Electrical Conductivity and Raman Spectroscopy Measurements of Electrodes for LiFePO$_4$ Battery

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The benefit of LiFePO$_4$ as a cathode material in rechargeable batteries has sparked considerable research interest. The 2015 Research Experience for Undergraduates (REU) in Physics at Howard University provided an opportunity to examine the electrical conductivity of carbon-coated LiFePO$_4$. 4-Point Probe resistivity testing shows that the cathode has an electrical conductivity value of $\sigma = 1.45 \times 10^{-7}$ S/cm which is in good agreement with values reported in the common literature. In later research, an increase in magnitude to $\sim 10^{-4}$ S/cm is expected with the insertion of gold nano-particles. This could place the LiFePO$_4$ combination in the class with high rate competitors such as LiCoO$_2$ and LiMn$_2$O$_4$.

I. INTRODUCTION

The many advantages of LiFePO$_4$ as a cathode material has made it a strong candidate to be examined, tested, and characterized at many institutions. Its capabilities include great thermal tolerance, strong charge and discharge cycling, inexpensive resourcing, and green advancing for the environment. These benefits, along with its impressive energy density[1], have enabled LiFePO$_4$ to be one of the best components for rechargeable hybrid vehicles. The performance of a battery depends heavily on the electrochemical potentials of its materials. Coin-Cell batteries are the simplest to investigate because they are easy to construct and consist of only one electrochemical cell. This cell stores chemical energy in two electrodes with different potentials, a reductant (the anode) and an oxidant (the cathode). The anode has a low potential with electrons at a high energy level whereas the cathode has a high positive potential that attracts electrons.

Inside the battery, these two electrodes are separated by a thin separator film, usually a porous electronic insulator, and an electrolyte that allows positive ions to freely flow through. Once the anode and the cathode are connected through positive and negative terminals and a metallic conductor, the highly energized electrons are forced to flow through the conductor, thus producing electricity. After powering through an external electrical load, the electrons continue flowing into the cathode where they remain at the higher, positive potential. The positive Li-ions, which were neutralizing the anode, simultaneously flow through the conductive electrolyte to recombine with electrons at the cathode.

To maximize the total voltage of a battery, the transport of electrons between cathode and anode has to be as smooth and efficient as possible. The unique olivine-structured LiFePO$_4$ allows oxygen ions to form sturdy bonds with phosphorous ($5^+$) atoms which create PO$_4^{3-}$ poly-anions in a tetrahedral configuration that stabilizes the three-dimensional construction and increases the overall durability of the molecule[2]. Although this capability enhances the endurance of the battery in temperate climates, it unfortunately decreases the electronic conductivity of the cell. The overall goal of the Williams research group is to find a way to enhance the electrical conductivity of LiFePO$_4$, while maintaining its positive characteristics.

II. BACKGROUND-OPERATION OF LIFEPO$_4$ BATTERY

LiFePO$_4$ batteries are a great competitor against other batteries because of their ability to handle hundreds of cycles of charge and discharge. This cycle begins from the material in the anode and reaches its halfway point at the cathode before being reversed. To get the best performance out of the battery, the components must allow as many electrons and positively charged Li-ions to flow at an optimal rate in every aspect of the chemical reaction. Graphitic carbon has been known to work competently as the main, active ingredient in the anode. It provides a low electrochemical potential for electrons and is also very affordable. This influenced the decision to use carbon black powder (CB) in the recipe for crafting the anode.

Once a circuit is completed, the electrons enter discharge phase and flow to a higher potential at the LiFePO$_4$ cathode. There, the electrons interact with positive Li-ions until no more electrons can be accommodated. At this point, the battery is unable to provide any more electricity. Charging is done by applying an outside current that reverses the electrochemical reaction to its initial state. The reversible process is shown here: LiFePO$_4$ $\equiv$ FePO$_4$ + Li$^+$ + e$^-$. When the electrons leave the cathode, the Li-ions become positive again which forces them follow the electrons on a different route through the electrolyte-soaked separator. The strong bonding of the FePO$_4$ molecules that are left behind prevents impurities in the cathode that causes charging and discharging performance to decrease. This

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enables the battery to endure many repetitive cycles.

![FIG. 1. The internal construction of a LiFePO₄ battery.](image)

**III. CONSTRUCTION OF ELECTRODES**

Each electrode goes through a similar process when being constructed. All powders are first stirred together in a beaker then placed on a vortex machine for approximately 8 minutes. The result is a uniform, solid-colored powder. Next, the blend of powders is placed into a beaker and stirred by hand with just enough N-Methylpyrrolidone (NMP), a solvent used to dissolve the binder material called polyvinylidene fluoride (PVDF). PVDF adds a great deal of viscosity whereas NMP liquefies the solution to achieve the target viscosity. All ingredients are then placed onto a vortex machine for about 30 minutes or until the solution is homogenized and contains no visible beads. A doctor blade is set for a thickness of approximately 0.080mm and used to spread the slurry on either a copper foil substrate (anode) or an aluminum foil substrate (cathode). The solutions were dried on a hot plate for approximately 15 minutes at a temperature of 70°C. The final dried product has a solid, smooth texture that enables it to be cut into small, 19mm discs for CR2032 battery assembly.

