

Methods for Improved Energy Density in Li Ion Batteries via Utilization of Thick Electrodes

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Abstract:

Global climate change has brought about an increased need for the use of more sustainable modes of transportation. Developing lithium ion batteries with improved energy and power densities, without increasing cost, is important in increasing the widespread use of electric vehicles. To achieve this feat, engineering thick electrodes such that higher energy densities can be achieved without sacrificing power density is imperative. A method utilizing 3D printing was used to create high performance, thick electrodes which achieved high energy densities while maintaining high power densities. This method shows the potential of strategically engineering electrode materials for improved performance.

1. Introduction

The transportation sector accounts for 29% of greenhouse gas emissions in the United States [1]. To avoid catastrophic consequences to our environment, it is necessary to find a way to reduce the impact of vehicles. One such option is the widespread integration of electric vehicles (EV). EV can convert 60% of the electricity drawn from the grid into operational energy, compared to the only 20% conversion efficiency of the typical internal combustion engine [5]. Additionally, EV do not produce harmful chemicals which are exhausted from a tailpipe and have the ability to utilize energy from renewable sources such as wind and solar. Development of the electric vehicle has seen great strides in the recent years, however “range anxiety,” or fear of having only a limited driving range before requiring a time-consuming recharge time, has limited their widespread adoption [2]. Reducing this range anxiety involves the development of better batteries. Li ion battery technology is currently utilized in EV.

The US Department of Energy has announced the goal of reducing battery prices to less than \$80/kWh, while increasing range to greater than 300 miles on a full charge, and decreasing the time to recharge to less than 15 minutes [4]. These goals provide opposing challenges. Increasing range requires that the battery is able to hold more energy, but this requires a longer time to recharge the battery to full capacity, unless the recharging power is also increased.

Accomplishing this while decreasing battery cost is a tall order and will require significant effort from the research sector. Additionally, this needs to be accomplished without a significant

increase in the mass of the battery, which if increased, would decrease the efficiency of the car (miles per kWh). This means the overall energy density, or kWh/kg, need to be improved.

Ideally, reaching these goals can be accomplished with existing Li ion battery technology through clever engineering of the battery cell. A lithium ion battery consists of several key components. Two electrodes, an anode (typically graphite) and a cathode (a layered metal oxide) are submerged in a liquid electrolyte solution containing a Li-based salt. A separator is placed between the two electrodes to prevent short circuits in the cell and the electrodes are connected by an external circuit which allows electrons to flow during charging and discharging. During discharge, electrons flow from the anode to the cathode through an external circuit. In order to avoid a build up of negative charge on the cathode from the excess electrons, positive Li ions will flow through the electrolyte solution into the cathode material to provide charge compensation. When the material is recharged, the electrons flow from the cathode to the anode and the Li ion will follow through the electrolyte solution (Figure 1). In addition to the parts of the battery integral to the chemistry associated with charge storage, there are many additional components of the battery necessary for its successful operation. These include current collectors, onto which the electrode materials are coated, and cell casing which houses the formerly-mentioned parts. Battery packs are typically assembled in the form of multiple cells strung together in series to increase voltage and in parallel to increase capacity. For example, to make up the 85 kWh battery pack in the Tesla model S battery, the base of the car contains 16 modules wired in series, each containing 6 groups, also wired in series, of 74 cells wired in parallel, for a total of 7,104 lithium ion battery cells, weighing 1,200 pounds (Figure 2). The battery pack is estimated to cost 21-22% of the cost of the car (~\$15,000) [8].

Strategically engineering batteries can provide a method of improving energy density of the battery without changing battery chemistry. The mass of the electrodes, which store the energy in a battery, should be increased while simultaneously decreasing the mass from inactive components (separator, cell casing, current collectors, etc.). There are several strategies to attempt to accomplish this. Reducing the weight associated with cell casing or separator thickness is associated with safety concerns. The amount of electrolyte solution utilized in the cells has already reached an essentially minimized volume. This leaves increasing the thickness of the electrodes. By increasing electrode thickness, the amount of active material in the cell

increases without a mass increase in other cell components, resulting in an increase in the energy which can be stored in the cell normalized to the weight of all cell components. Current cells have electrodes of with a thickness of approximately 25 μm , corresponding to about 8 mg of active material per cm^2 . If electrodes were increased to 200 μm , the mass loading would increase to about 64 mg/cm^2 . The inactive components of the cell would decrease from making up about 44% of the weight of the cell to only 12% of the weight of the overall cell, and over 30% by weight increase in the active material in the cell [4].

