
A Thesis submitted in partial satisfaction of the requirements for the degree of Master of Science

in

CHEMISTRY AND CHEMICAL BIOLOGY

by

Eunbit Cho

Committee in charge:

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Professor Min Hwan Lee
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2016
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The thesis of Eunbit Cho is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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2016
DEDICATION

To my parents, sister, and people who helped me throughout my struggles
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I would also like to thank the University of California, Merced and the dean of graduate division, Dr. Marjorie Zatz for the financial support. I was extremely lucky to have supportive staff members in Natural Science department throughout graduate career: Joy Sanchez-Bell and Paul Roberts.

My sincere thanks also goes to Jun Shin, Kohei Tomita, and Celina Mikolajczak for offering and having me as an intern in the Battery Technology group at Tesla Motors Inc. for past 8 months of my graduate studies. I am grateful for time spent with brilliant members of many different groups on amazing engineering projects.

Last but not the least, I would like to thank my family for all of their love and encouragement. And most of all for my supportive and patient sister Eungyeol whose faithful support is much appreciated.
Resume/ CV

EDUCATION

Master of Science, Chemistry 2014 –2016
College of Natural Sciences, University of California, Merced, Merced, CA

Bachelor of Science, Chemistry 2011 –2012
College of Science and Engineering, University of Minnesota-Twin Cities, Minneapolis, MN

Pre-Pharmacy, Transferred to UMN 2008 –2010
College of Pharmacy, University of Arizona, Tucson, AZ

PATENTS AND PUBLICATIONS

Patents: 6 pending patents as main inventor – Confidential and belongs to LG

• Electrode coating enhancement, electrode treatment, cell design and fabrication for specific functionalities, stack design of battery cell, and cathode material fabrication.


LABORATORY TECHNIQUES


PROFESSIONAL AFFILIATIONS

American Chemical Society
PROFESSIONAL EXPERIENCE

Industrial Research Experience:
Engineering project Management, battery supply chain, li-ion cell development, evaluation and manufacturing

*Tesla Motors, Palo Alto, CA, US*

- Manage and outline project deliverables for next-generation products (MX, M3, and prototypes.)
  - Managed prototype sample deliveries between Engineering labs, Fleet, and GA lines.
  - Wrote engineering specifications and legal documentation for vendor RFP and RFQ.
  - Evaluated testing protocols and secured samples to assess supplier viability.
  - Drove cost reduction efforts through supplier market research and contract negotiation.
  - Launched policy studies and business case evaluation of potential domestic/foreign markets for internal assessment.
- Created logistics dashboards for purchasing and supply chain data to facilitate management of build plans.
  - Identified and adverted critical production issues on the manufacturing line through independently developed tracker that integrates data from supply chain, logistics, shipment receiving reports, and field count. Interfaced with Purchasing and Logistics to prevent recurrence.
- Wrote an interactive Excel model to allow for rapid sensitivity study and visualization of battery material costs [S/cell] with respect to LME index pricing
  - Tuned and validated model to 99% accuracy by integrating theoretical and experimental parameters.
  - Supply data to senior management for preliminary valuation and cost reduction of purchasing agreements.

Mobile Battery Development – Li-ion Polymer Battery Platform Technology Team  
*LG Chem Research Park, Korea*

- Performed in a special task force project team, achieved 3% increase in energy density through redesigning chemistry and coating technology of electrode
- Conducted 7 different DOE to study sensitivity of electrode layouts and design parameters, achieved cost savings while not impacting cell chemistry and performance.

Corporate Materials Research Laboratory- Materials & Coating Division  
*3M Headquarters, Maplewood, MN, US*

- Conducted ROI studies for cost optimization on new glass cleaning formula, achieved 70% cost reduction.
Academic Research Experience:
Renewable energy, electrochemistry, lithium ion batteries, biomaterials, renewable polymeric materials, and nanomaterials

Graduate Student Researcher
Menke Group – Solar Cell & Battery Laboratory, UC Merced, Merced, CA
• Lithographically Patterned Nanowire Electrodeposition (LPNE) method for battery research.

Noy Group – Bionanoelectronics Laboratory, Lawrence Livermore National Lab, Livermore, CA
• Nanofluidic transport studies with carbon nanotube and artificial membrane channels.

Undergraduate Research Assistant (UGRA)
Severtson Group - Bioproducts and Biosystems Engineering, Center for Sustainable Polymers University of Minnesota-Twin Cities, Minneapolis, MN, US
• Developed renewable and sustainable pressure sensitive adhesives (PSA) with biodegradable polymeric materials for USPS
• Worked on prototype laboratory reactors for scale-up process at an industrial company in OH.

Undergraduate Researcher (Researcher I)
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SCHOLARSHIP AND HONORS

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Bobcat Graduate Fellowship, UC Merced  Spring 2016, Summer 2015
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Undergraduate Research Assistantship, Seoul National University  Fall 2010
Laboratory Assistantship, University of Arizona  Fall 2008 – Spring 2009
Abstract of the Thesis

The Synthesis of Lithium-Ion Micro-Batteries and an Industrial Market Analysis of Low Voltage Battery Systems

By

Eunbit Cho

Master of Science in Chemistry and Chemical Biology

University of California, Merced, 2016

Professor Erik Menke, Advisor

Improved electrochemical devices are needed to satisfy the growing demand for more sustainable and efficient energy sources for various industrial electronic products. Lithium-ion batteries are one of the top candidates, but this technology faces many challenges to meet specific engineering requirements for consumer devices. Chapter I describes the synthesis of lithium-ion micro-batteries via lithographically patterned nanowire electrodeposition (LPNE), which would allow future studies to fundamentally characterize electrochemical reactions at the electrode surface level while charging and discharging via in-situ atomic force microscopy (AFM). Chapter II critically assesses the potential of lithium-ion batteries to replace lead acid batteries in vehicular low voltage systems, which an emphasis on the key material characteristics of both platforms, including self-discharging and power performance at low temperature. A cost analysis of each system is also described.
CHAPTER I

The Use of Lithographically Patterned Nanowire Electrodeposition for Nanowire-Based Microbatteries

1. Introduction

1.1. Objective of Chapter I

The main objective of Chapter I is to develop a method of simulating and testing power performances or lithium-ion batteries via Lithographically Patterned Nanowire Electrodeposition. This novel LPNE method allows for easy and cheap fabrication of electrodes while maintaining high controllability, making it a powerful tool for in-situ characterization studies of electrodes during operation. In addition, a newly developed LPNE procedure will support intricate property studies based on various cell designs at the electrode level.

