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Abstract approved:

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Electrical double layer capacitor (EDLC) is a major group of supercapacitors. The capacitance of EDLC comes from the pure electrostatic charge at the electrode interface. Therefore, the capacitance of EDLC depends on the surface area of the electrode materials accessible to the electrolyte ions. Porous (Activated) carbons are ideal materials to make electrodes not only because of its good electrical conductivity, high surface area, and chemical stability, but also because they can be derived from sustainable resources. Herein, this project first describes the general information of EDLCs including basic theory, history, components and materials. The second achievement of this project is to build "green" supercapacitors with porous carbon. In order to achieve the green approach of supercapacitors, the porous carbon is made from starch, a cheap and reproduceable carbonaceous material. By using hydrothermal carbonization (HTC) and KOH activation, the process of making porous carbon requires less carbon input and produces less toxic byproduct. The electrochemical properties of the electrodes made were characterized using cyclic voltammetry (CV). The various characterization schemes used revealed that the utilization of KOH during activation process yielded carbon sponge possessing large surface areas and with substantial capacitances over 150 F/g in 1.0 M Na₂SO₄ electrolyte. In all, this capstone not only achieves the intended goal of building a "green" supercapacitor with high capacitance, but also proposes a simplified path for activating carbon.

Starch Based Supercapacitors

by Fangqiong Yuan

A CAPSTONE REPORT

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I understand that my Capstone Report will become part of the permanent collection of the University of Pennsylvania Master of Chemical Sciences Program. My signature below authorizes release of my final report to any reader upon request.

Fangqiong Yuan, Author

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Introduction

Over the last several decades, the need for electric power sources and storage systems has increased rapidly due to the miniaturization and portability of electronic devices. The next step forward of this scenario is the advantage of the Internet of Things (IOT), which will further increase the demand of miniaturization and decentralized small and long lasting (high energy density) energy sources.¹ Such demand raises concerns regarding manufacture, usage and disposal of new components and devices. The public is worried not only about the economic aspects like raw material availability and energy costs, but also the carbon (and its oxides) generation and input during manufacture, disposal and safety during use.

Due to its high energy density, the most common power source nowadays is the battery. Unfortunately, its power density is low due to chemical kinetic. Supercapacitors, invented in the 50s, with low energy density, but excellent power density, were at the time mostly considered memory backup power for computer systems.² These EDL are physical devices.

Since the performance of supercapacitors depend on high surface area materials, the advantage of nanostructure materials has led to a renaissance of research on the subject after the turn of the 21st century.³

Capacitor and Parallel Plate Capacitor

A capacitor is an electronic component that can store energy in its electric field. It usually consists of two conductive plates separated closely by non-conductive material (such as a dielectric). The non-conductive area can be either vacuum or electrical insulator such as plastic, glass, ceramic, or air.⁴ When a DC voltage is applied across an uncharged capacitor, electrons will accumulate instantly on the plate connected to the negative terminal of power supply, and the same number of electrons will be removed from the other plate. The amount of positive charges and negative charges are the same on the two plates, and thus the capacitor remains neutral overall. Once the capacitor is fully charged and reaches its steady state, current can neither flow through the capacitor nor through the circuit due to the insulating material separating between the two plates.²

The ability of a capacitor to store electrical energy on the surface of its two plates is described as capacitance C, in unit of Farad (F). It is defined as:

$$C = \frac{Q}{V} \tag{1}$$

where Q is the amount of electrons that is stored in the capacitor at steady state (maximum number of charges), and V is the voltage applied across the plates.⁵ An ideal capacitor has no energy loss during charging and discharging, thus has a constant capacitance.

The parallel plate capacitor is the simplest model of capacitors (**Figure 1**). It consists of two parallel metal plates with area *A*, separated by a uniform dielectric material with thickness *d* and permittivity of the dielectric material ε .⁶ Then, the capacitance of such parallel plate capacitor can be defined as:

$$C = \frac{\varepsilon A}{d} \tag{2}$$

Equation 2 describes the relations between capacitance *C*, metal plates area *A*, dielectric thickness *d* and permittivity ε . Permittivity ε is a fundamental parameter of a material. It describes the ability of a material to store an electric field in an electric field in the polarization of the material. The unit of permittivity is farad per meter (F·m⁻¹). Based on the equation, capacitance *C* is proportional to ε and *A*, while inversely proportional to *d*. Therefore, the capacitance of a capacitor can be improved by reducing the separation between the plates, using high permittivity dielectric material, or enlarging plate surface area.



Figure 1. A parallel plate capacitor consists of two metal plates that has area *A*, and separated by gap of *d*. The separation can be vacuum or any other dielectric materials such as air, gases, ceramic or plastic.

Supercapacitors

A supercapacitor, also known as an electrochemical capacitor (EC), is a high-capacity capacitor that stores electrical charges at the interface of surface and electrolyte of high surface area electrodes. It was first developed, and patent granted to General Electric's H.I. Becker in 1957.⁶ EC was described as storing electrical energy by holding the charges in the interfacial of double layer at a porous carbon material. It was considered not practical by the industry because the device had to immerse in large amount of aqueous electrolyte. After Becker, Robert A. Rightmire, a chemist at the Standard Oil Company of Ohio (SOHIO), developed a double-layer capacitor using high surface area carbon in tetraalkylarnmonium salt electrolyte dissolved in non-aqueous solvent.⁶ SOHIO did not find applications for the capacitor at the time, but the design model of standard EC design is still being used today.⁷ The first commercially viable EC was sold by a Japanese company Nippon Electric Company (NEC) in 1975.⁶ The supercapacitor had working voltage of 5.5 V with capacitance up to 1 F. It was

used as battery substitutes and power backup for volatile CMOS computer memory.⁷ Nowadays, there are commercial products that have capacitance up to 9,000 F at 2.7 V, with the size that can be easily hold in one hand.⁷

Based on how the electrical energy is stored, supercapacitors can be categorized as electric double-layer capacitors (EDLCs) and pseudo-capacitors. A pseudo-capacitor stores energy by electron charge transfer between electrode and electrolyte.⁸ It achieves high capacitance by adding electrochemical pseudo-capacitance to the double-layer capacitance. The pseudo-capacitance comes from Faradaic electron charge-transfer with redox reactions, intercalation or electrosorption.⁶ In other words, there are chemical reactions at the electrode of pseudo-capacitor, and thus pseudo-capacitor stores electric energy chemically. Electric double-layer capacitors (EDLCs) on the other hand, store electric energy electrostatically.

