which get adsorbed to the surface. An example of such adsorption is very much prevalent in the inhibitor systems where the adsorbed ions retard the rate of corrosion. [1, 2, 42]

In Supercapacitors the double layer capacitance depends on the actual area of the surface exposed to the electrolytes. An example of high surface area substrates is Carbon black and Activated Carbon. These Carbon substrates possess a three dimensional porous structure, surface of which the ions get adsorbed. The specific
surface area can go as high as 1000m²/g [1, 2, 7, 8]. Thus by keeping the geometrical area constant the surface area of adsorption charge can be increased. Since the charge separation between the residual charges is of the order of nanometers, the capacitance goes up by orders. However the structure of the double layer is not as simplistic as a parallel plate capacitor. The structure of the double layer is shown below in Figure 1.3. Supercapacitors in their earliest form stored energy by the use of Double Layer capacitance. Double Layer capacitance uses high surface area materials such as Carbon Black, Activated Carbon, graphene etc. to increase the area in the formula of capacitance.

1.1.3 Pseudo capacitance:
Pseudo capacitance is mechanism where the energy is stored via the transfer of electron/charge through the double layer. The phenomenon is quite similar to the faradaic charge transfer in batteries. The mechanism employs fast redox reaction to store the energy. Most common materials that are applied for the pseudocapacitance are transition metal oxide. Common materials are RuO$_2$, CuO, NiO and MnO$_2$ [10, 12, 28, 29, 16, 30 and 31]. Of these oxide compounds such as Cobalt oxide, Manganese Oxide, Ruthenium oxide etc. [28, 29, 15, 30, and 31] have multiple valence states and thus provide huge boost in energy density. One of the prime example is of Ruthenium Oxide which is shown in Figure 1.9 and 1.13 below which shows really high capacitance just by itself. One of reasons for its major hurdles for the commercial application is the scarcity of the oxide. Thus other alternatives are being heavily investigated in which one of alternatives are binary and ternary oxide such as NiCoO$_4$ solid solutions which can yield their individual redox reaction in the overall electrochemical behavior [19, 20, and 21].

1.1.4 Hybrid Capacitance:
Latest generation of Supercapacitors also utilizes fast redox reactions in tandem with double layer capacitance to store energy. The mechanisms as described previously are:
1. Double Layer Capacitance

2. Pseudo capacitance

Recently, the combination of Carbon and pseudocapacitive materials have attracted a lot of attention [12, 13, and 17]. Carbon materials not only provide the double layer capacitance they also provide charge transfer pathway for the pseudocapacitive materials. This results in improving the capacitance by the huge margin and thus increasing the overall capacitance of the system. An example of this has been shown in Figure 8 with Carbon substrate amplifying the RuO2 response.

Our current study of Barium Cuprate revolves around studying forming multiple oxide system and to evaluate their electrochemical properties. Barium Cuprate was chosen as it present opportunity to dope on both cationic location with Bi on the Barium position and Copper can be doped Sn. These dopants can provide extra redox transition apart from Copper, which is being investigated. Herein current study only Bi doping is covered. Also, there are cases in literature where similar compound like Strontium Cuprate can be made semiconducting by sintering in low partial pressures of oxygen [11]. The study ultimately aims to develop a Carbon (graphite), Polymer (Poly Ethylene Oxide) and Barium Cuprate as the pseudocapacitive element.

1.2 Background

1.2.1 Theory of Double Layer Capacitance

The capacitance of any system can be represented by the following equation:

\[
C = \varepsilon \cdot \frac{A}{d}
\]  

(1-1)

Here,

A= Surface area where the charge is stored

d = Distance between two electrodes
There are several models that describe the structure and distribution of ions in the electrical double layer. The three simple models that explain the basics of compact zone and diffused zone are further elaborated as:

I. Helmholtz model
II. Gouy Chapman model
III. Stern Model

Helmholtz Model: This is the simplest of the models, which assumes that the potential distribution is linear throughout the double layer. This theory assumes the distribution of charge in the double layer is just like the case of a capacitor. Figure 4, below shows an example of the model showing the distribution of ions on the surface of the electrode and linear variation of potential between the ionic layer and surface of the electrode.

 Rather than considering only a diffused layer, the Helmholtz model assumes a charge present on the electrode surface is neutralized by the ions present in the electrolyte. As the general equation for Capacitance would suggest, the capacitance would then only depend on the dielectric constant of the electrolyte and the charge separation. The model however, takes little account of the diffused layer formation.

Figure 1.4. Helmholtz model of double showing linear variation of potential in double layer thickness.
due to thermal movement of ions in the electrolyte, thus it is not considered to fully analyze the double layer systems that are present.

Gouy Chapman model [1]: This model takes consideration of the thermal movement of the ions within the electrolyte. The thermal energy does not allow the ions to form a monolayer of opposite charges in the electrolyte at the surface. This fact also explains the potential dependence of the double layer capacitance, which could not be fully explained in the Helmholtz theory.

Gouy Chapman model assumes the speed of the molecules have a Boltzmann distribution [1, 2 and 42]. This thermal energy does not allow the oppositely charged ions in the electrolyte to be bound rigidly to the electrode surface, and form a compact layer. Thus, the model predicts that the concentration of the oppositely charged ions will decrease exponentially as the distance from the electrode increases, as shown in Figure 1.5.

Stern Modification to the Gouy Chapman Model: The Stern model is a further improvement on the Gouy Chapman model. It assumes that ions in solution can only approach the electrode surface up to a finite distance. It also takes into account that ions in the solution have a finite size, which relates to the fact that ions in an aqueous solution or any polar solutions are usually solvated. Further, it suggests that initially there is a linear decay profile of the potential, as displayed in Helmholtz model. An exponential decay of the potential follows this compact layer which is depicted as a diffused layer in Figure 5. Stern assumed that a number of ions could become adsorbed in the surface due to its charged state. Stern Layer therefore, consists of these
adsorbed counter ions. The potential at the Stern layer, with respect to the solution, is also known as the Zeta Potential. This Zeta Potential is studied very extensively in surface and colloidal chemistry [42]. The diffused layer primarily consists of solvated ions.

All the three models of the electrical double layer demonstrate the presence of a potential profile at the surface of the electrode, indicating capability for electrostatic energy storage. This energy storage mechanism is popularly known as double layer capacitance. The circuit for a double layer has been shown in Figure 1.6. R1= resistance of the double layer, and R2= Series resistance of the solution. This resistance is composed of resistance of ionic movement in the solution and resistance of the participating electrodes.

Some of the double layer systems are shown in Table 1.1 with the respective capacitance ranges. Table 1.1 shows that the highest capacitance that could be achieved with high surface area Carbon material is about 370 F/g for the activated Carbon fibers in the aqueous electrolyte. The supercapacitors are expected to store much higher energy per unit mass to become a commercial device. Table 1.1 also indicates that there is a limit up to which these carbon materials can provide the capacitance and there is a pressing need for other mechanism of energy storage in order to increase the energy density of the electrodes.
Table 1.1 showing the different materials applied for EDLC based supercapacitor electrodes.

| Capacitances of Carbon Electrode Materials and Electrolytes at Room Temperature |
|---------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| **Aqueous Electrolyte**               | **Organic Electrolyte** |
| **Materials**                         | **Specific Surface Area (m².g⁻¹)** | **Density (g.cm⁻³)** | **F.g⁻¹** | **F.cm⁻³** | **F.g⁻¹** | **F.cm⁻³** |
| Commercial activated carbons (ACs)   | 1000 to 3500    | 0.4 to 0.7      | < 200    | < 80    | < 100    | < 50    |
| Particulate carbon from SiC/TiC      | 1000 to 2000    | 0.5 to 0.7      | 170 to 220 | < 120 | 100 to 120 | < 70 |
| Functionalized porous carbons        | 300 to 2200     | 0.5 to 0.9      | 150 to 300 | < 180 | 100 to 150 | < 90 |
| Carbon nanotube (CNT)                | 120 to 500      | 0.6             | 50 to 100 | < 60   | < 60   | < 30   |
| Templated porous carbons (TC)        | 500 to 3000     | 0.5 to 1        | 120 to 350 | < 200 | 60 to 140 | < 100 |
| Activated carbon fibers (ACF)        | 1000 to 3000    | 0.3 to 0.8      | 120 to 370 | < 150 | 80 to 200 | < 120 |
| Carbon cloths                        | 2500            | 0.4             | 100 to 200 | 40 to 80 | 60 to 100 | 24 to 40 |
| Carbon aerogels                      | 400 to 1000     | 0.5 to 0.7      | 100 to 125 | < 80   | < 80   | 40    |

*Ref. [3]*
1.2.2 Pseudo capacitance:  
Pseudo capacitance is a charge storage mechanism in which a change in the oxidation state of the electrode species occur. The phenomenon arises from the occurrence of red-ox reactions and enhanced electron/ion transfer across the double layer. The free electrons, are mainly responsible for the surface charge which results into double layer capacitance [42]. The density of free electrons per atom is orders of magnitude lower, when compared to redox reactions, where the value is integral. Thus, the greater availability of charges provides capability for higher energy storage. Pseudo-capacitance is a process very similar to a rechargeable battery, the difference being that it relies on faster reversible reactions and multiple oxidation states. Commonly used oxides and polymer are Ruthenium Oxide, Nickel Oxide and Manganese oxide, Polyaniline.

\[
\begin{align*}
Me &= Me^{n+} + ne^- \\
Red &= Ox + ne^- 
\end{align*}
\]  

Although, they possess potentially higher energy storage capability, the pseudocapacitive compounds are usually mixed with double layer inducing agents such as activated carbon, carbon black, graphite, etc. These are electrochemically inert species that can provide greatly enhanced charge transfer pathways throughout the system. They have also been found to exhibit a positive effect on the charge transfer rates of the combined electrochemical reactions. Electrochemically active materials fall into two categories [1, 2]:

1) Adsorption of pseudocapacitive agents such as metal oxide or conjugated polymers onto high surface area carbon/conducting substrates.

2) Intercalation of the pseudocapacitive agents as evident in case of Lithium ion batteries where the proton can traverse through the lattice.
An example of the pseudocapacitive system, well established in literature during the past years, are the organic conjugated polymers Polypyrrole and Polyaniline [2]. The P-type doped polymeric salts of these polymers yield the following redox reactions [2]:

\[
[\text{PPy}^+\text{A}^-] + e^- \leftrightarrow [\text{PPy}] + \text{A}^- \quad (1-4)
\]

Polypyrrole coatings have yielded capacitance values as high as 533 Fg\(^{-1}\) [4]. Major defects with such electrodes are the volume changes that are associated with the redox reactions. Volumetric fluctuations led to poor cyclic durability. Thus these polymer particles needed to be deposited onto carbon substrates such as Carbon Nanotubes, Graphene and graphite [5, 6, and 7].

Figure 1.7 gives an example of both pseudocapacitive and double layer capacitive material existing in tandem with each other. Figure 1.8 (i) shows a typical curve and the variation of the curves with scan rate. Figure 1.8 (ii) shows the variation of potential during the test. Figure 1.9 shows a RuO\(_2\)
based capacitor, where it is seen to be less than half as potent in terms of storing energy, as when it is coupled or combined with graphene oxide, which typically will contribute significant double layer capacitance of its own. Likewise, PANI based pseudo-capacitors are more effective charge storage electrode when applied along with a suitable double layer providing agent such as graphite or Carbon Nanotubes. Figure 1.10 shows a CV curve for CuO hierarchical structures shows the effect of scan on the Copper’s redox reactions. The voltammograms shown in Figure 1.10, yields about 94F/g which is almost one third of the specific capacitance reported for the Copper oxide and graphene oxide Nano- composite-245 F/g [18]. These examples indicate the pivotal role played by the double layer capacitance not only in the energy storage electrostatically but also towards the assistance to storage of energy by pseudocapacitance. Ideally there is no system where there is no double

Figure 1.10. Cyclic Voltammograms (100 mv/s) of (1) RuO2 and (2) Graphene oxide + RuO2 illustrating the effect of pseudo capacitance and double layer in tandem. (1) Exhibits the behavior when the pseudo capacitance alone. [16]
layer capacitance can be separated but their individual contribution dictate which mechanism dominates energy storage [42]. So when any material is referred as pseudocapacitive in nature that does not necessarily mean that it has not double layer capacitance. An electrode that has significant contributions from both mechanisms is known a Hybrid supercapacitor electrode. The equivalent circuit in Figure 1.11 represents electrical circuit for a hybrid system of double layer capacitance and pseudocapacitance. The individual elements are described below.

1) \((C_{dl})\) - Double layer capacitance.
2) \((C_{\phi})\) associated with pseudocapacitance.
3) \(R_F\) – faradaic resistance.
4) \(Rs\) - Solution resistance
5) \(R_o\) - Resistance accounting for discharge.

![Figure 1.11. Equivalent circuit of a supercapacitor electrode including double layer and pseudocapacitance [18].](image)

1.2.3 Electrochemical Cell Design:
Three electrode cell, as shown in Figure 1.12, has been used in the used in all the experiments. The electrolyte used is Potassium Hydroxide; the concentration of Potassium Hydroxide used is 2M in Deionized water. Counter electrode used is a graphite electrode. Standard Calomel electrode is used Reference electrode.

![Figure 1.12. A typical 3 electrode cell used to test the electrode material.](image)

1.2.4 Electrode Material for Supercapacitors:
The general requirements for the electrode for supercapacitors are:
1) Conductivity of the electrodes must be high for double layer capacitance.

2) The Electrode must have constituents which can produce both anodic and cathodic reactions.

3) The Electrode must be durable and flexible enough to withstand the volume changes due to the redox reaction. (Particularly common with Organic Polymers PANI, PolyPyrrol)

Optimizing the content of Carbon (Graphite, Activated Carbon, and Graphene oxide) and Polymer (Polytetrafluoroethylene, Polyethylene Oxide, and PVDF etc.) solves the 1 and 3. Since Carbon materials provide electrostatic charge for the double layer, and the polymer provides durability to the electrode. Redox-reaction supplying compounds. Their interaction with the double layer capacitance materials, is the most actively researched part in today’s supercapacitor research of energy. Transition metal oxide and Organic polymers are being heavily explored for maxim storage. Choice of oxide is typically based on three parameters:

1) Conductivity of the oxide.

