STUDYING ACTIVATED CARBONS OF NATURAL SOURCES FOR SUPERCAPACITOR APPLICATIONS

A Thesis by

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The following faculty members have examined the final copy of this thesis for form and content, and recommend that it be accepted in partial fulfillment of the requirement for the degree of Master of Science with a major in Mechanical Engineering.

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DEDICATION

To my father—my inspirer, the most honest, generous, thoughtful, and kindest person that I have ever met—and to the rest of my family
ACKNOWLEDGEMENTS

First, I would like to express my sincere gratitude to my advisor, Dr. Ramazan Asmatulu, for his continuous support of my Master’s study and related research, and for his patience, motivation, and immense knowledge. His guidance helped me during the entire time of my research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Master’s study.

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ABSTRACT

Activated carbon (AC) can be produced from natural sources such as pistachio and acorn shells, which can be an inexpensive and good use of natural waste, and used in energy storage devices, such as supercapacitors. The carbonaceous materials used in this thesis were carbonized at two high temperatures, 700°C and 900°C. Carbonized nutshells were chemically activated using 1 wt% potassium hydroxide (KOH). Activated carbon powders with polyvinylidene fluoride (PVdF) were used to construct carbon electrodes. 1M of tetraethylammonium tetrafluoroborate (TEABF₄) and propylene carbonate (PC) were used as electrolytes. Electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used for characterization of the supercapacitors. Scanning electron microscopy (SEM) was used to inspect the surface texture of the activated carbons.

Activated pistachio and acorn shells carbonized at 700°C showed more porous surface texture than those carbonized at 900°C. Carbonization temperature effects were studied for their electrochemical characteristics. Pistachio and acorn shells carbonized at 700°C showed better electrochemical characteristics than those carbonized at 900°C in their use as electrode materials. Results indicated approximately 50,000 µF/g and 27,083 µF/g specific capacitance for activated acorn and pistachio carbons, respectively, at a scan rate of 10 mV/s. Acorn and pistachio shells showed approximately 80% and 60% carbon yield, respectively. This study showed promising results for using these activated carbons produced from natural waste for supercapacitor applications.
TABLE OF CONTENTS

Chapter                                                                 Page

1. INTRODUCTION ......................................................................................... 1

   1.1 Motivation ......................................................................................... 1
   1.2 Historical Background ........................................................................ 2
   1.3 Research Objectives ........................................................................... 3

2. LITERATURE REVIEW ............................................................................ 4

   2.1 Principles of Supercapacitors .............................................................. 4
   2.2 Advantages of Supercapacitors over Batteries ..................................... 4
   2.3 Types of Supercapacitors .................................................................... 5
       2.3.1 Pseudocapacitor ........................................................................ 5
       2.3.2 Electric Double-Layer Capacitor ............................................... 5
   2.4 Supercapacitor Models ........................................................................ 6
       2.4.1 Helmholtz Model ........................................................................ 6
       2.4.2 Gouy-Chapman Model ................................................................ 7
       2.4.3 Stern Model .............................................................................. 8
       2.4.4 Current Model ........................................................................... 9
   2.5 Construction of EDLC .......................................................................... 10
       2.5.1 Electrode Materials .................................................................... 10
           2.5.1.1 Carbon ............................................................................. 10
           2.5.1.2 Metal Oxides .................................................................... 14
           2.5.1.3 Conducting Polymers ......................................................... 15
       2.5.2 Electrolyte Materials ................................................................. 15
           2.5.2.1 Organic Electrolytes ............................................................. 16
           2.5.2.2 Aqueous Electrolytes ........................................................... 16
           2.5.2.3 Ionic Liquid Electrolytes ......................................................... 17
       2.5.3 Separator .................................................................................... 17
   2.6 Applications of EDLC .......................................................................... 17
       2.6.1 Automobiles ............................................................................... 18
       2.6.2 Starters ....................................................................................... 18
       2.6.3 Memory Backups ........................................................................ 18
       2.6.4 Adjustable-Speed Drive Ride-Through ........................................ 19
       2.6.5 Micro-Grids ................................................................................ 19
       2.6.6 Mobile Devices .......................................................................... 19
       2.6.7 Electromechanical Actuators ....................................................... 20

3. EXPERIMENTAL ..................................................................................... 21

   3.1 Supercapacitor Model ......................................................................... 21
   3.2 Materials Used in Model ..................................................................... 21
## TABLE OF CONTENTS (continued)