The benefits to this method are vast, but increasing electrode thickness corresponds with large drawbacks. An increasing electrode thickness typically correlates to decreasing electrode rate capabilities, or how fast the battery can be charged/discharged, which has been identified as a factor of battery technology that the DOE wants to improve. This decrease in rate capability is due to the large ion and electron diffusion lengths resulting from the thickness increase. The Li ion needs to travel further through a thick electrode in order to compensate negative charges. Diffusion through electrode pores and bulk active material is already regarded as a slow, often rate limiting process. Additionally, electrons will have a further path to travel to reach the current collector and there will be a greater resistance in the cell. Increased resistance will result in a greater IR drop in the voltage, causing the cell to reach cut-off voltages in charge/discharge sooner, and will result in incomplete charge/discharge. This effect will be multiplied with employment of faster rates, or higher current being drawn from the cell [4].

To allow for the use of thicker electrodes, previous work had been done nanoscaling materials to shorten diffusion pathways of the Li ions through bulk material. In these nanoparticles, electron transport had been shown to be the rate-limiting step. This was improved upon by coating the particles in a conductive carbon coating. Following this, the rate of ion transport at the electrolyte electrode interface became the limiting factor, which was addressed by creating an artificial electrode electrolyte interface which allowed fast transport of the ions from the liquid to the solid phase. Finally, the transport of Li ions in the solution can be limiting in cases of changes to the liquid environment, in thick electrodes, and at very fast rates [5]. Taking the findings of previous work into consideration, Hu *et. al.* sought to improve the overall energy density of a battery using a 3D printing method [6]. Their reported method improved the

performance of their cathode materials over cathodes made by conventional methods due to improved ion transport through their strategic electrode design.

2. Methods

Hu *et. al.* looked to 3D printing of cathode materials as a way to create high performance, thick electrodes. 3D printing has a number of advantages including rapid prototyping, low cost patterning, and ability to easily control thickness of printed material. They took advantage of the technology to print 3D $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4 @\text{C}$ nanocrystal cathodes. $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ possess a high energy density and high working voltage, making it an ideal cathode material if rate capabilities can be improved. They compared their 3D printed cathode with a traditional $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4 @\text{C}$ cathode which is applied to a current collector using a doctor's blade technique, wherein the electrode is mixed with a solvent to form a slurry with paint-like consistency, and subsequently spread onto a current collector. The material was characterized by x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and thermogravimetric analysis. The materials were assembled into coin cells and used for device testing [6].

3. Results

The curves corresponding to the charging and discharging of the batteries displayed two plateaus and 4.1 and 3.4 V vs. Li/Li^+ , corresponding with the electron transfer event associated with the Mn and Fe metal centers in the cathode. When the rate capabilities of the two cathodes were compared, the improved performance of the 3D printed material compared to the traditional electrode was demonstrated. Rates used in this study were described as C-rates, where 1 C corresponds with a current capable of discharging the theoretical capacity of the battery in 1 hour. At 100 C, corresponding with a discharge time of $1/100^{\text{th}}$ of an hour or 36 seconds, the 3D printed material maintains a capacity of 108 mAh/g while the traditional cathode only achieves a capacity of 70 mAh/g (Figure 3). Additionally, the 3D printed cathode showed significant improvements in retained capacity compared to the traditional electrode, when the material was charged and discharged for 1000 cycles.

To understand the improved rate performance of their 3D printed material, the researchers used computer modeling to simulate a cell where they could change the thickness of their electrode.

With increased thickness, they found there was slower diffusion of Li ions in the electrode due to increased concentration polarization in the cell. This results in decreased Li ion transport in the cell, meaning that in the model cell, the active particles have a greater reliance on Li ion diffusion in the electrolyte. They compared the calculated capacities at different rates and thickness to their experimental results, and found the two were in good agreement, giving them confidence in their calculations. Their calculations showed an increasing drop off in capacity with increasing thickness as a cell of a given thickness was tested at higher rates.

Using the overlap observed in their experimental and theoretically calculated results, the authors observed a relationship between thickness and C-rate that allowed them to calculate an equivalent diffusion coefficient. Their calculations showed that the equivalent diffusion coefficient can be broken into three parts in which diffusion in different regions is differently weighted. In thin electrodes (Zone 1) or slow rates of discharge, the diffusion of ions will be limited by bulk diffusion, or diffusion of the ions through the solid electrode material. Diffusion of the ions through the liquid electrolyte in the pores of the electrode material is significantly faster and will not limit the performance of the battery. This is not true for thick electrodes or fast rates of discharge. During discharge, a concentration gradient of Li ions builds up in the electrolyte solution. This results in a depleted concentration of Li ions at the surface of the electrode material such that the Li ions are not readily available to diffuse through the active material particles. The electrochemical reaction must wait to occur until more Li ion can diffuse through the electrolyte solution, to the surface of the active material such that bulk diffusion can occur. In this situation, the diffusion through the electrolyte and the electrode pores is considered to be limiting. The 3D printed material has improved porosity, which allows for better ion diffusion in the electrolyte solution in the pores of the material. Thus, the performance of the 3D printed electrode remains in Zone 1 for faster rates of discharge/thicker electrodes [6].

