Lithium Ion Batteries and their Manufacturing Challenges

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Abstract

There is no single one "*lithium ion*" battery. With the variety of materials and electrochemical couples at our disposal as shown in the previous talks, we have the opportunity to design battery cells specific for their applications. Such applications require optimization of voltage, state of charge utilization, lifetime needs, and safety considerations. Selection of specific electrochemical couples also allow for designing power and energy ratios and available energy for the application.

Integration in a large format cell requires optimized roll to roll electrode manufacturing and active material utilization. Electrodes are coated on a metal current collector foil in a composite structure comprised of active material, binders, and conductive additives which requires careful control of colloidal chemistry, adhesion, and solidification. These added inactive materials and the cell packaging reduce energy density. Degree of porosity and compaction in the electrode can impede or enhance battery performance.

Pathways are explored to bring batteries from currently commercially available 100Wh/kg and 200Wh/L at $500/kWh to 250Wh/kg and 400Wh/L at $125/kWh.

Fundamentals of lithium ion batteries

The one common aspect of lithium ion batteries is that during charge lithium ions travel from the positive electrode or cathode through a solid or liquid electrolyte to the negative electrode or anode and during discharge in the opposite direction. At each respective electrode, the ion maintains its ionic form and intercalates into the crystal structure occupying interstitial sites in existing crystals on the anode side or re-occupying a vacant site in the cathode which formed when the lithium ion left that crystal. While transferring that ion, the host matrix gets reduced or oxidized which releases or captures an electron. If the ion would change its state of charge, it would be called a conversion battery such as air batteries. (Daniel et al., 2011)

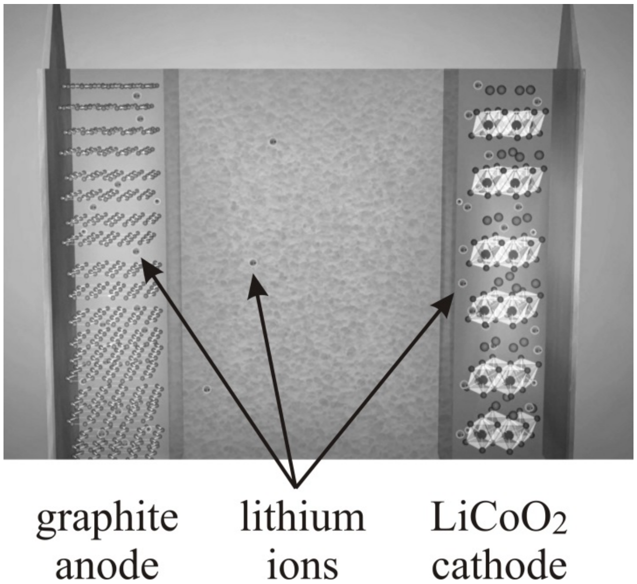


Figure 1: Inner structure of a battery and its lithium ion movement
for an animation go to: http://youtu.be/e7ZpvyJhMHM

The lithium ion battery was made possible by the discovery of $LiCoO_2$, which allows the extraction of lithium ions and creation of large amounts of vacancies without a crystal change up to the removal of half of the existing ions, and graphite, which allows the intercalation of lithium ions in between the graphene layers occupying the interstitial site between every hexagonal ring of carbon atoms. (Besenhard et al., 1976; Whittingham et al., 1976; Mizushima et al., 1980)

Variety of cathode materials

The search for new cathode materials is driven in part by notable disadvantages of $LiCoO_2$. $LiCoO_2$ is very reactive and an excellent oxygen source for what the community calls a thermal runaway reaction. With core temperature of the battery around 40-70°C, some low temperature reactions start to occur, but with temperatures around 105-135°C, highly exothermic reactions create temperature spikes and accelerate fast due to the release of extra heat during the reaction. (Roth, 2000) This is called thermal runaway and poses a safety hazard.