![FIG. 2. (a) Delamination due to excess PVDF. The anode film can closely resemble a piece of a black plastic bag. (b) Brittle cracking due to excess carbon black and not enough binder.](image)

**A. Anode-Carbon Black**

The viscosity of the anode slurry should be in the range between 4,500 and 5,500 cps (about Karo syrup) before baking in an oven or on a hot plate. Figure 2a displays delamination of anode paste due to slurry preparation which occurs when there is an excess of PVDF. Figure 2b displays a cracking effect that can result from a lack of PVDF or an excess amount of CB and NMP. The weight percentages that seemed to work the best with CB and PVDF were 64 : 36 wt%.

![FIG. 3. (a) SEM reveals the granules of LiFePO₄. (b) TEM image of the very thin carbon-coating.](image)

**B. Cathode- LiFePO₄**

The cathode slurry, made with LiFePO₄, PVDF, CB, should have a slightly thicker viscosity (approximately 6,000 cps) than the anode. It is important to keep LiFePO₄ as the most abundant ingredient in the composition so that the amount of Li-ions and overall energy density of the battery can be maximized. The weight percentages of LiFePO₄:PVDF:CB were 94.5 : 3.5 : 2.0 wt%. Figure 3a is an SEM image of the LiFePO₄ powder and figure 3b is a TEM image of the thin layer of carbon coating on a LiFePO₄ grain.

**IV. CHARACTERIZATION**

Raman spectroscopy was employed to investigate the vibrational modes of carbon and LiFePO₄. This allowed us to compare and contrast with common vibrational signatures. Results confirmed that our carbon black was truly carbon due to its characteristic bands. The LiFePO₄ spectra agree with others shown in the literature. 4-point probe resistivity testing provided quantitative data about the electrical performance of the cathode.
A. Raman Spectroscopy

A 720nm laser was used on the carbon black to excite its characteristic modes. The peaks are shown in figure 4a are the D-Band and G-Band readings at 1,600 and 1,300 cm\(^{-1}\), respectively. These modes represent the carbon’s in-planar stretching of the sp\(^2\) configuration.

For the LiFePO\(_4\), a 518nm laser was needed to penetrate the layer of carbon-coating that is placed by factory manufacturing standards. The coating helps facilitate the transport of electrons between the charge-discharge cycle. Figure 4b exhibits a tall peak between 900-1,100 cm\(^{-1}\) which is caused by a combination of P-O-P vibrations in the P\(_2\)O\(_7\) group and anti-symmetric PO\(_4\) stretching vibrations in the PO\(_4\) group[2]. The peaks that are observed below 600 cm\(^{-1}\) are a result of vibrational modes from free PO\(_4\) ions[2].

B. 4-Point Probe Resistivity Test

With the help of the Howard University nanotechnology lab, electrical conductivity measurements on the cathode were recorded using the four point probe method. Figure 5 is a schematic of the 4-point probe measurement apparatus. This method uses Ohm’s law, \(V=IR\), to measure the resistivity, \(\rho\), of the electrode. This result is then converted into the conductivity \(\sigma\). First, a current, \(I\), flows through the two outer probes, then the difference in voltage, \(V\), is measured between the two inner probes. The resistance, \(R\), is then calculated at different currents to obtain the average value.

In these measurements, the voltage was increased from 2.00nA to 10.00nA in five equal intervals. The resistance was calculated to be 3.0x10\(^4\)Ω. To calculate resistivity, the equation

\[
\rho = \frac{RA}{I}
\]

is used. The area \(A\) and thickness \(l\) of the LiFePO\(_4\) cathode are fixed dimensional values of the sample which are measured using a caliper.

After completing the series of four point probe measurements, the resistivity of the cathode was calculated to be 6.92x10\(^4\)Ω m, see Table I. The electronic conductivity is found by taking the inverse of the resistivity: \(\sigma = 1/\rho\). LiFePO\(_4\) is known for its sturdy framework that enables it to handle wider ranges of temperature and hundreds of charge and discharge cycles. However, LiFePO\(_4\) typically has an electronic conductivity of 10\(^{-9}\)S/cm[3]. Carbon-coated LiFePO\(_4\) has an electrical conductivity \(\sim 10^{-7}\)S/cm. Results from our work yielded a measurement of 1.45x10\(^{-7}\)S/cm which is in good agreement with carbon-coated LiFePO\(_4\).

<table>
<thead>
<tr>
<th>Test</th>
<th>Current(nA)</th>
<th>Voltage(mV)</th>
<th>Resistance(Ω)</th>
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<tr>
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<td>3.0x10(^4)</td>
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<tr>
<td>5</td>
<td>10.00</td>
<td>0.30</td>
<td>3.0x10(^4)</td>
</tr>
</tbody>
</table>

V. CONCLUSION

Results from this research portray promising progress to a balance of performance and endurance in LiFePO\(_4\) batteries. Good agreement was obtained between our electrical conductivity measurements and measured values obtained from the literature. Future endeavors include the introduction of gold nano-particles which will further increase the conductivity of these active materials.
A. Acknowledgment

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