2) No. of stable valence states of the compounds or available transitions between the existing valence states.

3) Reversibility of reactions.

4) Molar mass of the compound.

Conductivity of the oxide is clearly an important factor but not as critical as the choice of the oxide material. Better conductivity assists in the better charge transfer. Although insulating compounds like MnO$_2$ and Mn$_3$O$_4$ have been heavily utilized with materials like graphite and graphene oxide to compensate for the lack of electrical transport medium, and have been reported to have a capacitance of 349Fg$^{-1}$ [28, 29]. Ruthenium oxide is a semiconducting oxide which is a perfect
example of conducting oxides [15, 30, and 31]. Ruthenium oxide thins film also have posted a high capacitance value of 650Fg⁻¹[30, 31] with no filler for double layer capacitance. Interestingly, Ruthenium oxide is a compound with multiple oxidation state which makes it a very favorable choice for the supercapacitor electrodes. The following reaction shown below takes place in the Ruthenium oxide electrode.

\[
\text{RuO}_2 + x \ H^+ + x \ e^- \rightarrow \text{RuO}_{2-x} \ (\text{OH})_x
\]  

(1-5)

The reaction indicates that multiple oxidation state is a perfect example of the oxide materials for supercapacitor electrodes. The three most common oxidation states of Ruthenium are +2, +3 and +4. The charge \( x \) on the right hand side of the reaction is distributed among +2 and +3. Ruthenium

![Figure 1.13. CV plots for 2mV/s, 20mV/s and 50mV/s respectively for RuO2 thin films. [31] Figure also shows Ruthenium oxide thin films exhibiting transitions between +2, +3 and +4 at different scan rates.](image)
shows a perfect example (Figure 1.13) of multiple oxidation states, which enable them to form supercapacitor electrode oxide material. Fast reversible reactions are a must for a supercapacitance. As shown in the classical system of Ruthenium oxide, the fast reactions between oxidation states form excellent the fast reactions between oxidation states form excellent supercapacitor electrode materials.

Molar mass affects an electrode in number of atoms which can participate in the reaction it can accommodate in a given mass/weight. Thus smaller the molar mass the more number of atoms that can be fitted into a given mass, which can participate in the reactions.

One of the very interesting sub topics in creating symmetric electrodes is utilize binary and ternary oxide systems for supercapacitor electrodes [19, 20, and 21]. Multiple oxide systems such as NiCoO$_4$, CuO. SnO can also yield reaction over a much larger range of voltages over which the electrodes can operate. These multiple oxide compounds can lead to change of oxidation state in solid and can shut out the dissolution of the species on the electrodes. Dissolution/movement of ions across the electrode electrolyte surface has been a major problem with conducting polymers like Polyaniline and Polypyrrole. Thus these problems could be avoided by use of multiple oxide compounds.

1.2.5 Current Work:
Current work concentrates on exploring the ceramic compound, Barium Copper Oxide or Barium Cuprate (BaCuO$_2$) for standpoint of pseudo capacitor material. As shown in the phase diagram below (Figure 1.14), Barium Cuprate forms in the middle (50:50) BaO and CuO phase lines. The phase diagram is particularly of interest as the eutectic composition of BaCuO$_2$ (BC) and CuO at 1163K at 71.5% Copper oxide (Figure 13) has been used for the densification of Barium Titanate. The densification temperature was brought down to 1050 °C and was attributed to the dissolution
of Barium Titanate in BC and CuO [BCC]. It was reported that 2 - 2.5wt. % of BCC caused above 95% densification [12]. In the literature, it has been found that higher temperature such as 900°C, the compound Barium Cuprate is formed as a parasitic phase while synthesizing YBa$_2$Cu$_3$O$_7$. It has been found as a resistive phase in terms of electrical transports. But there has been cases where the conductivity has been introduced in the similar compound from the group by heat treatment in reduced partial pressure of Oxygen. A perfect example is of p type semiconducting cuprate is Strontium Cuprate thin films. Strontium Cuprate thin films have been synthesized with MOCVD to produce transparent conducting films. Oxygen deficiency was cited as the reason for the surprising spike in the conductivity [11]. Also there have cases where Strontium is substituted at some cites by Barium and Calcium, which has been cited as the cause for the increase in the hole mobility in the system [9]. Since, Strontium Cuprate belongs to the same family and bears a similar
crystal structure, as similar behavior can expected out of Barium Cuprate. The crystal structure of Barium Cuprate is Body Centered Cubic and shown below in figure 1.15, 1.16 and 1.17. The crystal structure consists of two \( \text{Cu}_{18}\text{O}_{24} \) spherical cages (1 at the center and 1/8 at each corner), six \( \text{Cu}_6\text{O}_{12} \) rings center around the diagonal and midway between the center and corner. Finally six \( \text{CuO}_4 \) lone pairs are located on the face. Between the Copper structure Layer of Barium and Oxygen are present.

A similar trend has been observed in the infinite layered \((\text{BaCuO}_2)/ (\text{CaCuO}_2) \) \(n\) and \((\text{BaCuO}_2)/(\text{SrCuO}_2) \) \(n\) layered compound which were synthesized as High Temp. Superconducting Material but were found to be semiconducting at room temp with a resistance of around 300mΩ [13, 4]. Here two resistive material come together to form a layer semi-conducting compound at room temperature. Previously, Prabhu et al l have found that resistance of Barium Titanate can be reduced by sintering in reducing atmosphere (90:10, N2:H2) at 1050°C. Barium Titanate sheet

![Figure 1.15. Unit cell of Barium Cuprate. Green indicate Barium atom, Yellow indicates Cu, and red indicates oxygen.](image-url)
resistance data can be seen in the Table 2 below [15]. This was attributed to the polaron conduction in the Barium Titanate. A similar route is taken here to induce vacancies in the lattice, with the expectation of inducing some conductivity in the compound. As mentioned before that binary oxide materials such as NiCoO₄, CuO, SnO [19, 20, and 21] etc. are gaining prominence.

Table 1.2 Showing the resistivity change due to Heat treatment. [15]

<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 (heat-treated)</td>
<td>73.6 ohm</td>
<td>46.22 ohm/cm</td>
</tr>
<tr>
<td>4</td>
<td>CBT and Graphite (heat-treated)</td>
<td>15.4 ohm</td>
<td>0.980 ohm/cm</td>
</tr>
</tbody>
</table>

Figure 1.16. Copper atoms in the unit cell, with Cu 18O24 spherical cage in the center and Cu 6O12 clusters (rings) and six CuO4 lone pair. All atomics are constructed using Crystal maker software student edition.
The current study also aims to develop Barium Cuprate into on such compound by doping it with Bismuth Oxide (III).

1.3 Objective:
Current study aims exploring the electrochemical and electrical properties of Barium Cuprate (BaCuO$_2$). The potential applications are for supercapacitor electrodes. Although it is an insulator, similar compounds such as Strontium Copper oxide have shown improvement in conductivity by heat treatment in lower partial pressures of oxygen than ambient conditions. The goal is also to study the occurrence of similar behavior with Barium Cuprate. Conductivity will also affect the electrochemical properties and reaction rates, studying the electrochemical aspect of the Heat treatment will also be included. Finally, addition of dopants to create a multiple oxide solution is also investigated here. Addition of dopants/substitution elements such as Bismuth and their impact on electrical transport and electrochemical properties have also been covered. Individual effect of
Heat treatment and Substitution of dopant atoms on the electrical and electrochemical properties have been delineated and shown over course of the study.

Barium Titanate shows capacitance over larger ranges of potential but the heat treatment temperature for Barium Titanate is 1050°C [15], which is extremely high. Barium Cuprate synthesizes at a much lower temperature of 750°C, thus would also bring the temperature of synthesis down. One of the larger goals here is to synthesize a compound which can form a solution with multiple redox reaction yielding atoms in our case copper and bismuth. This enlarges the range of operation of electrodes, giving rise to reactions on both positive and negative side of Potential with respect to Standard Calomel Electrode.
2. Electro-analytical Techniques & Structural Characterization

2.1.1 Electrochemical Impedance Spectroscopy:

Electrochemical Impedance spectroscopy is a very popular technique amongst the electrochemist and Materials Scientists. The technique involves applying a sinusoidal perturbation at certain frequency around a fixed voltage vs. Reference electrode. The current response is measured simultaneously, thus measuring the impedance of the circuit. A range of frequencies are applied to the cell and measured impedance is plotted as shown in Figure 2.1.

\[ E(t) = E_0 \exp(j\omega t) \quad (2-1) \]

And,

\[ I(t) = I_0 \exp(i\omega t - i\phi) \quad (2-2) \]

\[ Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0 (\cos \phi + i \sin \phi) \quad (2-3) \]

Figure 2.1. Showing typical lag between the potential function and current function in an ac circuit.

In any AC circuit, impedance is a complex number. The two components of impedance are:

1) Real (\( Z' \))
2) Imaginary (\( Z'' \))
EIS data is represented in two popular ways:

1) Bode Plot (Log (Z’) vs Log (frequency) and, Log(Z’’) vs Log( Frequency))

2) Nyquist plot (Z’ vs Z’’ plot)

Examples of Bode and Nyquist plot is shown in a figure 2.2 (b) and (a) respectively,

![Nyquist and Bode plot](image)

In Nyquist plot, the capacitance of the Imaginary Impedance Z’’ is plotted on the y axis and real impedance is plotted on the x axis. The curves go from the higher frequency to lower frequency as we traverse away from the origin. These plots are called as Nyquist plots. A popular circuit that is employed in analyzing a chemical reaction’s kinetic or diffusion control is Randles Circuit (Figure 2.3). In the Randles Circuit,

C<sub>dl</sub> is capacitor associated with the double layer, R<sub>ct</sub>= Charge transfer Resistance, R<sub>s</sub>= Solution resistance and W= Warburg Impedance element. Any reaction with the reaction with infinite thickness for diffusion has following dependence of Warburg impedance:
Where

1) \( W = \text{Warburg impedance element} \),

2) \( F = \text{frequency} \)

3) \( \Sigma \text{ or } \sigma = \text{Warburg Coefficient} \)

Warburg impedance arises due to the diffusion of reaction to the electrodes in a reaction. Any reaction which is in kinetically controlled would have a Nyquist of plot as shown in figure 2.4(a) (b).

In theory, the reactions having infinite thickness for diffusion would have \( 45^0 \) slopes from the x-axis. In practice the slope of \( 45^0 \) is hardly observed, this is due to the fact the diffusion of length of infinite distances are not physically not possible. Thus, the slopes tend to be generally more or less than \( 45^0 \) indicating the thickness of the boundary layer.
2.1.2 Cyclic Voltammetry:
Cyclic is one of the most electrochemical techniques in electro-analytical chemistry for characterization of electrochemical reactions. The technique is most prominently employed in the studying the reduction potentials but has also been applied to study the reversibility of the reactions. The technique varies the applied potential on the working electrode vs. a reference electrode. The potential is varied at a constant scan rate between a ranges of potential. The current values are acquired and plotted against the voltage thus giving rise voltammograms. A typical cyclic voltammetry curve has been shown in Figure 2.6. The positive side pointed peak is the cathodic peak and negative side pointed peak is the anodic peak.
Generally when the potential is increasing (left to right scan in figure 2.7) then the scan is termed as cathodic scan and opposite scan is known as anodic scan. Theoretically, the reactions which are reversible should have their Anodic and cathodic peak are distant by:

\[
E_{pc} - E_{pa} = 59mV/n \quad [n= \text{no of electrons transferred in the reaction}]
\]

Another equation which predicts the position of the peaks is:

\[
E_{pc} = E^0 + (29.5mV/n)
\]

\[
E_{ac} = E^0 - \left( \frac{29.5mV}{n} \right)
\]

Figure 2.6. Potential (vs. Ref) variation with time for a typical cyclic voltammetry test. [24]

Figure 2.7. Typical Cyclic voltammograms showing cathodic and anodic currents and their respective peaks. [24]

\[E^0= \text{Reduction Potential}\]
N= no. of electrons involved in reaction. But these conditions are observed in very few systems and the peaks are distant by more than 59mV. General consideration for characterizing reactions is that the reduction potential lies midway between the cathodic peak and anodic peak potentials.

2.1.3 Chronopotentiometry:

Chronopotentiometry is a technique in which a constant current is supplied to the cell and the potential of the working electrode vs. the reference electrode is acquired. The acquired potential is plotted vs. time. This is a versatile technique to measure the energy storage and charging behavior of any material or electrode. A typical curve is shown in figure 2.8. The charge and discharge usually occurs at same current. In figure 2.8 the part of the curve with positive slope is the charging step and the negative slope of the curve indicates the discharging of the supercapacitor. During charging cycle the current is flowing into the cell and the flow is reversed during discharging.

![Chronopotentiometry curves of Copper oxide hierarchical structure based electrode.](image)

Figure 2.8. Chronopotentiometry curves of Copper oxide hierarchical structure based electrode. [17] Part of the curve with positive slope indicates the charging cycle and negative signifies discharging cycle.

2.2 Structural Characterization:

2.2.1 X-Ray Diffraction (XRD):

X-Ray diffraction works on the principle of superposition of diffracted beams from the planes.

Figure 2.9 shows a simple example of Bragg’s law. Bragg’s law is defined as
\[ n\lambda = 2d \sin \theta \quad (2-7) \]

Figure 2.9. Showing reflection of X-rays from the crystallographic planes.

The Bragg peaks or planes can be identified from ICDD PDF -2 (Powder Diffraction File). Also, XRD is used to calculate the lattice parameters and unit cell volume. The unit cell volume deviations and peak shifts from the stated positions in PDF could indicate toward presence of vacancies in the structure.