During the course of the development, replacements for $LiCoO_2$ have been found which are less prone to that failure. Those compounds either replace parts of the cobalt with nickel and manganese forming $Li(Ni_xMn_yCo_z)O_2$ compounds (with $x+y+z=1$) often referred to as NMC or exhibit a completely new structure in form of phosphates like $LiFePO_4$. (Daniel et al., 2014)

These cathode materials all exhibit capacities in the range of 120-160Ah/kg at 3.5-3.7V resulting in maximum energy density of up to 600Wh/kg. When packaged in real devices, much inactive material mass is added and the energy density tends to drop to 100Wh/kg on the pack level. In order to push for higher energy density, the community has been on the search for higher capacity and higher voltage and found lithium and manganese rich transition metal oxides. These compounds are essentially the same materials as NMC but demonstrate an excess of lithium and higher amounts of manganese replacing nickel and cobalt in the structure. Some have 20% higher amounts of lithium. This allows those compounds to have higher capacity.

(Thackeray et al., 2007) They also demonstrate a higher voltage and enable cathodes with up to 280Ah/kg when charged up to 4.8V. However, these new compounds show stability problems and tend to fade fast.

Balancing of materials in real cells

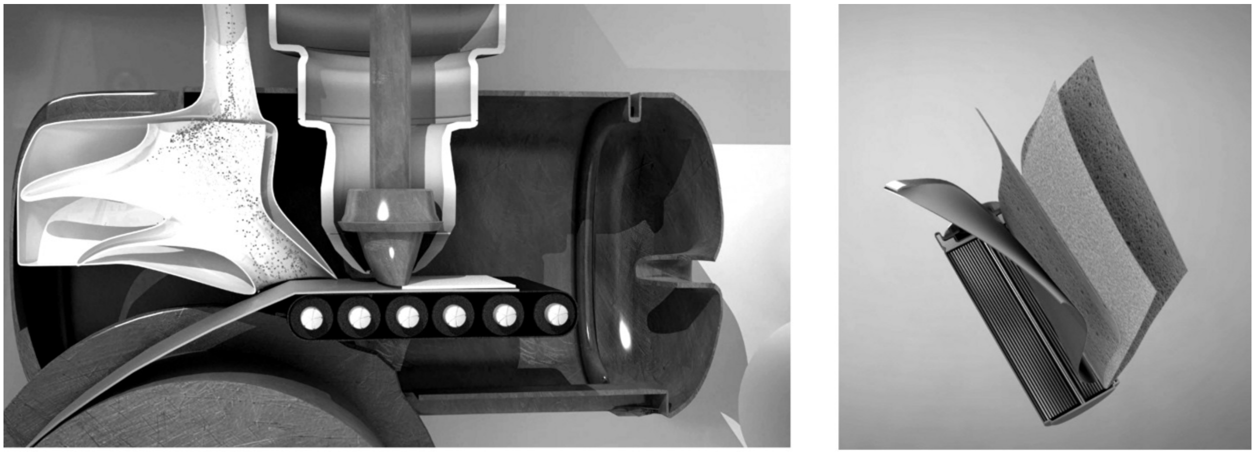
Lithium ion batteries are made of layers of porous electrodes on aluminum and copper current collector foils. (Daniel, 2008) The capacity of each electrode pair needs to be balanced in order to demonstrate a safe battery and not risk overcharge of the anode which can result in lithium metal plating and short circuiting, or over-discharge of the cathode which can result in a collapse of the crystal structure and loss of vacancies for lithium to re-intercalate dramatically reducing the available capacity.

Graphite has a theoretical capacity of 372Ah/kg which is double the amount of lithium compared to the available lithium in NMC cathodes. Therefore, in balanced lithium ion batteries, the cathodes typically exhibit double the thickness compared to the anode. This is an inherent flaw of the cell build which causes issues with mass transport and kinetics and therefore fostered the search for the above mentioned high capacity cathodes.

In order to increase the cell level energy density, inactive materials are being minimized in battery cells. One aspect of reducing inactive materials such as the current collector is to increase thickness of electrodes which further drives the problems of transport and requires a highly engineered porosity in those porous electrode layers.