Electric Double-Layer Capacitors (EDLCs)

An EDLC is one of the major groups of supercapacitors.⁹ Its capacitance comes from the pure electrostatic charge accumulation through the electrolyte and at the electrode interface.¹⁰ There is no chemical reaction in EDLCs. Therefore, the capacitance of EDLC is strongly depend on the surface area of the electrode materials that is accessible to the electrolyte ions.¹¹

The basic design of supercapacitors (**Figure 2**) consists of two electrodes separated by porous membrane. The two electrodes are ionically connected with each other by electrolyte.³ When voltage is applied to the electrodes, cations from electrolyte will form electric double layer at the electrode-electrolyte interface of the negative electrode. A charge-balancing layer of anions from electrolyte will be absorbed onto the positive electrode.⁶



Figure 2. Schematic presentation of an EDLC.

Components of EDLCs

Separator

The separator is usually ion-permeable membrane that can prevent short circuit by separating the two electrodes physically.⁶ In order to improve the conductivity of ions and minimize the equivalent series resistance (ESR), the separator is usually made of very thin and porous material. Also, the separator must be chemically and electrochemically inert so that it doesn't react with the electrolyte. Typical separator materials can be polymer films, paper, or glass fiber.¹²

Electrolyte

The electrolyte usually consists of solvent and solute that can dissociate into cations and anions when voltage is applied, and thus makes the electrolyte electrically conductive. The higher concentration of the electrolyte, the higher is the charge carrier concentration (ions), which means better conductivity, smaller ESR, and higher capacitance.⁶ In most cases, electrolytes are aqueous, but depending on different applications of the capacitors, the electrolyte can be solid, or organic.¹²

An aqueous electrolyte is mostly water based since water is a good solvent for inorganic salts. The number of ions in can provide increases as the concentration of electrolyte increases, which leads to higher conductivity. Typical aqueous electrolytes for EDLCs include inorganic salts such as Na₂SO₄, KNO₃, NaCl; or acids such as H₂SO₄.¹³ Under standard pressure, the boiling point of water is 100 °C. Furthermore, water dissociation into oxygen and hydrogen occurs when a potential difference of 1.2 V is applied. In order to avoid this reaction, aqueous electrolyte is mostly used in low voltage, low temperature environment but high specific power applications. Organic electrolytes are made of salts dissolving in organic solvents such as propylene carbonate, tetrahydrofuran, or urea.¹⁴ They have higher dissociation voltage and higher boiling point than water based electrolytes, but these are more expensive than aqueous electrolyte and some are toxic and or flammable.

In order to maintain the long-term stability of the EDLCs, electrolytes must be chemically stable and not react with any of the materials in capacitors. Both aqueous electrolytes and organic electrolytes have their own advantages and disadvantages. Therefore, electrolytes should be carefully chosen based on the desired performance and other requirements.

Electrode

The EDLC electrodes are made of a metal current collector covered by a thin coating. The current collector is usually made of metal with high conductivity such as stainless steel, platinum, or aluminum foil.¹³ In order to maintain the stability of the capacitor, both the coating and metal plate should be good

conductors, long-term chemically inert and high corrosion resistance.¹⁵ In **Equation 2**, the capacitance *C* is proportional to the surface area *A* of electrodes. Therefore, the materials with highest surface area are used to build EDLC electrodes, so that the number of electrolyte ions forming a double layer can be maximized.¹⁶ As the most common high surface area material, activated carbon was the first and most commonly used material to make EDLC electrodes.⁷ Other high surface area material commonly used to build electrodes include activated carbon fibers, graphene, carbide-derived carbon, carbon aerogel, and carbon nanotubes.¹⁷

Energy storage in the form of charge storage is commonly done by using electrochemical devices such as a battery. Pseudo-capacitors (redox supercapacitors) use this very technique, but the supercapacitor under discussion here, of the EDL type, is purely physical. The chemical reactions are kept to a minimum by using the electrical double layer as the energy storage mechanism.

All supercapacitors, such as the EDL supercapacitor, usually possess a high-power density. That is, they can be charged and discharged fast, as the process does not include chemical reactions which are limited by chemical kinetics. Fast charge and discharge process implies large current densities which also implies low output resistance. The resistivity of hydrothermally growth carbon electrodes from polysaccharides precursors usually show values around 1 Ω ·cm.

Carbon Material

Porous carbons are very good materials to make supercapacitors electrodes because of its good electrical conductivity, high surface area, porosity, and chemical stability. They usually made from carbonaceous materials such as wood, coal, fruit stones, and fruit shells.¹⁸ The carbonaceous material is first transformed into char, followed by further heat treatment and activation of the char. The process that transforming raw material into char is called carbonization. During the carboniasation, most of non-carbon species, oxygen, hydrogen and nitrogen are removed from the raw material.

Hydrothermal carbonization (HTC) is one of the common methods used to transform saccharides and polysaccharides into carbon. It is a low temperature/high pressure method that can transform organic materials into carbon with a considerable high yield.¹⁹ The carbonization reaction exothermic characteristic reduces the energy consumption during the process and increases its capability of adsorption. To further improve the surface area of carbon product, carbonization of carbonaceous precursors followed by physical or chemical activation is necessary. Usually the carbon activation processes are either chemical or physicochemical and all of them involve high temperature from 700 °o. to 1100 °rc thermal treatments.²⁰ The physical process involves the use of oxidizing gases (O₂, CO₂)/vapor assisted thermal treatment. It is the reaction between carbon atom and the gas that gives significant increase to the pore development.²¹ Such process uses gases such as O₂ and CO₂ activation agent, which does not produce toxic gases or by product. Therefore, physical activation takes

long time and involves high temperature treatment. And thus, it takes large amount of energy input to generate porous carbon using simple physical activation. To reduce energy input, chemical agent is added.

Generally, chemical activation is a single step process that involves using alkali metal hydroxides, alkali metal carbonates, transition metal salts or acids to attack the carbon material and followed by thermal treatments at lower temperatures than those needed for physical process.^{21–23} The product of chemical activation has been shown to perform quite well as an inexpensive molecular filter in the liquor and tobacco industry, to remove undesirable molecules (nicotine) or pigment molecules. The molecular filtering capability of activated carbon is due to its high specific surface are often in excess of 3000 m²/g. The electrical conductivity of these carbonaceous materials are typically not particularly high, but can be enhanced by pressure or doping to useful values as supercapacitor electrodes.