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1</td>
<td>Chemicals for Activation of Carbons</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Electrodes</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Electrolyte and Separator</td>
</tr>
<tr>
<td>3.3</td>
<td>Methods</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Preparation of Activated Carbons</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Construction of Electrodes</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Preparation of Electrolyte</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Assembly of EDLC</td>
</tr>
<tr>
<td>3.4</td>
<td>Characterization</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>4.</td>
<td>RESULTS AND DISCUSSION</td>
</tr>
<tr>
<td>4.1</td>
<td>Carbon Yield</td>
</tr>
<tr>
<td>4.2</td>
<td>SEM Analysis</td>
</tr>
<tr>
<td>4.3</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Specific Capacitance</td>
</tr>
<tr>
<td>4.4</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>5.</td>
<td>CONCLUSION AND FUTURE WORK</td>
</tr>
<tr>
<td>5.1</td>
<td>Conclusion</td>
</tr>
<tr>
<td>5.2</td>
<td>Future Work</td>
</tr>
<tr>
<td>REFERENCES</td>
<td></td>
</tr>
<tr>
<td>APPENDICES</td>
<td></td>
</tr>
<tr>
<td>A.</td>
<td>SEM IMAGES</td>
</tr>
<tr>
<td>K700 Non-Activated Shell</td>
<td>59</td>
</tr>
<tr>
<td>K700 Non-Activated Shell (10 µm magnification)</td>
<td>60</td>
</tr>
<tr>
<td>K700AC Electrode</td>
<td>61</td>
</tr>
<tr>
<td>K900AC Particles (200 nm magnification)</td>
<td>62</td>
</tr>
<tr>
<td>K900AC Particles</td>
<td>63</td>
</tr>
<tr>
<td>P700 Non-Activated (200 nm magnification)</td>
<td>64</td>
</tr>
<tr>
<td>P700 Non-Activated (10 µm magnification)</td>
<td>65</td>
</tr>
<tr>
<td>P900AC (200 nm magnification)</td>
<td>66</td>
</tr>
<tr>
<td>P900AC (1 µm magnification)</td>
<td>67</td>
</tr>
<tr>
<td>P900AC (10 µm magnification)</td>
<td>68</td>
</tr>
<tr>
<td>Chapter</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>B.</td>
<td>CYCLIC VOLTAMMOGRAMS</td>
</tr>
<tr>
<td></td>
<td>K700AC at Different Scan Rates</td>
</tr>
<tr>
<td></td>
<td>K900AC at Different Scan Rates</td>
</tr>
<tr>
<td></td>
<td>P700AC at Different Scan Rates</td>
</tr>
<tr>
<td></td>
<td>P900AC at Different Scan Rates</td>
</tr>
<tr>
<td>C.</td>
<td>SPECIFIC CAPACITANCE</td>
</tr>
<tr>
<td></td>
<td>K700AC</td>
</tr>
<tr>
<td></td>
<td>K900AC</td>
</tr>
<tr>
<td></td>
<td>P700AC</td>
</tr>
<tr>
<td></td>
<td>P900AC</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Ragone plot of energy storage system, adapted from [1]</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>Helmholtz double-layer model, adapted from [7]</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Gouy-Chapman diffuse model, adapted from [7]</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>Stern model, adapted from [7]</td>
<td>8</td>
</tr>
<tr>
<td>2.4</td>
<td>Double-layer model including layers of solvent, adapted from [20]</td>
<td>9</td>
</tr>
<tr>
<td>2.5</td>
<td>Basic construction of EDLC, adapted from [7]</td>
<td>10</td>
</tr>
<tr>
<td>2.6</td>
<td>Effect of pore diameter on specific capacitance [1]</td>
<td>13</td>
</tr>
<tr>
<td>2.7</td>
<td>Typical charge/discharge voltammetry of electrochemical capacitor [28]</td>
<td>14</td>
</tr>
<tr>
<td>3.1</td>
<td>Model of electric double-layer capacitor</td>
<td>21</td>
</tr>
<tr>
<td>3.2</td>
<td>(a) Potassium hydroxide and (b) hydrochloric acid</td>
<td>22</td>
</tr>
<tr>
<td>3.3</td>
<td>Electrode materials: (a) activated carbons, (b) polyvinylidene fluoride, (c) N,N-dimethylacetamide, (d) polyethylene terephthalate sheet, and (e) aluminum foil</td>
<td>22</td>
</tr>
<tr>
<td>3.4</td>
<td>Electrolyte materials: (a) tetaethylammonium tetrafluoroborate, (b) propylene carbonate, (c) lens tissue, and (d) porous paper</td>
<td>23</td>
</tr>
<tr>
<td>3.5</td>
<td>Natural sources: (a) pistachio shells and (b) acorn shells</td>
<td>24</td>
</tr>
<tr>
<td>3.6</td>
<td>Tube furnace (MTI Corporation/OTF-1200X) used for carbonization with argon gas flow</td>
<td>25</td>
</tr>
<tr>
<td>3.7</td>
<td>Construction of EDLC: (a) electrode layout on Al foil, (b) constructed carbon electrode with separator and PET sheet, and (c) assembled EDLC</td>
<td>26</td>
</tr>
<tr>
<td>3.8</td>
<td>(a) Scanning electron microscope used in this study and (b) thin-film gold-coated specimens</td>
<td>27</td>
</tr>
<tr>
<td>3.9</td>
<td>BioLogic SP-150 potentiostat/galvanostat used for CV technique</td>
<td>28</td>
</tr>
<tr>
<td>3.10</td>
<td>(a) Gamry Series G300TM potentiostat/galvanostat/ZRA for EIS technique and (b) leads connected to supercapacitor</td>
<td>29</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.1</td>
<td>Carbon yield of pistachio and acorn shells</td>
<td>30</td>
</tr>
<tr>
<td>4.2</td>
<td>SEM images of K700AC: (a) shell surface at 200 nm, (b) and (c) cross section of shell at 1 µm and 10 µm magnification, and (d) carbon electrode made from K700AC</td>
<td>31</td>
</tr>
<tr>
<td>4.3</td>
<td>SEM images of K900AC shell cross sections: (a) 200 nm, (b) 1 µm, and (c) 10 µm magnification, and (d) ground K900AC particles</td>
<td>32</td>
</tr>
<tr>
<td>4.4</td>
<td>SEM images: (a) non-activated K700 shell and (b) non-activated P700 shell</td>
<td>32</td>
</tr>
<tr>
<td>4.5</td>
<td>Cyclic voltammogram of P700AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s</td>
<td>37</td>
</tr>
<tr>
<td>4.6</td>
<td>Cyclic voltammogram of P900AC: (a) 10 mV/s, (b) 100 mV/s and (c) 500 mV/s</td>
<td>39</td>
</tr>
<tr>
<td>4.7</td>
<td>Cyclic voltammogram of K700AC: (a) 10 mV/s, (b) 100 mV/s and (c) 500 mV/s</td>
<td>41</td>
</tr>
<tr>
<td>4.8</td>
<td>Cyclic voltammogram of K900AC: (a) 10 mV/s, (b) 100 mV/s and (c) 500 mV/s</td>
<td>43</td>
</tr>
<tr>
<td>4.9</td>
<td>Steady-state curve I vs. Ewe for forward and backward voltage scan of K700AC</td>
<td>44</td>
</tr>
<tr>
<td>4.10</td>
<td>Specific capacitance of supercapacitors as function of scan rate</td>
<td>45</td>
</tr>
<tr>
<td>4.11</td>
<td>Electrical impedance spectroscopy plot for P700AC</td>
<td>46</td>
</tr>
<tr>
<td>4.12</td>
<td>Electrical impedance spectroscopy plot for P900AC</td>
<td>46</td>
</tr>
<tr>
<td>4.13</td>
<td>Electrical impedance spectroscopy plot for K700AC</td>
<td>47</td>
</tr>
<tr>
<td>4.14</td>
<td>Electrical impedance spectroscopy plot for K900AC</td>
<td>47</td>
</tr>
<tr>
<td>4.15</td>
<td>Electrical impedance spectroscopy plot for P700AC, P900AC, K700AC, and K900AC</td>
<td>48</td>
</tr>
</tbody>
</table>
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>AN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>ASD</td>
<td>Adjustable Speed Drive</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DMAC</td>
<td>Dimethylacetamide</td>
</tr>
<tr>
<td>EDLC</td>
<td>Electric Double-Layer Capacitor</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>NEC</td>
<td>Nippon Electric Company</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene Terephthalate</td>
</tr>
<tr>
<td>PRI</td>
<td>Pinnacle Research Institute</td>
</tr>
<tr>
<td>PVdF</td>
<td>Polyvinylidene Fluoride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SOHIO</td>
<td>Standard Oil of Ohio</td>
</tr>
<tr>
<td>TEABF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Tetraethylammonium Tetrafluoroborate</td>
</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 Motivation

With the advancement of technology, our dependency on energy storage devices is rapidly increasing. There are several ways to store electrical energy, batteries and capacitors being one. Both capacitors and batteries have been used extensively in various applications. Supercapacitors have the potential to be a major advancement in energy storage and can fill the gap between conventional capacitors and rechargeable batteries. The use of supercapacitors, also referred to as electric double-layer capacitors (EDLCs), ultracapacitors, etc.[1-6], is a promising option for charging and discharging energy rapidly whenever it is needed.

The type of electric energy storage typically requires an evaluation based on the application, life span, cost, performance in terms of energy density, and power density in terms of charging and discharging. In comparison to regular high-power lithium batteries, supercapacitors are able to deliver more specific power and higher specific energy. They also show very high life cycles and a wide range of operating temperatures compared to regular batteries [4]. Supercapacitors can charge and discharge so rapidly that they can provide a backup source of high peak power in seconds. Because they have longer life cycles, they do not require maintenance or replacement as do batteries. They are more environmentally friendly because there is no use of heavy metal and no toxic disposal issues. Because of these unique characteristics and with the increase of its energy density, supercapacitors are being viewed as an attractive alternative to regular batteries [5].

Figure 1.1 shows a Ragone plot of different energy-storing devices [1]. Conventional capacitors show higher power density but lower energy density, and batteries show a lower
power density but higher energy density. Supercapacitors fall in between these two choices of electric energy-storing devices.

![Ragone plot of energy storage system](image)

Figure 1.1. Ragone plot of energy storage system, adapted from [1].

1.2 Historical Background

Hermann von Helmholtz, a German physicist, first described the double-layer capacitor in 1853. In 1957, the General Electric Company first patented an electrochemical capacitor (U.S. Patent 2800616). This capacitor had double-layer capacitance and porous carbon for the electrodes [7-8]. In 1961, the Standard Oil of Ohio (SOHIO) Research Center (Cleveland, USA) started the commercial double-layer capacitor. SOHIO continued their development until 1971 and developed disk-shaped capacitors, but due to the lack of sales, they licensed their technology to Nippon Electric Company (NEC) of Japan, who first introduced their electrochemical products as memory-backup devices [7].

In 1978, Panasonic made a commercially successful electrochemical capacitor named “Goldcaps.” The next year, Elna Co. Ltd. introduced first-generation EDLCs called “Dynacaps,”
which had high internal resistance. These were used for data backup or low-current applications. The Pinnacle Research Institute (PRI) developed the first supercapacitor, called the “PRI Ultracapacitor,” with low internal resistance in 1982 for use in military applications. Later in 1992, Maxwell Laboratories took over the development of PRI Ultracapacitor for power applications. Apart from these companies, currently a few others around the world are manufacturing EDLCs. In the U.S., Kold Band International, Epcos, ELNA, and AVX are commercially manufacturing EDLCs [10, 14].