The thesis is specifically dedicated to exploring and validating the synthesis of lithium ion micro-batteries using LPNE. Potential future research topics are also explored in the conclusion.
1.2. Lithium-ion Battery

Batteries, electrochemical devices that convert chemical energy within active materials to electrical energy, are key components of modern devices. Due to their high energy density and conversion efficiency, they are ideal for consumer electronics and energy storage applications. Since batteries also bypass the theoretical thermodynamic efficiency limits of the Carnot cycle in internal combustion engines, they are even beginning to find a place in powering electric vehicles. Depending on their ability to recharge, batteries are categorized as primary or secondary batteries. Rechargeable batteries, commonly used for consumer electronic devices such as cell phones and digital cameras, are known as secondary batteries and include lead acid, nickel cadmium, nickel metal hydride, and lithium chemistries. Non-rechargeable batteries, such as the single-use types that go into military ordinance, are known as primary batteries and include dry carbon-zinc, lithium primary, mercury oxide, and silver oxide chemistries.
A battery, in its most basic form, can be viewed as a combination of cathode, anode, separator, and electrolyte. As shown in Figure 2b, an anode gives up electrons to the external circuit through oxidization in an electrochemical reaction. At the same time, the cathode accepts electrons through a reduction reaction. A separator provides physical separation between the anode and cathode and prevents a short circuit condition through electrical isolation. The porosity of a separator is a key factor as ions need to permeate and transfer through the separator for electrochemical reactions to occur. In addition, multiple safety factors need to be considered with separator material selection and design, as the IEEE 1725 Certification states. The separator should have sufficient stability to meet mechanical, chemical, electrochemical, and thermal requirements of a battery’s harsh
environment. For instance, a separator should be designed with sufficient thermal shrinkage allowance while extending beyond the electrodes and sufficient strength and thickness to prevent puncturing from foreign intrusions. Many industries use enhanced separators to increase the safety of their batteries by applying special coatings to the bare/original polymer. While the separator acts as a channel or bridge of ions in between a cathode and an anode, actual ionic conduction and charge transfer is done by the electrolyte solution. As such, the most common types of electrolyte are liquids with either water or other organic solvents with dissolved salts, acids, or alkalis for ionic conductivity. Some lithium ion cells use gel electrolytes and are often separately distinguished as polymer batteries. In academia, electrolytes are often substituted by ionic liquids in order to increase safety by lowering the thermal activity caused by organic solvents. In industrial applications, where fast charge and discharge rates are important, ionic liquids are non-ideal and are thus rarely used.

Figure 2. Left: Energy diagram of electrode chemical potentials, Right: Schematic diagram of Lithium-ion batteries. Reference [2]
Among all the four main components of batteries, the cathode and anode electrodes are generally the focus of most modern research since these sites are where the actual redox chemical reactions occur. For instance, development of new cathode/anode materials and electrode fabrication techniques promise to provide major advances in battery performance. Further explanation of the types of electrodes and their specific characteristics will be provided in the following Introduction section of this report.

1.3. Cathodes and Anodes

The cathode and the anode, as the primary sites of chemical reactions and the storage site for ions, could be viewed as the most critical factor in determining a battery’s performance specifications such as voltage windows, capacity, power, safety, and cost. As one of the most expensive components in a battery, the electrodes are also the focus of cost reduction efforts by industry and academia.

Since the negative electrodes store ions when a battery is fully charged, it is important to understand the fundamentals of anode chemistry to maximize high coulombic output (Ah/g) and conductivity when designing battery cells. Most lithium ion battery designs use carbon / graphitic materials for the negative electrode with proprietary additives. However, this material selection restriction of graphite limits the Coulombic output efficiency. Recent developments in negative electrode or anode materials have focused on nanostructure fabrication for special properties such as high surface area with carbon and Si-based materials with 0, 1, and 2D nanostructures. The resulting morphological effect on anode performance is of particular interest Reference [2]. Because ions are fully stacked when
fully charged, safety concerns associated with anode structure and expansion of Si-ion should be accounted for in the battery design.

Positive electrode or cathode materials should be a good oxidizing agent while being stable when in contact with the electrolyte through a useful working voltage potential. Most lithium ion batteries have a lithium metal oxide variant in use in its cathodes, some types as shown in Table 1.

<table>
<thead>
<tr>
<th>1-Dimension (Olivine)</th>
<th>2-Dimension (Layered)</th>
<th>3-Dimension (Spinel)</th>
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<td>LiFePO₄</td>
<td>LiCoO₂</td>
<td>LiMn₂O₄</td>
</tr>
<tr>
<td></td>
<td>LiNiₓMnᵧCo₂O₂</td>
<td>LiNi₀.₅Mn₁.₅O₄</td>
</tr>
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</table>

*Table 1. Various structural differences in lithium metal oxides. Reference [23].*

Commercially available cathode materials can be generally divided into three types; a rock salt-type structure, a spinel-type structure, and an olivine-type structure. The rock-salt structure is a layered form of lithium, transition metal, and oxygen atoms in octahedral form such as LiCoO₂, Li(NiMnCo)O₂, and Li(NiCoAl)O₂, as shown above in Table 1. Then, there is LiFePO₄, which was developed by the Goodenough group¹⁰ as the most famous olivine cathode material. This one-dimensional crystal morphology allows lithium atoms
to move along one dimensional tunnels, which gives poor rate capability with limiting ion mobility. LFP also has a low voltage which gives poor energy density. A well-known example of the 3D spinel structure is the LiMn$_2$O$_4$ cathode material. Lithium fills in one-eighths of the tetrahedral sites within the $\lambda$-MnO$_2$ structure and Mn-centered oxygen in octahedral fills one-half of the octahedral sites. \cite{11} However, LMO has a relatively low discharge capacity and difficulty in operating at high temperatures due to the sensitivity of manganese structures to heat. The manganese elution can be controlled by doping on the active material and many researchers have proposed increasing the lithium to manganese ratio. Because of structural differences in cathode materials, distinctive characteristics exist as shown in Figure 3 below.