Manufacturing of lithium ion batteries and aspects of cost challenges

Cost of lithium ion batteries are currently much higher than the automotive market could accept for a full penetration of electric vehicles in the market and a cost neutral product compared to cars which are run by internal combustion engines. The U.S. Department of Energy cost target for all electric vehicles is $125/kWh of usable energy. (Danielson, 2013) The current cost of commercial batteries is $400-500/kWh and projected cost of new experimental materials is $325/kWh. Most of the cost reduction in the past has been achieved by energy density increases at similar cost to the older generation products.



electrode coating
on current collector

electrode stack with anode, separator,
cathode, separator visible

Figure 2: Manufacturing schematic of electrode coating and battery electrode stack
for an animation go to: http://youtu.be/ZY7_EYrJrWg

Further cost reduction is possible through optimization of manufacturing schemes. Lithium ion batteries are manufactured in sets of electrodes and then assembled in cells. Active material is mixed with polymer binders, conductive additives, and solvents to form a slurry which is then coated on a current collector foil and dried to remove the solvent and create a porous electrode coating. Currently the solvent of choice, is N-methyl pyrrolidone (NMP) which is expensive, exhibits flammable vapors, and is highly toxic. It is also a material which the supply chain industry calls an indirect material, meaning that it is needed for the production of the product but it is not contained in the final device.

The flammable vapors of NMP require all processing equipment during the production of electrodes to be explosion proof, meaning all spark producing electrical components need to be shielded from the vapors and spaces need to be highly ventilated to keep vapor concentrations low. This increases the capital cost of such equipment considerably.

The third aspect of toxicity requires the electrode manufacturing plant to recapture the solvent from its exhaust stream, distil the product, and recycle it. This is again an additional cost.

Cost reduction by water based processing

The replacement of NMP by water is a tremendous opportunity to reduce cost in the production of lithium ion batteries. Cost of the water as a solvent is negligible compared to NMP; water is not flammable and does not produce flammable vapors; and water is environmentally benign. However, water is a polar solvent and demonstrates completely different behavior than the non-polar NMP. Active materials tend to agglomerate and metal current collector surfaces are hydrophobic which makes the coating process more difficult.

Understanding surface charges on particles by measuring zeta potential enables the design of polarity of those surfaces in presence of water by introducing small amounts of surfactants. In the case of cathode intercalation compounds, polyethylene imide was used successfully to introduce a large enough surface charge which resulted in particles to be repelled and not form unacceptable agglomerates. (Li et al., 2013)

Understanding the surface energy of metals and surface tension of the slurry as well as their interaction allows for optimization of the pair. It has been demonstrated that atmospheric plasma treatment of the metal surface by exposing it to a corona plasma enabled a cleaning of organic compounds on the metal surface and a slight etching and oxidation of that surface to dramatically reduce the surface energy to values below the surface tension of the slurry. This allowed perfect wetting of the surface by the slurry and created a coating with optimized adhesion. (Li et al., 2012)

Both aspects together have been demonstrated to enable a 75% operational and materials cost reduction on the electrode manufacturing resulting in a potential reduction of cost by up to 20% on the battery pack level for automotive applications. (Wood et al., 2014) This does not count for the lower equipment cost in which reduction of solvent recovery system and elimination of explosion proof requirement are much greater than the addition of the plasma processing equipment.

Future

Further cost reductions will be enabled by better understanding transport mechanisms and electrode architecture implications on electrochemical performance. Currently, the community is heavily engaged in modeling and simulation on all length scales to understand molecular mechanisms and enable a better design of electrodes, electrode stacks, and battery cells. It will enable thicker electrodes and a tremendous reduction in inactive materials further improving energy density at low cost and reducing cost directly and potentially enable much shorter and less energy intensive battery formation cycling.

Conclusion

Lithium ion batteries bear a tremendous potential for enabling a partial to full electrification of our automotive fleet, diversify energy sources for transportation, and enable a large amount of grid scale energy storage for a higher penetration of intermittent renewable energy supply. However, cost continues to be an issue and will need to be addressed by the development of a robust supply chain, standards in manufacturing, high manufacturing throughput, and streamlined low cost processing routes. Continued effort needs to be made in reduction of cost and a better understanding of molecular processes and transport issues in order to optimize the design and use of available energy in batteries and increase their life time.

As shown in this paper, increase in energy content and capacity in active electrode materials and reduction of indirect materials in the production are two ways to impact cost.

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Media for illustration

- Battery operation: http://youtu.be/e7ZpvyJhMHM
- Battery manufacturing: http://youtu.be/ZY7_EYrJrWg