1.3 Research Objectives

Compared to the other conventional energy-storing devices, the supercapacitor electrode has an extremely large surface area for storing electric energy. This has opened a wide range of options for using different materials having high surface area, such as activated carbons. Using natural wastes to produce activated carbons is also environmental friendly and less expensive. The objective of this study is to carbonize natural waste, such as pistachio and acorn shells, at two different high temperatures, chemically activate those carbons to fabricate EDLCs in an inexpensive way, and then characterize them through different physical and electrochemical analyses. A comparative study of pistachios and acorns can provide valuable information for the choice of producing activated carbons.
CHAPTER 2
LITERATURE REVIEW

2.1 Principles of Supercapacitors

Supercapacitors work on the same principle as conventional electrostatic capacitors. A conventional capacitor consists of two conductors separated by a non-conductive region called the dielectric. When electrical energy is applied across the conductors, energy is stored as a form of electrical charge and later acts as a source of energy when needed. In supercapacitors, the surface area of the conductors is much higher than in conventional capacitors.

The capability of a device for charge storage per unit voltage is known as capacitance. If voltage created across the conductors is \( V \) and charge is stored in conductors \( \pm Q \), then capacitance would be

\[
C = \frac{Q}{V} = \varepsilon \frac{A}{d}
\]  

(1)

where \( A \) is the conductors’ surface area, \( d \) is the distance between the conductors, and \( \varepsilon \) is the dielectric constant of the dielectric material [6-7], [16]. Also, the stored energy (\( E \)) in a capacitor can be calculated as

\[
E = \frac{1}{2} CV^2
\]  

(2)

2.2 Advantages of Supercapacitors over Batteries

Electrical energy can be stored in two different ways: indirectly in batteries, through Faradic oxidation and reduction which supplies energy throughout the electrochemical process, and also directly, by storing negative and positive charges in capacitors/supercapacitors, also known as non-Faradic electric energy storage. An important difference between capacitors and batteries is the reversibility. In batteries, the electric energy is produced from Faradic
electrochemical reactions through phase changes of chemical substances. Although the overall thermodynamic energy conversion can be conducted in a relatively reversible way, the charge and discharge processes often involve irreversibility in the interconversion of chemical reagents, which results in a restricted cycle life. Depending on the type of battery, cycles can be one thousand to several thousand. On the other hand, capacitors/supercapacitors have almost unlimited life cycles because chemical reactions or phase changes are not involved [6]. Again, from Figure 1.1, it is clear that supercapacitors have higher power densities than batteries. It should be noted that there has never been an aim to replace batteries with supercapacitors. But electrically coupling electrochemical capacitors in discharge and recharge with batteries offers complementary opportunities [6].

2.3 Types of Supercapacitors

Supercapacitors are divided into two groups depending on the mechanism for storing charge. One group is pseudocapacitors and the other group is electric double-layer capacitors.

2.3.1 Pseudocapacitor

The pseudocapacitor is based on the working principle of a battery. Electrical energy is obtained by progressive redox reactions between several oxidation states. Charge and discharge occurs not only on the surface of but also throughout the electrode. This capacitor is also called a Faradic supercapacitor [17, 18].

2.3.2 Electric Double-Layer Capacitor

The electric double-layer capacitor has two electrodes impregnated with an electrolyte. Its working principle is different from that of a conventional battery in that the EDLC directly stores electrical charges by physically separating the positive and negative charges on the electrode surface. When electric potential is applied on the electrodes, electrons from the
negative electrode move through the electrolyte to the positive electrode, and positive ions from the positive electrode move to the negative electrode. The charges are held statically. Unlike the pseudocapacitor, the EDLC holds charges only on its surface, not throughout the electrodes. Because the charge-and-discharge technique only involves the physical separation of ions, no chemical reaction occurs in the EDLC, which eventually leads to an almost unlimited cycle life [6, 17, 18].

2.4 Supercapacitor Models

Various supercapacitor models have been developed to explain the electrical process that occurs at the boundary of the solid conductor and the electrolyte. Three popular models that explain that process are discussed in this section.

2.4.1 Helmholtz Model

Helmholtz first introduced the “double-layer” model to explain the electrode/electrolyte interface in capacitors. Figure 2.1 illustrates the Helmholtz double-layer model.

![Figure 2.1. Helmholtz double-layer model, adapted from [7]](image)

In this model, the electrode will acquire a layer of positive charge on its surface, and next to that surface will be a layer of electrons in electrolyte. The same interface will occur at the other
electrode but with opposite charges. Because of this two-layer formation in the capacitors, Helmholtz called this double-layer behavior. The double layer can be thought of as a molecular capacitor [7, 14, 18].

According to the Helmholtz model, the differential capacitance \( C_l \) is given by [14]

\[
C_l = \frac{\varepsilon}{4\pi \delta}
\]

which implies that the differential capacitance is a function of dielectric constant \( (\varepsilon) \) and charge layer separation \( (\delta) \).

### 2.4.2 Gouy-Chapman Model

The Gouy-Chapman model proposes that capacitance is not constant but rather dependent on applied potential and ionic concentration. This model maintains that thermal motion creates a space distribution of ions in electrolytes. Both coulombic force and thermal motions influence the equilibrium distribution of counter ions. The counter ion concentration decreases, and a similar ion concentration increases from the electrode surface. This phenomenon is referred to as the diffuse electric layer [7, 14, 22]. Figure 2.2 shows the Gouy-Chapman diffuse model.

![Figure 2.2. Gouy-Chapman diffuse model, adapted from [7]](image)

This model was developed by combining Poisson and Boltzmann equations. According to this theory, differential capacitance \( C_G \) can be explained by equation (4):
\[ C_G = \frac{\varepsilon \kappa}{4\pi} \cosh \frac{z}{2} \]  

(4)

where \( z \) is the valence of ions, and \( \kappa \) is the reciprocal Debye-Hückel length and can be defined by

\[ \kappa = \sqrt{\frac{8\pi n e^2 z^2}{\varepsilon k T}} \]  

(5)

where \( T \) is the absolute temperature, \( n \) is the number of ions per cubic centimeter, and \( k \) is Boltzmann’s constant [14]. This double-layer model is not as compact as the Helmholtz model, because ions are considered as highly mobile point ions, and metal is a perfect conductor. This model leads to an overestimation of electric double-layer capacitance.

### 2.4.3 Stern Model

In 1923, O. Z. Stern combined the Helmholtz model and Gouy-Chapman model by introducing two regions of ion distribution. Figure 2.3 shows the Stern model.

![Figure 2.3. Stern model, adapted from [7]](image)

The inner region is a compact layer, or Stern layer, and the outer region is called the diffuse layer, or Gouy-Chapman layer. The total capacitance (C) of this EDLC can be calculated by combining the capacitance of these two regions [7, 22] as
\[ \frac{1}{c} = \frac{1}{c_i} + \frac{1}{c_G} \]  

(6)

where \( c_i \) is the Stern layer capacitance, and \( c_G \) is the Gouy-Chapman layer capacitance [14].

In a practical EDLC, the electric double-layer behavior is much more complex in porous electrodes. This behavior can be affected by a number of factors such as space constraints inside the pores, ohmic resistance of the electrolyte, wetting behavior of the porous electrode, and the mass transfer path [7].

2.4.4 Current Model

In 1963, Bockris, Devanathan, and Muller proposed a double-layer structure that considered the action of solvent. They proposed that specific adsorption occurs at the inner Helmholtz plane, hydrated anions and cations occupy the Gouy plane, and the occupancy of any ions in the inner Helmholtz and Gouy planes is prohibited. The surface potential decreases in both the inner Helmholtz and Gouy plane and the diffuse double layer [14, 20, 22]. Figure 2.4 depicts the double-layer model including layers of solvent.

