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BATTERY FUNDAMENTALS

he use of batteries as a portable power source has gained tremendous importance for powering mobile devices and for enabling greener and less energy-intensive transportation. Whether the demand is for a smart phone, laptop, tablet or the next wearable, the consumer demands a thinner and lighter battery while maintaining or increasing battery life at the lowest possible cost. This demand has caused many companies to increasingly consider the battery and its performance when designing their next device. While, in the past, it may have been acceptable to take an "off-the-shelf" battery that meets specifications and "plug it in", many companies are starting

to implement "smart" designs that take into account specific battery chemistries and characteristics to improve overall performance. This requires a knowledge of how a battery works. With this in mind, this article gives an explanation of battery fundamentals, why batteries degrade over their life, what limits their performance, the trade-offs between high power and high energy, and current efforts to build a better battery. While many of the overall properties are similar for many battery chemistries, here we will focus on the lithium-ion battery, specifically the cobaltdioxide/graphite lithium-ion battery, one of the most popular battery chemistries for mobile devices.

FROM CHEMISTRY TO ELECTROCHEMISTRY

Let us begin with basics. The study of batteries is in the field of electrochemistry, a subset of chemistry focused on understanding the relationship between chemical reactions and electricity. While the movement of electrons is present in all chemical reactions, electrochemistry deals with reactions on electrode surfaces where the movement of electrons and of ions is separated. Electrochemistry deals with the interconversion of chemical energy (in the form of chemical bonds) and electrical energy (in the form of electron movement, also known as electricity). To give an example, a chemical reaction

involves the transformation of one set of chemical substances to another, such as $A \rightarrow B$ or $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$. An *electro*chemical reaction is a chemical reaction that causes the creation and consumption of electrons such as

$$A \Rightarrow A^+ + e^-$$

and

$$A^+ + B + e^- \rightarrow C, \qquad 2$$

which can be added to become

$$A + B \rightarrow C$$
.

3

We can see that reaction 1 involves the production of an electron, while reaction 2 involves the consumption of an electron. If we mixed A and B in a vat, they would react via reaction 3 to make C. We can, however, make reactions 1 and 2 do work for us by splitting them up such as in Figure 1. Here, we have reactant A on the left and reactant B on the right. They are separated by a special substance called electrolyte, which is conductive to ions (in this case, A⁺), but is insulative to electrons. Because of this, the ion (A⁺) is allowed to flow through the electrolyte (following path [1]), but the electrons are forced through the external circuit (following path [2]), providing work for us in the form of electricity. The electron and the ion then react with reactant B, following reaction 2, to form our product, C.

The reader may have noticed that Figure 1 looks something like a battery, where the right side is denoted as the positive electrode (+) and the left side is denoted as the negative electrode (-) (also known as the cathode and the anode respectively). Indeed, every battery is made up of three components: a positive electrode, a negative electrode, and electrolyte, which must physically separate the positive and negative electrode and be conductive to ions and insulative to electrons.

The potential or voltage of the battery (measured in volts) is determined by the reactions occurring at each of the electrodes. If the reactants *really* want to be products, then the voltage will be high, but if the reactants have little desire to be products then the voltage will be low.

The capacity of the battery (measured in amp-hours) is determined by how much of each of the reactants are present. If, for example, we have a lot of both reactants A and B, then the capacity of our battery will be high, but if we do not have much of either, then our capacity will be low.

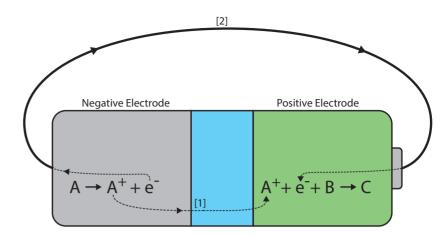


FIGURE 1. Generic battery with reaction 1 at the negative electrode (grey) and reaction 2 at the positive (green). The cation (A⁺) diffuses across the electrolyte (blue) via path [1] and the electron moves around the external circuit [2]. Both are reactants in reaction 2.

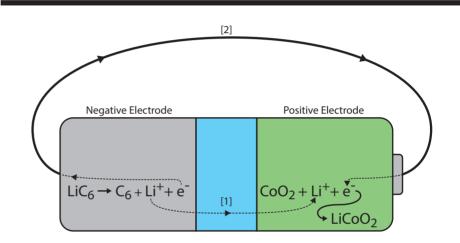


FIGURE 2. Basic lithium-ion battery moving from its charged state with lithiated graphite (LiC_6) at the negative electrode and cobalt dioxide (CoO_2) at the positive electrode to its discharged state with graphite (C_6) at the negative electrode and lithium cobalt dioxide ($LiCoO_2$) at the positive electrode.

However, if we have a lot of one reactant (i.e. A), but not much of the other (B), then the capacity will still be low and will be limited by the amount of B present.

