

ENHANCING LITHIUM ION BATTERIES THROUGH CATION DOPING  
AND GRAPHENE COATING

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An Honors Thesis

Presented to

The Faculty of the Department of Physics  
Sam Houston State University

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In Partial Fulfillment  
of the Requirements for the Degree of  
Bachelor of Science

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by

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July 2019

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## **DEDICATION**

This thesis is dedicated to my parents who have helped support me throughout my college career at Sam Houston State University. As well to my family who has influenced my character and are my motivation.

## ABSTRACT

Zavala, Caleb Alexander, *Enhancing Lithium Ion Batteries Through Cation Doping and Graphene Coating*. Bachelor of Science (Physics), July, 2019, Sam Houston State University, Huntsville, Texas.

$\text{LiFePO}_4$  has emerged as one of the most promising cathode materials for lithium ion batteries for a large variety of applications from smart phones and power tools, to electric vehicles. However, poor electronic conductivity and low lithium ion diffusion rate hinders its large-scale applications. It has been demonstrated that the electronic conductivity of  $\text{LiFePO}_4$  can be improved by several methods, including powder size reduction, carbon layer coating, and lattice doping. In this research, we investigate the effect brought by the combination of cation doping and carbon layer coating. Zr or Ti cation doped  $\text{LiFePO}_4$  is synthesized using solid-state reaction. Graphene or glucose is used as a carbon coating agent. Phase and morphology of as-prepared powder are characterized by X-ray diffraction. Electrochemical properties are characterized by charge-discharge measurement at various rate. Results of these measurements were analyzed and are represented in Figure 10 and Figure 11, which display the specific discharge and charge capacity per milliamperes an hour per gram ( $\text{mAh/g}$ ) for a 55-cycle number. These results determined that  $\text{LiFePO}_4$  with a glucose carbon coating agent was the cathode material with the best and most consistent results.

## **ACKNOWLEDGEMENTS**

First, I would like to thank my thesis chair, research mentor, and Professor Dr. Hui Fang, for allowing me to use his laboratory, instructing me in the research process, and helping me whenever I had questions. I would also like to thank the Ronald E. McNair scholars program, as well as, the Elliot T. Bowers Honors College for allowing me the opportunity to write this thesis and for all their assistance in preparing me for this research project. I also want to recognize my fellow student Clayton Ellinwood for his contribution in the research. Clayton excelled in battery assembly which helped tremendously with completing the project.

## PREFACE

A requirement for being a Ronald E. McNair scholar at Sam Houston State University is that each student needs to conduct a research project under a Ph.D. professor at Sam Houston State University; either a project in their same major or a project that the student is interested in. After my acceptance in the McNair program in the 2017 fall semester, I started searching for a research mentor in November of 2017. I knew from the beginning that I wanted a research project within the field of physics. I started searching for a research project by talking with each professor in the physics department to discuss their current research and future research projects, and the requirements for participating students. The two main research projects being conducted at the time was a particle physics project which entails extensive computer programming; however, I could not see myself pursuing the particle physics field. The second research project investigated lithium ion batteries. After I met with Dr. Hui Fang, I became very interested because this type of research was very applicable to modern technology and the entire research process was interactive. Once I decided on pursuing this lithium ion project, I talked with Dr. Hui Fang about when I could start on the research and he replied that I could start the project at the beginning of the spring 2018 semester. Dr. Hui Fang sent me research papers during this time to learn about the history, current status, and terminology of lithium ion batteries. He intended to adjust me to the research process during the 2018 spring semester, and to complete the research in the summer. The agenda for that semester was for two other students and I to meet every Friday in Dr. Hui Fang's lab and make the powder compounds.

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## CHAPTER I

### Introduction

A major issue the world faces is finding a reliable and safe energy source. A vital energy source used around the world is fossil fuels, and demand for the commodity has exponentially increased over the years. Fossil fuels are a non-renewable resource and a significant amount of this resource is exported from several politically unstable countries.<sup>1</sup> Using fossil fuels as a vital energy source has caused drastic change in weather patterns and is correlated to the steady rise of the earth temperature due to the CO<sub>2</sub> emitted from burning gasoline.<sup>1</sup>