![Double-layer model showing layers of solvent](image)

Figure 2.4. Double-layer model showing layers of solvent, adapted from [20]
2.5 Construction of EDLC

A practical double-layer capacitor is comprised of two electrodes connected to a current collector and separated by a separator soaked in electrolyte. A wide variety of materials is used for constructing an EDLC. This section focuses on the use and properties of various materials, and their significant importance in performance [7]. The basic construction of a carbon-based EDLC is shown in Figure 2.5.

![Figure 2.5. Basic construction of EDLC, adapted from [7]](image)

2.5.1 Electrode Materials

The key material to a high-performing EDLC is in its electrode material. The higher the surface area of the electrodes, the more charge they can contain. The selection of electrode material is very important. Supercapacitors are categorized based on the materials used for their electrodes: (a) carbon, (b) metal oxides, and (c) conducting polymers [7].

2.5.1.1 Carbon

Carbon is the most popular electrode material used for supercapacitors. Typically it is used with various modifications. Activated carbon (AC) is the most commonly used type of
porous carbon used for supercapacitors because of its high surface area, low cost, easy production in large quantities, great cycle stability, availability, wide operating temperatures, non-toxicity, and established electrode production technologies. AC in powders, woven cloths, felts, or fibers can have a surface area up 2500 m²/g. The charge storage in AC is mostly capacitive in the EDLC. Also, surface functional groups in activated carbons that can charge and discharge give rise to pseudocapacitance [1, 7].

Coal, pitch, and petroleum coke are the most commonly used materials for the commercial production of AC. But the scarcity of fossil fuels, environmental pollution issues, and cost have led AC productions to sustainable and renewable resources. Therefore, wood, nutshell, cellulose, corn grain, rice husk, banana fiber, sugar cane bagasse, etc. are popular in producing AC. The costs of some of these raw materials and carbon yields from pyrolysis of these sources are presented in Table 2.1 [23].

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Carbon Yield from Pyrolysis (wt%)</th>
<th>Raw Material Cost ($/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum Coke</td>
<td>90</td>
<td>1.4</td>
</tr>
<tr>
<td>Charcoal</td>
<td>90</td>
<td>1.2</td>
</tr>
<tr>
<td>Lignite</td>
<td>50</td>
<td>0.75</td>
</tr>
<tr>
<td>Coconut Shell</td>
<td>30</td>
<td>0.25</td>
</tr>
<tr>
<td>Wood</td>
<td>25</td>
<td>0.8</td>
</tr>
<tr>
<td>Potato Starch</td>
<td>45</td>
<td>1.0</td>
</tr>
<tr>
<td>Sucrose</td>
<td>&lt;45</td>
<td>0.25</td>
</tr>
<tr>
<td>Cellulose</td>
<td>&lt;45</td>
<td>0.65</td>
</tr>
<tr>
<td>Corn Grain</td>
<td>&lt;45</td>
<td>0.25</td>
</tr>
<tr>
<td>Banana Fiber</td>
<td>&lt;45</td>
<td>4</td>
</tr>
</tbody>
</table>
Since carbon materials can meet the requirements as electrode materials for an EDLC, various carbonaceous materials such as activated carbons, aerogels, xerogels, nanofibers, nanotubes, and graphite have been studied extensively [7].

Kalyani et al. [24] produced activated carbon from grass and used this AC as a catalyst for H$_2$ generation from the electrolysis of water. They also suggested that this AC be used as electrode material, an adsorbent for color, and odor and hazardous pollutants. Hou et al. [25] prepared controlled micro/mesopore interconnected structures of three-dimensional activated carbon with a high specific surface area as electrode material for supercapacitors from raw rice bran. These supercapacitors exhibited high specific capacitance at large current densities of 10 A/g and 100 A/g, i.e., of 265 F/g and 182 F/g in 6 M of potassium hydroxide (KOH) electrolyte, respectively. They showed that this AC can be prepared from agricultural by-products for high-performance energy storage devices like supercapacitors. Xu et al. [26] prepared two-dimensional porous carbon by pyrolysis of natural waste pistachio nutshells with KOH activation as electrode material for supercapacitors. They found a large real capacitance of 29.3/20.1 µF/cm$^2$ and a high energy density of 10/39 Wh/kg at a power of 52/286 kW/kg in 6 M KOH aqueous electrolyte. Natalia et al. [27] synthesized carbons from areca fibers and activated them with KOH and steam as electrode material for supercapacitors.

Theoretically, the higher the specific surface area of activated carbons, the higher the expected specific capacitance. But in reality, this situation is more complicated. One type of activated carbon with a small surface area can give larger specific capacitance compared with a larger surface area. This is because actual double-layer capacitance varies depending on the process used for activating the carbons. The porous texture of the carbon determines the conductivity of ions in a capacitor. The mobility of ions is more difficult in small pores than in
large pores, and this mobility is different than in the bulk of the electrolyte. The pore size must be chosen to suit the electrolyte and to ensure that it is optimal, based upon the size of the ions [28]. Figure 2.6 illustrates the effect of pore size on specific capacitance; for smaller pores it is very difficult for ions to show capacitance at high frequencies [1, 14].

![Figure 2.6. Effect of pore diameter on specific capacitance [1]](image)

Graphene is a two-dimensional carbon plane with one atomic thickness. Researchers have found it attractive because of its structure, preparation, mechanical hardness, electrical conductivity, and so on. Theoretically, graphene is an ideal electrode material, but experimentally, it is not yet well achieved [7, 18].

Electrochemical capacitors made from carbon are of two types, based on the kind of energy accumulated. One type is the electrical double-layer capacitor where only the electrostatic attraction between ions and the charged surface occurs, and the other type is a supercapacitor based on additional Faradic pseudocapacitance reactions. The performance of a supercapacitor simultaneously combines these two kinds of energy. Figure 2.7 illustrates the typical charge/discharge voltammetry of an electrochemical capacitor. An ideal double-layer capacitor is in the form of a rectangle, where the sign of the current is immediately reversed after reversing
the voltage sweep. But electrode materials with pseudocapacitance characteristics deviate from this rectangular shape, showing peaks caused by redox reactions [28].

![Diagram](image)

**Figure 2.7. Typical charge/discharge voltammetry of electrochemical capacitor [28]**

### 2.5.1.2 Metal Oxides

Metal oxides are mostly used as active electrode materials in supercapacitors because of their exceptional physicochemical properties. Redox reactions take place in these materials under the application of voltage. Metal oxides have low resistance and high specific capacitance that leads to high specific power for supercapacitors. Metal oxides such as RuO$_2$, MnO$_2$, Fe$_3$O$_4$, IrO$_2$, and V$_2$O$_5$ aid in supercapacitor applications. Among these metal oxides, RuO$_2$ shows excellent electrochemical capacitance characteristics. RuO$_2$ and IrO$_2$ were used in early electrochemical capacitors for military or space applications, but these metal oxides are not economically feasible, and almost 90% of the total capacitor cost is in the electrode material. Again, these materials are suitable for aqueous electrolytes and limit the nominal voltage to 1V. Numerous studies have used these favorable, but costly, noble metals at reduced costs by diluting them, forming metal compounds like nitrides, etc. [1], [29-30].
2.5.1.3 Conducting Polymers

Conducting polymers are also promising materials in supercapacitors because of the realization of high performance. Conducting polymers can stabilize a double-layer capacitor because they can change their physical structure by doping/de-doping. Conducting polymers such as polypyrrole, polyindole, polyaniline, and polythiophine are typical prototype materials for supercapacitors. These electronically conducting polymers use a charging process that occurs over the entire polymer mass, not just the surface like activated carbons. They show high conductivity in the charged state, and they usually charge and discharge processes fairly quickly. As a result, these polymers show high specific capacitance in their characterization. The most promising polymer supercapacitor is the n/p type. In the n/p doped polymer, the n-doped polymer is used as the negative electrode, and the p-doped polymer is used as the positive electrode. The charge and discharge processes in a conducting polymer supercapacitor are Faradic [7, 29].