In particular, the chemical activation process using potassium hydroxide (KOH) is a very promising method since it can produce carbon spheres with high surface areas up to 4000 m²/g.²⁴ In order to explain the mechanism for KOH activation process. A sequence of reactions were proposed by Yupeng and his coworkers.²⁵ In general, the chemical reaction during activation can be written as:

 $4 \text{ KOH} + \text{C} \rightarrow \text{K}_2\text{CO}_3 + \text{K}_2\text{O} + 2 \text{ H}_2 \tag{3}$

$$2 \text{ KOH} \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} \tag{4}$$

$$C + H_2O \text{ (steam)} \rightarrow H_2 + CO$$
 (5)

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{6}$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \tag{7}$$

$$K_2O + H_2 \rightarrow 2 K + H_2O$$
 (8)

$$K_2O + C \rightarrow 2 K + CO \tag{9}$$

$$K_2CO_3 + 2 C \rightarrow 2 K + 3CO$$
 (10)

For now, there is no previous research that has experimentally determined exactly what happened during the activation process. The reactions listed above (from **Equation 3** to **Equation 10**) were constructed to explain how KOH improved the surface area of carbon. The steam generated from decomposition of KOH transforms amorphous carbon into CO in **Equation 5** which leads to formation of pores. Carbon is also consumed by K and K⁺ (**Equation 9** and **Equation 10**). **Equations 5**, **9** and **10** are crucial because all the carbon consumption in those reactions contributes to the generation of significant amount of porous structure in the carbon. And thus, improve the surface area of carbon material. Other reactions (**Equations 3**, **4**, **6**, **7**, and **8**) will not be further discussed since they do not

contribute to development of pores. Some researchers have carried out experiments to study the effects of KOH/Carbon weight ratio.^{24,25} They mixed carbon and KOH with a KOH/C weight ratio ranging from 5 to 12. It was observed that the specific surface area increased with the increase of the KOH/C mass ratio and reached maximum when the mass ratio was 8. The specific surface area decreased slightly when the ratio was larger than 8.²⁵ Yupeng and his coworkers concluded that in the high KOH/C regime, excessive KOH consumed carbon, which led to excess activation and porous structure destruction, and decrease on the specific surface area of active carbon material.²⁵ Previous work demonstrated the synthesized carbon spheres using hydrothermal carbonization of rice husk²⁵, wood-derived saccharides²⁶,Miscanthus²⁷, glucose, and sucrose²⁸. Cristelle and his co-worker reported a high capacitance values of 180 F/g in organic electrolytes after chemical activation of carbide-derived carbons.²⁹



Figure 3. Experimental design of carbon activation.

This capstone project focuses on building supercapacitors with porous carbon synthesized using materials that are cheap, renewable, and abundant. The goal of this project is to build "green" supercapacitors, a technique that requires less carbon input, and produces less toxic byproduct is necessary. Starch is readily available carbonaceous material for the preparation of activated carbon as it is cheap, and easily extracts from plants. Thus, starch can easily be perfect material to produce activated carbon. The primary objective of the present work is to build supercapacitors that has specific capacitance of 100 F/g in inorganic salt electrolytes using starch as carbon source.

The experimental design (**Figure 3**) of this work consists of hydrothermal carbonization (HTC) of starch, annealing of carbon product, and KOH activation of carbon. As the first step of experimental design, HTC will be used to transform saccharides and polysaccharides into carbon. It is a low temperature/high pressure method that can transform organic materials into carbon with a considerable high yield.¹⁹ The carbonization reaction exothermic characteristic reduces the energy consumption during the process and increases its capability of adsorption. Different combinations of starch and acid will be used to improve the yield of HTC product. DI water and starch will also be used as material of HTC as reference. The next step is annealing. The aim of annealing process before the chemical

carbon activation is to solubilize and remove most of the eventually soluble tars leaving an almost pure carbon backbone, which not only improve surface area, but also present a great deal of active radicals at the surface.³⁰ Besides increasing carbon content, annealing can also reduce the diameter of carbon spheres, or obtain nitrogen-doped carbon spheres.^{28,31} Finally, the annealed carbon product will be further activated using KOH. The KOH chemical activation process will destroy carbon spheres and generate pores on the surface of carbon, which will significantly improve the surface area of carbon. The activated carbon will then be used to fabricate supercapacitor electrodes, and the electrochemical properties will be characterized using scanning electron microscope (SEM), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), and cyclic voltammetry (CV).

Materials and Methods

The general information of chemicals and equipment used are included in **Appendix 1**.

Preparation of Activated Carbon

The activated carbon was prepared using two major steps: 1) hydrothermal carbonization of starch, 2) annealing, and 3) chemical activation of carbon. After synthesizing, the carbon was made into electrodes and was measured using cyclic voltammetry method. The details of each steps are discussed in this section.



Figure 4. General procedure for hydrothermal carbonization (HTC), and carbon activation.

| Sample Number | Reaction Conditions | | | |
|------------------|--|--|--|--|
| 1 | Sucrose + DI H ₂ O 4h | | | |
| 2 | Sucrose + DI H ₂ O 6h | | | |
| 3 | Starch + DI H ₂ O 4h | | | |
| 4 | Starch + DI H ₂ O 6h | | | |
| 5 | Starch + H_2SO_4 4h | | | |
| 6 | Starch + H_2SO_4 6h | | | |
| 7 | Starch + H ₃ PO ₄ 4h | | | |
| 8 | Starch + CH ₃ COOH 4h | | | |
| 9 | Starch + CH ₃ COOH 6h | | | |

Step 1. Hydrothermal Carbonization of Starch

Table 1. Preparation conditions of carbonization using the HTC process.

The hydrothermal carbonization process started with making uniform 0.8 M starch paste. To make such mixture, 13.7 g of starch and 50.0 mL of DI water was mixed. The mixture was heated up and stirred in order to completely dissolve starch in water and form a uniform paste. The paste was then transferred into a stainless-steel autoclave, heated at 200 °C for 4 hours in an Iso-Thermal Oven (Model 655G, Fisher Scientific) and cooled to room temperature.²⁸ The product collected was then washed with ethanol, and soaked in ethanol overnight to remove all possible residues. The product was collected using vacuum filtration and dried at 110 °C for 2 hours. For comparison, 1 M of acid solution (sulfuric acid, phosphoric acid, and acetic acid) was used to make 0.8 M starch mixture instead of distilled water to produce varying results. **Table 1** contains the sample number and reaction conditions of acid and starch combination.