The importance of lithium ion batteries is their reliability and environmental safeness. Over the past 30 years, lithium ion batteries have become extremely popular due to their electrochemical properties and have been the most commonly chosen for rechargeable batteries.<sup>1</sup> Since the 2000's, rechargeable lithium ion batteries have risen as the most favorable battery to be used in portable devices due to their energy density and safeness. Lithium ion batteries have also made major advancements and have become safe, efficient, and powerful enough to be used in electric hybrid cars.<sup>1</sup>

The number of applications for lithium ion batteries keeps rising, which increases their potential to replace energy sources like fossil fuels in vehicles and machinery. Lithium ion batteries are becoming a major energy source due to its reliability, affordability, energy density, and environmental safeness. The production of lithium ion batteries has exponentially risen over the last 25 years and have been used as the energy source for the majority of portable electronic devices such as cell phones, tablets, power tools, etc. Due to its versatility, lithium iron phosphate (LiFePO<sub>4</sub>) has emerged as the

most popular choice for the cathodes used in lithium ion batteries.  $\text{LiFePO}_4$  has a stable and safe olivine structure and is a prime choice for cathode material because of its high capacity, cycle life, safety, power, and low cost.<sup>2</sup>

## CHAPTER II

### Methods

In my research I created cathodes for lithium ion batteries, which is the main element that determines the performance of lithium ion batteries.<sup>3</sup> I created several different types of  $\text{LiFePO}_4$  cathodes using the compounds lithium carbonate ( $\text{Li}_2\text{CO}_3$ ), Iron II Oxalate Dihydrate ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ), ammonium phosphate dibasic ( $(\text{NH}_4)_2\text{HPO}_4$ ), titanium IV methoxide ( $\text{Ti}(\text{OCH}_3)_4$ ) or zirconium ethoxide ( $\text{Zr}(\text{OC}_2\text{H}_5)_4$ ), as well as, carbon coating elements glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) or graphene. A total of five compounds were used to make the basic compound powders used for the cathodes. Each powder was synthesized by a solid-state reaction to create compounds of  $\text{LiFePO}_4$  and all the cathodes created are listed in table 1. Table 1 lists  $\text{Li}_{0.96}\text{Ti}_{0.01}\text{FePO}_4$  or  $\text{Li}_{0.96}\text{Zr}_{0.01}\text{FePO}_4$ , and the Zr 0.01 or Ti 0.01 represent a 1% doping with titanium of zirconium. The reason for a small dosage of titanium or zirconium is because it has been shown to optimize the cathodes electrochemical performance.<sup>4</sup>

$\text{LiFePO}_4$  belongs to the olivine group which is a material with low electronic conductivity, meaning that the particles have low electrochemical properties.<sup>3</sup> One way that this project tried to deal with this problem was through, "Cation Doping on  $\text{Li}^+$  and  $\text{Fe}^+$  and carbon coating which have been shown to increase the electronic conductivity up to an order of magnitude  $10^8$ ."<sup>4</sup> Another way that this project tried to improve the electronic conductivity was through carbon coating. The carbon coating was done by adding and alternating between graphene, a 2-dimensional material made of carbon, and alternated with glucose, another material which contains a high amount of carbon. The carbon from these materials created a carbon film over the cathode surface, with the

purpose of helping the flow of electrons from the current collector, and improving the surface conductivity of the cathode.<sup>2,3</sup>

The goal of this research was to create a cathode material with improved electrochemical abilities, such as improving the charging/discharging rate and cycle life. In this research, the cathodes were the only variable changed. The cathode was paired with a lithium ribbon anode, a 25 $\mu$ m microporous monolayer membrane, and a battery electrolyte (lithiumhexafluorophosphate in ethylene carbonate: diethyl carbonate 1:1). The cathode materials were synthesized by solid state reactions and were tested for the correct lattice structure by using a Rigaku MiniFlex 600 X-ray diffractor. That data was then compared to the lattice structure of LiFePO<sub>4</sub>. Since the cathodes were slightly doped with titanium or zirconium, the lattice peaks differences should not have been changed much, so comparing the structure against the lattice peaks of LiFePO<sub>4</sub> was a good way to check that the cathodes were the compounds desired. After verifying the compound, a pestle and mortar were used to mix the cathode together using the synthesized compound, carbon black, and teflon (biding agent), for a 1 gram ratio of 75:20:5. The cathode was then flattened and had ¼ cm holes punched into the flattened cathode to make around 4-7 cathodes to be used in the batteries. The cathode was left to dry for a day and was weighed and labeled the following day. The next step was to assemble the batteries in an airtight glove box filled with argon. Argon was used because it is a noble gas and does not react with the compounds, which was especially important when using a lithium ribbon anode because the element lithium corrodes and is flammable when exposed to oxygen. Once the batteries were assembled, they were taken out of the glove box, wiped down, labeled with the corresponding cathode, and then each battery voltage was checked