![figure 3](image)

*Figure 3. Expected benefits from different types of lithium metal oxides.*

These are well-known benefits of each lithium metal oxide material, and it would be ideal to select the right type of electrode for a specific targeted functionality. Having multiple options with many types of chemical compounds for materials allow researchers to customize the lithium ion battery to their application’s needs. Unfortunately, cell design is
not as simple as “mixing and matching” due to other chemical compatibility concerns from combinational reactions with electrolytes, binders, and additives. Most importantly, when fabricating cell designs with cathodes and anodes, the reversible charge capacity of the negative electrode must be always greater than the positive electrode (N/P Ratio) and the active area of the negative electrode must always fully physically cover the positive electrode. This factor is a really important safety consideration to prevent lithium plating. As such, an application specific lithium-ion battery can only be developed with a deep understanding of material properties and chemical reactions.

1.4. Fundamental Characteristics of Lithium-ion Battery

Most secondary batteries, not just lithium-ion variants, should retain their performance characteristics over repeated charge-discharge cycles and various storage conditions to be viable. Their rechargeability makes them well suited for use in energy storage devices or consumer electronics. In fact, their prevalence in consumer electronics has helped drive and standardize specification and performance requirements for lithium-ion batteries. In general, they should have a good energy retention rate, high power density, high discharge-charge rate, flat discharge curves, high energy density, and good low-temperature performance. However, depending on the application, performance goals will vary. For instance, the cycle life requirement for a cell phone’s battery will be drastically different from that of a vehicle’s ignition system battery. Chapter II of this Thesis will discuss a low
voltage system for a vehicle system that requires good storage life and low-temperature performance. Consumer electronic devices, such as cell phones, laptops, and watches, prioritize high C-rates and increased energy densities.

1.5. Lithographically Patterned Nanowire Electrodeposition

The Penner group at UC Irvine developed a new nanowire fabrication method called Lithographically Patterned Nanowire Electrodeposition (LPNE), which uses both a top-down and bottom-up approach for an easy, highly controlled, and customizable procedure for synthesizing noble-metal, semiconducting, and conducting polymer nanowires on glass or oxidized silicon surfaces. [6-8]

Figure 4. Gold nanowire synthesis via lithographically patterned nanowire electrodeposition, Reference [6].
As shown in above Figure 4, LPNE sacrifices nickel nanoband electrodes using optimal lithography and subsequently electrodeposits the desired nanowire at the electrode.\textsuperscript{[6]} The optical diffraction from optical lithography limits the spacing between nanowires to define the position of the nanowires. The thickness of the nanowire is set by the height of the nickel nanoband while the width is controlled through the deposition time. Also, as shown in Figure 5 below, high density LPNE can be performed to grow multiple nanowires with several electrodepositions.

*Figure 5. High-density gold nanowire fabrication with LPNE method.*
By using the LPNE method, arrays of nanowire can be made quite easily and relatively cheaply compared to other methods of nanowire fabrication. Also, because the LPNE fabrication method is highly customizable and easy to perform, arrays of nanowire can quickly be made for both cathode and anode electrodes. This allows one to make a micro-size battery which can be a powerful tool for studying in-situ intercalations of lithium-ion at charge and discharge conditions. Because lithium is extremely sensitive to air and has relatively high energy density characteristics, opening a fully charged cell is a dangerous procedure for researchers, especially within the confines of a glovebox. Furthermore, a standard glovebox makes it quite difficult to physically see what is happening at the electrode sites when the cell is cycling or at different states of charge (SOC). Much cell research is often carried out by cycling a cell through simple charge/discharge profiles using testing machines produced by companies such as ARBIN and MACCOR. This methodology provides current and voltage information while a battery is in operation, but yields little insight into exactly what is happening physically inside the cell. With this easily fabricated LPNE method, lithium intercalation or de-intercalation at the nano-level can be observed live with in-situ AFM to understand morphological behaviors while a cell is being charged or discharged.

Cells have dynamic and variable power performance at different SOCs. In other words, if the same battery cells at differing SOCs are put through a rate test, they behave differently due to the variable discharge curve of lithium ion. With this in mind, how does the speed and reactivity of lithium change as a function of SOC? Another interesting question to be answered can be followed by electrode modification. As mentioned before in the Introduction, there can be many hybrid forms of batteries with different chemistries or
loading levels within a fixed electrode material selection. For instance, if we were to take LCO and LFP electrodes with differing initial voltage levels, we would hypothetically be able to see lithium filling into LFP first during in-situ operation. The same holds true for different loading levels. If we fix a chemistry for a certain cathode type, increased loading levels would cause higher resistance within an electrode. It will be interesting to explore further with rate or temperature tests to investigate further the expected outcomes introduced in Section 1.2.

Figure 6. Proposed initial research plan for the LPNE micro-battery model, a) one electrode LPNE electrochemical device, b) both electrodes in full micro-battery model, c) modified electrode system in full micro-battery model, d) hybrid electrode in full micro-battery model, and e) for testing and characterization with in-situ AFM.
Figure 6a) demonstrates a basic electrochemical cell device with one electrode, either metal oxide or carbon for cathode or anode, to allow us to test functionality of the cell and see simple intercalation through in-situ AFM in e). Then the full micro-battery model can be made as shown in Figure 6b). The cell will have two overlaying electrodes in one system to behave like a battery. This configuration will allow us to study the battery as a function of different SOC levels. Also, with different electrode designs as shown in c) and d) above, we will be able to different test battery designs to investigate electrochemical properties and functionalities within a cell. Unfortunately, this research concept was not verified but remains as a future research topic. The focus of this paper is validating the viability of synthesis and fabrication of cells using LPNE. Making metal oxide nanowires has previously been done successfully by many researchers in the Menke group. However, making the anode was the bottle-neck for fabricating micro-batteries that replicate conventional battery models. Most anode materials for conventional lithium-ion batteries are carbon based graphite. However, growing carbons as a form of nanowire or nanofiber arrays was considered difficult with this system. Since intercalation of lithium during charging and SEI layer growth after initial cycle happens all at the anode, developing a method of making anode nanowires was critical in validating the micro-battery model viability.
2. Experimental

