

The Li Ion Battery

The Issue in Short

Advanced

Presently (Oct. **2009**) the world at large is in the throes of the financial crisis; before and after it was (and will be) shaken by the **energy crisis**. The articles "[Terawatt challenge](#)" and "[Powering the planet](#)" provide some background of particular interest to Material Science and Engineering students.

- Every budding engineer knows, of course, that automobiles in the near future will run **electrically**, powered by **batteries** - at least this is the unavoidable conclusion if one just reads a newspaper occasionally or listens to news.
- Is that true? Are we all going to drive around in electrical cars (or at least serious hybrids) in a few years that have about the same cost / performance relationship than present gasoline powered cars? This module will provide a few essentials for pondering this question.

First, we realize that the energy source in a future car will be a **Li ion battery**? Why is that? We will find out by recalling some basic facts about cars and doing a little quiz.

Before you read on, you should try to figure out the answers yourself by doing the extremely simple but highly illuminating quizzes (far too simple to be called "exercise") provided in the links.

Quiz 1

How much energy is contained in **1 liter** of gasoline?
Find out by using data you know about your car.

- What you could get is shown in the following table.

Known Property	SI units	Stupid units
Mileage	10 km/l	23.5 miles/gallon
Range with full tank	500 km	311 miles
Engine Power P	100 kW	135 PS or horse powers
Average speed in going 500 km	120 km/h	74.6 miles/h
Average capacity of engine used	50 %	
Average efficiency η of engine used	0,3 or 33%	
Time t to cover 500 km	4.17 h	
Energy E consumed = $0,5Pt$	208 kWh	
Energy E_G contained in 1 l of gasoline = $E/50 \text{ l} \cdot \eta$	12.6 kWh/l	

Not bad! The "official" number is $E_G \approx 10 \text{ kWh/l}$.

- The " \approx " sign alludes to the (small) differences between premium, diesel, and so on. Who cares. We are only concerned about orders of magnitude here.

Is a specific energy of around **10 kWh /l** a *large* or *small* number? Find out yourself in the next quiz:

Quiz 2

How large or small are **10 kWh /l** - in comparison to known energy (densities).

- Here are some answers: **1 kWh** energy is stored or used up in

- 0,1 l gasoline
- Large (**85 Ah**) truck battery.
- 0,25 kg dry wood
- 7,3 t H_2O in a reservoir with **50 m** height difference.
- A weight of **367 t** lifted to **1 m**.

- **9,5 l** brought to a boil (**100 °C**) from **10°C**.
- **100 h** of bicycling at **100 W** uses up the **10 kWh**, moves you about **2.000 km**, and works off about **17 Big Mac's**.

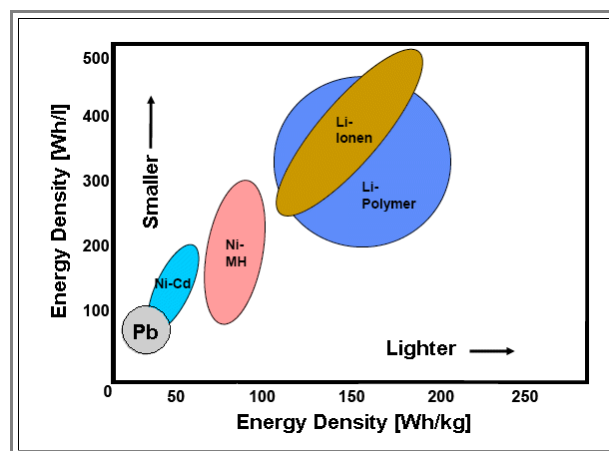
In other words: The chemical energy contained in gasoline is *absolutely huge* compared to typical mechanical energies we can directly relate to! It is, by the way, larger than the energy stored in **1 kg** of a solid high explosive.

So what is the energy density of a decent battery? Well - it depends. Do you mean energy *per liter* or *per kilogram*? There is a big difference from the view point of the user.