2.2.2 Scanning Electron Microscopy:

The Scanning Electron Microscopy (SEM) is one of the most versatile instruments for investigating the microstructure of materials. Under electron bombardment, a variety of different signals is generated (including secondary electrons, backscattered electrons, characteristic x-rays, and long-wave radiation in the ultraviolet and visible region of the spectrum) that can be used for materials characterization. Using secondary electrons, scanning electron microscopy (SEM) expands the resolution range to a few nanometers (under favorable conditions), thus bridging the gap between optical (light) microscopy and transmission electron microscopy. In addition to the
higher lateral resolution, SEM also has a much greater depth of field compared to optical microscopy. Scanning electron microscopy offers possibilities for image formation that are usually easy to interpret and will reveal clear pictures of as-polished and etched cross sections as well as rough surfaces and particles. **Energy-dispersive x-ray microanalysis** using equipment routinely attached to the scanning electron microscope. Due to the relatively easy handling, SEM has found a wide range of applications in materials research, materials development, failure analysis, and quality control. There are several excellent monographs available on physical fundamentals, instrumental details, and applications of the scanning electron microscope.
3. Experimental

3.1 Materials:

Barium Oxide:
This is purchased from Fisher Scientific and has purity level of 99.99%.

Copper oxide (II):
99.99% pure Copper oxide is purchased from Fisher Scientific.

Bismuth Oxide (III):
99.99% pure Bismuth oxide was procured from the Fisher scientific.

Graphite:
Graphite with a very high conductivity and fine particle size was purchased from Ashbury Carbons. The surface of the electrodes from BET measurements is reported to $115 \text{m}^2/\text{g}$.

Polyethylene Oxide (PEO):

\[ \text{HOCH}_2\text{CH(OH)}_n \text{OH} \]  

(3-1)

The chemical formula of the polymer is shown above. The PEO is purchased from the Fisher scientific and the molecular wt. of the polymer purchased is 4000.

3.2 Mixing of Native powders (Barium Oxide, Copper Oxide) by Ball milling:
All the powders of any composition of Barium oxide and Copper oxide are milled for 10 hours.

60% Isopropyl alcohol and 40% DI water solution is used as the solvent for ball milling. Also, 1% Darvan C is added as the dispersant. Zirconia balls are used as the milling media and Ball to powder weight ratio is 1:5.
3.3 Synthesis of Barium Cuprate and Cuprous oxide pellet:
All composition of Barium Oxide and Copper oxide are prepared by ball milling procedure as explained in section 3.2. Five composition of Barium Oxide and Copper oxide with following compositions (% by mole):

1. Barium Oxide-50%, Copper Oxide-50% (BC 50)
2. Barium Oxide-40%, Copper Oxide-60% (BC 60)
3. Barium Oxide-30%, Copper Oxide-70% (BC-70)

Pellets are pressed on a Carver Laboratory hydraulic press in a 0.5” die at a load of 5000 pounds. Weight of the powder pressed is kept at 0.5g. The pressed pellets are loaded in a ceramic boated and heat treated as it is in 90% Nitrogen and 10% hydrogen at different temperature. Five compositions and five temperature variation are tested with this procedure. Temperature variations are done with Barium oxide (40%) and Copper Oxide (60%) are 450°C, 500°C and 550°C.

3.4 Synthesis of Barium Cuprate and Bismuth doped Barium Cuprate by air sintering:
As in the section 3.3, pellets are pressed on a Carver Laboratory hydraulic press in a 0.5” die at a load of 5000 pounds. Weight of the ball milled powders is the same at 0.5g. The composition of Barium Oxide and Copper oxide used is at 50-50% by mole. Also 5% and 10% Bismuth (metallic ion % by mole) doped samples are also sintered in exactly same way. Barium Cuprate and 5% Bismuth doped Barium Cuprate pellets are air sintered at a temperature of 750°C and 600°C for a duration of 10hrs. The pellets have also been sintered at750°C for 2 hours. The pellets are air-cooled to room temperature.
3.5 Heat treatment of the air sintered Barium Cuprate (BC) and Bismuth doped Barium Cuprate:
The air sintered pellets in the section 3.4 are kept in a ceramic boat and heat treated in a tube furnace with an atmosphere of 90% Nitrogen and 10% Hydrogen. These pellets are heat treated at a temperature of 500°C for a time span of 2 hours. The pellets are allowed to air-cool to room temperature before they are taken out of the furnace. List of all the pellet barium cuprate and doped pellets synthesized is shown below:

<table>
<thead>
<tr>
<th>Pellet type / Conditions of synthesis</th>
<th>Abbreviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (Air sintered (AS) at 750°C for 10 hrs.)</td>
<td>BC 750-10</td>
</tr>
<tr>
<td>Heat Treated (HT) Barium Cuprate (Air sintered (AS) at 750°C for 10 hrs.)</td>
<td>HTBC 750-10</td>
</tr>
<tr>
<td>Barium Cuprate (AS at 750, 2 hours ),</td>
<td>BC 750-2</td>
</tr>
<tr>
<td>Barium Cuprate (HT &amp; AS at 750, 2 hours ),</td>
<td>HTBC 750-2</td>
</tr>
<tr>
<td>Barium Cuprate 5% Bi doped (AS at 750°C for 10 hours )</td>
<td>BC(5) 750-10</td>
</tr>
<tr>
<td>HT Barium Cuprate 5% Bi doped (AS at 750°C for 10 hrs.)</td>
<td>HTBC(5) 750-10</td>
</tr>
<tr>
<td>Barium Cuprate 5% Bi doped (AS at 750°C for 2 hrs.)</td>
<td>BC(5) 750-2</td>
</tr>
<tr>
<td>HT Barium Cuprate 5% Bi doped (AS at 750°C for 2 hrs.)</td>
<td>HTBC(5) 750-2</td>
</tr>
<tr>
<td>10 % Bismuth doped Barium Cuprate (AS at 750°C for 10 hrs.),</td>
<td>BC(10)750-10</td>
</tr>
<tr>
<td>HT 10 % Bismuth doped Barium Cuprate (AS at 750°C for 10 hrs.)</td>
<td>BC(10)750-10</td>
</tr>
</tbody>
</table>
3.6 Synthesis of Powders for the thin film electrodes:

Powders are synthesized in a similar way as the pellets are synthesized. The native powders of Barium Oxide and Copper oxide are mixed in a ball mill with zirconia balls for 10 hours. The mixed powders were extracted using vacuum filtration and subsequently vacuum drying at 60℃. The resulting powders were air sintered at 750℃ and 600℃ for 10 hours. Also powders were sintered at 750℃ for 2 hours to study the effect of time. Barium Cuprate and 5% Bismuth doped Barium Cuprate powders were synthesized at all three conditions. 10% Bismuth doped Barium Cuprate was synthesized only at 750℃ for 10 hours. These powders are also heat treated for 2 hours at 500℃ in a reducing atmosphere of 90% Nitrogen and 10% Hydrogen.

Table 3.2. Showing the list of powders used with PEO and graphite to make thin film electrodes.

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (synthesized by Air sintered (AS) at 750℃ for 10 hours)</td>
<td>BC 750-10</td>
</tr>
<tr>
<td>Barium Cuprate(Heat Treated (HT) and synthesized by AS at 750)</td>
<td>HTBC 750-10</td>
</tr>
<tr>
<td>Barium Cuprate (synthesized by AS at 750, 2 hours ),</td>
<td>BC 750-2</td>
</tr>
<tr>
<td>Barium Cuprate (HT &amp; synthesized by AS at 750, 2 hours ),</td>
<td>HTBC 750-2</td>
</tr>
<tr>
<td>Barium Cuprate 5% Bi doped (synthesized by AS at 750℃ for 10 hours)</td>
<td>BC(5) 750-10</td>
</tr>
<tr>
<td>Barium Cuprate 5% Bi doped (HT and synthesized by AS at 750℃ for 10 hours)</td>
<td>HTBC(5) 750-10</td>
</tr>
<tr>
<td>Barium Cuprate 5% Bi doped (synthesized by AS at 750℃ for 2 hours)</td>
<td>BC(5) 750-2</td>
</tr>
<tr>
<td>Barium Cuprate 5% Bi doped (HT and synthesized by AS at 750℃ for 2 hours)</td>
<td>HTBC(5) 750-2</td>
</tr>
<tr>
<td>Barium Cuprate 10% Bismuth doped(synthesized by AS at 750℃ for 10 hours)</td>
<td>BC(10)750-10</td>
</tr>
<tr>
<td>Barium Cuprate 10% Bismuth doped(HT and synthesized by AS at 750℃ for 10 hours),</td>
<td>BC(10)750-10</td>
</tr>
</tbody>
</table>
Finally before the thin film preparation all the powders are ball milled with zirconia balls for 3 hrs.

3.7 Synthesis of thin film electrode of BC and doped BC, PEO and graphite:
100 ml of 90% Isopropyl Alcohol and 10% Acetone was taken and 6.33g of PEO is added to and stirred for 10 mins. 0.33g of Graphite is added to this solution and vigorously stirred using a mixer for 10 mins. 14ml of this dispersed solution is taken and stirred for 15-20mins using a magnetic stirrer and then 0.70g of BC or doped BC powders are added to this solution. The solution was allowed to be stirred for another 10-15 mins.

A stainless steel substrate is cleaned using a 30% Hydrochloric acid for 15 mins. The substrate is then taken out of the solution and then cleaned in DI water. After cleaning the 0.5” X 0.5” substrate was used for to spin coat on. The solution described in the first part is spin coated, allowed to dry and then heat treated at 250°C. Two coating are formed one after the other, spun and each coating was cured at 250°C after the coating.

3.8 Electrochemical characterization
3.8.1 Cyclic Voltammetry:
A three electrode setup is used to run the experiment. Electrolyte used during the test is 2M KOH. The scan rates at which the tests are run is at 5mV/s, 30mV/s and 50mV/s. The range of voltage which is applied on the working electrode is 0 to -0.6V. The range is chosen considering the electrolyte and the potentials at which the copper redox reactions and potentials found in the literature.

One very important parameter is calculated from these cyclic voltammograms is the charge storage and specific capacitance. Figure below shows a general voltammograms. The integrated area in the curve is represented in the formula as A.

\[
Q = \frac{A}{(scan\ rate)} \quad (3-2)
\]
\[ c = \frac{Q}{(\Delta V) \cdot a} \]  

(3-3)

Figure 3.1. General cyclic voltammograms. Area enclosed within the boundaries of curves is indicative of charge stored by the cycle.

Q=Charge storage; \( \Delta V \)= range of the potential; \( a \)= geometrical area of the electrode (cm²).

Charge storage per unit is just \( Q \) divided by the geometrical area of the electrodes.

3.8.2 Electrochemical Impedance spectroscopy:

EIS is a test where, as explained in the Chapter 2, the potential oscillates in a sinusoidal format around a specified potential. The potential is selected using the CV curves. The reduction potential is usually the potential around which the test is conducted. The reduction potential is located midway between the anodic and cathodic peaks in the CV plot. Thus using this potential from the CV test results is used to run EIS. During the course of experiments the range of potential in which EIS was conducted is -0.32V to -0.43V vs SCE. The Nyquist plot in the EIS is mostly studied to
calculate the charge transfer resistance in the circuit. The circuit which is used to fit the Nyquist plot is shown below.

The modified Randles circuit (Figure 19) uses a finite thickness of diffusion for reactant for fitting rather than an infinite thickness of boundary layer. Typical curves are shown the EIS section in chapter 2. The software used for fitting is Gamry Echem Analyst.

3.8.3 Galvanostatic Charge/ Discharge:
Galvanostatic charge/discharge in the current set of experiments has been performed at 1mA/cm². The techniques provides a much realist picture of the energy storage. The area under Voltage vs time curve in the charging cycle, i.e. when the current applied is 1mA/Cm² is the charging capacitance and area under the discharging cycle (when the current is -1mA/cm²) is known as the discharging capacitance.

![A typical Chronopotentiometry (CP) curve is shown.](image)

Although these numbers are calculated at only for a few experiments, the comparison between different systems are made qualitatively. Figure below clearly shows the charging and discharging
Current along with the potential variation with time. The part where the potential and time curve’s slope is positive is the charging cycle and the area under the curve is indicative of the energy stored in the charging cycle. The negative slope part is discharging cycle and area under curve is indicative of energy stored in the discharge cycle. Energy calculation is shown below:

\[ E = i \times A \]  

(3-4)

E= Energy stored per unit area; i = Current density (1mA/cm²); A= Area under the V vs t curve in the charging or discharging cycle.

3.9 Electrical Resistance testing of Pellets:
A two probe measurement was made using a multi-meter to measure the resistivity and a multimeter was used to measure the resistance across the terminal. Resistance is measure along the thickness of the pellet.

3.10 X-Ray Diffraction:
X-ray diffraction was performed on the crushed powder samples to confirm the structure. The equipment scan between 10⁰ and 70⁰ at a scan rate of 2.0⁰/min.

3.11 Scanning Electron Microscopy and Energy dispersive spectroscopy:
Scanning electron microscopy is used to study morphology and size of powders. It also provides information about the surface of pellets and phase distribution on the surface. Also it has been used to see the particle distribution on the surface of the film and also film’s morphology.
4. Results and Discussion:

4.1 Composition optimization with pellets:
Barium Cuprate has been reported to form at 500°C under low partial pressures of oxygen or reducing conditions [34, 35]. Since reducing the sintering temperature of Barium Cuprate is one of the major objectives of the current study, this facet of the study is very pivotal. To achieve this following compositions around 50% BaO and 50% CuO are sintered in a reducing atmosphere of 10% Hydrogen and 90% Nitrogen:

1) 50% Barium oxide and 50% Copper oxide

2) 40% Barium oxide and 60% Copper oxide

3) 30% Barium oxide and 70% Copper oxide

The excess Barium Oxide composition was found to be unsuitable because of very high resistivity of Barium Oxide, Copper oxide (I) and Copper oxide (II) are both n and p type semiconductors. Their presence is thus not as detrimental. Pellet of composing mixed powders were pressed and heated treated at a temperature of 500°C for a duration of 2 hours. The resulting pellets were air...
cooled back to room temperature, followed by electrochemical & electrical characterization. X-ray diffraction was also performed to determine the phases present in the final mixture, the patterns are shown in Figure 4.2. X-ray diffraction plots show characteristic peaks of Barium Cuprate (BC) and Copper oxide (I) for all the compositions. Barium Oxide is only found in 50% Barium Oxide and 50% Copper Oxide (II). Major, Minor phases and ratio of integrated intensity ratio of the two major phases are shown in the Table 4.1. Table is obtained from the phase analysis performed on the X-ray diffraction patterns shown in Figure 4.2. Table 4.1 also show the Integrated Intensity ration of the strongest peaks of Copper (I) oxide and Barium Oxide which suggests higher Copper oxide (I) content in final phase as the Copper Oxide (II) concentration increases in the initial mix.

