Highly - Conductive Cathode for Lithium-Ion Battery Using M13 Phage - SWCNT Complex

By

Melanie Chantal Adams

Submitted to the Department of Materials Science and Engineering in partial fulfillment of the requirements for the degree of

Bachelor of Science

at the

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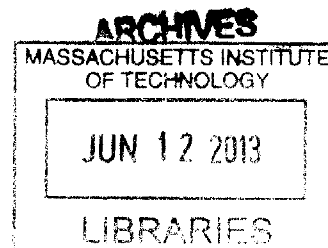

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Abstract

Lithium-ion batteries are commonly used in portable electronics, and the rapid growth of mobile technology calls for an improvement in battery capabilities. Reducing the particle size of electrode materials in synthesis is an important strategy for improving their rate capability and power density (which is the capacity at high rates). Using biological materials as a template during synthesis allows us to achieve this, improving synthesis methods. Utilizing biological materials makes it possible to synthesize nano-scale particles, and using the M13 virus has shown to be an early solution. The addition of conductive material, such as single-walled carbon nanotubes (SWCNT or CNT), also improves the conductivity of the electrode, further improving the battery's rate capabilities (Lee et al., 2009). In this study, our goal is to improve the conductivity of the LIB battery cathode using M13-carbon nanotube complexes.

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1. Introduction

1.1 Lithium-ion battery

The lithium-ion battery (LIB) is used in most common portable electronic devices, such as cellphones, laptop computers, and music players. The rapid growth of the mobile communication market demands further improvement of LIB capabilities. Though the LIB has superior energy density and self-discharge rates, one major challenge in this area is increasing the conductivity of the electrode active material to boost the capacity and the power of the battery. LIBs convert chemical energy to electrical energy, through the oxidation and reduction of lithium ions at the electrodes. Therefore, increasing transport of Li^+ ions and electrons would play a vital role in improving energy storage and charge/discharge rates.

In LIBs, the anode is the source of lithium ions and the cathode is the sink for the lithium ions. The choice for the cathode can vary depending on desired parameters. $FePO_4$ is a well-studied active material that is inexpensive, easy to fabricate, and environmentally benign which makes it an ideal for the applications of this project. Previous work has shown that the use of amorphous $FePO_4$ allows for a reduction in energy during fabrication because it can be synthesized at room temperature and ensures that at room temperature the material remains chemically active. At higher temperatures, an olivine crystalline structure can form which is much less effective and has been shown to have has a lower rate capability than amorphous $FePO_4$ [1]. While the active material is a major component of the electrode, electrochemically active materials are typically poor conductors, so carbon black is used for improved conductivity. For the physical structure of the electrode, a binder such as polytetrafluoroethylene (PTFE) is used to hold the carbon and active material together. Most electrodes of this nature are porous composites. For electrodes with these components, an electrochemical reaction can only

occur near those points where the active material, the conductive diluent (carbon black), and electrolyte meet [2]. The reaction can occur away from these points, but relies on Li diffusion and electron conduction through the active material, which can be slow.

1.2 Function of Phage

Decreasing the size of the active materials into the nanoscale regime, increases contact area which helps to boost the performance of the battery. Even with recent progress in synthesis methods, reducing the size of the particles is a challenge. However, utilizing biological materials make it possible to have nano-scale sized particles, and using the M13 virus has shown to be an early solution [3].

M13 is a filamentous bacteriophage that is composed of circular single stranded DNA and 6 proteins. Five of these are coat proteins and pV (p5) which is inside binding the DNA. It offers a genetically tunable platform to engineer binding specificities that facilitate the synthesis of electrochemical nano-scale active materials. The M13 capsid, almost a micron long, proves to be multifunctional with 2,700 copies of the pVIII (p8) protein, five copies of the pIII (p3) and pVI (p6) proteins each at the proximal end of the phage, and roughly five copies each of the pVII (p7) and pIX (p9) proteins forming a blunt distal end (Figure 1).

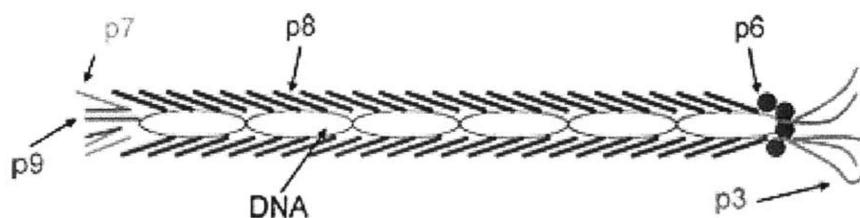

Figure 1. Schematic of the M13 phage and the location of protein groups [4].

All five surface exposed proteins are genetically modifiable, with p3, p8, and p9 being the most solvent exposed. Through biopanning, the desired protein can be obtained by exposure to the target substrate [5]. Biopanning is a process that isolates viruses with high binding affinity to the target molecules in a coated plate. The targets for use in this type battery are the nanotubes. The phage that do not bind to the target strongly are washed away at a lower pH and the remaining phages are amplified though bacterial infection.. Biopanning continues until a phage that has the most effective DNA fragment for binding to the target is selected [6]. The two phage types used are M13 phage clones, named DSPH and EFE. Genes that code for proteins in the phage, namely p3 and p8 are modified to serve as templates for amorphous iron phosphate growth [3]. These are accomplished by synthesis processes involving the use of DSPH and EFE. DSPH corresponds to attaching SWCNT to the p8 protein and EFE to p3.