Step 2. Annealing

The HTC carbon product collected in **Step 1** was divided into three portions. One of the three portions was thermally annealed (**S1**) at 800 °C with a heating rate of 20 °C·min⁻¹ and 2.5 hours activation time under constant flow of nitrogen gas in a tube furnace. A second portion of the black precipitate was annealed (**S2**) at 1000 °C for 2.5 hours under the same condition. The third portion was kept as is and characterized via thermal gravimetric analysis (TGA) (SDT Q600, TA Instruments) to measure mass loss of the samples over time from room temperature to 1000 °C. After annealing **S1** and **S2**, product was washed and soaked in iso-propanol to remove any possible residue. Three samples were made from each group of annealed carbon product. Each sample was then used to build the working electrode of an electrochemical cell for cyclic voltammetry (CV) experiments. CV was used to evaluate the performance of the different samples. Details of CV setup used will be elaborated later in **Electrochemical Setup section**. Detailed assignment of sample number was listed in **Table 2**. **Table 3** contains the amount of product collected and yields were calculated for further analysis.

| Sample Number | Reaction Conditions | Sample Number | Reaction Conditions |
|------------------|---|------------------|--|
| 4.0 | Starch + DI H ₂ O 6h 800 °C | 4B | Starch + DI H ₂ O 6h 1000 °C |
| 44 | annealing | 4D | annealing |
| 5.4 | Starch + H ₂ SO ₄ 4h 800 °C | 5 B | Starch + H ₂ SO ₄ 4h 1000 °C |
| JA | annealing | JD | annealing |
| C A | Starch + H ₂ SO ₄ 6h 800 °C | 6 B | Starch + H ₂ SO ₄ 6h 1000 °C |
| 0A | annealing | 00 | annealing |
| 7.0 | Starch + H ₃ PO ₄ 4h 800 °C | 7B | Starch + H ₃ PO ₄ 4h 1000 °C |
| | annealing | 7.0 | annealing |
| 84 | Starch + CH ₃ COOH 4h 800 | <u>9</u> D | Starch + CH ₃ COOH 4h 1000 |
| 8A | °C annealing | оD | °C annealing |
| 0.4 | Starch + CH ₃ COOH 6h 800 | 08 | Starch + CH ₃ COOH 6h 1000 |
| JА | °C annealing | 3D | °C annealing |

| Table 2. | Preparation | conditions | of annealing | step. |
|----------|-------------|-------------|--------------|-------|
| TUDIC L. | ricpuration | 00110110110 | or armouning | otop. |

Step 3. Carbon Activation

The carbon product collected from carbonization of starch (**Step 1**), and KOH pellets were mixed in mass ratios of 1:1, 2:1, 4:1, 6:1, and 8:1 (KOH: Carbon). Distilled water was added to the solid mix, and then the carbon was left impregnated in the KOH solution for 2 hous.²⁴ The mixture was then dried at 110 °C until the weight was constant. The activation process was carried out in constant nitrogen flow (rate of 1 L·min⁻¹) in a tube furnace at 800 °C for 1 hour with a heating rate of 20 °C·min⁻¹, and then cooled to room temperature in the furnace. After KOH activation, the carbon was collected and washed with 1 M HCl until the pH value was lower than 7 to remove alkali residue, followed by washing with warm distilled water to remove the salt residue. The final products of activated carbon (AC) were collected with vacuum filtration and dried in the oven at 110 °C for 2 hours. Three samples were made from each group of activated carbon product. Each sample was then used to build the working electrode of an electrochemical cell for CV experiments.

Material Characterizations

Images of surface of the activated carbon were taken using Scanning Electron Microscope (JSM-6360LV, JEOL USA). All samples were sputter coated with gold, and the system was operated under accelerating voltages above 7 kV

to avoid surface charging during the measurements. Images were taken with 1000x magnification. Thermal gravimetric analysis (TGA) was used to determine the weight loss of HTC carbon product over time as temperature increased. For each sample, the temperature was ramped from room temperature to 1000 °C under N₂ gas flow. The structural characterization was done using X-ray diffraction (XRD). XRD was performed using X-ray diffractometer with Cu Kα radiation (40 kV, 20 mA). Each sample was scanned with a scan range of 3-30 degree with a scan rate of 1 degree per minute.



Figure 5. Schematic of sample holder assembly for activated carbon-based electrode. (a) Top view of the cover of the sample holder. (b) Top view of the bottom of the sample holder with sample loaded. (c) Side view of the sample holder with sample loaded. (Design done by Prof. Cyro Ketzer Saul, Visiting Scholar of University of Pennsylvania, ESE Department)

Electrode Assembly

The activated carbon (AC) collected was grinded into fine powder and mixed with agar in mass rations of 1:16 (agar: AC). Distilled water was added to the mixture and heated to form a thick paste. The thick paste was then painted using microspatulas on filter paper as thin as possible. The filter paper should be fully covered by the carbon paste. To hold the particles together, the filter paper was covered with punched holes using laser machining equipment (PLS6.75, Universal Laser System). The filter paper covered with AC was then dried and cut into 12 × 12 mm samples. The fabricated sample was placed in a sample holder and characterized electrochemically with CV. The design of sample holder is shown in Figure 5. The sample holder was made of acrylic using the same machining IR laser (PLS6.75, Universal Laser System). Stainless steel was used as current collector (marked green in Figure 5). The 12 × 12 mm sample was placed at one side of the current collector (marked red in Figure 5). To apply pressure and improve contact between the carbon surface and the current collector, three screws were used to assemble the two parts of the holder. To further apply the pressure evenly over the sample, a 12×12 mm grid was made

with laser in the top part of the holder. The grid was placed right above where the sample was placed.

Electrochemical Setup

The performance and characteristics of constructed carbon electrodes were measured using CV after assembly. A schematic representation of electrochemical cell is illustrated in **Figure 6**. A stainless steel plate was used as counter electrode, a silver/silver chloride (Ag/AgCI) electrode was used as reference electrode, and 1 M Na₂SO₄ was used as electrolyte. The three electrodes were connected to the potentiostat. Once the electrochemical cell was assembled, the experimental parameters were selected through the control program made using National Instrument's LabView 2018 (developed by Prof. Cyro Ketzer Saul, Visiting Scholar of University of Pennsylvania, ESE Department). Detail of the program is attached in **Appendix 3**.



was used as reference electrode, and 1 M Na₂SO₄ was used as electrolyte.

Electrochemical measurements

A LabView program developed by Prof. Cyro Ketzer Saul was used to control the potentiostat. Detail and coding of the program is included in **Appendix 3**. The control panel of the program was presented in **Appendix 4**. To avoid

Faradaic effects at low voltages and water splitting at high voltages, the voltage range was set from -0.3 V to 0.3 V with scan rate of 0.01 V/s, 0.02 V/s, and 0.005 V/s. Every measurement had two cycles. Measurements were done in triplicate and the largest specific capacitance was used for data analysis. To obtain the specific capacitance, the samples were dried in a hot plate until its weight m_1 remained constant before loading to the sample holder. After measuring the capacitance, electrodes were washed with distilled water to remove all the activated carbon, dry on the hot plate, and weighed the mass m_2 of filter paper. The specific capacitance of samples was calculated by equation:

$$C_{\rm se} = \frac{C}{m} \tag{11}$$

where *C* is the capacitance recovered from the simulation program.

CV curve fitting

The CV curve fitting was developed using Excel Visual Basic for Application (VBA), so that the experimental data was able to fit with a CV curve of a simple equivalent electric circuit of EDLC shown in **Figure 7**. In **Figure 7**, V_s is the external source voltage, *C* is the capacitor, R_s is the series resistor, and R_p is the parallel resistor. V_c is the capacitor voltage, *i* is the current that flows to the circuit, i_p is the capacitor that flows through the parallel resistor and i_c is the current that goes to the capacitor.