Generally the typical cyclic voltammogram of a polymer supercapacitor is not rectangular, but rather gives a current peak at the respective redox potential of the polymer, which is not expected in a capacitor. This characteristic gives rise to the debate over whether it should be called a battery or a capacitor. But compared to metallic oxides, it can be termed as a capacitor. Swelling and shrinking of electroactive polymers is well known and can lead to degradation during cycling [1].

2.5.2 Electrolyte Materials

The choice of electrolyte is an important factor for the electrochemical performance of EDLCs, as stated earlier. Here, different types of electrolytes used for activated carbon
electrodes are discussed. Electrolytes that have been used with activated carbon electrodes are organic, aqueous, and ionic liquid.

2.5.2.1 Organic Electrolytes

Organic electrolytes are the most common electrolytes used commercially in EDLCs. Organic electrolyte-based EDLCs offer a high life cycle of 5,000,000, a wide range of operating temperatures from −30°C to +50°C (with acetonitrile solvent), and a moderately high operational voltage of 2.2 to 2.9V. The most common organic electrolyte is an ammonium salt called tetraethylammonium tetrafluoroborate (TEABF₄), with anhydrous propylene carbonate (PC) or acetonitrile (AN) as the solvent. Together with solvent acetonitrile, TEABF₄ is widely used in most commercial supercapacitors [7]. The main advantage of this electrolyte is its low viscosity, which leads to high conductivity, but it has drawbacks such as high volatility and flammability. Organic electrolytes have a significantly higher specific resistance compared with concentrated aqueous electrolytes [1]. Although organic electrolytes have good electrochemical characteristics, their high flammability, toxicity, and low thermal stability limit its use in high-performance supercapacitors [7].

2.5.2.2 Aqueous Electrolytes

Aqueous electrolytes limit the unit cell voltage of electrochemical capacitors typically to 1V, which is less than organic electrolytes [1]. Aqueous electrolytes are advantageous because of their low cost and high ionic conductivity. But a serious disadvantage in using acid-based electrolytes is that they lead to corrosion of EDLCs at high temperatures and voltages, which limits the life cycle and operating voltage [7].
2.5.2.3 Ionic Liquid Electrolytes

Ionic liquid electrolytes are room-temperature molten salts completely made with anions and cations. Ionic liquid-based electrolytes have high voltage stability, which leads to the high energy density of EDLCs. They show good conductivity above a temperature of 60°C. Also, these electrolytes are nonvolatile, nonflammable, and nontoxic. They facilitate using EDLCs in mobile applications, but have low ionic mobility at room temperature and are also expensive [7].

2.5.3 Separator

The separator in an electric double-layer capacitor prevents contact between the electrodes and allows ions to transfer between them. It is important for the separator material to possess both strong ion conductance and electronic insulation. It should be chemically resistant to corrosion with electrolytes or any other elements in the capacitor. A separator must be mechanically durable, in order to prevent the migration of electrode materials, and it should be thin while maintaining its mechanical durability. Commercially used common separators are cellulose paper, glass wool, ceramic, and polymer. A separator is selected based on the choice of electrolyte. For an organic electrolyte, cellulose paper or microporous polymer is chosen, and for an aqueous electrolyte, a glass-, mica-, or ceramic-based separator is chosen. Cellulose paper has high porosity and low equivalent series resistance but it has low mechanical durability [31].

2.6 Applications of EDLC

Electrochemical supercapacitors are still new devices and have yet to experience widespread use. Due to its limited power and energy capabilities, originally they were used in low-power applications. But recent development in improving energy and power density has increased its use in many applications [14]. In this section, the applications of supercapacitors as electric energy storage device are discussed.
2.6.1 Automobiles

One of the popular applications of supercapacitors is in automotive vehicles. Supercapacitors opened new possibilities for energy efficiency in hybrid electric vehicles and pure electric vehicles. For regenerative braking techniques, supercapacitors are exceptionally suitable to utilize and save the vehicle’s kinetic energy. When vehicles start to move, initially high power is required, and supercapacitors have both superior output and input power capability. Automotive manufacturers like Honda have been proactive in hybrid electric vehicles. Honda developed its own suitable supercapacitor to improve vehicle performance and implemented it in the Honda FCX [34].

2.6.2 Starters

Today, the energy required to crank a small or large engine is stored in lead or nickel-cadmium batteries. The high internal resistance in this type of storage limits their peak current, and for this reason they need to be oversized. Cold environmental temperature and fast discharging may also affect their properties. In their place, supercapacitors have better power behavior and a wide range of operating temperatures [32].

2.6.3 Memory Backups

The most common application of a supercapacitor is in semiconductor memory backup for any electronic equipment that contains a complementary metal-oxide semiconductor (CMOS), RAM, or microprocessor. Any power interruption may lead to the loss of stored information in the device. To prevent a power disruption, lithium batteries have been used as backup power for several years. But these batteries were not an ideal solution due to their short cycle life and limited operating temperature range. To meet this demand, supercapacitors can perform well with a longer cycle life, low cost, and very little maintenance [36].
2.6.4 Adjustable-Speed Drive Ride-Through

Many electronic devices, from home appliances to industry, face critical power disturbance problems caused by voltage sags and momentary interruptions. Voltage sags do not harm equipment, but they can easily interrupt the operation of sensitive loads such as electronic adjustable speed drives (ASDs). This interruption can cause tripping of the ASDs, which in turn may lead to loss in continuous-production industries. Different solutions such as lead-acid batteries, flywheels, and supercapacitors have been suggested to solve this issue. Supercapacitors have been found to be the best candidate for this issue considering cost, safety, cycle life, high power density, and low energy density [36].

2.6.5 Micro-Grids

Micro-grids are considered to be the next-generation energy networks. They have the capability of reducing carbon emissions through green energy harnessing. Popular electrical power generators are wind turbines, fuel cells, photovoltaic cells, and micro-turbines, and commonly used electrical energy storage devices would be batteries and supercapacitors. Because micro-grids can be interconnected to power grids, they are able to supply or demand power from power grids. This type of configuration is known as a smart grid [34-35].

2.6.6 Mobile Devices

Some mobile devices use a xenon flash, which is built into the device to facilitate good picture quality for the camera. This xenon flash consumes a considerable amount of power for an instant. To meet this demand, rather than making a larger battery, some mobile manufacturers have incorporated supercapacitors into devices to ease the temporary high power requirement. Here, the supercapacitor performs the peak load, although the battery supplies the total energy requirement but does not realize the high power demand [34].
2.6.7 Electromechanical Actuators

Electromechanical actuators convert electrical energy to mechanical energy, which requires a large amount of power. Supercapacitors, which have a higher capacitance than ordinary capacitors, are a better option to be used as electromechanical actuators. Both electromechanical actuators and supercapacitors consist of two electrodes (anode and cathode) separated by ionic conducting material. Faradic and non-Faradic materials have served as actuators. For more than two decades ago, Balakrishnan and Subramanian have proposed conducting polymer actuators based on electrochemical dopant intercalation. Artificial muscles in robots, biomimetic robots, microsensors, microscopic pumps, and optical fiber switches are some of great potential applications of electromechanical actuators [36].
CHAPTER 3
EXPERIMENTAL

3.1 Supercapacitor Model

The supercapacitor or electric double-layer capacitor model in this study consisted of two activated carbon electrodes, two layers of electrolytes, and a separator sandwiched in the middle. Two aluminum foils were attached with electrodes as charge collectors. The outer sides of the supercapacitor were covered with polyethylene terephthalate (PET) sheets to insulate them from any other media outside. Figure 3.1 shows a model of the EDLC.