1.3 Single walled carbon nanotubes

Uniformly attaching single wall carbon nanotubes (SWCNTs) to the M13 virus p8 protein and synthesizing the active material on this complex will help to increase the material conductivity. Through the use of an engineered bacteriophage, a specific number (1-10) of the SWCNTs can attach to the major protein coat (p8) of M13 [7]. Controlling the number SWCNTs allowed to bind to the protein will allow for incremental monitoring of the impact that nanotubes have on improving battery function.

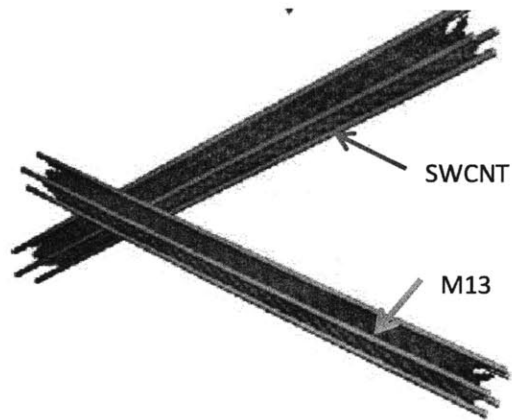

Figure 2. The virus/SWCNT complex. The SWCNTs are shown in blue and the M13 phage is shown in purple [7].

Attaching carbon nanotubes to p8 will increase surface contact to the active material, improving upon the impact of carbon black to increase conductivity. Though p3 is less abundant, attaching carbon nanotubes there will also function to increase surface contact to the active material. This should allow for a decrease in carbon black content in forming the electrode while obtaining similar or better results.

2. Materials and Methods

2.1 Phage amplification

Procedure followed for amplification of DSPH and EFE is based on "Protocol for amplification of virus in large-scale" by Hyunjung Yi – January 25th, 2010.

For 1L of culture: final virus concentration is about 10^{13} pfu total (or 10^{14} based on nano-drop measurement).

Overnight culture (O.C.)

The work area is cleaned with 70% ethanol. A small amount of cells were taken and spread using a pipet on an agar plate. The plate was kept at 37°C for 12-16 hours for cells to grow. ER2738 cells are used because they grow quickly. *Steps for amplification*

Day 0. 10 ml of O.C. is needed for 1 L of amplification volume (1:100 diluted O.C.). For 10 ml of O.C., put 10 ml of LB medium, 10 ul of TET (antibody) and single colony of ER2738 cells. 1 L of LB medium is prepared and autoclaved and allowed to cool down to room temperature. Solutions of PEG/NaCl and TBS were prepared. We needed 125 ml of PEG (120 ml + 5 ml) and 31 ml of TBS (30 ml + 1 ml).

Day 1. 1 ml of TET and 10 ml of O.C. was poured in 1 L of LB medium. The virus is then poured in (around 1011 pfu total). The culture was incubated in the 37'C shaker at around 225-250 rpm for about 6 hours. 500 ml of cell + virus culture was poured into each large centrifuge tube. The tubes were centrifuged at the largest rotor (JLA 81,000) at 7000 rpm for 30 min. 360 ml of supernatant was transferred to fresh tubes and combined with two 360 ml in one tube (720 ml total). 120 ml of PEG/NaCl was added to the 720 ml supernatant and put the 4 'C refrigerator overnight.

Day 2. The phage solution was centrifuged at 7,500 rpm (~12,000 rcf) for 30 min. The phage solution was not disturbed as the supernatant was discarded. The phage was centrifuged again for 5 min. The white pellet was dissolved completely with 30 ml of TBS solution. The solution was transferred to 50 mL centrifuge tubes and centrifuged at 10,000 rpm for 5 min to remove residual impurities. The supernatant was transferred to new centrifuge tubes and 5 ml of PEG/NaCl solution was added. The solution was mixed until it was homogeneous. The PEG/NaCl/TBS/phage solution was put in the 4' C refrigerator overnight.

Day 3. The phage solution was centrifuged at 1,100 rpm for 30 min. Without disturbing the phage solution the supernatant was discarded and the solution centrifuged again for 5 minutes. The white phage pellet was dissolved completely with 1 ml of TBS solution. (This determines your phage concentration) The solution was transferred to 1.5 ml eppendorf tubes and centrifuged at 10,000 rpm for 5 min to remove residual impurities. The supernatant was transferred to new centrifuge tubes. This is the final phage solution. The unused amount of phage was refrigerated when not in use.

To measure the concentration of phage:

The Nanodrop ND-1000 Spectrometer instrument was used to measure the concentration of the phage after amplification. In the ND-1000 software ,the UV-Vis setting was selected. A water sample was used first to initiate/calibrate the instrument. The control or blank sample should then be measured to provide a baseline for all subsequent measurements. For the phage samples, DSPH and EFE, TBS was used. To calculate the concentration using the absorbance, the formula is:

$$x = \frac{Abs\ \lambda_{269} - Abs\ \lambda_{320}}{7225} \times 60000$$

Equation 1. Calculation for concentration using absorbance

where x is multiplied by 10^{10} pfu/μL.