and recorded. The batteries were placed in an Arbin Instrument Bt-2000, which ran several tests on the batteries and gave the results used for the data analysis for the cathodes electrochemical properties. The results from this instrument were in terms of galvanic charge and discharge, cycle life power density, and capacity.<sup>4</sup>

Table 1

Cathode Materials: Different Compounds Created

| Compounds added to $\text{LiFePO}_4$ | Compounds Synthesized                           | Carbon Coating Element |
|--------------------------------------|-------------------------------------------------|------------------------|
| Titanium                             | $\text{Li}_{0.96}\text{Ti}_{0.01}\text{FePO}_4$ | Glucose                |
| Zirconium                            | $\text{Li}_{0.96}\text{Zr}_{0.01}\text{FePO}_4$ | Glucose                |
| None                                 | $\text{LiFePO}_4$                               | Glucose                |
| Titanium                             | $\text{Li}_{0.96}\text{Ti}_{0.01}\text{FePO}_4$ | Graphene               |
| Zirconium                            | $\text{Li}_{0.96}\text{Zr}_{0.01}\text{FePO}_4$ | Graphene               |
| None                                 | $\text{LiFePO}_4$                               | Graphene               |

*Note:* In total, six different compounds were created for my part of the project.

## CHAPTER III

### Experimental Process

#### Powder Creation

The research process was a challenge and required a lot of patience because every step was very hands on, and a lot of the cathode process required several steps with precise measurements. For the completion of a synthesized  $\text{LiFePO}_4$  compound, I had to weigh 5 different compounds and each compound was measured to  $\pm .0001$  of a gram. Making the compounds varied slight depending on if the material was made with glucose or graphene for the carbon coating agent. The compounds were placed in a steel vial with steel balls, which was weighed each time to be around 60 – 59.000 g. The purpose of this measurement was to ensure that the ball to powder mass ratio was 20:1, to insure a good mixture of the compounds. If the compound was made with glucose as the carbon coating agent, then glucose would have been weighed and placed in the with the other elements as seen Figure 1.



Figure 1. Compounds and steel balls in a steel vial. M. Semmlinger, B.S. thesis, Sam Houston State University, 2015.<sup>5</sup>

The vial would then be filled approximately 1/3 with ethanol, as seen in Figure 2 and placed for 90 minutes in a SPEX 8000 Mixer machine. After this step, the liquid compound, if made with glucose, was placed in a beaker and left to sit in a hot oven box and left-over night to dry. If the compound had graphene as a carbon coating agent, then after the ball milling stage the compound was placed in an Erlenmeyer flask and a weighed amount of graphene was added to the compound. The flask would then be sealed as seen in Figure 3: placed in a sonicator for 120 minutes to create a good mixture between the compound and graphene.



Figure 2. Base compounds in a steel vial filled 1/3 way with ethanol. M. Semmlinger, B.S. thesis, Sam Houston State University, 2015.<sup>5</sup>

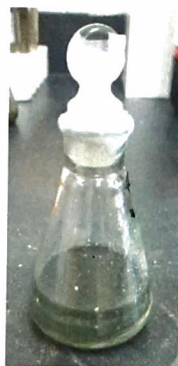


Figure 3. Base compounds mixed with graphene in Erlenmeyer flask

The compound was then placed in a beaker or ceramic dish and was set to dry in a hot oven box overnight. The dried compound is demonstrated in Figure 4.



Figure 4. Dried compound material made with graphene.

The dry compound would then be set in a glass pipe filled with flowing argon and heated in a furnace. The furnace would start at room temperature, increase to 350 degree C° and stay at 350 degree C° for 10 hours. The furnace would then be increased to 700 degree C° and stay there for 5 hours. After that, the furnace will be cooled down to a room temperature. The purpose of this process is to synthesize the compounds by a solid-state reaction and create the desired compound. The result of this process is portrayed in Figure 5. The compound in Figure 5 would then be crushed into a fine powder and placed in a small glass container.