2.1 Chemicals

Two types of monomers were used for the polymer synthesis in this experiment; 3,4-ethylendioxythiophene (EDOT) and 2,6-dimethylphenol (PO). These monomers and acetone, lithium perchlorate were all purchased from Aldrich and used as received. Millipore MilliQ water ($\rho > 18.0 \text{ M}\Omega \text{cm}$) was used for all preparation. Diluted nitric acid (0.8 mol/L) from Aldrich was used for etching process. Positive photoresist and developer were both obtained from Rohm and Hass, Nickel rod (99.995 % pure) was purchased from Kurt J. Lesker company, premium microscope slides were purchased from Fisher Scientific Company, and liquid nitrogen was purchased from Praxair.

2.2 Equipment

2.2.1 Denton Vacuum BTT-IV

A Denton Vacuum BTT-IV was used as the physical vapor deposition device, to deposit nickel layer on the glass slides and silicon wafer substrates.
2.2.2 SQM-160 Thin Film Deposition Monitor

SQM-160, thin film deposition monitor from INFICON was used while samples were prepared in PVD, to measure rate and thickness of the coating. Sensor is specific for material types and it can be assigned for different materials by average number/rate.

2.2.3 Laurell Spin Coater

Spin coater, Model WS-400-BZ-6NPP/LITE was purchased from Laurell Technologies to coat fluorescence on top of physical vapor deposited nickel layer.

2.2.4 OAI Model 30 UV light

OAI Model 30 UV light was used for the patterning in photolithography. It has a stand-alone light source with constant intensity controller and shutter timer. This device allows various beam sizes up to 24 inches square with output spectra ranging from 220 nm to 450 nm, with appropriate lamp.

2.2.5 Electrochemical Cell

Electro-deposition and characterization can be done by one electrochemical cell with three-electrode composed of Pt, Ag/AgCl, and nickel strips coated on glass slides. These electrodes work as the counter electrode, reference electrode, and working electrode for nanowire preparation.
2.3 Experimental Procedure

2.3.1 Synthesis of nanowires

The listed steps below for LPNE procedure is implemented shown as follows. [6-9]

a) Glass slides Cleaning: soda-lime glass microscope slides were diced into 1x1 squares then the squares were submerged into the aqueous Nochromix solution for 24 h for deep cleaning and then air dried.

b) Nickel Layer Deposition: physical deposition of a 40-nm-thick nickel film (ESPI, 5N purity) by hot-filament evaporation at a rate of around 0.7 A/s. The film thickness and evaporation rate were controlled by SQM-160

c) Photoresist Coating: the nickel-covered glass squares were then coated with a positive photoresist layer (Shipley 1808) by spin coating. Photoresist (1 ml) was dropped onto each nickel square, which was then rotated at 2,500 rpm for 80 seconds. Then the sample is heat-treated in oven at 90 °C for 30 min. This produced about ~0.8 μm thick photoresist coating.

d) Developer Treatment: after cooling at room temperature, a transparent contact mask was placed on top of photoresist with a quartz plate to be selectively exposed to the OAT UV light source at 0.5 mW/cm² for 3.3 seconds. Then the slides were soaked in an aqueous developer solution from Shipley MF-24A for another 30 seconds. After rinsing with pure H₂O, samples were dried with a stream of air.

e) Nitric Acid Etching: slides were etched with diluted nitric acid (0.8 M) for 8 minutes to remove exposed nickel then washed with pure H₂O.
f) *Electrodeposition of Polymer (PEDOT or PPO):* one compartment of three-electrode electrochemical cell was used for electrodepositing PEDOT or PPO nanowires. The glass slides or silicon wafer slides with above preparation would have nickel bands in pattern which will grow nanowires with electrodeposition method via computer-controlled Gamry Instrument’s potentiostat/galvanostat. Cyclic voltammetry and chronamperometry were utilized for PEDOT and PPO nanowire preparation. An example of experimental setting for PEDOT deposition is shown in below figures. [9]
Figure 7. Cyclic voltammetry setting for PEDOT synthesis. Reference [9]
Figure 8. Chronoamperometry setting for PEDOT synthesis. Reference [9]
3. Results and discussion

3.1 Electrodeposition Methods

As explained above in experimental part, monomer of poly(3,4-ethylenedioxythiophene) (PEDOT) was used for electrodeposition method. Monomer form, 3,4-ethylenedioxythiphene (EDOT) has the 3- and 4- positions of the thiophene ring blocked by oxygen which allows minimization of unwanted polymerization at two beta-carbon cites. Also the oxygen with its electron-donating characteristic increases the electron density of the thiophene ring, which allows the conjugated polythiophene ring to be positively charged by the anion dopants. \[^3\] Synthesis of PEDOT in chemical polymerization requires several methods and oxidants; typically using oxidizing agents such as FeCl$_3$ or Fe(OTs)$_3$. \[^3\text{-}4\]
Electrochemical polymerization is trivial so long as there is a conductive substrate. With nanostructures, we are able to fabricate high capacitance electrochemical surface for PEDOT polymerization via electrodeposition. For the electrodeposition method, both cyclic voltammetry and chronoamperometry are utilized to electrodeposit conductive polymeric nanowires. From previous research done on synthesizing PEDOT nanowires, it was clear that the deposition methods have an impact on the width and morphology of the nanowires. Both of cyclic voltammetry and chronoamperometry methods were done and characterized with the optimal microscopy set as 100x/0.8, as shown in figure 10 and figure 11. It was clear that chronoamperometry produces more uniform and wider nanowires because of more charge was accumulated through chronoamperometry that more EDOT monomers were oxidized and polymerized.