2.2 SWCNT Dispersion Protocol

A solution of 2 wt% of sodium cholate was prepared in a beaker. Using 1g/mL as the density of water, 500 mL of water would require 10g of sodium cholate. Some of this solution should be set aside and stored for dilutions and UV-Vis testing. 400 mg of Hipco SWCNT was dissolved in 200 mL of the 2wt% sodium cholate solution and placed in a homogenizer for 1 hour at level 2 or 3. After homogenization, the solution was sonicated at 90% power for 10 minutes using a cup-horn sonicator. The appropriate probe tip procedure uses a 6mm tip at 40% power amplitude and should be sonicated for 1 hour. The tip should be dipped in water and the initial run on the sonicator used for cleaning. The sonicated solution was centrifuged in 35-40 mL amounts in 5 tubes at 30,000 rpm for 4 hours when using the SW-Ti32 bucket, which can be 25,000rpm for 318 minutes when using SW28. This was decanted and the top half was taken from each centrifuged solution. This solution should be approximately 20 mL. The total from the entire solution should be approximately 100mL from the initial 200mL. To test the concentration of SWCNT in the solution DU800 software was used. The method for testing the solution was "wavelength scan II." Ascan mode ofwith a start wavelength of 200, an end wavelength of 1100, and a scan speed of 240nm/min was used. The first sample measured was a blank sample consisting of 100μL of the plain 2wt% sodium cholate solution.. The concentration of the solution can be found by the formula:

$$Abs_{632} \times 27 = Concentration\left(\frac{\mu g}{mL}\right)$$

Equation 2. Calculation for CNT concentration using absorbance

The concentration of SWCNT in the solutions used for virus complexation was 10 μg/mL. This value can vary but for this study this was the maximum concentration used , to prevent aggregation during virus complexation and synthesis. The solution was diluted using the sodium cholate solution and the concentration measured with the DU800 until the desired concentration is achieved.

2.3 Virus Complexation

2.3.1 DSPH (p8)

For adding the virus to the SWCNT, a process involving dialysis is used. This process adds CNT to the p8 regions of the virus and is typically used with DSPH. The phage to SWCNT ratios used were 1:5 and 1:10. The appropriate amount of SWCNTs needed wasbased on the total phage desired for each ratio. The volume of the appropriate amount of solution needed to get these values were then calculated The number of SWCNTs was given by using the molecular weight and atomic density of the SWCNT, which are $1.14*10^{-12}$ μg and $3.76*10^{19}$ C/cm^2, respectively. Once these values are determined, the appropriate amount of virus and SWCNT are mixed. More sodium cholate may need to be added to ensure that the concentration remains approximately 2wt% SC. The minimum SC concentration allowable is approximately 0.5wt% to prevent aggregation. For this reason, the virus solution should be added to the SWCNT and not SWCNT to virus. The solutions are then transferred to SpectraPor dialysis bags of 12-14,000 MWCO. The ionic strength and pH of the dialyzing solution is controlled by adding NaOH and NaCl, in addition to HCl. The changes to the dialyzing solution schedule are shown in a chart below. After 48 hours, the solution was removed from dialysis bags and refrigerated until needed for electrode synthesis.

Table 1. Conditions for dialysis for virus complexation

Time	Ionic strength	pH	
0 hr	10 mM NaCl	5.3	200 µL of 0.1 M HCl per 5 L of DI water
1.5 hr	10 mM NaCl	5.3	200 µL of 0.1 M HCl per 5 L of DI water
3 hr	10 mM NaCl	5.3	200 µL of 0.1 M HCl per 5 L of DI water
4.5 hr	10 mM NaCl	5.3	200 µL of 0.1 M HCl per 5 L of DI water
6 hr	10 mM NaCl	5.3	200 µL of 0.1 M HCl per 5 L of DI water
7-8 hr	10 mM NaCl	10	2 mL of 1 M NaOH per 5 L of DI water
24 hr	10 mM NaCl	10	2 mL of 1 M NaOH per 5 L of DI water
48 hr	10 mM NaCl	10	2 mL of 1 M NaOH per 5 L of DI water

During the dialysis process, any noticeable aggregation requires changing of the bath before the designated change point and increasing the pH. The dialysis allows for the phage to replace the sodium cholate and bind to the proper domains, because SC is a surfactant for the SWCNTs and prevents the surfaces from adhering. After this process, the SWCNTs are attached to p8.

2.3.2 EFE (p3)

The virus complexation using EFE occurs after the $FePO_4$ has already been formed. When the final step of synthesis was complete, the $FePO_4$ solution with EFE as a template was reacted at room temperature for 3 hours with the appropriate number of SWCNTs.

2.4 Electrode Synthesis

2.4.1 Active Material

2.4.1.1 $FePO_4$ without phage or CNT:

Ammonium iron sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) was used to incubate Fe for $FePO_4$ To obtain material for multiple electrodes 300 mL of 1mM $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ solution used, along with 300 mL of 1mM of $LiPO_4$. This mixture was allowed to react in a cold

room overnight. When the reaction was finished, the solution was centrifuged for 30 minutes at 3300-3500 rpm. The supernatant was thrown away and the pellet rinsed with water. The material was placed in a smaller eppendorf tube dispersed in water and centrifuged again for 10 minutes at 11,000 rpm using a microcentrifuge. The supernatant was thrown away and rinsed again with water and centrifuged. After the last centrifugation, the tube was placed, uncovered, in the vacuum oven overnight or for at least 6 hours. The material obtained is the active material, $FePO_4$.