Table 4.1. Major and minor phases of different composition sintered at 500°C for 2 hours in reducing atmosphere.

<table>
<thead>
<tr>
<th>Initial Composition of the pellets</th>
<th>Major Phase in sintered pellets</th>
<th>Minor phase(s) in sintered pellets</th>
<th>Integrated Intensity ratio of I_{600BC}/I_{111 Cu2O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% CuO 50% BaO</td>
<td>Barium Cuprate</td>
<td>Barium oxide, Copper oxide (I)</td>
<td>4.23</td>
</tr>
<tr>
<td>60% CuO 40% BaO</td>
<td>Barium Cuprate</td>
<td>Copper oxide (I)</td>
<td>1.16</td>
</tr>
<tr>
<td>70% CuO 30% BaO</td>
<td>Copper oxide (I)</td>
<td>Barium Oxide</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 4-2 show the electrochemical and resistivity data. The table shows resistivity’s decreasing trend with increasing Copper oxide (II) concentration in the initial composition of the pellet. Electrochemical properties suffer with increasing Copper Oxide (II) concentration in the initial composition.

Table 4.2. showing the resistance of the different composition pellets sintered in reducing atmosphere.

<table>
<thead>
<tr>
<th>Composition of pellet sintered in reducing atmosphere</th>
<th>Resistance</th>
<th>Resistivity</th>
<th>Charge Storage at 5mV/s (/cm3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% CuO 50% BaO</td>
<td>2.2MΩ</td>
<td>0.077 MΩ m</td>
<td>21.25mC</td>
</tr>
<tr>
<td>60% CuO 40% BaO</td>
<td>603Ω</td>
<td>14.003 Ω m</td>
<td>164.43mC</td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
<td>------------</td>
<td>----------</td>
</tr>
<tr>
<td>70% CuO 30% BaO</td>
<td>513Ω</td>
<td>11.95 Ω m</td>
<td>92.06mC</td>
</tr>
</tbody>
</table>

The structural data (Table 4.1, Integrated Intensity ratio) dictates a higher Copper oxide (I) concentration as the concentration in the final composition as Copper oxide (II) concentration increase in the reactants. This highlights that Copper oxide (I), though not as detrimental as Barium Oxide (see 50% BaO and 50% CuO), does have a negative impact on the electrochemical properties of Barium Cuprate. Copper oxide (I) has been identified as an oxide with very poor pseudocapacitve properties and has been found to electrochemically dormant here too. The plots supporting the tables have been shown in Figure 4.1 (Cyclic voltammetry). The plots show the Copper’s redox reaction in 60% Copper oxide, 70% Copper but no redox reactions for the 50% Copper oxide composition. Formation of Copper oxide (I) is due to reduction of Copper oxide (II) in reducing atmosphere causes the presence of excess Barium Oxide in the final composition for the sintered stoichiomertic 50% Barium Oxide and 50% Copper oxide composition. This is evident
from the x ray diffraction data in Table 4.1 and Figure 4.2 where the stoichiometric composition has Barium Oxide as a minor phase in the final overall phase. This is also the reason for very high resistivity in these particular pellets. The competing reaction of reduction of Copper oxide (II) does not allow the formation of isolated Barium Cuprate without any parasitic phases (Cu₂O and BaO). Between all the tested compositions 60% Copper oxide and 40% Barium Oxide is the

![Graphs showing CV at 30 mV/s for different compositions.](image)

Figure 4.1. CV at 30 mV/s for the different composition sintered in reducing atmosphere.
optimum composition with maximum electrochemical activity and charge storage. Thus this composition is used in the optimization of temperature in reducing atmosphere.

4.2 Sintering temperature Optimization in reducing atmosphere:
The temperature optimization is important as it helps in minimizing the temperature of formation of the compound and also provides important information about the electrochemical behavior and structural details at different temperatures. 60% Copper oxide and 40% Barium Oxide composition is pressed in the form of a pellet and then sintered in the reduced atmosphere at following temperatures for 2 hours at 450°C, 500°C and 550°C. X-ray diffraction was performed on the as synthesized pellets and pattern for the respective samples are shown in Figure 4.3. The diffraction pattern shows formation of Barium Cuprate at all temperatures. Copper oxide (I) was the other phase that was also found. Also, variation in the integrated intensity of Barium Cuprate and
Copper oxide (I) which is indicative of varying phase composition. Minor and Major phase present are drawn from Figure 4.3 and are tabulated below. The table below also shows the variation in integrated intensities ratio of BC and Copper oxide (I).

![X ray diffraction pattern](image)

**Table 4.3.** showing the major and minor phase present in the 60% CuO; 40% BaO sintered in reducing atmosphere for 2 hours.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Major Phase</th>
<th>Minor phase</th>
<th>Ratio of Integrated Intensities of most intense peaks of Cu2O and Barium cuprate (I_{600 BC} / I_{111 Cu2O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>Barium Cuprate</td>
<td>Copper (I) Oxide</td>
<td>0.71</td>
</tr>
<tr>
<td>500</td>
<td>Barium Cuprate</td>
<td>Copper(I) Oxide</td>
<td>1.16</td>
</tr>
<tr>
<td>550</td>
<td>Copper oxide(I)</td>
<td>Barium Cuprate</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Figure 4.3. X ray diffraction pattern of the 60% CuO and 40% BaO sintered at different temperatures.

Table 4.3 suggests an increasing share of Copper oxide (I) in overall final phase as the sintering temperature increases. Figure 4.4 shows the CV pellets sintered at different temperatures. Copper’s redox reaction are retained in the CV plots. The charge storage (from the CV plots Figure 4.4)
results from the pellets are tabulated below in Table 4.4 As, Copper oxide (I)’s concentration in overall phase increases the resistivity decreases and electrochemical performance suffers (see Table 4.4).

This phenomenon was also observed in the section 4.1 (Composition optimization), which would indicate that Copper oxide (I) does not assist in improving charge storage. As Copper oxide (I) is present in all the synthesized pellets, results from these sections (4.1 and 4.2) does not give an explicit idea of Barium Cuprate’s pseudocapacitive capability due to the absence of isolated Barium Cuprate phase. Thus it becomes imperative to determine the electrochemical performance of

<table>
<thead>
<tr>
<th>Temperature of sintering (°C)</th>
<th>Charge storage (mC/cm²)</th>
<th>Resistivity (Ω.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>79.01</td>
<td>1315.26</td>
</tr>
<tr>
<td>500</td>
<td>95.94</td>
<td>1083.6</td>
</tr>
<tr>
<td>550</td>
<td>81.95</td>
<td>959.78</td>
</tr>
</tbody>
</table>

Table 4.4 Charge storage at 5mV/s and electrical resistivity for 60% CuO; 40% BaO sintered in reducing atmosphere for 2hours.

Figure 4.4. CV for 60% Copper oxide 40% Barium oxide sintered in reducing atmosphere at different temperatures. Copper’s cathodic can be found between (-0.30 - 0.20 vs SCE) and anodic reaction can be seen in the range of (-0.50 - 0.40 vs SCE).
4.3 Air sintered Barium Cuprate pellets:
As explained in the section 4.2, there is a requirement of estimation of electrochemical capability of Barium Cuprate. Thus, Barium Cuprate (BC) pellets has been synthesized by sintering the stoichiometric Barium Oxide and Copper Oxide (1:1) at 750 °C for 2 hours and 10 hours. The phase composition is investigated using X-ray diffraction. The plots are shown in Figure 4.5. The plots show the formation of Barium Cuprate as the major present. Barium Oxide and Copper oxide are found in traces in 2 hours sintered pellets. Summarized results from X-ray diffraction analysis are shown in Table 4.5.

These pellets have been subsequently been electrochemically characterized using Cyclic voltammetry, EIS and RCP. The resistivity of these pellets was also measured. The results from Table 4.5. Major and minor phases present in the Barium Oxide and Copper oxide (1:1) synthesized by air sintering

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Major Phases</th>
<th>Minor phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate synthesized at 750°C, 10 hr. (BC-750C-10h)</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
<tr>
<td>Barium Cuprate synthesized at 750°C, 2 hr. (BC-750C-2h)</td>
<td>Barium Cuprate</td>
<td>Barium Oxide , CuO</td>
</tr>
</tbody>
</table>

The Cyclic Voltammetry analysis are tabulated in Table 4.6 below and plots can be seen in Figure 4.6. The redox transition that take place is following one:

\[
Cu^{2+} + e^- \rightarrow Cu^{+1}
\]

The individual anodic peaks and cathodic peaks can be located around -0.50V vs SCE and (-0.17- -0.1 V vs SCE) in Figure 4.6. Table 4.6 shows the charge storage at 5mV/s.
The resistivity data in Table 4.6 can be explained more explicitly with the final phase composition of the pellets. The resistivity of the 2 hours sintered pellets is higher than 10 hours because of the unreacted Barium Oxide still present in sintered pellets (Table 4.5). Barium Oxide has much higher

Figure 4.6. XRD for the Barium Cuprate synthesized by sintering at 750°C for 10 hours and 2 hours air sintered pellets.

Figure 4.5. CV plots at 30mV/s for the Barium Cuprate synthesized by sintering at 750 °C. The Cathodic and anodic peaks of Copper’s redox reaction are marked by blue and red markers on the plots respectively. Unreacted Barium Oxide still present in sintered pellets (Table 4.5). Barium Oxide has much higher
resistivity in excess of $5000 \, \Omega \text{cm}$ at room temperature [36] thus increases the equivalent resistance of the pellets just by the presence in such low concentrations.

Table 4.6. Showing the Charge storage and resistivity for Barium Cuprate pellets.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Charge storage mC/cm² (5mV/s)</th>
<th>Resistivity (Ω.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate synthesized at 750°C, 10 hr. (BC-750C-10h)</td>
<td>148.5165</td>
<td>1401</td>
</tr>
<tr>
<td>Barium Cuprate synthesized at 750°C, 2 hr. (BC-750C-2h)</td>
<td>108.5975</td>
<td>1877.32</td>
</tr>
</tbody>
</table>

The EIS plots can be seen in Figure 4.7. The plots show a straight line behavior in low frequency zone, which is indicative of diffusion limited reaction. The curved part in the high frequency zone is indicative of kinetics limited reaction. The shape of the curve is typical of a Randles circuit type behavior. EIS results are shown in Table 4.7 which shows parameters from a modified Randles circuit. Charge transfer resistance ($R_{ct}$) is indicative of curved part of EIS curve. Lower Charge transfer resistance ($R_{ct}$) would indicate transition to diffusion limited zone at higher frequency. 2 hours sintered barium Cuprate show higher $R_{ct}$ and the effect can be attributed to the presence of Barium Oxide.

Table 4.7. EIS results for the Barium Cuprate pellets.

<table>
<thead>
<tr>
<th>Sample type (Barium Cuprate)</th>
<th>Solution resistance, $R_s$ (Ω)</th>
<th>Charge transfer resistance, $R_{ct}$ (Ω)</th>
<th>% error in fitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered at 750°C for 10 hours</td>
<td>5.2</td>
<td>55.4</td>
<td>2.05%</td>
</tr>
<tr>
<td>Sintered at 750°C for 2 hours</td>
<td>6.8</td>
<td>74.6</td>
<td>4.36%</td>
</tr>
</tbody>
</table>

RCP plots in Figure 4.8 show qualitatively that there is more charge storage for 10 hours air sintered samples. Figure 4.8 clearly shows that the area under $V$ vs $t$ curve is higher for the 10 hour sintered pellets in comparison to the 2 hours sintered pellets. Thus it can be concluded that Barium
Cuprate can yield redox reactions pertaining to Copper transition from +1 to +2 and back. 10 hours sintered time yields better electrochemical and electrical properties due to the complete consumption of reactants.

**4.4 Bismuth doped Barium Cuprate pellets:**

As stated in the Objectives and background, the goal is to create binary or ternary oxide solid solution which can yield multiple redox transitions over large ranges of voltages. Addition of Bismuth in the form of Bismuth oxide to Barium Cuprate serves as a step in this direction. Two doping concentrations are used here:

1) 5% Bismuth (III) 45% Barium 50% Copper (II)
2) 10% Bismuth (III) 40% Barium 50% Copper (II)
In the reactants, Bismuth is added in the form of Bismuth Oxide (III) but here for convenience of understanding the Metallic ionic concentration is noted. For 5% Bismuth doping, pellets are prepared at two sintering times at 750°C, 10 hours (BC (5)-750-10h) and 2 hours – (BC (5)-750-2h). 10% Bismuth doped pellets (BC-10-750-10) are only sintered four 10 hours at 750°C. X ray diffraction was performed on the pellets sintered at aforementioned conditions. The plots are shown in Figure 4.8 and Table 4.8 shows the major and minor phase present in the pellets. Figure

Table 4.8. Major and minor phase in the 5% and 10% Bismuth doped Barium Cuprate synthesized by sintering at 750°C.