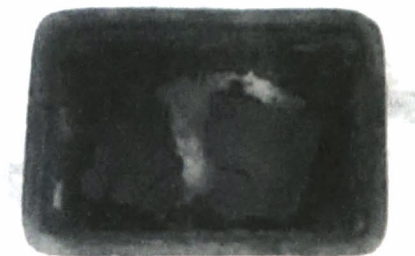


Figure 5. Compound after the furnace process. M. Semmlinger, B.S. thesis, Sam Houston State University, 2015.<sup>5</sup>

## Cathode Preparation

In creating the cathodes 1 gram worth of substances were measured and contained the powder compound, carbon black, and Teflon (binding agent) for a ratio of 75:20:5. The weighed substances were then placed in pestle and mortar and a few drops of ethanol were added. Next, I mixed the materials together for approximately 20 minutes to create a cathode as depicted in Figure 6. Once I could tell that the compounds were mixed well, I proceeded to roll out and flatten the cathode with a metal rod. Then as depicted in Figure 7, I punched out  $\frac{1}{4}$  cm holes from the rolled-out cathode and on average was able to get 4 to 7 cathodes made per 1 gram.



Figure 6. Cathode material after the pestle and mortar process. M. Semmlinger, B.S. thesis, Sam Houston State University, 2015.<sup>5</sup>

The cathodes were then placed in an oven box to dry overnight and the following day each cathode was weighed and labeled.

## Battery Assembly

The final step of the experimental process was battery assembly. The materials used in making a battery were a coin cell battery shell, one of the made cathodes, two 25 $\mu$ m microporous monolayer membranes, a punched-out lithium ribbon anode, three nickel mesh spacers, and a battery electrolyte (lithiumhexafluorophosphate in ethylene carbonate: diethyl carbonate 1:1).

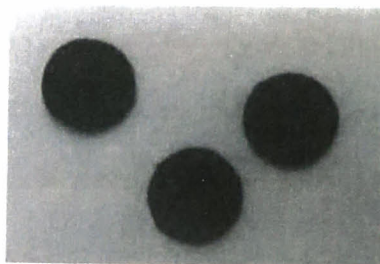


Figure 7. Three punched out cathodes. M. Semmlinger, B.S. thesis, Sam Houston State University, 2015.<sup>5</sup>

An example of how the batteries would be built is shown in Figure 8. All these materials were prepared in bulk, placed inside an airtight glove box filled with argon to prevent the corrosion of any of the materials, and were assembled. After all the batteries were completed for the day, the batteries would be taken out of the glove box, cleaned, labeled, and then each battery's voltage was checked.

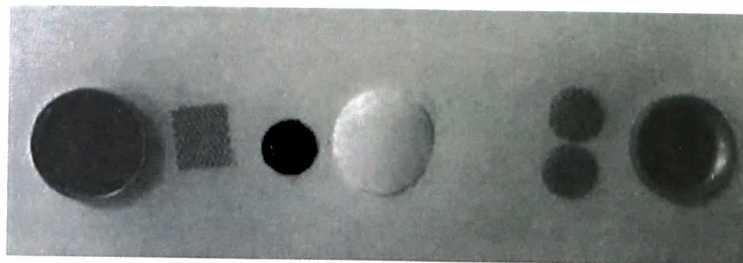


Figure 8. Example of the materials used in the battery assembly process. M. Semmlinger, B.S. thesis, Sam Houston State University, 2015.<sup>5</sup>

## CHAPTER IV

### Data Analysis

#### X-Ray Diffractions

The first data analysis dealt with checking the X-ray diffraction patterns of each powder compound created and comparing them to that of the X-ray diffraction pattern of  $\text{LiFePO}_4$ . Figure 9 is a chart of peaks vs degree with the six-powder compounds created. The X-ray diffractor started at  $15^\circ$  and rotated to  $80^\circ$  and the results are as seen in Figure 9. All the X-ray diffraction patterns are stacked on top of each to compare their peaks because the slight amount of differences in the compounds should not have changed its peak structure much. This graph was then checked against a computer database to compare against the X-ray diffraction pattern of pure  $\text{LiFePO}_4$ . The powders that did not have large peak discrepancies were used in creating the cathodes.