THE ELECTROCHEMISTRY OF LITHIUM-ION BATTERIES

Let us now move to a battery that is a bit more relevant: the lithium-ion battery. Again, we must have a negative electrode, a positive electrode, and electrolyte. In the case of a lithium-ion battery, the material at the negative electrode (see Figure 2) is lithiated graphite (LiC_6). For the positive electrode, lithium-ion batteries have several

different chemistries that are common, however, for this example, we will choose lithium cobalt dioxide (LiCoO₂), as it is one of the more common materials for smart phone applications. The simplified reactions during discharge are

$$\text{LiC}_6 \Rightarrow \text{C}_6 + \text{Li}^+ + \text{e}^-$$
 4 at the negative electrode, and

5

$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$$

at the positive.

Similar to our battery in Figure 1, during discharge, the lithium in the negative electrode reacts to release a lithium ion following reaction 4 (see Figure 2). The lithium ion moves into and across the

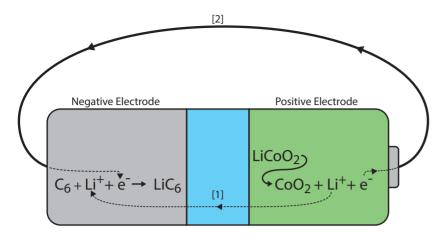


FIGURE 3. Basic lithium-ion battery being forced, via an external power source, from its discharged state to its charged state.

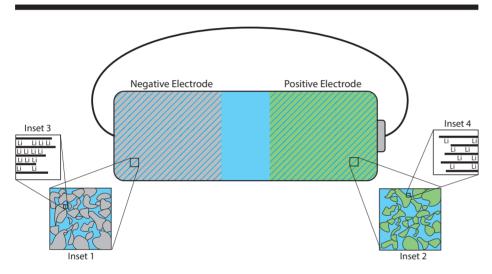


FIGURE 4. Lithium-ion battery showing the porous nature of the electrodes. Insets 1 and 2 show a partially zoomed-in view of the active material particles at the electrodes. The particles are on the order of 10 μ m. Insets 3 and 4 show a cartoon of the lithium sitting between the crystalline layers of the active material.

electrolyte (which is a liquid that is conductive to ions, but insulative to electrons) following path [1] and the electron is forced through the external circuit following path [2]. The electron then reacts with the lithium ion that came across the electrolyte from the negative electrode to form LiCoO_2 following reaction 5.

During charge, the reverse happens (Figure 3 and reactions 6 and 7); a lithium ion is removed from the $LiCoO_2$ positive electron following reaction 7, the ion passes into and across the electrolyte following path [1], and the electron is forced along the external circuit following path [2].

$$C_6 + Li^+ + e^- \rightarrow LiC_6$$
 6
 $LiCoO_2 \rightarrow CoO_2 + Li^+ + e^-$ 7

Once they reach the negative electrode, the electron and the lithium ion react with the graphite to form lithiated graphite following reaction 6. This brings the battery back to its initial, charged state. Because the lithium would much rather be in the positive electrode as LiCoO₂ than in the negative electrode as LiC₆, there is a driving force for reactions 4 and 5 to occur. As these reactions occur, the battery discharges and we are able to extract usable electrical work from these favorable chemical reactions. Once all the useable lithium is

transferred from the negative electrode to the positive electrode (all the reactants are used up, becoming products), the battery is fully discharged and must be charged back up again (the work we got out of the battery must be put back in). Since nothing is free, we must put additional electrical work back into the battery in order to charge it, thereby forcing the lithium back into its less chemically favorable LiC₆ state via reactions 6 and 7 following Figure 3.

Since reaction 4 and 6 are really the same reaction run in opposite directions (as are 5 and 7), we say that the reactions are reversible and use a bidirectional arrow to lump these reactions into two overall reactions (8 and 9):

 $LiC_6 \leftrightarrow C_6 + Li^+ + e^-$ 8

and

$$CoO_2 + Li^+ + e^- \leftrightarrow LiCoO_2$$
. 9

ELECTRODES IN MORE DETAIL

Let us now look at the positive and negative electrode in more detail. In both Figures 2 and 3, we saw that the reactions involved with discharging and charging the battery include reacting the lithium into and out of the liquid electrolyte. In fact, all of the reactions in our battery occur at the interface between our solid electrode materials (LiC₆ and LiCoO₂) and the liquid electrolyte. Because of this, the more surface area that we have where the liquid electrolyte contacts the solid electrode materials, the more area we have to react and the faster our reactions can take place. In Figures 2 and 3, the electrodes were shown as large blocks to simplify the diagram. In an actual battery, however, the electrodes are very porous and the LiC6 and LiCoO₂ active material are actually small particles pressed together and surrounded by liquid electrolyte (see insets [1] and [2] in Figure 4). The electrodes can be thought of as soaked sponges or pebbles in a bucket full of water (in our case electrolyte). We now show the electrodes in Figure 4 as striped with blue (our electrolyte material) to denote the fact that the electrodes are porous with electrolyte filling the pores.