2.4.1.2 $FePO_4$ with phage only:

To understand the effect of the phage, the same quantities of $LiPO_4$ and $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ are used but phage solution with the desired concentration is added before the addition of $LiPO_4$.For this part of the study we used DSPH. The concentration of the phage solution is used to calculate the volume of phage needed.. This is the pfu value used for all electrode syntheses containing phage. The phage and 300 mL of Fe^{3+} were incubated overnight in a cold room. The phage acts as a template for the formation of $FePO_4$. When this incubation was completed, 300 mL of $LiPO_4$ was added and the entire solution left overnight in a cold room again. When this reaction was completed, the material was centrifuged in the same manner as above.

2.4.1.3 $FePO_4$ using DSPH with CNT:

After the completion of dialysis to attach the phage to CNT in the ratios of 1:5 and 1:10, the proper amount of the phage-CNT complex to get the desired amount is used and added to 300 mL of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$. This solution is incubated overnight in a cold room. 300 mL of $LiPO_4$ was then added and the entire solution is reacted overnight in a cold room. When the final

reaction was complete, the material was centrifuged in the same manner and the final pellet was dried in a vacuum oven.

2.4.1.4 $FePO_4$ using EFE with CNT:

EFE is synthesized in a similar manner to phage without CNT. When the reaction with $LiPO_4$ is completed, before being centrifuged, it is left to react to with a solution of CNT in the ratio of 1:5 and 1:10 phage to CNT particles for 3 hours at room temperature. It is important to maintain a sodium cholate concentration of at least 0.5% with the optimal value around 2%. When this reaction is completed, the solution is centrifuged in the same manner and the final pellet is left in a vacuum oven to obtain the active material.

2.4.2 Fabrication of electrode

Each electrode contained 70% active material, 20% Super P (conductive carbon black), and 5% binder which is poly(tetrafluoroethylene) or PTFE for these electrodes. These values are calculated based on the mass of the dehydrated active material. The calculated mass of Super P and the active material without PTFE are ground and mixed using a mortar and pestle until the powder is uniform. The powder is transferred to a stainless steel plate and mixed with PTFE. This mixture is rolled to form a uniform electrode. When possible, 3/8-inch hole punch is used to cut a circular piece to fit inside the button cell. The weight of each electrode was recorded for calculations for charge/discharge during testing. Ideally, the mass of each electrode should be between 2-3 mg but slightly higher is also acceptable.

2.5 Battery Synthesis

Components: Case, cap, washer, spacer, separators, lithium as anode, $FePO_4$ -CNT complex as cathode.

The battery is made inside a glove box with O_2 and H_2O levels below 1ppm. If levels rise, the glove box must be purged. The electrodes with different conditions were contained in glass vials held inside a vacuum oven or in the glove box to ensure that any excess moisture is removed. Prior to placement in the glove box, the final weight was recorded for use in calculations. When assembling the battery, there are separate tools for use with the lithium and for use with the other components of the battery. Lithium tape was cut and the oxide scraped off using designated lithium tools. A 9/16 inch hole punch was used to get a circular piece to fit inside the button cell case. The large component of the case is the base for the other materials. A spacer was the first part placed within it, with the FePO4or other cathode material placed on top. A plastic separator was placed on top and 80-100μL of electrolyte, LM $LiPO_4$, was put on the separator. Another separator was placed on top of the liquid and the lithium anode was placed on top as the final reaction component. The washer was placed on the lid prior to placement on the cell to ensure that the anode and cathode don't make contact. The washer-lid unit was placed on top of the lithium and was hermetically sealed with a crimping machine. When removing the battery from the glove box, the cells were wrapped in non-metallic materials, individually if more than one cell is made, before placement in the materials tray to prevent discharging. Once outside the glove box, ensure that the cell does not come in contact with a metal surface prior to testing.

2.6 Battery Testing

Solartron Analytical Cell Test software was used to test the battery. For the cells made, a galvanostatic test was used which uses a constant current. For each cell, a schedule needs to be created detailing the processes for the battery to undergo to obtain the needed data. In the schedule, an initial rest step is included to get the resting voltage of the battery. The first step in the process for testing is a discharge. An initial discharge step was used at the rate of a tenth of the current (C/10) needed to discharge the battery, which is calculated for each device based on its mass. This is known as the C-rate. For the case of C/10, the battery is discharged at a rate equal to 1/10 of the battery capacity. This means that there is a 10 hour discharge. The battery capacity varies with the discharge rate and the higher the discharge rate, the lower the cell capacity [9]. The minimum voltage required for the discharging is 2 volts to prevent exhaustion of the material. The discharge step is followed by a charging step and the process is repeated two times to get results for capacity after a number of cycles.. For the safety limits of testing, the voltage should not exceed 10 V while the current should not exceed 4 A. For analysis, the data was saved to files in .csv format.