Figure 7. Schematic diagram of circuit used to simulate/fit the EDLC behavior.

In **Equation 12**, the source voltage change was considered at a constant rate of φ , which corresponds to the scan rate in V/s and it was positive during charge and negative during discharge. The current *i* that flowed in the system could be described by the following differential equation.

$$\frac{di}{dt} = \left[\frac{\varphi}{R_s} + \frac{V}{C \cdot R_s \cdot R_p} - \frac{1}{C} \left(\frac{R_s + R_p}{R_s \cdot R_p}\right) i\right]$$
(12)

In an iterative calculation, the current *i* after a small interval of time *dt* was given by

$$i_{t+dt} = i_t + di \tag{3}$$

where di was given by

$$di = \left[\frac{\varphi}{R_s} + \frac{V_t}{C \cdot R_s \cdot R_p} - \frac{1}{C} \left(\frac{R_s + R_p}{R_s \cdot R_p}\right) i_t\right] dt$$
(4)

This approximation converged for time steps (dt) smaller than the characteristic circuit time constants.

For the data fitting, the experimental results obtained during the second CV cycle were compared with the second cycle theoretical CV model results. The differences were squared, added and then square rooted to generate an Error parameter. The VBA program scanned each fitting parameter (C, R_s , R_ρ , C_0) changing it and measuring the Error parameter, if the Error was reduced the process was repeated until the Error increases again stopping the process. The C_0 parameter created a slight displacement of the CV curve up or down (positive or negative). Its value was usually small (few percent) compared to the C parameter. Since its value could be positive or negative there was no known physical meaning to it.



Figure 8. Screenshot of Excel stimulation program dashboard (developed by Prof. Cyro Ketzer Saul, Visiting Scholar of University of Pennsylvania, ESE Department). Detail and coding of the program attached in **Appendix 3**.

All parameters were set to be initially increased of a preset value, if the Error is not reduced the parameter was then decreased from the same preset value and the process restarts. After all parameters are tested the program stops, allowing the change of the preset value for each parameter. The preset value was a percentile of the parameter value. For example: If the Capacitance parameter is 0.23 F and the preset change is set to 1%, it means that at each program iteration the increase or decrease in the Capacitance will be of 0.0023 F.

For each program iteration the whole CV curve was calculated and compared with the experimental data, generating a new Error parameter. For every CV measurement, only scan rate of 0.01 V/s data sets were used to perform the simulations.

Results and Discussion

Yields of Hydrothermal Carbonization (HTC)

Different combinations of acids and saccharides were used to figure out whether the acids added have effect on the yield of carbonization. **Table 3** summarizes the yields of the different samples prepared by HTC using different acids. Sucrose is a monosaccharide, which means non-carbon elements such as hydrogen and oxygen can be removed from sucrose molecule directly by inputting energy and break the chemical bonds. Starch is polysaccharide. Before breaking the chemical bonds inside the molecule, more energy is required to break the alpha-linkages between glucopyranose units first. It is the reason why **Sample 2** and **Sample 4** were hydrothermal treated for the same amount of time, but **Sample 2** had a higher yield. They have the same amount of energy input, but **Sample 2** was starch, it required more energy to fully transformed into carbon. For the same reason, **Sample 3** did not fully transform into carbon. Using acidic aqueous solutions instead of pure DI water to dissolve starch, helped breaking chemical bonds, and thus reduce the hydrothermal treatment time and save energy.

Samples 5 and **6**, were produced using starch as a starting material in sulfuric acid. These reaction conditions resulted in relatively low yield compared to when other acids were used (**Samples 7, 8, and 9**). It is hypothesized that sulfuric acid is responsible for low yield of **Samples 5** and **6**. The carbon elemental composition of starch is $44.44\%^{30}$, which means that the maximum amount of carbon can be recovered from 13.69 g of starch is 6.09 g. For starch in 1 M sulfuric acid, H₂SO₄ oxidizes carbon at high temperature. In this case the reaction is

$$C + 2 H_2 SO_4 \rightarrow CO_2 + 2 SO_2 + H_2 O$$
 (15)

The amount of carbon consumed by sulfuric acid in **Equation 15** can be calculated using

$$\Delta m = 12.0 \frac{g}{mol} \times \frac{1 M \times 50 mL}{2 \times 1000 mL/L} = 0.3 g$$
(16)

Since 0.3 g of carbon is consumed by sulfuric acid (**Equation 16**), the calculated product for **Samples 5** and **6** should be 0.3 g less than for other starch-acid combination. Phosphoric acid is weak acid which is not able to oxidize carbon. As a result, the theoretical amount of crude product for starch in phosphoric acid should be the same as starch in distilled water.

Samples 8 and **9** had the highest yields among all groups. It is due to the carbon elemental composition of acetic acid (CH₃COOH), since it has 3 carbon atoms per molecule. During carbonization, the hydrogen and oxygen are removed from acetic acid molecule. The amount of carbon can be recovered from carbonizing acetic acid in theory can be calculated using

$$\Delta m = 3.0073 \, g \times \frac{24}{60.052} = 1.2 \, g \tag{17}$$

From **Equation 17**, the theoretical yield for starch in acetic acid should be 7.29 g. It is the highest theoretical yield among all groups, which agrees with the experimental data collected. In order to recover as much carbon product as possible during HTC, starch and acetic acid seems to be the best combination. However, the effect of different carbon products on the results of carbon activation remains unknown and will be discussed in the followed sections.

| Sample | crude | | | | Grude Group A | | | | Group B | | |
|--------|--------------|-------------|----------------------|------------------------------|------------------|-----------|--------|-------------------------------|-----------|--------|--|
| Number | | | | | 800 °C Annealing | | | 1000 [°] C Annealing | | | |
| | Material (g) | Product (g) | Yield ^[a] | Calculated Product (g) | Before (g) | After (g) | Yield | Before (g) | After (g) | Yield | |
| 1 | 13.6965 | 4.7194 | 34.46% | 6.0867 | | | | | | | |
| 2 | 13.6948 | 5.4954 | 40.13% | 6.0860 | | | | | | | |
| 3 | N/A | | | | | | | | | | |
| 4 | 13.6915 | 5.3196 | 38.85% | 6.0845 | 1.7512 | 0.8263 | 47.18% | 1.7991 | 0.8582 | 47.70% | |
| 5 | 13.6960 | 3.0360 | 22.17% | 5.7865 | 1.0308 | 0.5038 | 48.87% | 1.0443 | 0.5086 | 48.70% | |
| 6 | 13.6958 | 3.0757 | 22.46% | 5.7864 | 1.0529 | 0.5187 | 49.26% | 1.0640 | 0.5325 | 50.05% | |
| 7 | 13.6964 | 4.0300 | 29.42% | 6.0867 | 1.3890 | 0.6948 | 50.02% | 1.3744 | 0.6860 | 49.91% | |
| 8 | 13.6933 | 4.1850 | 30.56% | 7.2886 | 1.4329 | 0.7229 | 50.45% | 1.4264 | 0.6883 | 48.25% | |
| 9 | 13.6937 | 5.5410 | 40.46% | 7.2886 | 1.8997 | 0.9829 | 51.74% | 1.8598 | 0.9466 | 50.90% | |

Table 3. Preparation conditions and yields of carbonization and annealing procedure.