Figure 10. Nanowires grown under CV, seen from the microscope with magnification 100.
Figure 11. Nanowires grown under chronoamperometry, microscope with magnification 100. [9]

Specific width and height measured data of the PEDOT nanowire synthesis under different deposition time can be found in table 2, below.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Height (nm)</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>40</td>
<td>N/A</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>150</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>330</td>
</tr>
<tr>
<td>80</td>
<td>40</td>
<td>387</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>530</td>
</tr>
<tr>
<td>120</td>
<td>40</td>
<td>544</td>
</tr>
</tbody>
</table>

Table 2. The width and height measurement of PEDOT under different deposition time, measured with AFM. [9]
Synthesizing PEDOT was done by following the suggested conditions in previous research. Deposition voltage as 1.0 V vs a standard Ag/AgCl reference electrode, and the deposition time as 300 seconds. This is equivalent or comparable to the total time throughout five cycles in cyclic voltammetry.

One of the biggest benefits that LPNE method offers is controllability of the physical parameters of the nanowires. As Table 2 shows, there is a linear correlation between width and deposition time. Thus, expanding on the previous research done by Menke group to find the impact of electrodeposition voltage and time on PEDOT nanowire synthesizing via chronoamperometry, we were able to develop controlled conductive polymeric nanowire arrays with fixed width in high aspect ratio (>200), as shown in Figure 12.

*Figure 12. Left: PEDOT sample on glass, Right: PEDOT sample on Si-wafer.*
PEDOT is often used as battery and solar cell materials, but the proposed micro-battery model for this research would need a carbon based anode and lithium metal oxide form of cathode, as shown in Figure 6. Thus, pyrolysis was necessary to create carbon nanowires for the anode. Because PEDOT was not durable after the pyrolysis on either glass or wafer, a different polymer was used to synthesize the anode material. For a new conductive polymer with higher thermal durability, poly-phenylene oxide (PPO) was found through literature review, \cite{12} as shown in Figure 13. PPO has high resistance to high temperatures and with a glass transition temperature as high as 210 °C.

![Chemical structure of PPO](image)

*Figure 13. A new suggested conductive polymer, poly(p-phenylene oxide) (PPO).*

Based on Glarum’s paper in 1985, NaOH (0.15 N) and 4-tert-butylphenol (TBP) (0.02 M) samples were made for electrodeposition of PPO on silicon substrates. After multiple trials on cyclic voltammetry, potential optimization was done to be in the region of 0.25 V to 0.45 V, as shown in Figure 14.
As cyclic voltammetry analysis was done to find a very specific oxidation peak for PPO, we were able to grow PPO nanowires through cyclic voltammetry and determine that 0.45 V is the specific oxidization peak for PPO. The first cycle shows larger current in graph with bare nickel contacting the solution, causing electron donation of the monomer in faster rate, which happens with PEDOT as well. Because the sweep rate was 20 mV/s for 5 cycles in cyclic voltammetry, 300 seconds for electrodeposition time was calculated and considered in potential static method for PPO synthesis at 0.45 V at first. However, PPO is not the end product for the micro-battery fabrication procedure. We would need to go through pyrolysis in order to make carbon/graphite based anode nanowires. With voltage fixed condition PPO, different electrodeposition time was suggested to create different sizes of nanowires. As shown in Figure 15, various electrodeposition times were used, from 200 seconds to 900 seconds with increments of 100 seconds to create PPO LPNE.
3.2 Pyrolysis Method

Unfortunately, PEDOT did not show any traces after pyrolysis. After switching the substrates from glass slides to silicon wafer, we also had to switch materials from PEDOT to PPO. After all, PPO sample was successfully turned into carbon after pyrolysis. Pyrolysis conditions for both PEDOT and PPO were same for the apparatus shown in

Figure 15. PPO samples on silicon wafer substrates after electrodeposition, seen from microscope using the magnitude of 100 x / 0.8.
Figure 16. Samples were treated in Argon during the preparation and pyrolysis process and temperature was set for 650 °C with a 30-minute dwell.

Figure 16. Pyrolysis apparatus used for experiment.

Samples with different deposition times were used to find optimized width of PPO for anode preparation. From many trials of pyrolysis with different width of PPO nanowire
samples, 600 second deposition time was minimum requirement to successfully prepare carbon anode samples. As Figure 17 indicates, clear carbon lines were observed, from the microscope using the magnification 100.

Figure 17. Finalized anode nanowires after pyrolysis: previously PPO nanowires prepped with electrodeposition (600 seconds) in figure 16.
4. Conclusion

Using lithographically patterned nanowire electro-deposition method (LPNE), electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) and phenylene oxide (PO) to synthesize PEDOT and PPO nanowires was done. This suggests the potential feasibility of fabricating micro-battery systems to establish a direct relationship between charging and intercalation at electrode levels during cell operation. Through the LPNE method, nanowires of different sizes and morphologies were successfully fabricated while maintaining controllability of physical parameters to allow for flexibility in designing cells. With the pyrolysis technique, carbon based nanowire arrays were made irreversibly from PPO, suggesting an easy design of anode in the proposed micro-battery. From earlier experiments and fundamental studies on PPO with various parameters including deposition methods, deposition voltage, time, and template, we found that a linear relationship between the deposition time and the width of PEDOT nanowires, allowing us to find the optimal synthesis condition for PEDOT. With PPO having similar characteristics to PEDOT, similar approaches were applied and tuned to synthesize PPO.

After trials of cyclic voltammetry results, we were able to find the optimal synthesis conditions for the anode of the proposed micro-battery system; 600 seconds of deposition time with potential static method followed by pyrolysis at 650 °C with 30 minutes of dwell time. With successfully synthesized carbon based anode nanowires, further analysis can be done with the system in electrolyte. While showing the feasibility of micro-battery fabrication with LPNE method already yields interesting results, further experimentation
and validation will be required to fully characterize LPNE nanowire electrodes and confirm their viability in detailed cell-level design studies. A detailed morphological and electrical characterization of the anodes produced via the pyrolysis would help in refining the fabrication technique. Critical questions such as the electrical and mechanical continuity, and dimensional controllability of the nanowires can be answered through SEM and AFM. This is of particular interest as there are concerns of physical damage to the anode post-pyrolysis, along with the repeatability of the width of wires for testing. Ideally, the device will be investigated with in-situ AFM to show controlled lithium intercalation movement at specified depth of discharge (DOD) and state of charge (SOC), to show specific power rate. The process of collecting and interpreting the electrical results of a cell through IV curves during operation is already well defined. However, we do not have a clear idea of what is physically occurring at the surface level of the electrode during this period. This tool will allow novel investigations into power performance as a function of cell design characteristics on the electrode level. So far, this thesis covers the initial stage of micro-battery development and the current research only validated the possibility of nanowire electrodes in the form of controlled fabrication. Future research will be expanded to in-situ characterization the hybrid electrodes, either with different chemistries or loading levels to confirm electrochemical activities in atomic level.
CHAPTER II

An Industrial Comparison of Lithium-Ion and Lead Acid-Based Low Voltage Battery Systems

1. Introduction

1.1. Objective of Chapter II.

The main objective of Chapter II is to explore the use of lithium-ion chemistries in low voltage battery systems in the automotive industry. Most manufacturers currently source lead acid batteries despite their low energy density and toxicity.