3. Results

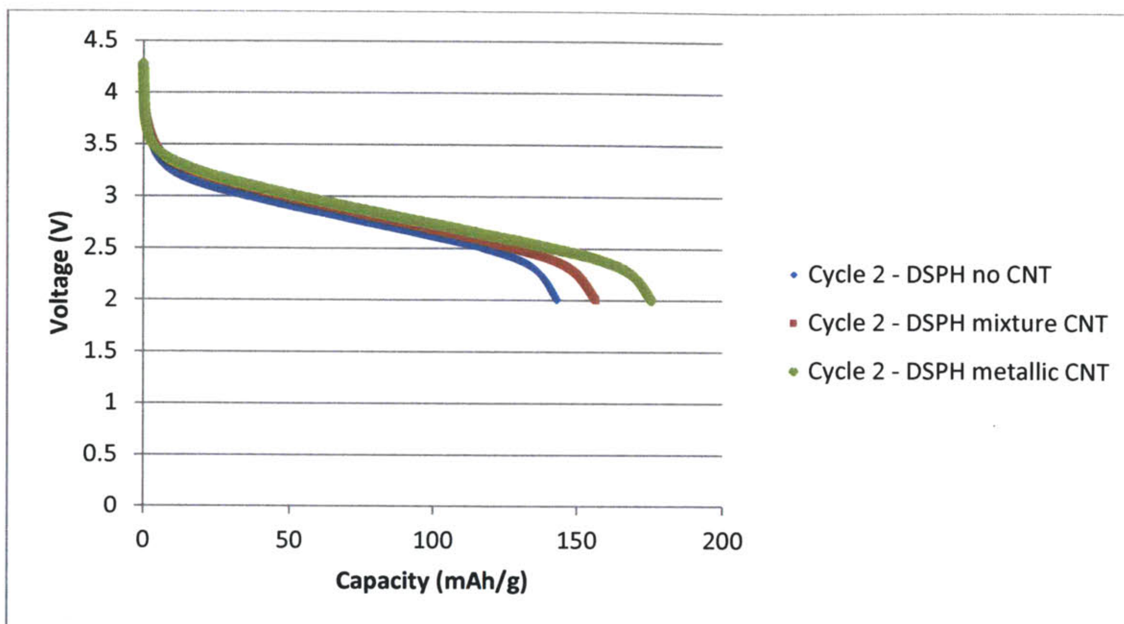

Figure 3. Cycle 2 discharge capacities of batteries with DSPH templating at C/10 discharge rate.

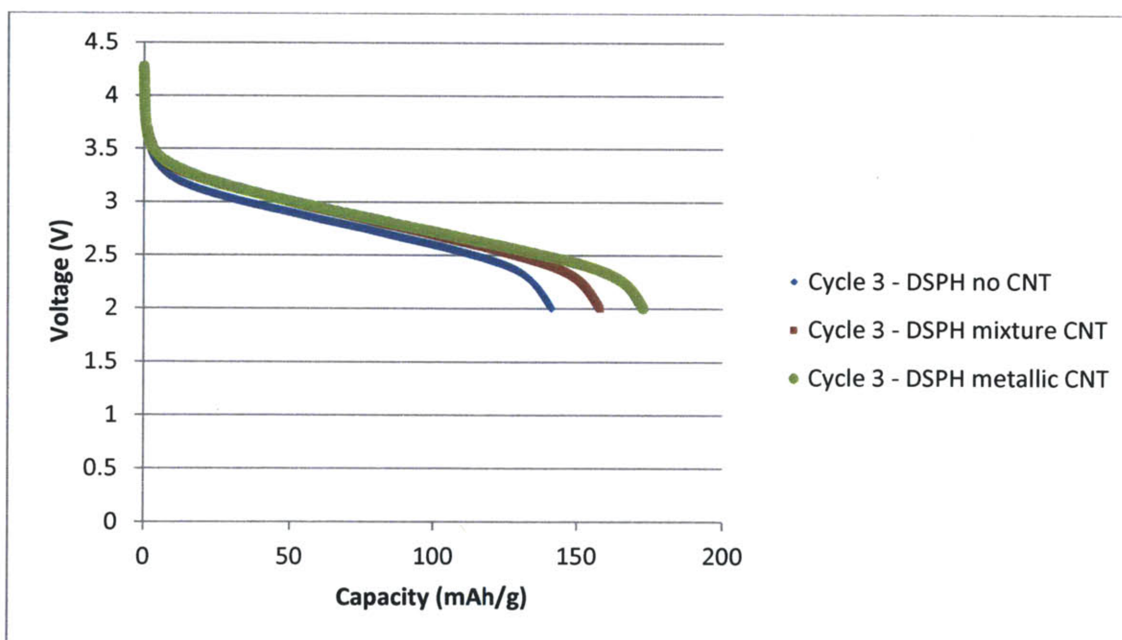

Figure 4. Cycle 3 discharge capacities of batteries with DSPH templating at C/10 discharge rate.