![Figure 3.1. Model of electric double-layer capacitor](image)

3.2 Materials Used in Model

3.2.1 Chemicals for Activation of Carbons

Potassium hydroxide and hydrochloric acid (HCl; normality 12.1) were purchased from Fisher Scientific. These are shown in Figure 3.2.
3.2.2 Electrodes

Activated carbons produced from pistachios and acorns shells were used as electrode materials. Polyvinylidene fluoride (PVdF) (average Mw-180,000 by gel permeation chromatography) purchased from Sigma-Aldrich was used as a binder for the activated carbon powders. Aluminum foil was used to collect electrons from the carbon electrodes. The solvent N, N-dimethylacetamide (DMAC, reagent grade) and acetone (high performance liquid chromatography grade) were purchased from Fisher Scientific. Polyethylene terephthalate used to cover the outer sides of the supercapacitor was manufactured by M. G. Chemicals Ltd. (416-T laser printer transparency film). Figure 3.3 shows the electrode materials used in this study.

Figure 3.2. (a) Potassium hydroxide and (b) hydrochloric acid

Figure 3.3. Electrode materials: (a) activated carbons, (b) polyvinylidene fluoride, (c) N, N-dimethylacetamide, (d) polyethylene terephthalate sheet, and (e) aluminum foil
### 3.2.3 Electrolyte and Separator

Electrolyte tetraethylammonium tetrafluoroborate (MW 217.06 g/mol) and solvent propylene carbonate (anhydrous, 99.7%) were purchased from Sigma-Aldrich. The lens tissue was manufactured by ShieldMe®. Special thin porous paper manufactured by Sepp Leaf Products, Inc. was used as the separator. Figure 3.4 shows the materials used for the electrolyte and separator.

![Figure 3.4. Electrolyte materials: (a) tetraethylammonium tetrafluoroborate, (b) propylene carbonate, (c) lens tissue, and (d) porous paper](image)

### 3.3 Methods

#### 3.3.1 Preparation of Activated Carbons

The natural waste of pistachio and acorn shells was chosen as the raw material to produce activated carbons. Pistachios were purchased from a local store, and acorns were collected from the Wichita State University campus. The shells were separated from the seeds. Figure 3.5 shows the collected pistachio and acorn shells.
Figure 3.5. Natural sources: (a) pistachio shells and (b) acorn shells

The procedure for making activated carbon from both pistachios and acorns is identical for both. After collecting the nutshells, they were washed several times, soaked in deionized (DI) water overnight, and then dried in an oven (Precision Scientific/Thelco Laboratory Oven) for two hours at 105°C to evaporate all water content. Following that, they were stabilized in an oven at 240°C at 5°C/min heating rate for two hours to evaporate any volatile content in the shells. The stabilized nutshells were immersed in a 1 wt% KOH solution, and the soaked shells were placed in a vacuum desiccator at 22 inHg pressure for 30 minutes to evacuate any trapped air. Then the nutshells were soaked in the KOH solution for twelve hours for chemical activation. Following this, the solution was drained out, and the nutshells were dried in an oven at 85°C for two hours prior to carbonization. The dried shells were carbonized in a tube furnace (Figure 3.6), holding it at 700°C for two hours at 5°C/min heating rate with a continuous flow of argon gas. The argon gas flow was used to ensure that the carbonization process would occur in an inert environment. The carbonized nutshells were washed at least three times with a 36% HCl solution to neutralize any KOH content in the shells, and then the shells were washed again at least three times with DI water to remove any additional HCl content. The shells were dried in oven at 105°C for two hours to evaporate the water content and collect the activated carbons, which were ground using
a mortar and pestle for thirty minutes to make activated carbon powders. Carbonization at 900°C was followed similarly for both pistachio and acorn shells. Activated pistachio shells carbonized at 700°C and 900°C were labeled P700 and P900, respectively, and activated acorn shells carbonized at 700°C and 900°C were labeled K700 and K900, respectively.

![Figure 3.6. Tube furnace (MTI Corporation/OTF-1200X) used for carbonization with argon gas flow](image)

### 3.3.2 Construction of Electrodes

Layouts 2 cm by 2 cm and 0.13 mm thick were created using Scotch tape on aluminum foil. Polyvinylidene fluoride was used as a binder with the activated carbon powders. The DMAC solvent and acetone (70:30 weight ratio) were mixed with 5 wt% PVdF and stirred with a magnetic stirrer for four hours at 50°C on a hot plate. Then the AC was dispersed into a PVdF solution (50:50 weight ratio) using a magnetic stirrer for five minutes. The slurry was placed on the aluminum foil layouts, maintaining the dimensions, to construct the carbon electrodes. Finally, the electrodes were kept in oven at 120°C for four hours to dry the slurry mixture and make the solid carbon electrodes. Figures 3.7 (a) and (b) show steps in the electrode construction of the EDLC, and Figure 3.7 (c) shows the assembled EDLC.
3.3.3 Preparation of Electrolyte

The organic electrolyte was prepared using 1 M TEABF$_4$ and PC. Lens tissues (2 cm by 2 cm) were immersed into the electrolyte and kept in a vacuum desiccator for 30 minutes, in order to be properly soaked.

3.3.4 Assembly of EDLC

After preparing the electrodes and electrolyte, all components of the EDLC were assembled, as shown previously in Figure 3.1. One carbon electrode was placed on a PET sheet, then a TEABF$_4$-soaked lens tissue was placed on top of that. One porous paper used as a separator was placed on top of the lens tissue, and the remaining symmetric part of the EDLC was followed in a similar fashion. Figure 3.7 shows the complete assembly of the EDLC.

![Figure 3.7. Construction of EDLC: (a) electrode layout on Al foil, (b) constructed carbon electrode with separator and PET sheet, and (c) assembled EDLC](image)

3.4 Characterization

3.4.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to inspect the surface texture of the activated pistachio and acorn carbon shells and powders. A Zeiss Sigma variable pressure field emission scanning electron microscope, as shown in Figure 3.8, was used in this study. Before
the scanning process the specimens were thin-film coated with gold to make the surfaces conductive.

![Figure 3.8](image)

**Figure 3.8.** (a) Scanning electron microscope used in this study and (b) thin-film gold-coated specimens

### 3.4.2 Cyclic Voltammetry

Cyclic voltammetry (CV), a technique that is widely used in electrochemistry for its versatility, involves applying an electric potential to a working electrode which changes over time. This technique records the current flowing through the electrode as a function of applied potential, and a plot of the current vs. the applied potential, called a voltammogram, is constructed. Usually the initial potential is selected so that the chemical reagents in the capacitor are not previously oxidized or reduced. The potential of the working electrode begins with an initial potential ($E_1$) and starts to increase linearly with time to the final potential ($E_2$). Then it starts to scan reversely from the final potential ($E_2$) to the initial potential ($E_1$) value. From this, a voltammogram plot is constructed [37-39]. Cyclic voltammetry was carried out using a BioLogic SP-150 potentiostat/galvanostat (Figure 3.9). A constant pressure of 82.41 gm/cm² was kept on the sample to ensure good contact between the components during the experiment.
Figure 3.9. BioLogic SP-150 potentiostat/galvanostat used for CV technique

3.4.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful technique to analyze a component’s performance under the frequency domain. Applying alternate current impedance in an electrochemical system can also provide detailed information about the electrochemical reactions. Electrochemical measurement systems typically consist of a potentiostat together with a frequency response analyzer. Alternate current amplitude perturbation is added to a constant direct current signal with a changing frequency. By scanning the frequency, the impedance change can be recorded, and each value can be obtained. Impedance can be plotted using a Nyquist diagram as a negative value of the imaginary part on the Y-axis and the real value on the X-axis [14, 40-41].

A Gamry Series G300TM potentiostat/galvanostat/ZRA was used in this study (Figure 3.10) to perform potenti-electrochemical impedance spectroscopy. In this technique, the experiment parameters were the frequency range of 10 Hz to 300 kHz, AC voltage of
1000 mV/rms, and DC voltage of 1 V. A constant pressure of 82.41 gm/cm² was kept on the sample to ensure good contact between components during the experiment.