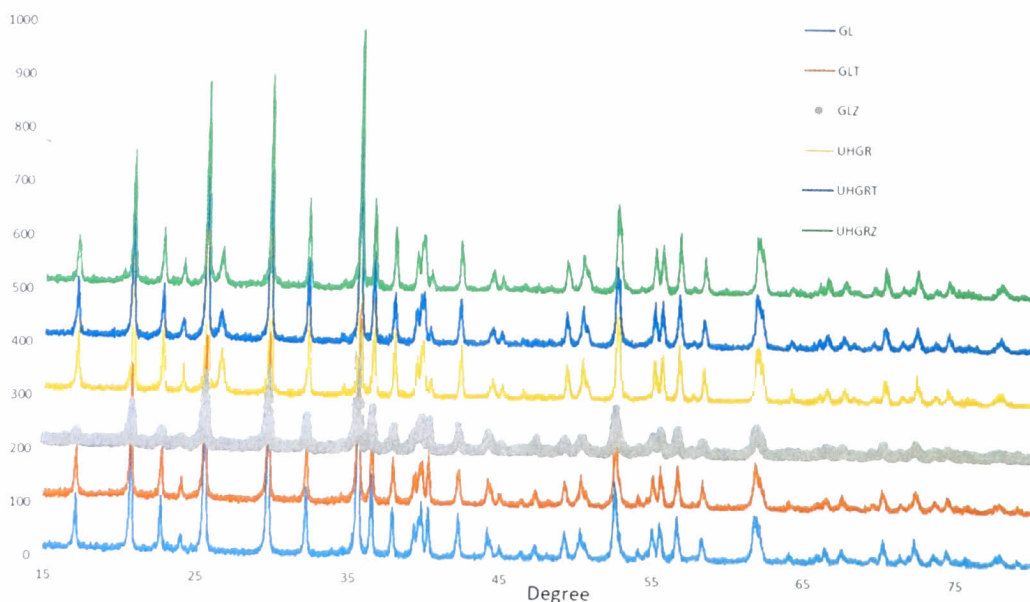


Figure 9: X-ray diffraction patterns of the 6 powders. The labeling of the table is as so cathode made from Glucose only (GL), Glucose with titanium (GLT), Glucose with Zirconium (GLZ), Graphene added only (UHGR), Graphene and titanium (UHGRZ), and

Graphene with zirconium. (UHGZ).

## **Battery Results**

In this project 6 different types of cathodes were created and approximately 4 to 6 batteries of each cathode were made per round. The 4 batteries from each batch with the best voltages were placed in an Arbin Instrument BT-2000. The batteries were tested in this machine for approximately a week, charging and discharging faster as time increased. The machine increased and decreased in voltage over a 55-cycle number period. Over 3 months, the battery assembly process was repeated 3 times due to difficulties with the glove box and other small errors. The first batch of batteries assembled led to little to no results because the glove box was contaminated with outside elements, such as oxygen and effected several materials used in the battery. The glove box problem was fixed by purging the glove box with two tanks of argon, this process cleansed the air and ensured that only pure argon was left inside, and was completed right before the battery assembly process. The second batch of batteries assembled lead to poor results that were much lower than anticipated and had to be redone. The problems with the second batch was caused by an undetermined step during the battery assembly process and the battery electrolyte used was thought to be a cause for poor results. This problem was resolved in the third batch by neatly assembling each battery and using a newly purchased battery electrolyte. By the end of the summer, about 110 batteries where made for this research project. Figures 10 and 11, show the best result from each type of cathode and are displayed in a specific discharge and charge capacity per milliamperes an hour per gram (mAh/g) for a 55-cycle number. These results determined that  $\text{LiFePO}_4$  with a glucose carbon coating