Quiz 3

This and That

- If you think about electric cars, the **weight** of the battery is what you are concerned with. The volume is not all that important. You have plenty of space because you do no longer need a bulky engine, transmission, drive train and so on. Electric motors are much smaller than comparable gasoline counterparts.
 - If you want to power your submarine, it's the the other way around. If the batteries are too light weight, you have trouble to "sink" it. If you want to power your cell phone, it's volume you are concerned about. If you want to store huge amounts of energy (e.g. to get through the night if your major energy source are solar cells), weight and volume are not confining - the price is!
- Let's look at both specific energy densities in one diagram



- It looks like the best we can come up with is at present (Oct. 2009) the **Li ion** battery with a specific capacity around **0.5 kWh per liter** or **0,15 kWh per kg**. In other words: **1 l** of gasoline beats the best battery we have by a factor of **20** with respect to the specific volume and by more than a factor of **100** with regard to the specific weight.
- OK - that simply means we have to find room for a **Li ion** battery with a volume of **1000 l** or **1m x 1m x 10 cm** to run a car. That should be possible in a decent sized car.
- Unfortunately, if we look at the figure, the weight of such a battery would be around **3 000 kg** or so (and the price would be totally prohibitive). Twice the weight of your old-fashioned standard car!
- The conclusion is easy:

If cars are to be powered by batteries in the near future, we need to improve batteries at at least by a factor of 5 or so with respect to the energy density.

As a material scientist you now wonder what exactly determines the energy density of a battery. For finding out we need to look at the basic working principle of a battery.

Working Principle of a Battery

The energy stored in a battery is chemical energy, i.e. the energy released by a chemical reaction. We will only consider **Li** based batteries here, so we have a reaction [of the type](#):



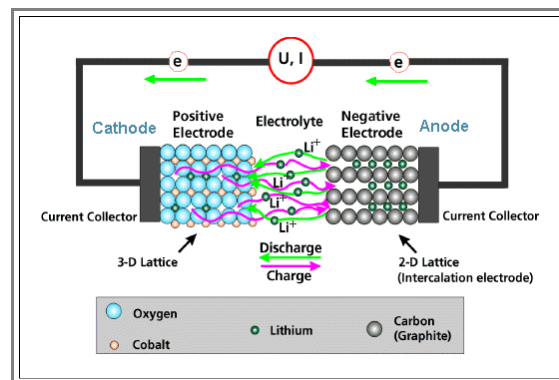
So take a piece of **Li** and a "piece" of **F**, separate it by an electrolyte that cannot pass electrons but only ions, put it into a box with contacts to the **Li** and the **F** - you have a battery.

It's not so easy, of course. The general principle of forcing the electrons to go through an outer circuit from one reaction partner to the other one, while the ions move through the electrolyte is certainly correct. But:

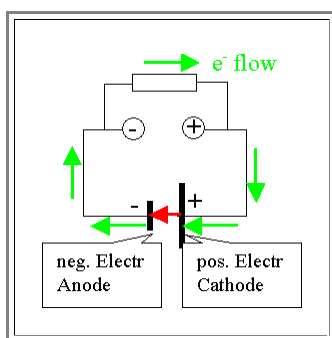
1. How do you keep and contact an (extremely corrosive) gas like **F₂**?
2. How do you keep your **Li** from reacting with the oxygen in the air?
3. Will the reaction actually take place? Will a piece of metallic **Li** in a **F₂** atmosphere start to react without being "triggered" somehow (like **H₂ + O₂**)?
4. Can you reverse the reaction by running a current through your battery, i.e. charge it again?
5. and so on. and so forth.

Making a real battery with "**Li ions**" is not all that easy - Point 2 will always a problem, for example, demanding airtight sealing and a lot of security features.

So let's look at the working principle of a **Li ion battery** in a very general way.



We have a **negative electrode**, also called **anode**, where **Li** is present as a "metal".