If we zoom in even closer to the active material particles (insets [3] and [4] in Figure 4), we see that both the graphite at the negative electrode and the LiCoO_2 at the positive electrode are actually layered crystalline materials with the lithium

sitting between the layers. This means that there is a continuously variable amount of lithium sitting between either the graphite or cobalt dioxide layers. For example, you can have a lot of lithium fitting between the layers (inset [3]), a small amount of lithium fitting between the layers (inset [4]), or anything in between. So, in actuality, our active material at each electrode is $\rm Li_y \ C_6$ at the negative electrode, and $\rm Li_x \ CoO_2$ at the positive electrode, where x and y are variables which show the variability of the lithium in the electrodes.

We now update reactions 8 and 9 to reflect this variable amount of lithium to get $\text{Li}_y \, \text{C}_6 \leftrightarrow \text{Li}_{y\text{-}x} \, \text{C}_6 + x \text{Li}^+ + x \text{e}^- \qquad 10 \\ \text{at the negative electrode, and} \\ \text{CoO}_2 + x \text{Li}^+ + x \text{e}^- \leftrightarrow \text{Li}_x \, \text{CoO}_2. \qquad 11 \\ \text{at the positive electrode.}$

PUTTING IT ALL TOGETHER: LIMITS ON BATTERY PERFORMANCE

Now that we have an idea of how a battery works, let us talk a bit about the performance of the battery, or the trade-off between power and energy. Using Figure 4 as our basis, we can see that we have a finite amount of space to fit our necessary components: the negative electrode, positive electrode, and electrolyte. There are, of course, many more practical items that are necessary such as terminals to attach our leads, casing to protect the battery (and us!), circuitry to monitor and control the voltage and current, current collectors to more easily pass the electrons from the active material to the terminals. etc. But, for now, let us concentrate on the three electrochemically necessary items. In order to optimize our battery, we first want to match the capacity of positive and negative electrode. As we charge and discharge our battery, we take the lithium out of one side and put it into the other side; we can think of this as shuttling books from one bookshelf to another. Since our capacity is limited by the total quantity of lithium (books) that we can shuttle across, we want both of our electrodes (bookshelves) to be equally sized. If one electrode is much larger than the other then we have wasted space. Since CoO₂ cannot fit quite as much lithium between its layers as graphite can, we need to have slightly more CoO₂ than graphite in order for both

ELECTROCHEMISTRY IS A LARGE FIELD THAT INCORPORATES MANY DIFFERENT DISCIPLINES

electrodes to have the same overall capacity. Given this constraint, we now have only one variable to play with. We can increase the total amount of active material available (increasing our capacity), which decreases the space for our liquid electrolyte, or we can decrease the amount of active material (decreasing our capacity) to make room for more electrolyte. The more electrolyte we have, the faster we can move the lithium back and forth (meaning better power capability), but less lithium is available to move. To make another analogy, we can think of a city where houses are our active material, roads are our electrolyte, and cars are our lithium. If we build only a few small roads, then we have lots of room for our houses (high energy density), but it will be difficult to get from one place to another quickly (low power). Conversely, we can build a ton of freeways and make it very easy to quickly get from one place to another, but there will be little room for houses (high power).

This is the conundrum between high power and high energy; we would like to be able to quickly charge (and discharge) our battery, but we also want a single charge to power our device for a long time (high energy). Within a given chemistry, we can balance between the two options to optimize for a given situation, but, in order to make further progress, we need to increase the total amount of lithium in each electrode, giving us both improved power and energy. It is precisely this that battery companies are working on. This work generally falls under two categories: fit more lithium into the current chemistry, and find a new chemistry that can fit more lithium. Actually most of the "new" chemistries have been known for quite a while, but do not currently work well or are too expensive. An example of the first option is coming up with a way to allow the LiCoO₂ to go to higher voltages. This would allow us to access more of the lithium that currently remains trapped inside the LiCoO₂, increasing the capacity

of the battery while the size and weight remains the same. The difficulty, however, is that the electrolyte starts to break down at high voltages. Therefore, much of this work focuses on protective coatings or new electrolyte mixtures that can withstand these intense conditions.

An example of the second option (finding a new chemistry that can fit more lithium) is the use of a silicon electrode in place of graphite at the negative electrode. Silicon can store much more lithium than graphite can (though its mechanism for storing it is very different), but the silicon particles tend to crack as they are charged and discharged. As the particles crack they can become electrically isolated from the rest of the battery meaning that the lithium contained in them is no longer accessible. This quickly degrades the electrode causing the capacity of the battery to decrease and the life of the battery to be short. Many companies are attempting to get around this issue through improvements to the silicon particle properties or by strategies such as mixing a small amount of silicon into the graphite at the negative electrode. There are, of course, many more examples of battery research and development, but that is a topic for another article.

SUMMARY

From this article, I hope that the reader gains a basic understanding and appreciation for the complexities involved in creating a great battery. It is a difficult and arduous process and, unfortunately, there is no Moore's Law for batteries (the lead acid battery which we use to start our cars was invented in 1859!). Though we briefly discussed the basics of electrochemistry, explored how a battery works, examined the trade-off between high energy and high power, and looked at current efforts to build a better battery, we have only scratched the surface. Electrochemistry is a large field that incorporates many different disciplines and I hope that this article has shed some light on the topic. ■