<table>
<thead>
<tr>
<th>Sample type (synthesis temperature.-750°C)</th>
<th>Major Phases</th>
<th>Minor phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Bismuth (III) 45%Barium 50%Copper (II) (10hrs.)</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
<tr>
<td>5% Bismuth (III) 45% Barium 50% Copper (II) (2hrs)</td>
<td>Barium Cuprate</td>
<td>Barium Oxide and Copper oxide</td>
</tr>
<tr>
<td>10% Bismuth (III) 40% Barium 50% Copper (II) (10hrs)</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
</tbody>
</table>

4.9 embodies characterstic peaks of Barium Cuprate. The X-ray diffraction patterns (Figure 4.9) also show that the peaks of Barium Cuprate are slightly shifted away from origin with respect to their expected position and thus making a case for substitution of Bi in the lattice. The shifts in the peaks is quantified in terms of change in the unit cell volume. The change in unit cell volume signifies the extent of Bismuth substitution in the Barium Cuprate lattice. Bismuth substitution at Barium site would cause the unit cell to shrink as the ionic diameter of Bismuth is 1.03Å and which is considerably less than Barium’s 1.35Å.
Table 4.8. showing the change in the unit cell volume.

<table>
<thead>
<tr>
<th>Type of pellet</th>
<th>Unit cell Volume (nm³)</th>
<th>Change in the unit cell Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (750°C, 10hr and 2hr.)</td>
<td>6.209</td>
<td>0</td>
</tr>
<tr>
<td>5% Bi doped Barium Cuprate (750°C, 10hrs)</td>
<td>6.092</td>
<td>-1.89</td>
</tr>
<tr>
<td>5% Bi doped Barium Cuprate (750°C, 2hrs)</td>
<td>6.12</td>
<td>-1.44</td>
</tr>
<tr>
<td>10 % Bi doped Barium Cuprate (750°C, 10hrs)</td>
<td>6.083</td>
<td>-2.03</td>
</tr>
</tbody>
</table>

The electrical (Resistivity) and electrochemical results (CV, charge storage) are shown in the Table 4.9. The relevant CV plots are shown in Figure 4.10. Table 4.9 shows that the resistivity of the Bismuth doped BC pellets is less than that of respective (sintering condition) air sintered BC pellet. 2 hours sintered BC pellets show higher resistivities due to presence of Barium Oxide. Charge storage (Table 4.11) of Bi doped BC pellets exhibit a maximum of 41.7% (5% Bi, 750°C, 10 hrs.) enhancement on the best performing air sintered BC (750°C, 10 hrs.). 5% Bismuth doped pellets are found to have 19% better charge storage and less electrical resistivity than the 10% Bismuth doped BC.
Table 4.9. showing the charge storage and resistivity data for the 5% and 10% Bismuth doped Barium Cuprate.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Temperature of synthesis (°C)/time (hrs.)</th>
<th>Resistivity (Ω.cm)</th>
<th>Charge Storage (mC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (5% Bi doped)</td>
<td>750/10</td>
<td>1362.02</td>
<td>210.43</td>
</tr>
<tr>
<td>Barium Cuprate (5% Bi doped)</td>
<td>750/2</td>
<td>1781.854</td>
<td>171.16</td>
</tr>
<tr>
<td>Barium Cuprate (10% Bi doped)</td>
<td>750/10</td>
<td>1340.16</td>
<td>176.66</td>
</tr>
</tbody>
</table>

The CV plots are shown in figure 4.10 exhibit a Bismuth redox reaction on the positive half of the range (0-0.45V vs SCE reference electrode). This significantly improves the charge storage on the positive half of the range (0-0.45V vs SCE) and thus increased the overall capacitance of the system. The CV plots also show that the Copper’s redox reaction are retained and are enhanced.
by the bismuth doping in Barium Cuprate. Tables 4.10 shows the peak current in CV plots (30mV/s) for the Barium Cuprate and Bismuth doped Barium Cuprate. Bismuth doped Barium Cuprate pellets have much higher peak height than the pure Barium Cuprate pellets. One of the examples is highlighted in blue in the table. Although this is not always true for cathodic peak for all the Bismuth doped

Table 4.10. showing the peak current in CV plots (30mV/s) for BC and Bi doped BC.

<table>
<thead>
<tr>
<th>Pellet type</th>
<th>Copper’s Cathodic reaction peak current (mA)</th>
<th>Copper’s anodic reaction peak current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (750°C and 10hrs)</td>
<td>10.4</td>
<td>-6.3</td>
</tr>
<tr>
<td>Barium Cuprate (750°C and 2 hrs)</td>
<td>8.4</td>
<td>-7.2</td>
</tr>
<tr>
<td>5% Bi doped Barium Cuprate (750°C &amp; 10 hrs)</td>
<td>29.3</td>
<td>-36.4</td>
</tr>
<tr>
<td>5% Bi doped Barium Cuprate (750°C and 2 hrs)</td>
<td>4.3</td>
<td>-15.7</td>
</tr>
<tr>
<td>10% Bi doped Barium Cuprate (750°C &amp; 10 hrs)</td>
<td>6.8</td>
<td>-9.0</td>
</tr>
</tbody>
</table>

Barium Cuprate cases. For 10% Bismuth doped pellet the enhancement is only seen in the anodic peak only. But this signifies that the Bismuth has effect on the reactions of copper.

The EIS plots are shown in Figure 4.11 and show Modified randles circuit type behavior with a straight line behavior in the low frequency zone and curvature towards the high frequency zone. Randles circuit parameter are shown in the Table 4.11 for the Bismuth doped BC pellets. $R_{ct}$ is the base of comparison and 5% Bi doped pellets show lowest $R_{ct}$. The $R_{ct}$ of the 2 hours sintered 5% Bi doped pellets is high due to the presence of Barium Oxide. Lowest $R_{ct}$ was observed for the 5% Bi doped BC (750 °C, 10 hrs).
Table 4.11. EIS results from the 5% and 10% Bismuth doped Barium Cuprate pellets.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Temperature of Air sintering (^\circ)C/time (hr.)</th>
<th>Solution resistance ((\Omega))</th>
<th>Charge transfer Resistance ((\Omega))</th>
<th>Error%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (5% Bi doped)</td>
<td>750/10</td>
<td>1.16</td>
<td>64.48</td>
<td>1.8%</td>
</tr>
<tr>
<td>Barium Cuprate (5% Bi doped)</td>
<td>750/2</td>
<td>2.79</td>
<td>417.23</td>
<td>2.68%</td>
</tr>
<tr>
<td>Barium Cuprate (10% Bi doped)</td>
<td>750/10</td>
<td>1.03</td>
<td>78.39</td>
<td>2.66%</td>
</tr>
</tbody>
</table>

RCP curves are shown in Figure 4.12 and the material exhibit good charging/discharging characteristic. 10% Bi doped BC does not show a stable behavior as the capacitance decrease with each cycle. 10 hours sintering time is found to be better performing since the charging area is much higher for it when compared from the 2 hours sintered 5% Bismuth doped BC.

This concludes that 2 hours sintering time for Bi doped Barium Cuprate is not sufficient for obtaining optimum electrochemical and electrical properties for supercapcitor electrode. The enhanced electrochemical behavior is attributed to the supposed Bismuth susbtituiton of the
Barium site in the lattice as suggested by the unit cell shrinkage. Since the no. of Oxygen atoms in the lattice remains fixed, Bismuth (+3 oxidation state) substitution on Barium site (+2 oxidation state) would cause Copper (+2 oxidation state) to change the oxidation state from +2 to +(2-∂) to accommodate extra charge on Bismuth. (2-∂) oxidation translates to presence of both +1 and +2 oxidation states in Bismuth doped Barium Cuprate. Thus it is concluded that introduction of more Cu (+1) oxidation state in the lattice improves charge storage. In the latter part of results and discussion further proof for Bismuth substitution has been presented.

4.5 Heat treated Barium Cuprate:
The effect of Bismuth doping on Barium Cuprate’s electrochemical properties is supposedly attributed to the perturbation of oxidation state of Copper from +2 to +(2-∂). Similar changes in the oxidation states can be introduced by heat treating Barium Cuprate in low partial pressures of oxygen. Following reaction is expected to take place:

$$\text{BaCuO}_2 \rightarrow \text{Ba (Cu}^{+1})_x (\text{Cu}^{+2})_{2-x}\text{O}_{2-x(2)} + (x/4) \text{O}_2$$ (4-2)

The pellets prepared in the section 4.3 at 750°C (2hrs and 10hrs) are now heat treated at 500°C for 2 hours. X-ray diffraction (Figure 4.13) has been performed on these heat treated pellets. In figure

Figure 4.12. RCP for the 5% Bismuth and 10% Bismuth doped Barium Cuprate pellet.

Figure 4.13. RCP for the 5% Bismuth and 10% Bismuth doped Barium Cuprate pellet.
4.13, the crystal structure remains intact and the same peaks appear as in the case of Barium Cuprate. However they are shifted from their expected position (as shown in the figure) and away from the origin indicating shrinkage in unit cell volume. Shrinkage in the unit cell volume would suggest reduction partial reduction of Copper (+2) to Copper (+1). The summarized results from the structural characterization can be seen in the table 4.14 and 4.15.

Table 4.12. Major and minor phase in the Heat treated Barium Cuprate for 2hours in reducing atmosphere at 500°C.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Major Phases</th>
<th>Minor phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treated BC [synthesized at 750°C, 10 hr.]</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
<tr>
<td>(HTBC -10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat treated BC [synthesized at 750°C, 2 hr.]</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
<tr>
<td>(HTBC-2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The table 4.13 shows the change in the unit cell volume. The decrease in the unit cell volume (Table 4.13) is indicative of the partial reduction of copper’s oxidation state (+2 to +1) resulting into non-stoichiometry in Copper’s state. This will present itself in the form of smaller unit cell volume than expected for air sintered Barium Cuprate. These pellets were electrochemically and electrically characterized.

Table 4.13. Unit cell volumes and shrinkages for the Heat treated Barium Cuprate pellets.

<table>
<thead>
<tr>
<th>Type of pellet</th>
<th>Unit cell Volume (nm³)</th>
<th>Change in the unit cell Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (750°C, 10hr and 2hr.)</td>
<td>6.209</td>
<td>base of comparison</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate (750°C, 10hrs)</td>
<td>6.088</td>
<td>-1.95</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate (750°C, 2hrs)</td>
<td>6.108</td>
<td>-1.63</td>
</tr>
</tbody>
</table>
The effect of heat treatment on Barium Cuprate has been very profound in terms of electrical resistivity and electrochemical activity. The effect of this has been shown in Table 4.14. In Table 4.14, the electrochemical and electrical resistivity improves by a significant margin in the 10 hours sintered pellets. The effect is not so prominent in the 2 hours sintered pellets but still positive. The charge storage shows a similar trend and heat treated pellets show a 25% and 47.2% increase for 10hrs and 2hrs non-heat treated BC pellets respectively. The CV, EIS & RCP plots are shown in figure 4.14, 4.15 respectively. The CV plots show the Cu (+1)/Cu (+2) transitions as evident in air sintered Barium Cuprate pellets. These reaction are indicated on the plots. Charge storage is much higher for the heat treated pellets 10 hours sintering BC than 2 hours sintered BC.

Figure 4.13. X-ray diffraction pattern comparison showing shifted peaks in heat treated pellets.
Heat treated pellets show higher peak currents for copper’s cathodic and anodic reactions than non-heat treated Barium Cuprate pellets. Table 4.15 shows the Copper’s cathodic and anodic peak currents from the CV plots at 30mV/s. Barium Cuprate in comparison to air sintered. Again, as seen in the Bismuth doped Barium Cuprate pellets, the reaction peak height much is higher for the heat treated BC as highlighted (in blue ) in Table 4.17. This effect is prominent only for the 10 hours sintered pellets, 2 hours sintered pellets (BC and heat treated BC) only show the effect for anodic reaction.

RCP plots are shown in Figure 4.15. The plot shows that the good charging discharging characteristics for the heat treated BC pellets and also indicate 10 hours sintered BC pellets show more energy storage than 2 hours sintered BC after heat treatment too. The EIS curves are shown in Figure 4.15 and show a typical behavior of modified Randles circuit. The Randles circuit’s

### Table 4.14 Charge storage and Resistivity comparison for Barium Cuprate and heat treated Barium Cuprate

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Synthesis Temperature / air sintering (°C)/ Time (hr.)</th>
<th>Heat treatment temperature (500°C/ 2hrs)</th>
<th>Resistivity (Ω.cm)</th>
<th>Charge Storage (mC/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate</td>
<td>750/10</td>
<td>None</td>
<td>1401</td>
<td>148.5165</td>
</tr>
<tr>
<td>Barium Cuprate</td>
<td>750/2</td>
<td>None</td>
<td>1877.32</td>
<td>108.5975</td>
</tr>
<tr>
<td>Barium Cuprate (HTBC-750C-10h)</td>
<td>750/10</td>
<td>yes</td>
<td>1246.8313</td>
<td>185.5865</td>
</tr>
<tr>
<td>Barium Cuprate (HTBC-750C-2h)</td>
<td>750/2</td>
<td>yes</td>
<td>1720.8848</td>
<td>160.27</td>
</tr>
</tbody>
</table>
parameters evaluated from Figure 4.15 are shown in Table 4.16. In the Table 4.16, Charge transfer resistance is the parameter that is the base of comparison.

Table 4.15 Showing variation in the peak currents for the heat treated Barium Cuprate and non-heat treated Barium Cuprate pellets.

<table>
<thead>
<tr>
<th>Pellet type</th>
<th>Copper’s Cathodic reaction peak current (mA)</th>
<th>Copper’s anodic reaction peak current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (750°C and 10hrs)</td>
<td>10.4</td>
<td>-6.3</td>
</tr>
<tr>
<td>Barium Cuprate (750°C and 2 hrs)</td>
<td>8.4</td>
<td>-7.2</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate (750°C and 10hrs)</td>
<td>16.7</td>
<td>-22.6</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate (750°C and 2 hrs)</td>
<td>5.3</td>
<td>-8.5</td>
</tr>
</tbody>
</table>

Figure 4.14. CV at 30mV/s for the Heat treated Barium Cuprate. HTBC-10 (air sintering for 10 hours), HTBC -2 (air sintering for 2 hours).
Heat treated 10 hours sintered BC posts much lower charge transfer resistance than heat treated 2 hours sintered BC pellets. This reiterates the better electrochemical behavior of 10 hours sintered BC pellets (heat treated or just air sintered).

Table 4.16 EIS results are shown in the table below for the Heat treated Barium Cuprate pellets.