The thesis assesses the feasibility of using lithium-ion cells for the low voltage system given low temperature power (LTP) performance, shelf storage performance, and cost efficiency. Vendor supplied data was used for the analysis and vendor/model names were redacted to conform to non disclosure agreement (NDA) restrictions.
1.2. Low Voltage System Battery

Today’s vehicle is composed of many electronic parts and it is not an exaggeration to say that an automobile is a fine result of modern electrical, mechanical, and chemical research combined. Whether it is electric vehicle or traditional gasoline vehicle, many parts of a vehicle need an electric energy source with low voltage system, which makes having low voltage system battery necessary in electrical vehicles as well. Traditionally, automotive batteries are required to be rechargeable, able to start an engine, and have enough power to supply other low voltage electrical energy to the vehicle while in operation. Basically whether 12 V batteries can have SLI function (starting, lighting, ignition of engine) is basic criteria. Most of SLI batteries are lead acid with nominal voltage of 12.0 V in modern market. Porsche was the first car maker to introduce Li-ion starter battery for 911 GT3, 911 GT3RS, and Boxter Spyder at $1,700 USD \textsuperscript{[15]}. There has been more research being driven to use lithium ion chemistry for the 12 V automotive battery system due to many benefits. Yet, most of current 12 V automotive batteries are based on lead acid chemistry. Because basic chemistry of lithium-ion battery was described in previous introduction part in Chapter I, lead acid chemistry will be briefly discussed in below with comparison chart.

For lead acid batteries, there are two design types of lead acid batteries; sealed/flooded and VRLA using absorbed glass mat (AGM). Generally, AGM batteries are more expensive
but show better performance in cycling and deep discharging. Though each battery manufacturers have their own design and chemistry, lead dioxide is active material for positive electrode and metallic lead in porous structure is used for negative electrode.

\[ Pb + PbO_2 + 2H_2SO_4 \leftrightarrow 2PbSO_4 + 2H_2O \]

Each cell has nominal voltage of 2.0 V and six of the cells are connected in series in a single case. By the weight analysis of acquired samples, flooded batteries have active materials and grid components as about 70 % of the total weight. AGM batteries, on the other hand, have active materials and grid components around 85 % of total weight\textsuperscript{[11]}.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Pb Acid</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Lead</td>
<td>Carbon</td>
</tr>
<tr>
<td>Cathode</td>
<td>PbO\textsubscript{2}</td>
<td>Li-Metal Oxide</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Diluted H\textsubscript{2}SO\textsubscript{4} (Aqueous)</td>
<td>Organic solvents with additives</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Properties</th>
<th>Pb Acid</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal V</td>
<td>2</td>
<td>3.7 (average)</td>
</tr>
<tr>
<td>Operating V</td>
<td>2.0 to 1.8</td>
<td>Various</td>
</tr>
<tr>
<td>Operating T</td>
<td>-40 to 55 °C</td>
<td>-20 to 50 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy Density</th>
<th>Pb Acid</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volumetric (Wh/L)</td>
<td>40</td>
<td>203</td>
</tr>
<tr>
<td>Gravimetric (Wh/kg)</td>
<td>80</td>
<td>570</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Power Density</th>
<th>Pb Acid</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td></td>
<td>Moderate to High</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Pb Acid</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varies</td>
<td></td>
<td>2000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Self-Discharge/ Calendar Life</th>
<th>Pb Acid</th>
<th>Li-ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate, Few Months</td>
<td>Moderate, Few Months</td>
<td></td>
</tr>
<tr>
<td>Low, Good</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 3. Simple comparison chart of lead acid battery and lithium-ion battery.*
1.3. **Low Voltage Requirements**

From the chart above, we know what are the chemical and physical differences of both types of batteries. Whether the characteristic of lithium-ion or lead acid is beneficial for the low voltage application in automobiles can be only determined after evaluating critical requirements in specification. The very basic purpose of SLI batteries is to start the engine until power can be supplied via alternator, which requires a high burst of current. Also, typical SLI batteries do not need cycling. Battery chemistry can be selectively selected for the vehicle requirements, but certain performance metrics should be guaranteed to be considered for application.

2. **Experimental Results**

An automotive 12 V battery traditionally handles engine starting, vehicle lighting, and engine ignition (SLI) functions and is often simply referred to as an SLI battery. These tasks are critical to the function of a vehicle and require the SLI battery to meet certain performance metrics to guarantee nominal operation. The most common industry standard metrics are “Cold Cranking Amps (CCA)” and “Reserve Capacity (RC).” Due to the significant amount of power required to start the engine by the starter motor, power is more valued than energy density in this application. SLI batteries are rarely discharged more than 20% under normal operating conditions\textsuperscript{[16]} leaving deep discharge capabilities as a
non-critical performance metric. As such, we will discuss the most critical performance points relevant to power in this report. Low temperature power and shelf storage will be discussed in section 2.1. and 2.2. of this report, respectively. Then normalized values of both gravimetric and volumetric energy densities will be used to compare lead acid and lithium ion designs.