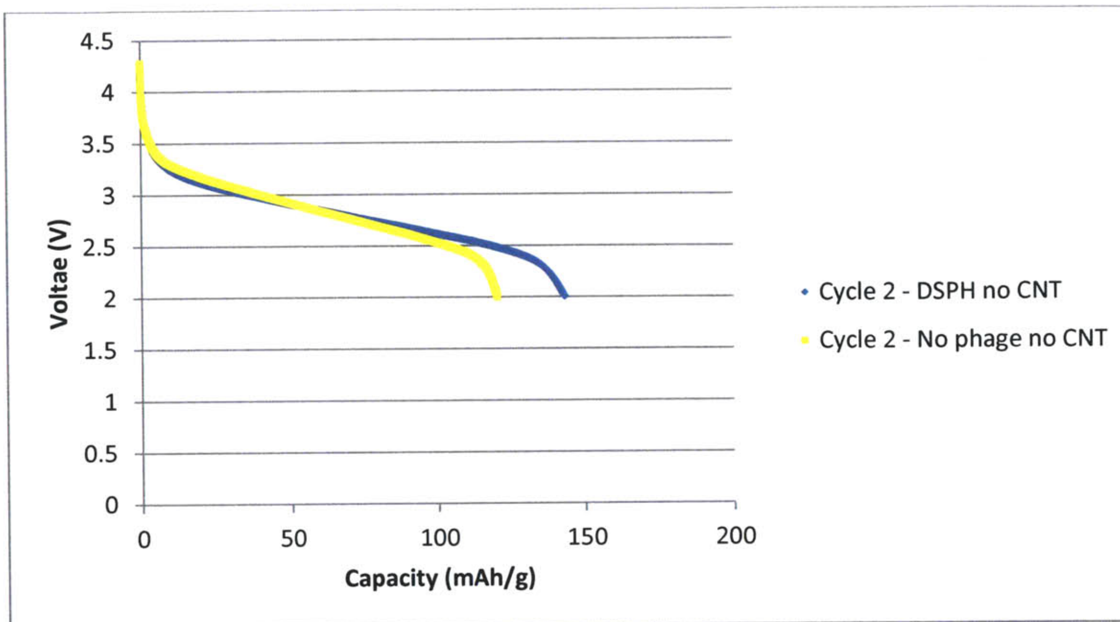

Figure 5. Cycle 2 discharge capacities of batteries with and without phage templating at C/10 discharge rate.

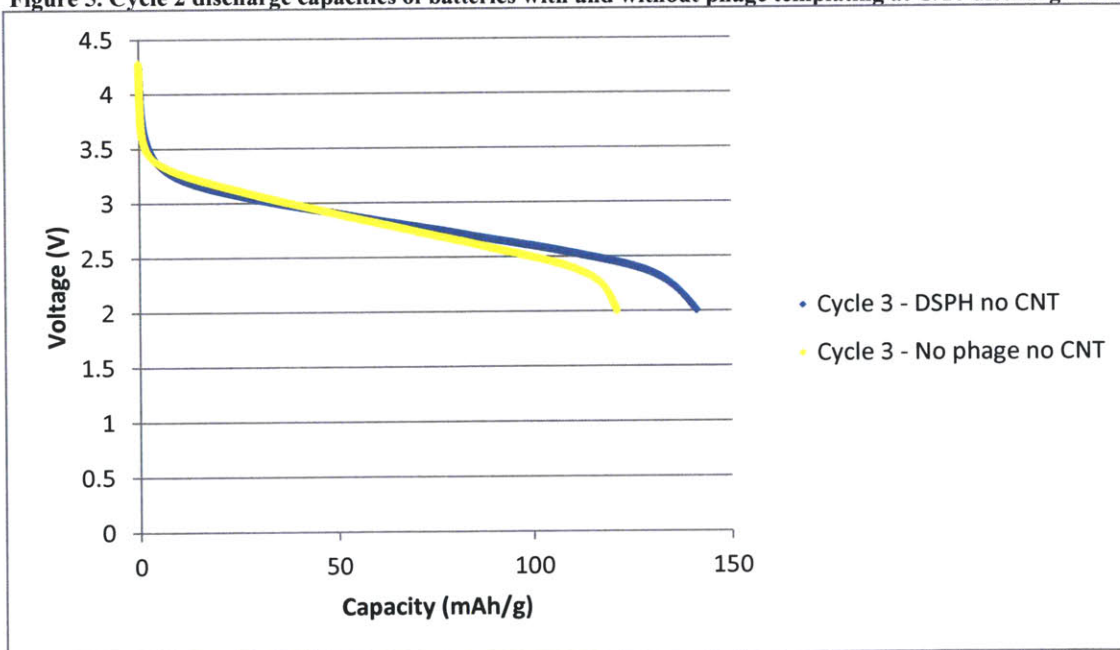

Figure 6. Cycle 3 discharge capacities of batteries with and without phage templating at C/10 discharge rate.