<table>
<thead>
<tr>
<th>Pellet type</th>
<th>Solution resistance (Ω)</th>
<th>Charge transfer resistance (Ω)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treated Barium Cuprate synthesized at 750°C, 10 hr. (HTBC-10)</td>
<td>1.29</td>
<td>43.34</td>
<td>2.91%</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate synthesized at 750°C, 2 hr. (HTBC-2)</td>
<td>1.82</td>
<td>62.4</td>
<td>3.43%</td>
</tr>
</tbody>
</table>

The overview of this section is that heat treatment shows similar electrochemical changes with respect to pure BC as observed with the Bismuth doped Barium Cuprate pellets. Similar unit cell volume shrinkage was also observed with the heat treatment of BC in reducing atmosphere. This strongly suggests that Copper is partially
reduced to +1 state in the lattice and its oxidation state has changed to 2−δ from 2. Since both contribute towards a similar phenomenon and aids in the improving pseudocapacitance, the combined effect of both should maximize the capacitance. The electrochemical and electrical properties shows a dependence on the oxidation of state of Copper.

4.6 Heat treated and Bismuth doped pellet:
Since introduction of Bismuth and heat treatment both improve the electrical and electrochemical and electrical characteristics. The combined effect of both should maximize the charge storage in system, therefore this step becomes very crucial. To observe effect of the both in tandem, following three Bismuth doped variant from the section 4.4 are synthesized at 750°C and then heat treated in reducing atmosphere (90% Nitrogen 10% Hydrogen).

1. 5% Bismuth (III) 45% Barium 50% Copper (I) (750°C sintering time-10hrs)
2. 5% Bismuth (III) 45% Barium 50% Copper (I) (750°C sintering time-2hrs)
3. 10% Bismuth (III) 40% Barium 50% Copper (I) (750°C sintering time-10hrs)

The three different pellets were structurally characterized using the X-ray diffraction studies. The plots are shown below in Figure 4.16. The plot shows the presence of Barium Cuprate in all three phases and no other phases were found. The major and minor phase are shown Table 4.17 below.

Figure 4.16 also show peak shifts of the characteristic BC peaks from their expected position away from the origin. These peaks shift are again quantified in terms of change in unit cell volume.
Table 4.18 shows the comparison of the unit cell volume and embodies all the structural effects associated with shifting of peaks. It is also indicative of Bi substitution on Barium site in the Barium Cuprate lattice and partial reduction to Copper (+2 to +1) in Bi doped due to heat treatment.

Table 4.17. showing the major and minor phase present in the Heat treated Bismuth doped Barium Cuprate.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Major Phase</th>
<th>Minor phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treated 5% Bismuth doped BC(750°C/2hrs)</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped BC (750°C/10hrs)</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
<tr>
<td>Heat treated 10% Bismuth doped BC(750°C/10hrs)</td>
<td>Barium Cuprate</td>
<td>None</td>
</tr>
</tbody>
</table>
Table 4.18 shows that there is not much difference between the Unit cell volume of Heat treated 5% Bismuth doped Barium Cuprate (750°C, 10hrs) and Heat treated 10% Bismuth doped Barium Cuprate (750°C, 10hrs). This is indicative of the saturation of Bi solubility in Barium Cuprate lattice.

Table 4.18. Table showing the unit cell volume change due to heat treatment of Bismuth doped BC

<table>
<thead>
<tr>
<th>Type of pellet</th>
<th>Unit cell Volume (nm³)</th>
<th>Change in the unit cell Volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (750°C, 10hr and 2hr.)</td>
<td>6.209</td>
<td>base of comparison</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped Barium Cuprate (750°C, 10hrs)</td>
<td>6.072</td>
<td>-2.21</td>
</tr>
<tr>
<td>Heat treated 5% Barium Cuprate (750°C, 2hrs)</td>
<td>6.101</td>
<td>-1.74</td>
</tr>
<tr>
<td>Heat treated 10% Bismuth doped Barium Cuprate (750°C, 10hrs)</td>
<td>6.068</td>
<td>-2.28</td>
</tr>
</tbody>
</table>

These pellets are also characterized electrochemically and electrically. The CV, EIS & RCP plots are shown in Figure 4.17 and 4.18. The individual resistivity data is shown in Table 4.19. Figure 4.17 show the related CV plot at 30mV/s and the redox reactions of Copper and Bismuth are observed. The peaks are indicated on the plots. The charge storage and electrical resistivity is shown in Table 4.21. The table shows that the heat treated pellets of 5% Bismuth doped BC (750°C and 10hrs.) stores 19% more charge and has lower resistivity than 10% Bi doped BC. 2 hours sintering time again yields around 23% less charge storage and higher electrical resistivity.

The EIS plots can be seen in Figure 4.18. These plots show a modified Randles circuit type behavior and the associated parameters for each pellet are shown in Table 4.22. The charge
transfer resistance is seen to be the base of comparison and is seen to be reducing by more addition of Bismuth in Barium Cuprate.

Table 4.19. Showing the charge storage and electrical resistivity of the heat treated Bismuth doped Barium Cuprate.

<table>
<thead>
<tr>
<th>Pellet type</th>
<th>Charge storage (mC/cm²)</th>
<th>Resistivity (Ω.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat Treated 5% Bismuth doped BC (750°C/10 h)</td>
<td>210.43</td>
<td>1242.39</td>
</tr>
<tr>
<td>Heat Treated 5% Bismuth doped BC (750°C/2h)</td>
<td>171.16</td>
<td>1648.37</td>
</tr>
<tr>
<td>Heat Treated 10% Bismuth doped BC, (750°C-10h)</td>
<td>176.66</td>
<td>1203.87</td>
</tr>
</tbody>
</table>

Figure 4.17. CV at 30mV/s for the Heat treated 5% (above) and 10% (below) Bismuth doped pellets showing the Bismuth and copper redox reactions.
Table 4.20. Showing the charge transfer resistance of heat treated Bismuth doped BC pellets.

<table>
<thead>
<tr>
<th>Pellet type</th>
<th>Solution resistance</th>
<th>Charge transfer resistance</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treated 5% Bismuth doped Barium Cuprate sintered at 750°C for 10 hours</td>
<td>2.46</td>
<td>48.83</td>
<td>3.56%</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped Barium Cuprate sintered at 750°C for 2 hours</td>
<td>1.87</td>
<td>31.23</td>
<td>5.62%</td>
</tr>
<tr>
<td>Heat Treated 10% Bismuth doped BC, BC(10)-750C-10h</td>
<td>1.16</td>
<td>15.68</td>
<td>2.83%</td>
</tr>
</tbody>
</table>

The RCP plots shown in the figure 4.18 show only one cycle of RCP test for ease of comparison. The rest of cycles were found to similar in terms of capacitance. The highest charge storage is for the 5% Bi doped BC (750°C, 10h) and then 10% Bi doped BC (750°C, 10h) and finally the 5% Bi doped BC (750°C, 2h). The charging/discharging characteristics seem fast enough all the different Bi doped pellets. Thus as seem in the previous sections 2 hours of sintering for synthesis is not suitable for obtaining optimum electrochemical and electrical properties.

![EIS and RCP of heat treated 5% Bismuth doped Barium Cuprate pellets. RCP shows that the area under the charging curve is more for 10 hours air sintered samples.](image)
4.7 Summary of electrochemical results of Pellets:
The electrochemical behavior of Barium Cuprate shows very interesting characteristics where copper which is situated inside the lattice, shows redox transitions between +1 and +2 state. These reactions are particularly different from the ones exhibited by Copper oxide (II) as the reduction potential is different (more negative). Thus these reactions are rather redox reactions of Barium Cuprate than just Copper making transitions from +1 to +2 and back. 5%, 10% Bismuth doping in BC and Heat treatment of BC enhances by charge storage by 41.8%, 18.9% and 24.9% respectively (comparison b/w 10hours sintering time). Bismuth substitution on Barium site and Heat treatment in reducing atmosphere of Barium Cuprate effectively introduces more Cu\(^{+1}\) ions in the lattice. Thus the electrochemical properties are found to be directly related to the concentration of these Cu\(^{+1}\) in the lattice, which is however difficult to calculate but has been observed qualitatively with unit cell volume and its shrinkage. Concentration of Cu\(^{+1}\) also reduces the resistivity of the Barium Cuprate which is an expected behavior in such compounds when sintered in reducing atmosphere. Heat treatment in reducing atmosphere and 5% Bismuth doping of BC together thus provide the lowest resistivity and charge storage which is about 46% higher than native BC (see Table 4.21). Bismuth doping also yields its own reaction too. Table 4.21 below show the individual charge storage of each of the pellets tested. Table shows the absolute values and summarizes the results from the last few sections.

Now that the electrochemical properties of Barium Cuprate and Bismuth doped Barium Cuprate pellets have been established the focus is to achieve similar structural characteristics in the powders. Following section discuss the synthesis of powders and these powder based thin films. Also, the films will reiterate the similar phenomenon which will add further proof to the claims made above.
Table 4.21. Summary of Charge storage for the pellets.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Temperature of synthesis(℃)/time (hr.)</th>
<th>Charge Storage (mC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (BC)</td>
<td>750/10</td>
<td>148.5165</td>
</tr>
<tr>
<td>Barium Cuprate (BC)</td>
<td>750/2</td>
<td>108.5975</td>
</tr>
<tr>
<td>5% Bi doped BC</td>
<td>750/10</td>
<td>210.43</td>
</tr>
<tr>
<td>5% Bi doped BC</td>
<td>750/2</td>
<td>171.16</td>
</tr>
<tr>
<td>10% Bi doped BC</td>
<td>750/10</td>
<td>176.66</td>
</tr>
<tr>
<td>Heat treated BC</td>
<td>750/10</td>
<td>185.5865</td>
</tr>
<tr>
<td>Heat treated BC</td>
<td>750/2</td>
<td>160.27</td>
</tr>
<tr>
<td>Heat Treated 5% Bi doped BC</td>
<td>750/10</td>
<td>216.8925</td>
</tr>
<tr>
<td>Heat Treated 5% Bi doped BC</td>
<td>750/2</td>
<td>182.38</td>
</tr>
<tr>
<td>Heat Treated 10% Bi doped BC</td>
<td>750/10</td>
<td>191.257</td>
</tr>
</tbody>
</table>

4.9 Structure studies for the powders:
Powders are synthesized using the same conditions used to synthesize the pellets. X-ray diffraction analysis was performed and is shown in figure 4.19, 4.20 and 4.21. Barium Cuprate was successfully synthesized in the powder at the same conditions at 750℃. The corresponding heat treated powders also show similar crystal structure but with slight shift in characteristic peak in XRD pattern away from the origin as it was found in the case of pellets. Preservation of crystal structure and shifting of the characteristic peaks away from the origin was observed in the bismuth doped BC powders too. This is indicative of the phenomenon of Bismuth substitution at Barium positions in lattice as observed in the case of pellets. Table 4.22 and 4.23 presents the major, minor phases and unit cell volume data in the powders synthesized.
The change in the unit cell volume is close to what is observed for the pellets. This shows the powders bear the similar characteristics as observed in the pellets.

Table 4.22. Major, minor phase in the powders sintered and their respective unit cell volume changes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Major Phase</th>
<th>Minor Phase</th>
<th>Unit cell Volume (nm(^3))</th>
<th>% Δ unit cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate doped with 5% Bismuth synthesized at 750°C for 10 hrs.</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.084</td>
<td>-2.01</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate doped with 5% Bismuth synthesized at 750°C for 10 hrs.</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.068</td>
<td>-2.26</td>
</tr>
<tr>
<td>Barium Cuprate doped with 5% Bismuth synthesized at 750°C for 2 hrs.</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.109</td>
<td>-1.61</td>
</tr>
</tbody>
</table>

Table 4.23. Major, minor phase in the powders sintered and their respective unit cell volume changes.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Major Phase</th>
<th>Minor Phase</th>
<th>Unit cell Volume (nm(^3))</th>
<th>% Δ unit cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat treated Barium Cuprate doped with 5% Bismuth synthesized at 750°C for 2 hrs.</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.095</td>
<td>-1.83</td>
</tr>
<tr>
<td>10% Bi doped Barium Cuprate air sintered 750°C 10h</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.082</td>
<td>-2.03</td>
</tr>
<tr>
<td>Heat treated 10% Bi doped Barium Cuprate air sintered 750°C 10h</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.066</td>
<td>-2.29</td>
</tr>
<tr>
<td>Barium Cuprate synthesized at 750 °C for 10 hours</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.211</td>
<td>0.04</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate synthesized at 750 °C for 10 hours</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.087</td>
<td>-1.95</td>
</tr>
<tr>
<td>Barium Cuprate synthesized at 750 °C for 2 hours</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.209</td>
<td>0</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate synthesized at 750 for 2 hours</td>
<td>Barium Cuprate</td>
<td>None</td>
<td>6.106</td>
<td>-1.65</td>
</tr>
</tbody>
</table>
Figure 4.19. XRD of 10% Bi doped Barium Cuprate powders synthesized at different temperatures and times. Corresponding heat treated Barium Cuprate is also shown.

Figure 4.20. XRD of Barium Cuprate powders synthesized at different temperatures and times. Corresponding heat treated Barium Cuprate is also shown.
4.10 Electrochemical results for thin films
4.10.1 Base line with graphite and PEO:
Thin film electrodes are synthesized by spin coating of BC, HTBC, Bismuth doped BC, and heat treated Bismuth doped BC with PEO and graphite onto a 0.5’ x 0.5’ Stainless steel (SS301) substrate. PEO and graphite used as the conductive base for the HTBC powders. Partial solution mixing technique [41, 42] has been used to synthesize the PEO and graphite composite solution. The solution used consists of Acetone and Isopropyl alcohol (1:9 by volume). This solution is thus taken as the base and the ceramic powders are added to this solution. Further this solution carrying graphite, PEO and Ceramic powders is spin coated onto a Stainless Steel substrate (Section 3.7 for complete procedure). The final electrode composition of the ceramic-polymer-graphite composite is 50% Ceramic powder, 47.5% PEO and 2.5% Graphite (by wt.). Since
Polymer and graphite are added in significant amounts a baseline has to be defined for the differentiation between the contribution from the ceramic powders and PEO & graphite composite. The charge storage value for the PEO and graphite based electrode is 20.73 mC/cm². This forms the baseline for all the electrodes that are formed via spin coating route as explained in experimental section. A typical CV for large and small range is shown in Figure 4.22.