2.1 Low Temperature Power Performance

A common industry standard for rating the performance of SLI batteries in vehicle applications is cold-cranking amperes (CCA). The CCA test evaluates whether the battery is capable of delivering the power to crank an engine in low temperature conditions. This is because battery power delivery capabilities generally drop drastically due to increased internal resistance from reaction and transport rates at low temperatures. In extreme cases, the increased viscosity of automotive oil at low temperature would also require more current from the starter motor to apply sufficient torque to the crank. The cranking period could also be increased due to the need for several cycles to burn off condensed fuel on the cylinder walls and warm the block to achieve proper atomization needed for combustion. The combination of these factors mean that the same battery that started a vehicle on a hot day may fail to perform the same thing on a cold morning. The CCA testing standard requires a fully-charged battery, after a shipping charged condition at vendor’s specified profile, at -18 °C to deliver a set current for 30 seconds without dropping below 7.2 V (Standard SAE Requirements, J537).\textsuperscript{[22]} This set current is the CCA rating. Engine size
and compression are some of the most critical factors in determining CCA requirements, as larger engines with heavier parts means more inertia for the starter motor to overcome. Likewise, a diesel engine with higher compression ratios will require a more powerful starter motor. Since multiple design parameters can impact CCA, including both mechanical and chemical designs, mass was used to normalize vendor supplied data to better isolate from factor from this study. Ideally, this gravimetric value will not differentiate between a larger and smaller battery having identical internal designs and allow for a better generalization of SLI lead acid CCA performance. A market analysis yielded an average gravimetric CCA value of 33.98 A/kg, as shown in Table 4 below. This data represents commercially available lead acid SLI product lines from seven distinct vendors.

<table>
<thead>
<tr>
<th>Vendors</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normalized CCA (A/kg)</td>
<td>31.16</td>
<td>28.29</td>
<td>33.31</td>
<td>38.87</td>
<td>33.31</td>
<td>38.87</td>
<td>34.07</td>
<td>33.98</td>
</tr>
</tbody>
</table>

*Table 4. CCA at -18 °C as described by given procedure in above, normalized to be A/kg. Data used by 12 V lead-acid battery vendor supplied data.*

While this gravimetric CCA does indicate some variation in initial performance, we will generalize this average CCA value as a typical lead acid SLI 12 V battery’s capability for the purposes of this comparison.

For analyzing the CCA of lithium-ion automotive batteries, several batteries from vendors in development were used. There are many different lithium-ion chemistries that are being
used in cell design and the voltage range would be determined and differentiated by types of lithium metal oxide. As shown in Figure 18 below, potential cell-level voltage windows differ by cathode types. In the current market, however, LiFePO₄ is most actively considered chemistry for 12 V SLI development due to its intrinsic safety properties. This limits the sample size of existing li-ion 12 V products that would allow lithium-ion discussions with LFP chemistry. A further confounding factor to this comparison is that most li-ion SLI vendors advertise “LCA”, Lithium-ion Cranking Amperes, instead of CCA. While this will be explained in further detail below, this is due to the CCA testing specifications not being directly translatable to li-ion designs due to differences in voltage windows. Because there is no standardized procedure or guideline for LCA, vendor specified LCA values do not give us normalized gravimetric LCA data from different vendors is highly variable, as shown in Table 5.

<table>
<thead>
<tr>
<th>Vendors</th>
<th>Normalized LCA (A/kg)</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>282.19</td>
<td>247.06</td>
<td>67.91</td>
<td>90.00</td>
<td>171.79</td>
</tr>
</tbody>
</table>

*Table 5. LCA at -18 °C as described by given procedure in above, normalized to be A/kg. Data used by 12 V li-ion battery vendor supplied data*

With such a wide range of values in data set, we cannot directly compare the LCA to CCA, which makes a numerical comparison between li-ion and lead acid 12 V batteries difficult. Manufacturer datasheets generally state that non-normalized LCA values should be multiplied by 1.5 to estimate the real current that lithium ion can deliver, as the vendors are taking the consideration of potential window in voltage difference from both chemistries. To explain further in detail, voltage difference from two different chemistries
were rated by 1.5x as Figure 18 in below specifies the potential difference. The tested CCA values are compared to find the voltage deliverable throughout the specified performance but they are not necessarily an ultimate test or measurement for true cranking current. With $V=IR$ and $P=IV=I^2R$, current multiplied by voltage would be actually producing the power to perform work (watts). Considering what we care about is power deliverable in watts, the rating system was evaluated to compare an equivalent CCA-rated lead acid battery’s performance.

![Figure 18. Comparison graph for discharging of LFP and PbA batteries.](image)

<table>
<thead>
<tr>
<th></th>
<th>Pb Acid</th>
<th>Li ion</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volumetric CCA</strong> (A/L)</td>
<td>66.23</td>
<td>158.07</td>
</tr>
<tr>
<td><strong>Gravimetric CCA</strong> (A/kg)</td>
<td>33.98</td>
<td>171.79</td>
</tr>
</tbody>
</table>

*Table 6. Comparison of normalized CCA of lead-acid and lithium ion chemistries in current 12 V batteries.*
It was thus necessary to perform an internal evaluation of the batteries with customized testing methods and specifications to validate individual battery SLI performance independent of chemistry. The charging profile was tailored to match observed vehicle usage patterns and benchmark data was supplied to vendors to follow for performance evaluation. With current level of lithium ion cells in market with high power capabilities, 30 A per 18650 cell as maximum continuous discharge current is already a possible, as shown in Figure 19.

![Li-ion Evaluations for Power Performances](image)

*Figure 19. High power li-ion cells in market for evaluation for maximum continuous discharge current per capacity. C-rate would be calculated from the graph as well.*
One factor to consider would be Series-Parallel [SP] configuration of these cells in a system. The current technology limitations of lithium ion chemistries at -18 °C is another concern, especially when we consider how different cathode chemistries allows us more room to play in potential ranges.

![Figure 20. Map of voltage densities for different lithium metal oxide commonly used in cathode. Reference [20]](image)

With its higher energy and comparable power density, lithium ion seems like a viable contender against lead acid for SLI applications. If we consider electrical and hybrid vehicles, which have much lower starting requirements due to less inertial mass for the starter to overcome (or no starter motor at all), a high CCA may no longer be necessary with proper system design and makes lithium ion option more appealing. However, we
should know that lithium ion costs much more than lead acid option, which will be discussed later in Discussion section of this report. Also, one of the advantages from lead acid is its low energy density making the battery system a lot safer in an application. [8] This can be done by regulating voltage within battery management system to control, so the discussion will only consider cost evaluation in perspective.