agent (represented by B44 in Figure 10 and 11) was the best and most consistent cathode material. Even though  $\text{LiFePO}_4$  with a glucose carbon coating agent (B44 in Figure 10 and 11), is shown to have lower specific discharge and charge capacity than  $\text{Li}_{0.96}\text{Ti}_{0.01}\text{FePO}_4$  with a glucose carbon coating agent (B62 in Figure 10 and 11), it was chosen as the best material because it was more stable than  $\text{Li}_{0.96}\text{Ti}_{0.01}\text{FePO}_4$  with glucose and produced the second highest results. The stability was determined by viewing the specific discharge and charge capacity vs cycle number for each cathode type. The cathode material  $\text{Li}_{0.96}\text{Zr}_{0.01}\text{FePO}_4$  with a graphene carbon coating agent, showed to be the most stable, but had a low specific discharge and charge capacity.  $\text{Li}_{0.96}\text{Ti}_{0.01}\text{FePO}_4$  with a glucose and graphene carbon coating agent both showed to be the most unstable of the cathode materials produced, and was the most difficult to mix during the pestle and mortar process.  $\text{LiFePO}_4$  with a graphene carbon coating agent and  $\text{Li}_{0.96}\text{Zr}_{0.01}\text{FePO}_4$  with a glucose carbon coating agent both showed to have similar specific discharge and charge capacity, but  $\text{LiFePO}_4$  with graphene had more consistent results.

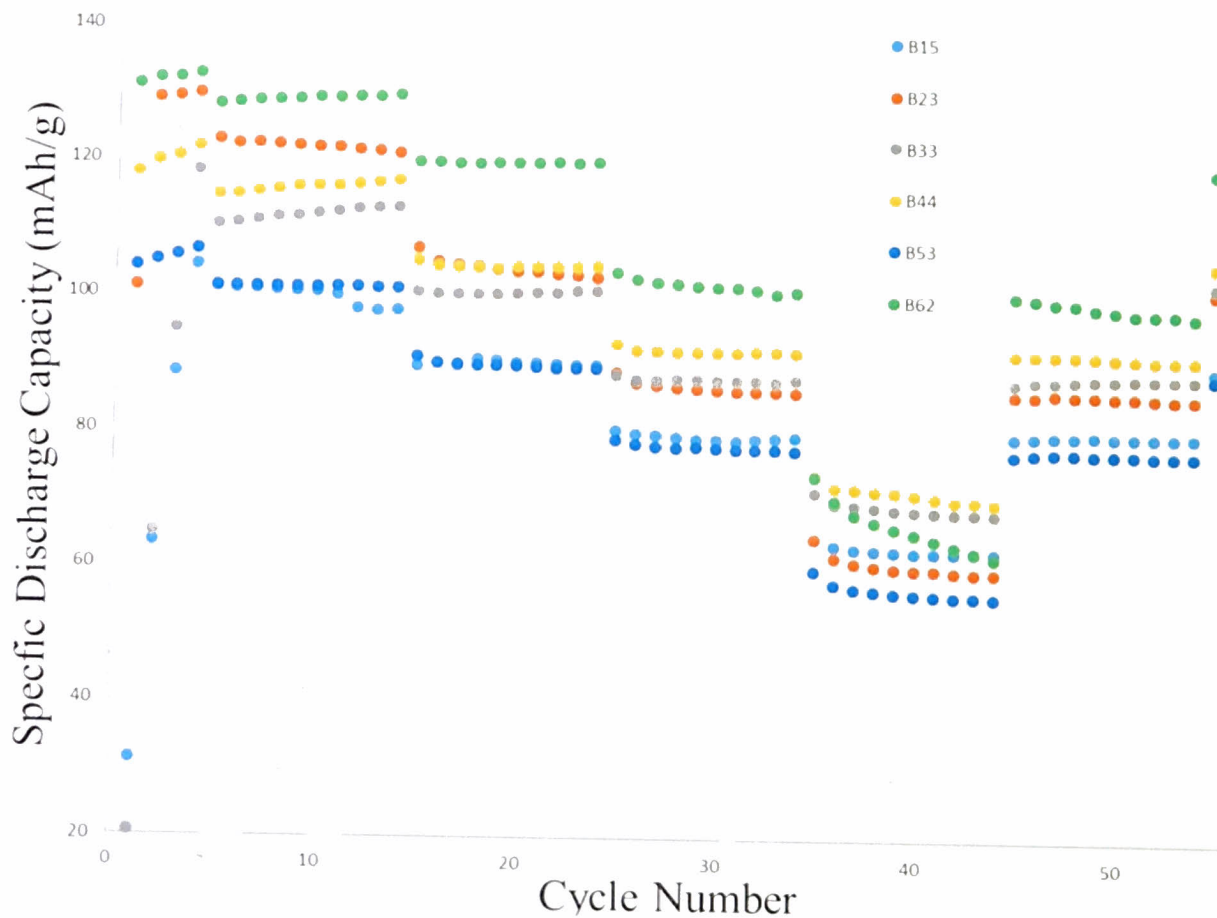


Figure 10: Specific Discharge Capacity v. Cycle Number. The labeling of the table is graphene carbon coating with titanium (B1), graphene carbon coating (B2), glucose carbon coating with zirconium (B3), glucose carbon coating (B4), graphene carbon coating with zirconium (B5), glucose with titanium (B6).