Figure 3.10. (a) Gamry Series G300TM potentiostat/galvanostat/ZRA for EIS technique and (b) leads connected to supercapacitor
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Carbon Yield

Pistachio and acorn shells both were carbonized at both 700°C and 900°C. Acorn shells showed a 16–20% higher percentage of carbon yield than pistachio shells. This indicates that carbonizing pistachio shells at these temperatures will leave higher carbon residue than carbonizing acorn shells at this temperature. Pistachio shells showed 60–61% and acorn shells showed 76–80% of carbon yield at 700°C and 900°C. Because there was no significant effect observed in carbon yield at these two high temperatures, carbonization at 700°C can be followed, which is believed to be more economical. Figure 4.1 shows the carbon yield of pistachio shells (P700 and P900) and acorn shells (K700 and K900).

![Carbon Yield](image)

Figure 4.1. Carbon yield of pistachio and acorn shells

4.2 SEM Analysis

The purpose of KOH activation of the charcoal is to create more surface area than would be possible with non-activated charcoal. The activation effect can be observed in SEM images
for both types of shells. An enormous surface area was created by activating the carbon shells. Figures 4.2(a), (b), and (c) depict the surface textures of activated acorn shells (K700AC) carbonized at 700°C. SEM images at different magnifications showed the porous structure created all over the surfaces. The same characteristics can be observed in activated acorn shells (K900AC) at 900°C in Figures 4.3(a), (b), and (c). But the non-activated carbonized shells of both acorns and pistachios (i.e., K700 and P700), shown in Figures 4.4(a) and (b), respectively, did not indicate any porous surface texture. Only a lamella surface was created on P700, which is believed to be due to carbonizing at a high temperature, and there were no porous or lamella structures observed in K700.

Figure 4.2. SEM images of K700AC: (a) shell surface in 200 nm, and (b) and (c) shell cross section at 1 µm and 10 µm magnification, and (d) carbon electrode made from K700AC
Figure 4.3. SEM images of K900AC shell cross sections: (a) 200 nm (b) 1 µm, and (c) 10 µm magnification, and (d) ground K900AC particles

Figure 4.4. SEM images: (a) non-activated K700 shell and (b) non-activated P700 shell
Figure 4.2(d) shows the SEM image of a carbon electrode made from K700AC. It was observed that the composite made with activated carbon particles and PVdF (as a binder) are closely connected to each other. The binder provided linkage among the porous carbon particles, formed a continuous network, and made it conductive with other activated carbon particles.

Ground carbon powders made from activated carbon shells were also examined. Figure 4.3(d) shows the SEM image of ground activated carbon particles made from acorn shells (K900AC) carbonized at 900°C. It was observed that the particles have a highly porous structure, indicating a larger surface area than non-activated particles. This larger surface area can contain more electric charges and provide more space for movement. A variation in particle size was also observed. It is believed that the hand-grinding process could not ensure homogenous particles.

In Figures 4.2 and 4.3, both activated acorns showed highly porous surfaces. But comparing SEM images of K700AC and K900AC, it was seen that K700AC showed more porous surfaces than K900AC. Again, the porous structure in K900AC looked stiffer with larger pores than the K700AC structure. The K900AC sample also experienced a more difficult grinding process than K700AC. It is believed that this might have occurred as the result of the high temperature (900°C) carbonization, which might melt more of the carbonaceous materials of the shells and create larger pores with a stiffer structure. A similar phenomenon was observed in pistachio shells, where P700AC showed a more porous surface area than P900AC. Additional SEM images of both activated and non-activated nutshells are provided in Appendix A.

4.3 Cyclic Voltammetry

Cyclic voltammetry, an important technique for electrochemical analysis of supercapacitors, involves scanning the potential of a stationary working electrode using a triangular potential waveform. During this potential sweep, the potentiostat measures the current
of the supercapacitor. A cyclic voltammogram is a current response plotted as a function of the applied potential, in order to determine the capacitance of the supercapacitor [54]. The cyclic voltammogram of an ideal capacitor is exhibited as a rectangular shape, but the voltammogram of a real capacitor, which has resistance, is a parallelogram or a similar shape [28]. Supercapacitors made with different activated carbon composites were analyzed for cyclic voltammetry. Figures 4.5 to 4.8 show cyclic pistachio and acorn shell voltammograms of P700AC, P900AC, K700AC, and K900AC, respectively, at three different scan rates of 10 mV/s, 100 mV/s, and 500 mV/s. In these figures, the X-axis represents the potential, and the Y-axis represents the current.

As can be seen in Figure 4.5, the P700AC pistachio shell supercapacitor tended to indicate more parallelogram shapes as the scan rates increased. The same phenomenon was also observed in Figure 4.7 for the acorn shell K700AC supercapacitor. It was observed that each curve has the same form of shape but total current increased with the increase in scan rate. This can be explained by the size of the diffusion layer and the scan rate. With a slow voltage scan rate, the diffusion layer will grow much faster compared with that of the fast voltage scan rate. Because current is proportional to the flux towards the electrode, the current will be smaller at the slow voltage scan rate and larger at the fast scan rate [6, 40, 60].

Both P700AC and K700AC showed good capacitive behavior in an analysis of their cyclic voltammograms. But comparing Figures 4.5 and 4.7, it was observed that Figure 4.7 (K700AC), showing an activated carbon composite from acorns carbonized at 700°C, revealed better characteristics than Figure 4.5 (P700AC). Also, in comparing Figures 4.6 (P900AC) and 4.8 (K900AC), it should be noted that P900AC, showing activated carbon composite from pistachios carbonized at 900°C, revealed little deviated parallelograms. These results are
reasonably attributed to the formation of larger porous structures in activated carbon shells at a high temperature of 900°C, which contributed less surface area than the shells carbonized at 700°C. A similar phenomenon was observed in acorn shells (K700AC and K900AC) in Figures 4.7 and 4.8, respectively. Also, K700AC deviated more than K900AC in forming parallelograms in the CV tests. Additional CV plots for different scan rates from 10 mV/s to 500 mV/s are provided in Appendix B.
Figure 4.5. Cyclic voltammogram of P700AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s (continued)
Figure 4.5 (continued). Cyclic voltammogram of P700AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s
Figure 4.6. Cyclic voltammogram of P900AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s (continued)
Figure 4.6 (continued). Cyclic voltammogram of P900AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s
Figure 4.7. Cyclic voltammogram of K700AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s (continued)
Figure 4.7 (continued). Cyclic voltammogram of K700AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s
Figure 4.8. Cyclic voltammogram of K900AC: (a) 10 mV/s, (b) 100 mV/s, and (c) 500 mV/s (continued)
Figure 4.8 (continued). Cyclic voltammogram of K900AC: (a) 10 mV/s (b) 100 mV/s, and (c) 500 mV/s

4.3.1 Specific Capacitance

The parameter of the CV technique is the scan rate $\frac{dE}{dt} = 100$ mV/s within a potential range of $\pm 0.75$V. The ohmic drop resistance is insignificant before the charge transfer resistance, and it can be neglected. Because the transport of the material does not limit the kinetics of the redox process, the transfer resistance is equal to the pseudocapacitance resistance. Assuming that the system could be modeled by a real capacitance and the resistance in parallel, equations can be calculated corresponding to the upper and lower part of the curve around the corrosion potential, which is equal to open circuit voltage. From these equations, anodic current ($I_a$) and cathodic current ($I_c$) can be extrapolated, and capacitance ($C_{dl}$) for the electric double-layer capacitor can be calculated as [10, 53]

$$\frac{I_a - I_c}{2} = C_{dl} \frac{dE}{dt}$$
For the K700AC sample shown in Figure 4.9, the capacitance, \( C_{dl} \), can be calculated as follows:

\[
I_a = 0.2 \text{ mA}, \quad I_c = 0.24 \text{ mA} \\
C_{dl} = 0.0022, \quad F = 2200 \mu\text{F}
\]

\[
\text{Specific Capacitance} = \frac{2200 \mu\text{F}}{0.24 \text{ g}} = 9166.666667 \mu\text{F/g}
\]

All specific capacitance calculations followed this same procedure.