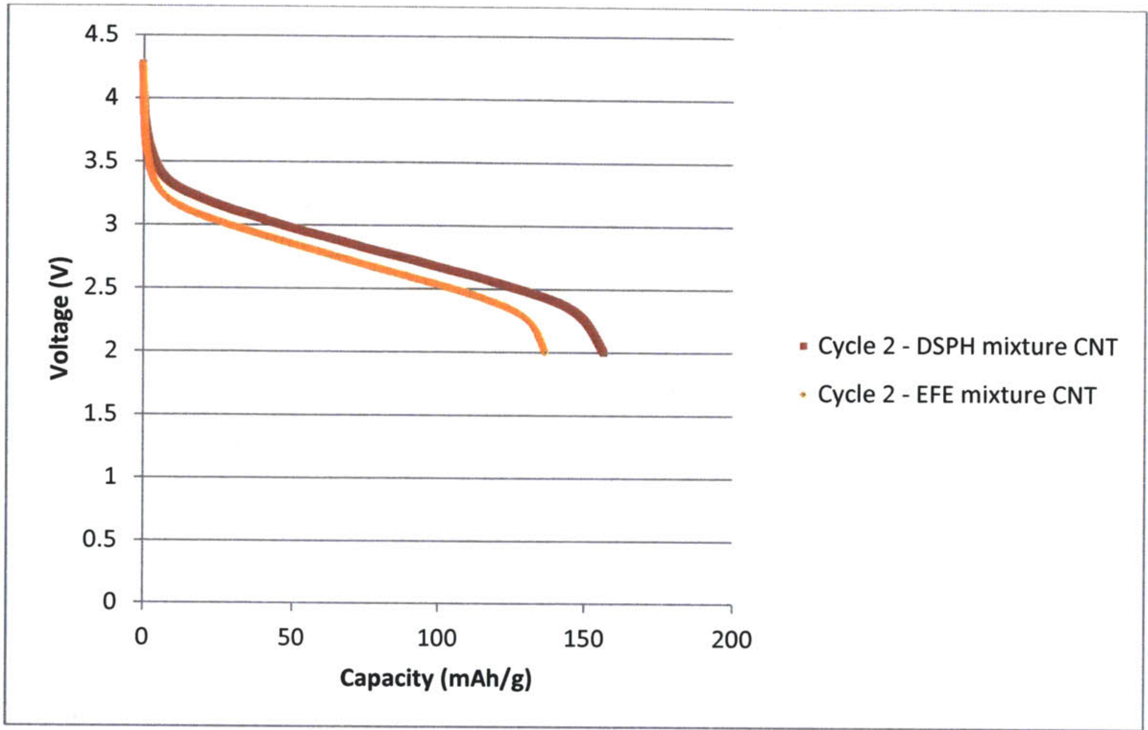

Figure 7. Cycle 2 discharge capacities of batteries omparing EFE and DSPH templating with mixed CNTs at C/10 discharge rate.

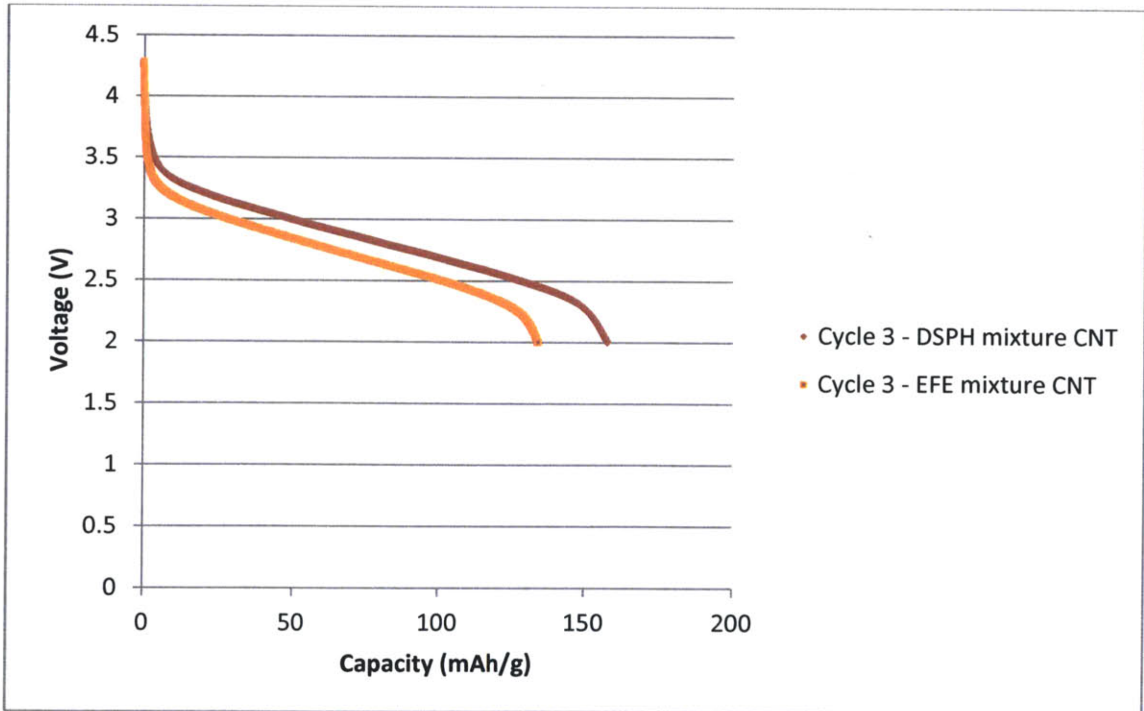

Figure 8. Cycle 3 discharge capacities of batteries omparing EFE and DSPH templating with mixed CNTs at C/10 discharge rate.

Table 2. Capacities and degradation of batteries for multiple cycles of selected batteries. Italicized data indicate use in charts above.