![Figure 4.22. CV at 30mV/s for spin coated film of PEO and Graphite.](image)

4.10.2 Barium Cuprate based thin films:

Four different Barium Cuprate powders are used to synthesize the thin films:

1) Barium Cuprate sintered at 750°C, 10 hours.

2) Barium Cuprate and Copper Oxide (1:1) sintered at 750°C, 2 hours.
3) Heat treated Barium Cuprate sintered at 750°C, 10 hours;

4) Heat treated Barium Cuprate sintered at 750°C, 2 hours;

The electrochemical characterization results from CV analysis are shown in Table 4.24. The associated CV plot are shown in figure 4.23. The CV plots shows Cu$^{+1}$/Cu$^{+2}$ transition as present in the pellets although. These transitions are indicated on the plot. The charge storage values are much higher than pellets as shown in Table 4.24. The major gain in charge storage is found to be in the positive range (0-0.45V vs SCE).which could be attributed to the introduction PEO and graphite, since the major portion of capacitance lies in the positive half of the range.

Table 4.24. Charge storage for the Barium Cuprate, graphite and PEO thin films.

<table>
<thead>
<tr>
<th>Thin film type</th>
<th>Charge storage (mC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate synthesized at 750 °C for 10 hours</td>
<td>193.26</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate synthesized at 750 °C for 10 hours</td>
<td>217.68</td>
</tr>
<tr>
<td>Barium Cuprate synthesized at 750 °C for 2 hours</td>
<td>163.49</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate synthesized for 2 hours</td>
<td>151.42</td>
</tr>
<tr>
<td>PEO and graphite baseline</td>
<td>20.73</td>
</tr>
</tbody>
</table>

The RCP and EIS curves are shown in figure 4.24 and 4.25. The EIS plots show straight line behavior in low frequency zone and circular behavior in high frequency zone. This type of curves are typical of a modified Randles circuit. Table 4.25 shows the summarized EIS results and parameters obtained from the EIS analysis of as specified Barium Cuprate powder based thin films. The table clearly shows the heat treated Barium Cuprate based thin films pose lower charge transfer resistance than the respective non heat treated Barium Cuprate based thin films. RCP plots shown in Figure 4.24 again shows that higher charging area seen is for the heat treated Barium Cuprate thin films than the respective non-heat treated Barium Cuprate.
Table 4.25. EIS results from the Barium Cuprate, graphite and PEO thin films.

<table>
<thead>
<tr>
<th>Powder used in thin film (Base- PEO and Graphite)</th>
<th>Solution resistance, $R_s$ (Ω)</th>
<th>Charge transfer resistance, $R_c$ (Ω)</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate (750°C;10 hours)</td>
<td>1.04</td>
<td>109.27</td>
<td>3.63</td>
</tr>
<tr>
<td>Barium Cuprate (750°C;2 hours)</td>
<td>1.26</td>
<td>147.11</td>
<td>3.15</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate(750°C;10hrs)</td>
<td>0.58</td>
<td>41.13</td>
<td>1.37</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate (750°C; 2 hrs.)</td>
<td>0.78</td>
<td>89.34</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Figure 4.23. CV plots of thin films based on Barium Cuprate powders sintered at 750°C for 2 hours and 10 hours. Their corresponding heat treated powders based thin films are also shown.
RCP plots shown in Figure 4.24 again shows that higher charging area seen is for the heat treated Barium Cuprate thin films than the respective non-heat treated Barium Cuprate. Here only one cycle of RCP curve is shown because the curve do not show any deviation in the following cycle.

Figure 4.25. EIS of the different Barium Cuprate and heat treated Barium Cuprate based thin films.

Figure 4.24. RCP of the different Barium Cuprate and heat treated Barium Cuprate based thin films.
4.10.3 Bismuth doped Barium Cuprate based thin films:
Similar to the Barium Cuprate based thin films, the 6 different variants are prepared for 5% and 10% Bismuth doped Barium Cuprate here:

1) 5% Bismuth doped Barium Cuprate (750°C; 10 hours )
2) Heat treated 5% Bismuth doped Barium Cuprate (750°C; 10 hours).
3) 5% Bismuth doped Barium Cuprate (750°C for 2 hours).
4) Heat treated 5% Bismuth doped Barium Cuprate (750°C, 2 hours )
5) 10% Bi doped Barium Cuprate (750°C, 10 hours)
6) Heat treated 10% Bi doped Barium Cuprate (750°C, 10 hours)

The summary of CV (plots shown in Figure 4.26 and 4.27) results can be seen in Table 4.26. The individual heat treated Bismuth doped BC powders based thin films have better performances than their just air sintered Bismuth doped Barium Cuprate counterpart as shown in Table 4.26.

Table 4.26. Charge storage for the Bismuth doped Barium Cuprate powders based thin films.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Charge storage (mC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Bismuth doped Barium Cuprate synthesized at 750°C for 10 hrs.</td>
<td>301.4</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped Barium Cuprate (synthesized at 750°C; 10hrs.)</td>
<td>343.6</td>
</tr>
<tr>
<td>5% Bismuth doped Barium Cuprate (synthesized at 750°C; 2 hrs.)</td>
<td>230.25</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped Barium Cuprate (synthesized at 750°C&amp; 2hrs.)</td>
<td>273.18</td>
</tr>
<tr>
<td>10% Bi doped Barium Cuprate (synthesized at 750°C; 10hrs.)</td>
<td>314</td>
</tr>
<tr>
<td>Heat treated 10% Bi doped Barium Cuprate (synthesized at 750°C; 10hrs.)</td>
<td>304.63</td>
</tr>
<tr>
<td>PEO and graphite baseline</td>
<td>20.73</td>
</tr>
</tbody>
</table>

The CV plots bear Bi⁺³/Bi⁺� transitions along with the existing Cu⁺¹/Cu⁺² transitions. The individual cathodic and anodic reactions can be seen in Figure 4.26 and 4.27. Between 5% Bi
doped and 10% Bi doped Barium Cuprate, the performance of 5% was found to be better for both Heat treated and non-heat treated powders. Heat treated Bi doped BC show better charge storage for 5% Bi doping but no major change is seen between the two films for the 10% Bi doping of BC. Therefore, in terms of charge storage the powders bear similar electrochemical characteristics as the pellets.

Figure 4.26. CV 30mV/s for Heat treated and non-heat treated 10% Bismuth doped BC based thin films.

![Graph showing EIS plots for 5% and 10% Bi doped BC](image)

Figure 4.27. CV at 30mV/s for 5% Bi doped BC based thin films.

The EIS plots of 5% and 10% Bi doped Barium Cuprate powders based thin films are shown in Figure 4.27 and 4.28 respectively. The figure show typical characteristics of a Randles circuit by
having a straight line behavior in the low frequency zone and circular curve in the high frequency zone. The Charge transfer resistance is shown in Table 4.27. The charge transfer resistance for the heat treated Bi doped BC powders is found to be less than the respective non heat treated Bi doped BC powder based films. Again heat treated and 5% Bi doped Barium Cuprate (sintering temp-750°C;10hrs) powder based films posted least charge transfer resistance. For similar synthesis conditions( air sintering and subsequent heat treatment) 5% Bi doped BC had lower charge transfer resistance in comparison to 10% Bi doped BC powder based films.

Table 4.27. Table showing the charge transfer resistance for the Bismuth doped Barium Cuprate powders based thin films.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Charge transfer resistance (Ω)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Bismuth doped BC synthesized at 750°C for 10 hrs.</td>
<td>14.31</td>
<td>3.66%</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped BC (synthesized at 750°C; 10hrs.)</td>
<td>7.52</td>
<td>4.07%</td>
</tr>
<tr>
<td>5% Bismuth doped BC (synthesized at 750°C; 2 hrs.)</td>
<td>213.54</td>
<td>1.82%</td>
</tr>
<tr>
<td>Heat treated 5% Bismuth doped BC (synthesized at 750°C; 2hrs.)</td>
<td>75.38</td>
<td>2.74%</td>
</tr>
<tr>
<td>10% Bi doped BC (synthesized at 750°C; 10hrs.)</td>
<td>17.32</td>
<td>1.44%</td>
</tr>
<tr>
<td>Heat treated 10% Bi doped BC (synthesized at 750°C; 10hrs.)</td>
<td>12.83</td>
<td>1.92%</td>
</tr>
</tbody>
</table>

RCP plots are shown in Figure 4.29 and 4.30. The figures clearly show that heat treated Bismuth doped BC films have more charging area which translates to more storage of energy. Although for heat treated 10% Bi doped BC powder based films discharging characteristics are poor compared to non-heat treated powder based films. For 5% Bi doped BC based films the heat treated powder have charging and discharging times as well as the energy.
Figure 4.28. EIS for the 5% (above, left–10 hours, right–2 hours) and 10% Bi doped BC powder based thin films (below).

Figure 4.29. RCP for the 10% Bi doped BC powder based thin films.
4.10 Summary of electrochemical results of thin films and Comparison with pellet: The electrochemical results typically reiterates the similar phenomenon seen in the pellets. Bi doped BC, heat treated BC and Bi doped BC all show similar shrinkage in unit cell as seen with the pellets. This signifies the structural similarity between the pellets and powders. The comparison between the thin film and pellets has been shown in Table 4.27. BC based thin films were found to producing the redox reactions of Copper( +1/+2), however charge storage is much more for films. In Table 4.28, heat treatment of BC powders shows about 10% increase in the charge storage than the non heat treated BC based films electrochemical properties on account of the more Cu$^{+1}$ species present in the lattice. Similarly 5% and 10% Bismuth doped Barium Cuprate based films have almost 50% more charge storage than undoped BC. The heat treatment of 5% Bismuth doped BC powders did shown an 10% increase in the charge storage on the non heat treated powder based films.. But with 10% Bismuth doped BC powders heat treatment showed a 3% loss in charge storage for films. Highest charge storage is obtained for heat treated 5% Bismuth.
doped BC powder based films which posted almost 75% increase on the BC powder based films (750 °C; 10hrs.) . The reoccurrence of improvement in charge storage due to Bismuth doping and heat treatment would infer a dependence of electrochemical properties on the concentration of Cu\(^{+1}\) in Barium Cuprate lattice. Bismuth doping also presents itself in the form of Bi (+1/+3) transition on the positive half of the range (0-0.45V vs SCE).

Table 4.28. Summary of Charge storage for Barium Cuprate, PEO and graphite thin films.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Temperature of synthesis(°C)/time (hr.)</th>
<th>Charge Storage (mC/cm(^2)) in pellets</th>
<th>Charge Storage (mC/cm(^2)) in films</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>750/10</td>
<td>148.5165</td>
<td>193.26</td>
</tr>
<tr>
<td>BC</td>
<td>750/2</td>
<td>108.5975</td>
<td>151.42</td>
</tr>
<tr>
<td>5% Bi doped BC</td>
<td>750/10</td>
<td>210.43</td>
<td>301.4</td>
</tr>
<tr>
<td>5% Bi doped BC</td>
<td>750/2</td>
<td>171.16</td>
<td>230.25</td>
</tr>
<tr>
<td>10% Bi doped BC</td>
<td>750/10</td>
<td>176.66</td>
<td>314</td>
</tr>
<tr>
<td>Heat treated BC</td>
<td>750/10</td>
<td>185.5865</td>
<td>217.68</td>
</tr>
<tr>
<td>Heat treated BC</td>
<td>750/2</td>
<td>160.27</td>
<td>163.49</td>
</tr>
<tr>
<td>Heat Treated 5% Bi doped BC</td>
<td>750/10</td>
<td>216.90</td>
<td>343.6</td>
</tr>
<tr>
<td>Heat Treated 5% Bi doped BC</td>
<td>750/2</td>
<td>182.38</td>
<td>273.18</td>
</tr>
<tr>
<td>Heat Treated 10% Bi doped BC</td>
<td>750/10</td>
<td>191.26</td>
<td>304.63</td>
</tr>
<tr>
<td>PEO and graphite baseline</td>
<td>-</td>
<td>-</td>
<td>20.73</td>
</tr>
</tbody>
</table>

Table 4.28 is also indicative of a general effect seen when a pseudocapacitive oxide is mixed with an EDLC material such as graphite. The effect multiplies the overall capacitance of the composite system rather than just the addition of capacitance of two components. The effect can be seen here too as graphite and PEO both enhances the capacitance of the system in a similar way as in the
case of non-heat treated and heat treated 5% Bi doped BC the charge storage rises by 45% and 59% respectively.

4.11 Scanning Electron Microscopy:
Scanning electron microscopy was done Barium Cuprate, 5% Bismuth doped Barium Cuprate and 10% Bismuth doped Barium Cuprate (750°C; 10 hrs.). Figure 4.32 show SEM micrographs for the Barium Cuprate pellets. Barium Cuprate pellets sintered at 750°C for 10 hours show presence of only one major phase which is Barium Cuprate as suggested by the x ray diffraction in the section 4.1.

![SEM micrographs for Barium Cuprate sintered at 750°C for 10 hrs. (5000X and 500X respectively; left to right). The Micrographs show only a one phase structure, the phase is identified as Barium Cuprate.](image)

It is also clear in the SEM micrographs that densification is not nearly complete, indicated by the pores seen in the 500X image. Bismuth doped (5% and 10%) Barium Cuprate pellets however show the presence of two phases as shown in Figure 4.32. The Backscattered electron images (Figure 4.32) show presence two phase as there are bright regions located between the dim regions. Figure 4.33 and 4.34 shows the EDS done on one such bright spot and a dark spot, the EDS (Figure 4.33 and 4.34) on the brighter phase reveals a much higher concentration of the Bismuth.
This concludes incomplete diffusion of Bismuth in Barium Cuprate in the lattice. This could be caused because of the introduction of Bismuth as reactant (Barium Oxide and Copper Oxide) in the form of Bismuth oxide (III, Bi$_2$O$_3$). The addition of Bismuth oxide particularly during the ball milling stages is in minute quantities because the doping is only 5% and 10% by mole. When such small quantities are involved a great number of new microstructural features starts to appear and become evident through EDS analysis.