![Figure 4.9. Steady-state curve I vs. Ewe for forward and backward voltage scan of K700AC](image)

Figure 4.10 shows the plot of specific capacitances of four supercapacitors—P700AC, P900AC, K700AC, and K900AC—as a function of different scan rates. An obvious decrease was observed in specific capacitance with the increase in scan rates using the cyclic voltammetry technique. An analysis of the results showed that P700AC and K700AC showed higher specific capacitance behavior; more specifically, K700AC showed the highest specific capacitance behavior. This phenomenon was expected after observing the CV test results. At the lowest scan
rate of 10 mV/s, K700AC showed 50,000 µF/g, P700AC showed 27,083 µF/g, and K900AC 14,583 µF/g of specific capacitance. At this scan rate, K700AC showed the highest and K900AC the lowest specific capacitance. Specific capacitance plots for every individual electrode are provided in Appendix C.

![Specific Capacitance vs Scan Rate](image)

Figure 4.10. Specific capacitance of supercapacitors as function of scan rate

### 4.4 Electrochemical Impedance Spectroscopy

Electrical impedance spectroscopy plots for electrodes P700AC, P900AC, K700AC, and K900AC are shown in Figures 4.11 to 4.14, respectively. Real impedances observed for P700AC, P900AC, K700AC, and K900AC were about 440, 600, 540, and 520 ohm, respectively. It was observed that P700AC showed the lowest real impedance of about 440 ohm, and P900AC showed the highest real impedance of about 600 ohm, indicating that P700AC had the smallest electrical energy loss and therefore should have the highest specific capacitance [12]. Again, P900AC showed the highest electrical energy loss and lowest specific capacitance. Also, apart from electrode K900AC, the other electrodes—P700AC, P900AC, and K700AC—
showed good semicircular behavior at high frequencies, meaning that all three should show good capacitive behavior at high frequencies.

Figure 4.11. Electrical impedance spectroscopy plot for P700AC

Figure 4.12. Electrical impedance spectroscopy plot for P900AC
Figure 4.13. Electrical impedance spectroscopy plot for K700AC

Figure 4.14. Electrical impedance spectroscopy plot for K900AC

Figure 4.15 shows a Nyquist plot for all four supercapacitors. It should be noted that all supercapacitors have a real impedance within 600 ohm.
Figure 4.15. Electrical impedance spectroscopy plots for P700AC, P900AC, K700AC, and K900AC
CHAPTER 5
CONCLUSION AND FUTURE WORK

2.1 Conclusion

The purpose of this study was to produce activated carbons from natural waste, such as pistachio and acorn shells. Finding a low-cost, environmentally friendly, easy-production procedure can provide a promising future for these supercapacitors. Also, a comparative study of the electrochemical characteristics of these activated carbons can suggest which one to choose.

Carbonization of pistachio shells at 700°C and 900°C showed that there was no significance difference in carbon yield. Both temperatures yielded 60–61% carbon, indicating that carbonizing can be followed using 700°C rather than 900°C, in order to be more economical. Carbonization of acorn shells at 700°C and 900°C showed that there was little difference (76-80%), in carbon yield. Carbonization of acorn shells can be followed using 700°C.

Analyzing the surface texture of the carbons by scanning electron microscopy showed that KOH activation produced a highly porous surface area for both pistachio and acorn carbons, whereas there was no porous surface observed in non-activated carbons. This highly porous surface area is the most important factor for carbon electrodes in supercapacitors. The K700AC and P700AC samples showed more porous surface textures and small pores than the K900AC and P900AC samples.

Cyclic voltammetry techniques showed more promising results for K700AC and P700AC carbon electrodes than K900AC and P900AC carbon electrodes. More specifically, K700AC electrodes showed more promising characteristics than any other electrodes. It is believed that the highly porous surface textures of K700AC and P700AC contributed good electrochemical behavior, with K700AC performing the best. This observation can also be justified in a
comparative study of specific capacitance of all electrodes. At a scan rate of 10 mV/sec, the specific capacitance of K700AC was 50,000 µF/g, and the specific capacitance of P700AC was 27,083 µF/g.

Results using the electrochemical impedance spectroscopy technique showed that P700AC showed the lowest real impedance of about 440 ohm, and P900AC showed the highest real impedance of about 600 ohm, thus indicating that P700AC has the smallest electrical energy loss and should have the highest specific capacitance, and P900AC has just the opposite characteristics. Also, apart from electrode K900AC, the other electrodes—P700AC, P900AC, and K700AC—indicated good semicircular behavior at high frequencies, implying that all three should show good capacitive behavior at high frequencies.

5.2 Future Work

In our ever-growing quest for energy storage, supercapacitors have opened a new dimension, and this field of study is still growing. There is considerable room for improvement of this technology, and this study was a beginning approach for doing that. Also, there can be many ways to improve this study. The activated carbon powders were not uniform in size because they were hand ground. A better grinding technique, such as ball mill grinding, might provide smaller and more uniform activated carbon powders.

It was noticeable at 200 nm zooming that tiny cracks appeared on the activated carbon surfaces. Zooming in further at 100 nm or less with more advanced equipment could provide more detailed information about the surface texture. The activation procedure could be further studied as well. By analyzing pore sizes and comparing them with electrolyte ion sizes, a more accurate combined electrolyte and activation procedure might be found. Because the binding material PVdF showed high resistances, a lower molecular weight PVdF or other binding
material such as poly(vinyl alcohol) could be studied. Also, the Brunauer-Emmett-Teller (BET) technique could be used to study the activated carbons for their textural characteristics, such as micro- and meso-pore sizes, pore volumes, etc.
REFERENCES
REFERENCES


REFERENCES (continued)


REFERENCES (continued)


REFERENCES (continued)


REFERENCES (continued)


[52] BioLogic Scince Instruments, Measurements of the double layer capacitance, Retrieved September 6, 2015, from http://www.bio-logic.info/assets/app%20notes/20101209%20-
%20Application%20note%2021.pdf.


APPENDICES
APPENDIX A

SEM IMAGES

K700 Non-Activated Shell
APPENDIX A (continued)

K700 Non-Activated Shell (10 µm magnification)
APPENDIX A (continued)

K700AC Electrode
APPENDIX A (continued)

K900AC Particles (200 nm magnification)
K900AC Particles
P700 Non-Activated (200 nm magnification)
APPENDIX A (continued)

P700 Non-Activated (10 µm magnification)
APPENDIX A (continued)

P900AC (200 nm magnification)
APPENDIX A (continued)

P900AC (1 µm magnification)
APPENDIX A (continued)

P900AC (10 µm magnification)
APPENDIX B

CYCLIC VOLTAMMROGRAMS

K700AC at Different Scan Rates

![Image of cyclic voltammograms]
APPENDIX B (continued)

K900AC at Different Scan Rates
APPENDIX B (continued)

P700AC at Different Scan Rates

![Graph showing the relationship between \( <i> \) vs. \( E_{we} \) at different scan rates.](image-url)
APPENDIX B (continued)

P900AC at Different Scan Rates

![Graph showing cyclic voltammetry results for P900AC at different scan rates. The graph plots the current density (mA) against the potential (mV vs. SCE). Multiple curves are shown, each representing a different scan rate.](image-url)
APPENDIX C

SPECIFIC CAPACITANCE

K700AC

![Graph showing Specific Capacitance (μF/g) for K700](image)

K900AC

![Graph showing Specific Capacitance (μF/g) for K900](image)
APPENDIX C (continued)

P700AC

Specific Capacitance (µF/g) P700

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P900AC

Specific Capacitance (µF/g) P900

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