2.2 Self discharging and Storage Performance

From industrial perspective, self discharge rate is quite important especially when we talk about energy storage in shelf life. Thermodynamically, electrode reaction equilibria are towards discharge direction, so the discharged state would be more stable. Also, this matters not just in shelf life while inventory depository but also while vehicle is not in use for a long time. Many conditions including depth of discharge (DOD) and state of charge (SOC) would affect storage life performance. [17] Because of this, each vendor has specified optimal charging condition for their batteries in application, as well as own proprietary charging conditions in battery manufacturing and shipping status. Typically shipped batteries have stable OCV and impedance as vendor states, as shown in Figure 21, as an example.
OCV of the cells fade eventually as storage time becomes longer. Typically, self-discharge rate with vendor shipped voltage for lead acid batteries decreases by 2-3 % per month in room temperature. \(^{[19]}\) If 2 % of capacity drops every month, then a battery with 12.73 OCV in shipping charge would be 11.98 V by 3\(^{rd}\) month in. The literature value was reestablished by random samples of lead acid batteries in stock for a discharge rate study. Self-discharged rate of lead acid batteries with OCV measurements concluded 1-2 % drop per month which would take six months to be 11.92 V. This was done by mostly electrolyte improvements and cell designs by vendors. Lead and lead dioxide are thermodynamically unstable in sulfuric acid solutions, which would still be affected in open circuit status. Oxygen would evolve in positive electrode whereas hydrogen would at the negative. The grassing rate increases with increasing acid concentration as follows in below equation. \(^{[17]}\)

\[
PbO_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O + \frac{1}{2}O_2
\]

\[
Pb + H_2SO_4 \rightarrow PbSO_4 + H_2
\]
This is temperature dependent and acid concentration dependent as well. At the positive electrode, PbSO₄ development by self-discharge would be slow, yet the negative electrode has relatively rapid reaction. There could be many discussions associated with design for better self-discharge performances including low-antimony alloy grids and acid concentration that can be done. On contrary, lithium ion has benefit in self-discharge rate. Literature claims that it would have 2\% decreasing rate monthly, but actual data shows less than 1\% drop per month. Having a wider voltage window for lithium ion allows lithium ion cell’s calendar life a lot longer, in addition, by controlling DOD.

3. Discussion

For SLI purpose, only two segments of 12 V SLI performance was discussed with explored test data. However, the fundamental comparison of two cannot be dismissed without cost evaluation in market research of these batteries. This is one of primary reasons why many manufactures are still sourcing lead acid batteries for the low voltage system in vehicle while lithium ion batteries meet and often exceeds some of test requirements in performance and specifications. Cost and commercial sides of two batteries will be discussed a bit closely in below section.
3.1. Cost Analysis

Lead acid batteries have an overwhelmingly dominant large market share due to their lower costs, and easy accessibility in market. There are as many form factors of lead acid batteries as vehicle sizes, and as such one must select from the correct “group size” to ensure performance and an easy installation. Lithium ion batteries are a lot smaller for the same capacity deliverable, but lead acid batteries have large by volume and heavy by mass as these factors depend on the size and requirements of vehicle power. Thus, sometimes vehicles need to make a room for those batteries that only fixed 12 V battery sizes would fit in a car. With different sizes and volumes of current 12 V batteries available, price was again normalized by weight and volume of the batteries. Thus, as below chart some of batteries were taken as sample and calculated to attain an average market cost. Note that this table is to show only market cost of lead acid batteries and lithium ion batteries by volume or mass, not to show cost per per active material. Also, Li-ion mass and volume are taken form complete configuration, not calculated based on cell sizes.

<table>
<thead>
<tr>
<th></th>
<th>$/kg</th>
<th>$/L</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lead Acid</strong></td>
<td>12.0</td>
<td>22.5</td>
</tr>
<tr>
<td><strong>Li-ion</strong></td>
<td>170.8</td>
<td>206.2</td>
</tr>
</tbody>
</table>

Table 7. Cost by weight and volume for both lead acid and lithium ion 12 V batteries in market average.
It is true that the lead acid batteries are much cheaper than li-ion batteries by volume and mass. Thus, the CCA analysis above and capacity value of lead acid compared to lithium ion can be reestablished with the cost of two batteries. From the Table 7, the cost difference between lead acid and lithium ion are tremendous, as lithium ion is 14 times more expensive than lead acid. However, we would need to look at the power deliverable per weight to run cost analysis. For example, if we want 350 A from both batteries, the average cost here would give us $123.59 for lead acid and $347.98 for lithium ion option, according to average values in Table 6 and Table 7. According to the cost analysis, lithium ion is about three times more expensive than lead acid batteries. A more efficient way to look at these cost comparisons will be comparing relative energy density and power density per USD.

The cost approximation can be done with lifecycle assessment of both batteries, as well. Especially in modern vehicles with consistent effort of reducing the weight of vehicle parts, quantitative value of having lighter battery should be considered in cost analysis. Also, if having a longer cycle or calendar life of 12 V battery is beneficial in vehicle or application, monetary values by cost analysis should also be calculated. Environmental impact of lead acid battery is also another important factor to count in when it comes to 12 V battery development. This is directly related to recycling fee of lead acid with strict regulations and policies in Europe and certain countries.
4. Conclusion

Lead acid is still a very attractive source for low voltage power system for SLI purpose in vehicles due to low cost, ready availability, proven safety with low energy density, and meeting the cranking requirements with high rate in broad range of operating temperature. However, environmental factor, lighter weight and smaller volume due to high energy density makes lithium ion quite attractive. Lithium-ion option would also meet power requirements with long cycle life and low self-discharge rate on shelf, depends on specific requirements by vehicle application. Future studies can be done to modify lithium ion chemistry and even combine with other energy storage system to overcome current limitations of lithium ion.
References


[16] J. X. Weinert, A. F. Burke, and X. Wei, “Lead-acid and lithium-ion batteries for the Chinese electric bike market and implications on future technology advancement”, J. Power Sources. 2007, 172, 938-945