		Capacity (mAh/g)		
		Discharging		
Sample	Composition	Cycle 2	Cycle 3	% decrease
11	*Only $FePO_4$*	*120.61*	*121.07*	*-0.38*
1	*DSPH – no CNT*	*143.16*	*141.15*	*1.40*
6	*DSPH – mix CNT*	*156.69*	*157.92*	*-0.79*
21	*DSPH – met CNT*	*175.46*	*172.64*	*1.61*
28	*EFE - mix CNT*	*136.79*	*134.27*	*1.84*
25	EFE – met CNT	158.06	145.74	7.79

Table 3. Degradation between cycles of DSPH - metallic CNT battery

Discharging capacities (mAh/g)						
Cycle 2	Cycle 3	% decrease	Cycle 4	% decrease	Cycle 5	% decrease
168.99	168.35	0.38	168.03	0.19	168.14	-0.06

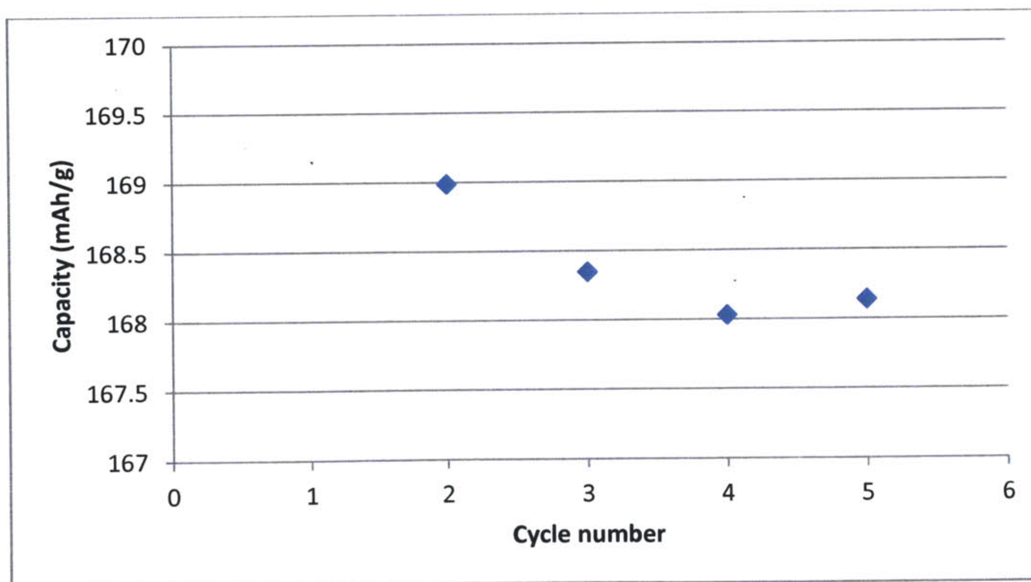

Figure 9. Changes in capacity for multiple cycles for a battery with DSPH and metallic SWCNTs. The discharge rate was C/10.

4. Discussion

Since the capacity is based on the mass of the active material of the electrode, all of the values are comparable. Based on the data obtained, DSPH allows for higher capacity than EFE when attached to CNTs. It can also be seen that the phage does have a positive impact on the overall capacity of the battery, measured at a constant rate, even when used without CNTs to attach to. Using metallic CNTs in place of a mixture which contained in a 70% metallic and 30% non-metallic CNTs, improved the capacity by approximately 9% , at the end of the third cycle of discharging, when used with the DSPH phage. This is an overall improvement of 22% from the battery that used no CNT with DSPH and an improvement of 42.6% from the capacity of the battery that only contained $FePO_4$ in the cathode. Although gains in EFE were not as large as those seen with DSPH, there was still improvement in the capacity of the battery. The appearance of the batteries did not show any signs of leakage or expansion.

Despite some steep degradation in some samples with DSPH, the capacity of DSPH batteries remains higher than that of EFE with metallic and with mixed CNTs. The cycling of one sample of DSPH with metallic CNTs has shown that there is very little degradation between cycles of testing. The results from 5 charge-discharge cycles indicate that the capacity, at least over short cycling, remains consistent.

5. Conclusion

The difference in the capacities for the different conditions for the active material is most likely a result of the number of differences in contact area between the active material and the SWCNT used. The gains in capacity may indicate that less Super P may need to be used in the construction of the electrodes. This allows for more active material content in the electrode to further improve battery capacity. Some of the data in Table 1 may come from batteries where tests were initiated a day later than the battery was made which could lead to slow discharging of the battery. This could also explain why in 2 cases there seemed to be an increase in capacity after 3 cycles instead of a decrease.

While the energy density of this system of LIBs is lower compared to that of $LiCoO_2$ and other battery types, the voltage range it operates within is similar and the material itself provides a safer alternative. The life cycle of these batteries also greatly exceeds what is possible for similar LIB systems at possibly more than 1000 cycles before the battery is exhausted barring any operational errors [9]. As with any battery, the capacity declines over time so further testing for the cyclability of the batteries is being done. Additional tests to confirm results and analyze the effects of metallic CNTs on the performance of batteries using the EFE phage as a template are also being performed.

The batteries used were tested at room temperature, so testing battery performance in different temperature conditions may give a full picture about the operation range. Since these batteries may be applicable in various situations, different temperature tests can indicate whether there may be expansion problems and whether a reduction in capacity is seen when shifted from the center of the battery's typical usable range. This would also allow us to determine whether

the phage templating allows for the material to withstand higher temperatures, as current $LiFePO_4$ batteries have a significant decline in capacity above 60°C.

Long term use also needs to be assessed through more testing of the batteries capacity with multiple cycles. It is normal for battery capacity to reduce over time and for less than 10 cycles the capacity remains almost constant. For longer use, the capacity cannot be extrapolated from current data. Batteries need to be continuously cycled under similar conditions to understand the behavior of this type of battery and whether or not EFE and DSPH prolong battery life as well.

6. References

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