^aYield is defined as: $\frac{Crude \ produt \ recoverd \ (g)}{Weight \ of \ starch \ used \ (g)} \times 100\%.$

Annealing

The yields of annealing are summarized in **Table 2**. For the convenience of referencing, carbon product annealed at 800 °C for 2.5 hours was labeled as **Group A**, and carbon product annealed at 1000 °C for 2.5 hours was labeled as **Group B**. Detailed assignment of sample number was listed in **Table 3**. All samples had about 50% mass reduction after annealing. During annealing, **Samples 4**, **6**, and **9** had close to 1% yield higher than **Samples 5**, **7**, and **8**. Although 1% is not significant different, it still indicates that more starch was fully transformed into carbon with longer time period of hydrothermal treatment applied.

TGA curve provide information on chemical composition and thermal stability of materials. It is usually displayed from left to right and a decreasing curve indicates sample weight loss. The TGA curves of **Samples 5** and **6** in **Figure 9** almost overlap with each other. The TGA curves of **Samples 3** and **6** in **Figure 10** also overlap with each other. The similarity of all curves indicates that the composition of different samples was similar, mostly carbon, water, and saccharide residue. The Δ Weight vs. Temperature curves of all samples were flat from 800 °C to 1000 °C, which means the mass of HTC carbon product over time remained constant as temperature increased from 800 °C to 1000 °C. The first major weight loss in both figures was at 70 °C, due to water evaporation. The second shift was the remaining organic compounds decomposition at around 450 °C. In Figure 9, The starch in 1 M H₂SO₄ curves show small amount of weight loss at 110 °C, which was caused by H₂SO₄ dehydration³². The carbon yield obtained after temperature reaches 1000 °C was approximately 50%, which consists with the 50% yield from the annealing process.



Figure 9. Thermal gravimetric analysis (TGA) curves of Samples 5 and 6.



The capacitance is proportional to the surface area of CS (**Equation 2**). In the case of spheres, the surface area of spheres is inversely proportional to the diameter of spheres. Therefore, small spheres indicate large specific capacitance. In order to achieve large capacitance, small CSs in size are expected. The SEM images (**Figure 11**) of different samples consist of large number of grey spheres in scale of micrometer. Each sphere represents one carbon sphere. **Figure 11c** has relatively larger diameter than **Figure 11a** and **Figure 11b**, which indicates smaller specific capacitance.



Figure 11. SEM images of carbon spheres annealed at 800 °C for 2.5 hours. Images were taken with 1000× magnification. System was operated under 5 kV of accelerating voltage. (a) SEM image of Sample 4A; (b) SEM image of Sample 6A; (c) SEM image of Sample 7A.

The annealed product was mixed with agar in mass ratio of 1:16 (agar:carbon), made into EDLC electrodes, and measured with CV. Comparison of ability for charge accumulation of the annealed carbon at scan rate of 0.01 V/s is presented in **Figure 12**. The voltammetry curve of an ideal supercapacitor

should be rectangular. In practice, the CV curves of supercapacitors have round corners due to energy loss in charging and discharging and tilts at high voltage due to potential chemical reactions. Although the voltammetry curves in **Figure 12** are not perfect rectangle, they still indicate that EDLC electrodes are successfully built using the annealed carbon.



Figure 12. Voltammetry characteristics of a capacitor electrode built from annealed carbon spheres at scan rate of 0.01 V/s. Electrolyte: Na₂SO₄. (a) CV plot of Sample 8A; (b) CV plot of Sample 8B; (c) CV plot of Sample 9A; (d) CV plot of Sample 9B; (e) CV plot of Sample 5B; (f) CV plot of Sample 7B.

| | 800 [°] C Annealing (F/g) | 1000 [°] C Annealing (F/g) |
|--|---------------------------------------|--|
| Starch + DI H ₂ O 6h | 0.061 | |
| Starch + H ₂ SO ₄ 4h | 0.121 | 0.074 |
| Starch + H ₂ SO ₄ 6h | | 0.162 |
| Starch + H ₃ PO ₄ 4h | | 0.164 |
| Starch + CH ₃ COOH 4h | 0.150 | 0.179 |
| Starch + CH ₃ COOH 6h | 0.110 | 0.172 |

Table 4. Specific capacitance of the carbon products made under different conditions at scan rate of 0.01 V/s, potential from -0.3 V to 0.3 V.

The specific capacitance of the carbon products made under different conditions are summarized in **Table 4**. In most cases, samples with 1000 °C annealing have larger specific capacitance than those with 800 °C annealing. The samples exhibit specific capacitance ranging from 0.06 F/g to 0.18 F/g, which is significantly smaller than the 100 F/g, goal of this project. Previous research reports that carbon annealing at high temperature under N₂ gas flow can increase the carbon content (higher yield), eliminate functional groups that greatly influence the conductivity , make the shape of carbon spheres (CS) more uniform, and reduce the their diameter.²⁸ In theory, the annealing process should increase the surface area of carbon. And thus, specific capacitance should be increased. However, the specific capacitance values illustrated in **Table 4** are so small that the increase in surface area is neglectable.

Effects of the KOH/Carbon weight ratio

A previous study established that the high specific surface area of activated carbon was made from graphitizable carbon using KOH as chemical activation agent.³³ Some researchers further reported that specific surface area of activated carbon increased with the increase in the ratio of KOH/C from 3 to 9.²⁴ Therefore, KOH was chosen to use as activation agent. The KOH/carbon weight ratio was chosen as 1:1, 2:1, 4:1, 6:1, and 8:1. Since larger surface area means more electrons can be stored in capacitors, it is safe to expect significant improvement on the capacitance.