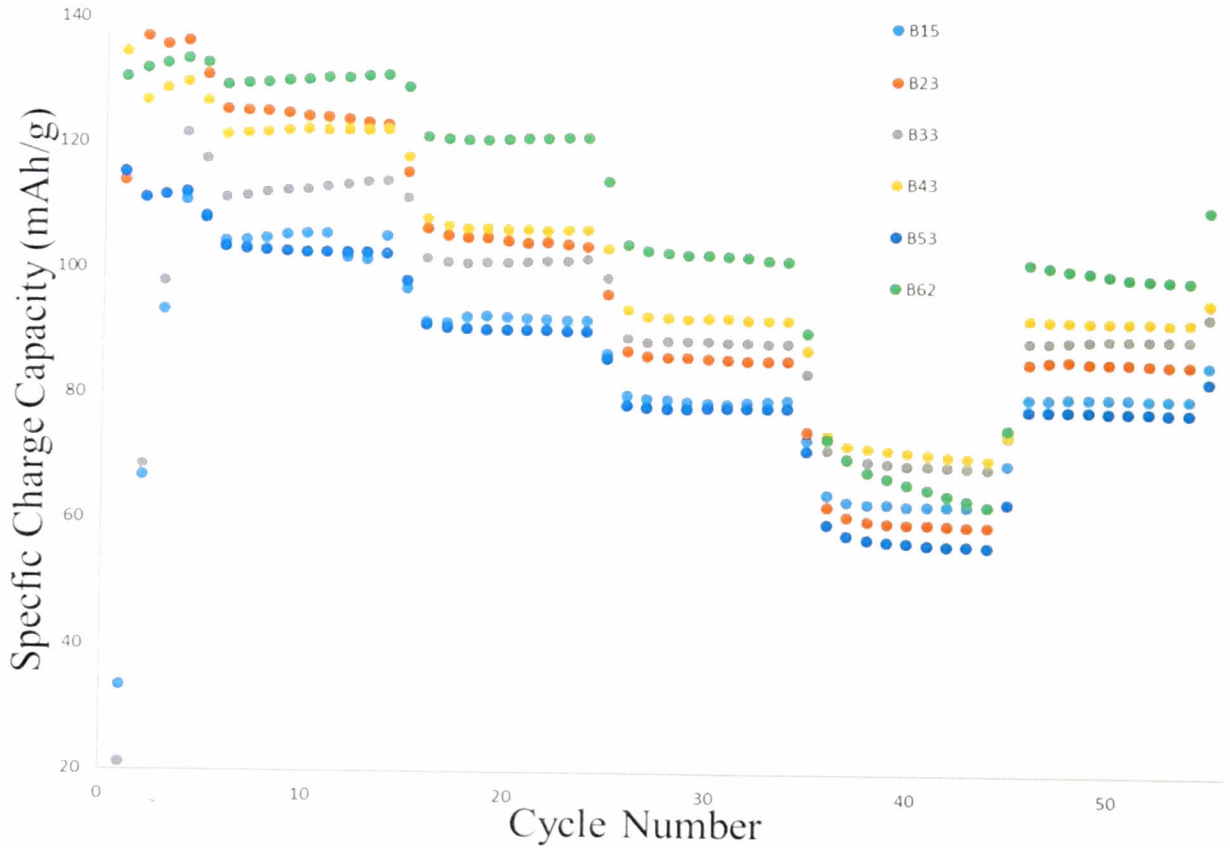


Figure 11: Specific Charge Capacity vs Cycle Number. The labeling of the table is graphene carbon coating with titanium (B1), graphene carbon coating (B2), glucose carbon coating with zirconium (B3), glucose carbon coating (B4), graphene carbon coating with zirconium (B5), glucose with titanium (B6).

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## **APPENDIX**

Some of the figures used in this thesis came from a thesis of a former Sam Houston State University student Michael Semmlinger. I was in direct contact with Michael Semmlinger via email and was granted permission to use photos that he had taken and used in his thesis.