4. Conclusion

To improve Li ion battery technology to meet future needs, energy and power density need to be improved while cost of the technology decreases. By employing thicker electrodes, energy density can be increased without a need for changes in battery chemistry. Although simply scaling up the thickness of electrode materials has resulted in negative consequences in terms of

power density, strategic engineering of thick electrodes has allowed for thicker electrodes with good rate performance. Herein, a method utilizing 3D printing was shown to improve thick electrode performance by improving Li ion transport through the battery material. Future work should be done to continue to develop new electrode engineering methods which results in improvement both the energy and power density of Li ion batteries.

Figures

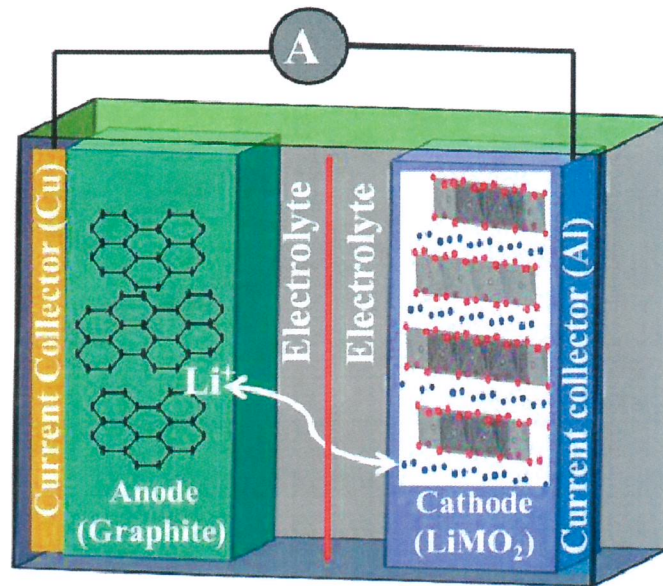


Figure 1. Schematic of lithium ion battery components. Figure obtained from [1]



Figure 2. Battery pack inside Tesla Model S, containing 7,104 lithium ion battery cells, to provide the car with 85 kWh of energy at full charge. Figure from: <https://insideevs.com/news/323682/rare-look-inside-a-tesla-model-s-battery-pack/>.

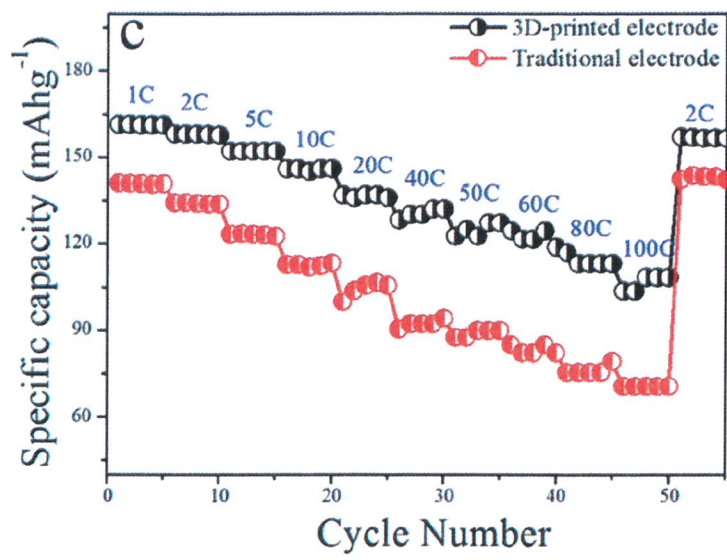


Figure 3. Rate testing of the 3D printed electrode overlaid with the results from a traditional electrode. The numbers in blue correspond with C-rates, or current densities, which are increased from 1 C to 100 C, followed by returning the rate to 2C for the final 5 cycles. From figure 2 in [6].

References

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8. Tesla Model S battery information is available on the “Tesla Model S” page on Wikipedia, < https://en.wikipedia.org/wiki/Tesla_Model_S>.