The SEM image in **Figure 13a** is the HTC sample. The image was not well focused. The spheres started charging and deforming the image. The charging indicated that the conductivity of the spheres was so bad that most electrons injected by the beam cannot readily flow to ground. With the KOH treatment (**Figure 13b**), the conductivity of carbon spheres increased so that the image is well focused. As the mass ratio of KOH incresed (**Figure 13c**), the spheres disaapeared and perforate sponge forms. This was reflected in the XRD diffractograms (**Figure 14**) of carbon and activated carbon. The broad carbon diffraction peak around $\theta/2\theta = 23^{\circ}$ and $\theta/2\theta = 26^{\circ}$ can be attributed to amorphous carbon structures, which means there was a small correlation between crystalline

carbon planes. The peaks disappeared completely after the KOH treatment, suggesting that the amorphous structures were destroyed. The material turned into completely uncorrelated material, in this case, a carbon sponge.



Figure 13. SEM images of Starch in CH₃COOH carbon before and after activating with KOH. (a) HTC product of starch in CH₃COOH; (b) After 1: 1 KOH activation; (c) After 4:1 KOH activation.

The voltammetry curve of an ideal supercapacitor should be rectangular. The current flow is reversed immediately upon reversing the potential, with a current independent of the electrode potential. In practice, the CV curves of supercapacitors have round corners due to energy loss in charging and discharging. The capacitive performance of the activated carbon was evaluated in electrochemical cells using 1 mol/L Na₂SO₄ electrolyte solution and scan rate of 0.01 V/s. Measurements were done in triplicate. The CV plots of samples that exhibited the largest capacitance in Sample 5, 7, and 9 were illustrated in Figures 15, 16, and 17. All figures show the typical capacitor profiles. They are parallelogram due to the resistive losses. When KOH/C ratio was smaller than 4, the curve shapes of all samples turned closer to rectangle, and larger area of the curves was obtained. These results indicates that as the KOH/C mass ratio increased, the capacitance of the active carbon electrodes increased, as well as charging and discharging speed. For Sample 5 and Sample 7, specific capacitance reached its maximum at KOH/C ratio was 4. After KOH activation, the capacitance considerably increased comparing with the annealed carbon samples. Large specific capacitance indicated large surface area. These results are also consistent with the SEM images (Figure 13) and XRD diffractograms (Figure 14). The carbon spheres were destroyed, and carbon sponge formed, and thus significantly improved the surface area of carbon.



Figure 14. XRD diffractograms of carbon before and after activating with KOH. (a) Complete XRD diffractogram; (b) Partial enlarge of XRD diffractogram from 0° to 30°.



 Figure 15. Voltammograms of activated carbon electrodes in 1 M Na₂SO₄ electrolyte. Carbon made from Sample 5. (a) KOH/C mass ratio 1:1, calculated specific capacitance 50.9 F/g; (b) KOH/C mass ratio 2:1, calculated specific capacitance 114.6 F/g; (c) KOH/C mass ratio 4:1, calculated specific capacitance 154.7 F/g; (d) KOH/C mass ratio 6:1, calculated specific capacitance 137.64 F/g; (e) KOH/C mass ratio 8:1, calculated specific capacitance 137.45 F/g.



Figure 16. Voltammograms of activated carbon electrodes in 1 M Na₂SO₄ electrolyte. Carbon made from Sample 7. (a) KOH/C mass ratio 1:1, calculated specific capacitance 34.28 F/g; (b) KOH/C mass ratio 2:1, calculated specific capacitance 58.68 F/g; (c) KOH/C mass ratio 4:1, calculated specific capacitance 146.43 F/g; (c) KOH/C mass ratio 6:1, calculated specific capacitance 139.02 F/g; (e) KOH/C mass ratio 8:1, calculated specific capacitance 126.30 F/g.



Figure 17. Voltammograms of activated carbon electrodes in 1 M Na₂SO₄ electrolyte. Carbon made from Sample 9. (a) KOH/C mass ratio 1:1, , calculated specific capacitance 44.38 F/g; (b) KOH/C mass ratio 2:1, calculated specific capacitance 83.82 F/g; (c) KOH/C mass ratio 4:1, calculated specific capacitance 130.82 F/g; (d) KOH/C mass ratio 6:1, calculated specific capacitance 137.55 F/g; (e) KOH/C mass ratio 8:1, calculated specific capacitance 174.29 F/g.



Figure 18. Specific capacitance (F/g) of samples activated in different KOH/C weight ratio (largest specific capacitance of three measurements).

Specific capacitance of all samples was summarized and plotted in **Figure 18**. Measurements were done in triplicate and the largest specific capacitance was used in the plot. **Figure 18** shows that when the ratio of KOH/C was smaller than 4, the specific capacitance of all samples increased with the increase of KOH/C ratio. When the KOH/C ratio is 4, the specific capacitance of **Sample 5** and **Sample 7** reached their maximum. When the KOH/C is larger than 4, the specific capacitance of **Sample 8** increased further with the increase of KOH/C mass ratio, while the other two groups of samples decrease gradually.

The decrease of specific capacitance of **Sample 5** and **Sample 7** can be explained by excessive loss of carbon during KOH activation.³⁴ Shen and his coworkers observed that KOH consumed carbon and created pores during the activation process. As a result, in the KOH/C ratio regime smaller than 4, more porosity was observed. In KOH/C ratio regime than 4, an excessive amount of carbon was consumed by KOH which led to shrinkage in the carbon structure and caused reduction in porosity. Results of Shen's work explained the reason why the specific capacitance starts decreasing after reaching the maximum in this work. Since less pores means less surface area, the reduction of pores leads to decrease of capacitance. The trend in **Figure 18** is in agreement with the literature.

Figure 19 shows the mean specific capacitance of all samples. The error bar represented the range of three measurements. There is scattering in every data point. The scattering of **Sample 9** activated with KOH/C ratio of 2, and 4 have larger deviation than other data points. It is hypothesized that the observed differences were due limited readability of balance scale that was used to measure

the mass of activated carbon used in each electrode. To obtain the specific capacitance, the samples were dried in a hot plate until its weight remained constant before loading to the sample holder. After measuring the capacitance, electrodes were washed with distilled water to remove all the activated carbon, put on hot plate to dry, and weighed the mass of filter paper. The balance scale used in this work had a readability of 4 numerical decimal (0.0001 g). The average mass of filter paper in each sample was 0.0020 g, which was the last 2 digits of the scale. Every 0.0001 g of difference from the scale contributed 5% of deviation of the mass of the filter paper. Therefore, the uncertainty of balance scale contributed a lot to the scattering of specific capacitance.



Figure 19. The mean specific capacitance plotted against KOH/C mass ratio.

Simplified Carbon Activation Process

The proposed synthesis route of activated carbon contained annealing. As discussed in 'High Temperature Treatment' section, the annealing process did not improve the specific capacitance of carbon. Since high temperature treatment consumed considerable amount of electrical energy, annealing process was removed from the process of generating porous carbon later during the experiments. The actual generation process was hydrothermal carbonization of starch, and KOH activation of carbon (**Figure 20**). Although the annealing process

was removed, the supercapacitor electrodes made from activated carbon demonstrated good electrochemical properties, high specific capacitance, and high surface area. Therefore, it is safe to say that annealing process is not necessary in the carbon activation process.