**Figure 4.32.** SEM and EDS of 10% Bismuth doped Barium Cuprate pellets. EDS analysis shows high Bi concentration in the bright regions.

**Figure 4.33.** SEM micrographs of 5% Bismuth doped Barium Cuprate (left) and 10% Barium Cuprate (right) sintered for 10 hours at 750°C. The analysis indicates a two phase structure. The bright phase is found out to be Bi$_2$O$_3$.
degree of mixing cannot be achieved. This could lead to low solubility of Bismuth in Barium Cuprate and would yield unreacted Bismuth in the final phase. Another factor that could lead to

Figure 4.34. SEM and EDS of 10% Bismuth doped Barium Cuprate pellets. EDS analysis shows high Bi concentration in the bright regions.

Figure 4.35. SEM micrographs of 5% Bismuth doped Barium Cuprate (top) and 10% Bismuth doped Barium Cuprate (air sintered at 750°C for 10 hours) (bottom). Bright region indicating Bismuth rich/unreacted Bismuth oxide in the pictures.
incomplete diffusion could be because the solid solubility limit of Bi in barium Cuprate has been achieved. It is difficult to distinguish between the two. Such features are also present in the 5% and 10% Bismuth doped Barium Cuprate powders as shown in Figure 4.35.

4.11. 2 SEM of Barium Cuprate powder:
The Barium Cuprate powders synthesized at 750°C for sintering time 2 and 10 hours showed a single phase structure and no other phase was found. No stark difference in morphology and phases was found in Heat treated Barium Cuprate powders (750°C, 10hrs.) in comparison to the Barium Cuprate powders (750°C, 10hrs.). Cuprate powders (750°C, 10hrs.). The micrographs are shown in Figure 4.36. Average particle size is of the order is 2-4 µm.

Figure 4.36. SEM micrographs of the Barium Cuprate (750°C, 10 hours, left), Heat treated Barium Cuprate (750°C, 10 hours, left) and Barium Cu(750°C, 2 hours). Only one phase (BC) was found in the SEM characterization.
4.11.3 SEM analysis of thin films:
The films show very uniform distribution of particles over the surface. The surface of films are shown in Figure 4.36. The films show uniform coverage of ceramic particles (bright phase) and black matrix is confirmed as graphite and PEO. Since graphite penetrates PEO when agitated aggressively and thus this penetration makes it very difficult to distinguish between graphite and PEO. This also proves that the percolation of graphite into PEO is very through and uniform.

![SEM micrograph of the Barium Cuprate (750, 10 hrs.), PEO and graphite thin films.](image)

4.12 Microstructural Features:
The density is calculated by normalizing the weight of the pellet with their volume. The density is further divided by the theoretical density of the Barium Cuprate to calculate the Densification. Densification data for different Barium Cuprate pellets is shown below in the Table 4.29. Bismuth doped BC pellets have been observed to yield more densification that undoped BC. This happens because of the fluxing nature of Bismuth Oxide which will decrease the melting point of the system and in turn increases the densification. This also suggests that Bismuth has substituted at Barium sites in BC lattice. The subsequent heat treatment does not increase the densification by much in all the cases. Bismuth doping’s effect can be clearly seen in the in the densification as 5% and 10% Bismuth doped pellet post higher densification than pure Barium Cuprate in air sintering (Table 4.29).
Table 4.29. Showing the densification of different Barium Cuprate pellets synthesized

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Temperature of air sintering (°C)/ Time (hr.)</th>
<th>Final Density (g/cm³)</th>
<th>Theoretical Density (g/cm³)</th>
<th>Densification (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium Cuprate</td>
<td>750/10</td>
<td>5.1293</td>
<td>5.68</td>
<td>90.30</td>
</tr>
<tr>
<td>Barium Cuprate</td>
<td>750/2</td>
<td>4.503</td>
<td>5.68</td>
<td>79.28</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate</td>
<td>750/10</td>
<td>5.173</td>
<td>5.68</td>
<td>91.07</td>
</tr>
<tr>
<td>Heat treated Barium Cuprate</td>
<td>750/2</td>
<td>3.882</td>
<td>5.68</td>
<td>80.14</td>
</tr>
<tr>
<td>5% Bi doped BC</td>
<td>750/10</td>
<td>5.161</td>
<td>5.68</td>
<td>91.01</td>
</tr>
<tr>
<td>5% Bi doped BC</td>
<td>750/2</td>
<td>4.47</td>
<td>5.68</td>
<td>80.70</td>
</tr>
<tr>
<td>Heat treated 5% Bi doped BC</td>
<td>750/10</td>
<td>5.186</td>
<td>5.68</td>
<td>91.32</td>
</tr>
<tr>
<td>Heat treated 5% Bi doped BC</td>
<td>750/2</td>
<td>4.561</td>
<td>5.68</td>
<td>80.30</td>
</tr>
<tr>
<td>10% Bi BC</td>
<td>750/10</td>
<td>5.191</td>
<td>5.68</td>
<td>91.30</td>
</tr>
<tr>
<td>Heat treated 10% Bi BC</td>
<td>750/10</td>
<td>5.194</td>
<td>5.68</td>
<td>91.46</td>
</tr>
</tbody>
</table>

4.13 Vibrational studies:
The spectra from Barium Cuprate (Air sintered for 10 hours at 750°C), 5% Bismuth doped Barium Cuprate (Air sintered for 10 hours at 750°C) and heat treated Barium Cuprate (Air sintered for 10 hours at 750°C) is presented. The peak shifts for respective vibrations is shown below in the table
below. This could be caused because of Bismuth substitution at Barium site in the lattice. Since number of Oxygen in the lattice is fixed and Bismuth is in $+3$ oxidation state and is substituting Barium which is in $+2$ oxidation, it would require one of preexisting ion to change oxidation state. Between Barium and Copper, only copper has the ability to exist in multiple oxidation states ($+1$ and $+2$). Therefore, slight deviation in oxidation state of Copper from $+2$ to $+2- \Delta$ would explain the shifts.

The table below shows the peak location for each sample. In Heat treated Barium Cuprate powders the peak shift would be caused due to the partial reduction of $\text{Cu}^{2+}$ to $\text{Cu}^{+1}$ due to reducing atmosphere, thus introducing non-stoichiometry in the Copper's oxidation state. This non-stoichiometry results in the shifting of Cu-O vibration peaks in the FTIR spectra. Figure 4.38 shows the corresponding FTIR spectra of the respective powder samples. Cu-O bond symmetric stretching, Cu-O asymmetric vibration and Ba-O vibration are indicated on the plot as 1, 2 and 3.

<table>
<thead>
<tr>
<th>Table 4.30. Summary of Vibrational spectra and shifts in characteristic peak. [34]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vibration mode</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Cu-O bond symmetric stretching</td>
</tr>
<tr>
<td>Cu-O asymmetric vibration</td>
</tr>
<tr>
<td>Ba-O vibration</td>
</tr>
</tbody>
</table>
4.13 Summary:
1) Synthesis of Barium Cuprate under reducing condition was performed and 450°C is found to be the lowest temperature for the formation of the compound. Another competing reaction of Copper oxide (II) reducing to Copper Oxide (I) was found to be active. This competing reaction does not allow an isolated formation of Barium Cuprate.

2) Barium Cuprate pellets were synthesized by sintering in air at 750°C for two time durations (2 and 10 hours) and electrochemical characterization of Barium Cuprate yielded Cu$^{2+}$ to Cu$^{+1}$ transition (and the reverse). A maximum charge storage of 148mC/cm$^2$ for the sintering time of 10 hours. 2 hours sintering time was found to be insufficient for obtaining optimum electrochemical and electrical properties.
3) Barium Cuprate pellets were heat treated and doped with Bismuth separately and together both. Both of these cause unit cell volume to shrink and is indicative of Copper presence of +1 state in the lattice.

4) Both Bismuth doping and Heat treatment individually and collectively reduce the electrical resistivity and enhance the electrochemical activity of Copper’s redox reactions in BC pellets. Also bismuth doped pellets show Bismuth reactions (+3 to +1 and back) peaks in cyclic voltammetry analysis. 5% Bismuth doping along with heat treatment in BC increased charge storage by almost 40% on the pure and non-heat treated BC pellets.

5) Powders were successfully synthesized at the same condition/temperature with similar structural features (unit cell volume) as for the respective pellets. Thin film electrodes using as synthesized powders (with PEO and Graphite) were successfully formed showing a uniform particle distribution on the surface.

6) Powders also show a similar relationship between the 2hours and 10 hour sintered powders with 10 hours sintered powder based thin films outperforming the 2 hours sintered powders. Also Heat treated powders are better than just their non-heat treated counterpart.

7) Bismuth doped Barium Cuprate powders enhance copper’s reactions and also yield their own redox reactions (+1/+3). Bismuth doped and heat treated both together improved the charge storage by more than 75% on the pure and non-heat treated BC films. A maximum charge storage of 343mC/cm² for the Heat treated 5% Bismuth doped Barium Cuprate was observed.

8) Bismuth doped Barium Cuprate powders based thin films also showed the Bismuth reactions (+1 to +3 and back) in the positive region vs Standard Calomel electrode. This provides charge storage on the positive side of 0V vs SCE.
9) Vibrational studies show heat treated Barium Cuprate and Bismuth doped Barium Cuprate shows signs of change in the Cu-O bond’s vibrational characteristics, indicating substitution and change in the oxidation state of Copper in the lattice.

10) Microstructural analysis of pellet and powders suggest that Barium Cuprate was successfully formed with no residual/parasitic phases at 10 hours sintering time. Bismuth doped barium Cuprate showed signs where unreacted Bismuth Oxide was found.

11) More densification of Bismuth doped pellets would also suggest Bismuth substitution in Barium Cuprate as Bismuth Oxide is fluxing agent and increased the densification rate.
5. Conclusions

1) Barium Cuprate has been established as a pseudo capacitive phase which gives reaction in negative range vs Standard Calomel Electrode. It produces transitions from Cu\(^{+1}\) to Cu\(^{+2}\) and the backward transition in the range of \((-0.3 \text{ – } -0.2 \text{ vs SCE})\) for the cathodic reaction and \((-0.60 \text{ - } -0.45 \text{ vs SCE})\) for the anodic reaction. This transition is different from the Cu \((+1/+2)\) transition which occurs in any Copper oxide system. This reaction is characterized as the redox reaction taking place in the lattice of Barium Cuprate.

2) Bismuth doping and heat treatment of Barium Cuprate leads to introduction of Cu\(^{+1}\) in the Barium Cuprate lattice. The electrochemical properties and electrical conductivity have been found to be enhanced by increasing the Cu\(^{+1}\) concentration. Bismuth doping also shows its effect in the form of its own redox reactions \((+1/+3)\) which lies in the range of \((0-0.45\text{ V vs SCE})\). Thus enhance the overall electrochemical behavior and charge storage. 5\% Bismuth doping in BC and subsequent heat treatment provide a 35\% increase in the charge storage.

3) As the last conclusion suggests the electrochemical properties of Barium Cuprate are heavily influenced by the oxidation of Copper in Barium Cuprate lattice. More so on the amount of Cu\(^{+}\) present in the lattice.

4) Solubility limit of Bismuth in Barium Cuprate is however not yet determined conclusively. Microstructural analysis showed trace of undiffused Bismuth oxide. This could also be attributed to the mixing limitations posed by ball milling when such low quantities of powders are involved.

5) Powders of Barium Cuprate and Bi doped Barium Cuprate have been successfully synthesized. Powders show similar structural characteristics as observed for the pellets with peak shifts in X-ray diffraction pattern. Using these powder thin films are fabricated with a very uniform distribution of the particles in the matrix of PEO and Graphite which yield significant charge...
storage. A very high charge storage of 343mC/cm$^2$ (~101F/g) was achieved with thin films which is high considering the long range of operation (1.15V).

6) Thin films show an increase of about 30%-70% in the charge storage upon the pellets. PEO and graphite are present in the capacity of facilitating charge transfer for Barium Cuprate rather than just providing double layer capacitance. Also PEO and graphite baseline electrodes exhibit their own reactions too. These reactions have been found to complementary to the overall system and is partly responsible for higher charge storage in films when compared to pellets.

7) As synthesized electrodes can function in much a larger voltage range of 1.15 V because of multiple reactions on either side of 0 V vs Standard Calomel Electrode. Such electrodes can be used symmetric electrodes in a supercapacitor due to symmetric charge storage on both side of 0 vs SCE. Finally, these electrodes present a very convenient way of synthesizing supercapacitor electrodes without use of any expensive organic chemicals.
6. Future work:
1. Optimization of time of sintering for synthesis Barium Cuprate powders is required. Since there is a difference between the electrochemical properties for different sintering times (10 hrs. and 2 hrs.). There could be a time in this interval of 8 hrs. (Between 2 hrs. and 10 hrs.) which can yield similar electrochemical properties. This would help significantly in reducing the cost of production of the powders.

2. Temperature of the synthesis of Barium Cuprate can reduced by co-precipitation of reactant powders (Barium Oxide and Copper Oxide). The extent of reduction of the sintering temperature has to be determined.

3. The solubility limit of Bismuth is still not clear as it could be due to the processing issues posed by the inadequate mixing of the reactant powders by ball milling. Co-precipitation of reactant would ensure a much thorough mixing and if more bismuth can substituted in the BC lattice. Also, if so the effect of more bismuth addition to the BC lattice on the electrochemical properties needs to be studied.

4. Copper’s oxidation state needs to be investigated in detail to get a confirmation of the presence of any Cu$^{+1}$ species present in the system. An X-ray photoelectron study would be ideal for such an investigation. Thus a correlation between electrochemical and these reduced ions must be also be studied.
7. References:


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