Figure 20. Activation process used in this work without annealing.

Conclusion and Future Work

In conclusion, a simplified method of preparing activated carbon with welldeveloped porous structure, and capacitance much higher than the intended value (100 F/g) has been developed via HTC and KOH activation. By adding acids during HTC process, the time of hydrothermal treatment has reduced, and yields has increased. The use of KOH during activation process resulted in carbon spheres obtained forming a carbon sponge with large surface areas. While these materials were used as supercapacitor electrodes in 1 M Na₂SO₄ electrolyte, these exhibited excellent electrochemical properties with capacitance over 150 F/g, which was much larger than expected. Furthermore, it was found that annealing process is not necessary in the carbon activation process. With the KOH chemical activation alone, carbon can be activated and form porous sponge. Significant amount of energy can be saved since the annealing process require high temperature and under dry gas flow or vacuum.

Further study includes finding the optimal thickness of the sample, so that specific capacitance of each sample can be further improved. In addition to study the effects of thickness on capacitance, using chemical agent such as $H_3PO_4^{35}$, NaOH³⁶, or alkali metal carbonates³⁷ (K₂CO₃, Na₂CO₃) activation agent to produce porous carbon can be another possible direction of study. Moreover, using the method proposed in this work, other carbon rich but cheap materials such as agar, used coffee grounds, and table sugar can be good material to produce activated carbon in the future.

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Appendices

| Name | Vender | Lot No. |
|---------------------------------|-------------------------------|------------|
| Starch | Sigma-Aldrich | SLBT3746 |
| Agar | Sigma-Aldrich | MKCG8706 |
| Sulfuric Acid | LabChem | H078-09 |
| Phosphoric Acid | Avantor Performance Materials | 0000176511 |
| Acetic Acid | Acros Organics | A0242075 |
| 2-Propanol | Fisher Chemical | 155225 |
| КОН | Fisher Chemical | 172338 |
| DI Water | Fisher Chemical | 183956 |
| Ethanol | Fisher Chemical | 179389 |
| Na ₂ SO ₄ | MP Biomedicals, LLC | QR14759 |

Appendix 1. List of vendors and lot numbers of chemicals used.

| Ap | pendix | 2. | List | of | vendors | of | equi | oment | used. |
|----|--------|----------|------|------------|----------|----|------|-------|-------|
| | PCHAIX | <u> </u> | LIUL | U 1 | VOLIGOIO | 01 | oqui | | uocu. |

| Name | Vender | Model |
|--|------------------------|---------------------------------------|
| Iso-Thermal Oven | Fisher Scientific | Isotemp® Oven Model 655G |
| Tube Furnace | Carbolite Gero | Horizontal Split Tube Furnace HST/HZS |
| XRD | | |
| (Laboratorio de Optica de Raios-X (LORXI) da Universidade Federal | Shimadzu Corporation | XDR 7000 |
| do Paraná (UFPR)) | | |
| SEM (Laboratorio de Optica de | | |
| Raios-X (LORXI) da Universidade | JEOL USA | JSM-6360LV |
| Federal do Paraná (UFPR)) | | |
| TGA | TA Instruments | SDT Q600 |
| Laser | Universal Laser System | PLS6.75 |

Appendix 3. Control program of potentiostat National Instrument's LabView (developed by Prof. Cyro Ketzer Saul, Visiting Scholar of University of Pennsylvania, ESE Department).







Appendix 4. Labview Cyclovoltameter

Appendix 5. Coding of CV simulation program (developed by Prof. Cyro Ketzer Saul, Visiting Scholar of University of Pennsylvania, ESE Department).

```
Private Sub CommandButtonl_Click()
    'Sets initial values ??of the variances according to the value chosen in the worksheet
    var ini = Cells(1, 5)
    cont_var_g = 0
    'Param 1
    Cap = Cells(4, 4)
Cap_v = Cap * var_ini
Cells(4, 5) = Cap_v
    'Param 2
    Rs = Cells(5, 4)
    Rs v = Rs * var_ini
    Cells(5, 5) = Rs_v
    'Param 3
    Rp = Cells(6, 4)
    Rp v = Rp * var ini
    Cells(6, 5) = Rp_v
    'Param 4
    CO = Cells(7, 4)
    C0 v = C0 * var ini
    Cells(7, 5) = COv
    'Erro+ initial
    Erro = Cells(8, 9)
    'Iniciate adjustment
    If CheckBox1.Value Then
        Param = 1
        Call Varia(Param, Cap, Cap_v)
    End If
    If CheckBox2.Value Then
        Param = 2
        Call Varia(Param, Rs, Rs v)
    End If
    If CheckBox3.Value Then
        Param = 3
        Call Varia(Param, Rp, Rp_v)
    End If
    If CheckBox4.Value Then
        Param = 4
        Call Varia(Param, CO, CO v)
    End If
End Sub
```

```
Private Sub Varia(par, valor, var)
Flag m = 0:
cont_var = 0: 'Variation Counter
 'Test in crease in value
Do While 1 = 1
   valor new = valor + var
   Erro = Cells(8, 9)
    'Test Erro
   Cells(3 + par, 4) = valor_new
   Worksheets("Sim").Calculate
   Err_new = Cells(8, 9)
    'Debug.Print "Err New = "; Err new; " Err = "; Erro
    '(Err * 0.99999) Then '(Varies more than 0.001%)
    If Err new < Erro Then
        'Debug.Print "Improved increasing"
       Flag_m = 1
       cont_var = cont_var + 1
       valor = valor new
   Else
        'Worse of no difference
       'Back to original
        'Debug.Print "Worse"
       Cells(3 + par, 4) = valor
       Worksheets("Sim").Calculate
       Exit Do
   End If
Loop
'Test for decrease in value
'Only if it has not risen (save time)
If Flag_m = 0 Then
   Do While 1 = 1
      valor_new = valor - var
Erro = Cells(8, 9)
      'Test Erro
      Cells(3 + par, 4) = valor_new
      Worksheets("Sim").Calculate
       Err_new = Cells(8, 9)
       'Debug.Print "Err New = "; Err new; " Err = "; Erro
       If Err_new < Erro Then</pre>
           'Improved
           'Debug.Print "Improved decreasing"
          Flag m = 2
           cont_var = cont_var + 1
           valor = valor new
       Else
        'Worse or no difference
        'Back to original
       'Debug.Print "Worse"
          Cells(3 + par, 4) = valor
          Worksheets ("Sim").Calculate
          Exit Do
       End If
   Loop
End If
 'ActiveSheet.
```

```
End Sub
```