- The term **negative electrode** is clear. The **Li** atoms incorporated or **intercalated** in the electrode material must leave an electron back so that they can move as **Li⁺** ion through the electrolyte if the battery is discharged and thus supplying energy to the outside world.
- But why is it also called **anode**? Isn't an anode always the positive pole towards which the electrons flow?
- Yeah - but only **outside** the battery as shown on the diagram. **Inside** the battery the electrons (or negative charges) must flow from **plus to minus**. The battery, after all, is an electron pump that moves the electrons "up" to a high energy level from which they can "flow down" towards the positive pole.
- Of course, it's not electrons flowing from plus to minus inside the battery but positively charged **Li⁺** ions in our case. But if you replace the battery by a generator, your electrons flow indeed in the "wrong" direction inside the generator.
- The general definition of an anode is therefore: An anode accepts electrons; it provides for a general oxidation reaction. The polarity is positive seen from an external user and negative as seen from inside a generator. In the picture you see that the internal electron (or negative charge) current does indeed flow into the anode (red arrows).

- ▶ We have a **positive electrode** also called **cathode** (now we know why) where **Li** reacts to whatever and is incorporated as **Li⁺**.
 - The chemical reaction to "whatever" - e.g. **LiCoPO₄** - provides the energy that drives the whole process.
- ▶ Between the electrodes is an **electrolyte** that allows **Li⁺** ions to pass but does not conduct electrons. That's why we have a battery. The electrons can only get from the anode to the cathode by flowing through electron conductors in the external circuit.
- ▶ The two electrodes must be intimately connected to some **current collector** (a metal like **Cu**) that conducts the electrical current out of the battery to the terminals.
 - This is not a simple issue! If you want to run a **100 kW** motor with a **3 V** battery, you are going to draw **100 000/3 A = 33 333 A** which is a lot of current. Even if you switch battery cells in series to achieve **300 V**, you still run **333 A** through the current collectors and wires.
- ▶ What kind of properties are we asking for concerning the electrode materials? It's a long list; most important for us at this point are
 - **General Properties:**
 - Specific capacity or how much **Li** (in **kg**) can you incorporate in **1 kg** or **1 l** of the the electrode material.
 - Electrochemical potential.
 - Conductivity; connection to current collector.
 - Long term stability; survives how many charge / discharge cycles?
 - Hazard potential (does it explode / burn if exposed to air?).
 - Price.
 - Ecological topics.

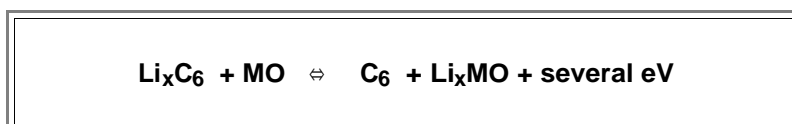
▶ Negative Electrode/Anode

- In principle one could use **Li** metal. In practice, however, one cannot, for many reasons. Consider just recharging after all your **Li** has been used up and is now incorporated in the cathode. You now have a "hole" on your anode side. How do you get your **Li** back?
- We therefore use an anode material that ideally can incorporate a lot of **Li** easily, **and** can release most of that incorporated **Li** easily. In other words, it shouldn't take much energy to get it out again. That implies that no strong bonds between the anode material and the **Li** must develop.
- The standard material at present is **graphite**. **Li** atoms are simply "intercalated" between the hexagonal **C**-layers. Another, very interesting material for anodes is **Si**. We will come back to that.

▶ Positive Electrode/Cathode Properties

- In principle same thing as above, except that we must produce a lot of energy whenever **Li⁺** is incorporated.
- What we use are metal oxides (**MO**) like **LiCoO₂**, **LiNiO₂**, **LiMn₂O₄**, **LiFePO₄**, **LiNi_xCo_yMn_zO₂**.

▶ The over-all reaction then is like this:



▶ All we do, in simple terms, is to "shuttle" **Li** back and forth between the two electrodes, gaining energy in one direction (discharge) and using energy (charge) in the other.

Capacity of a Battery

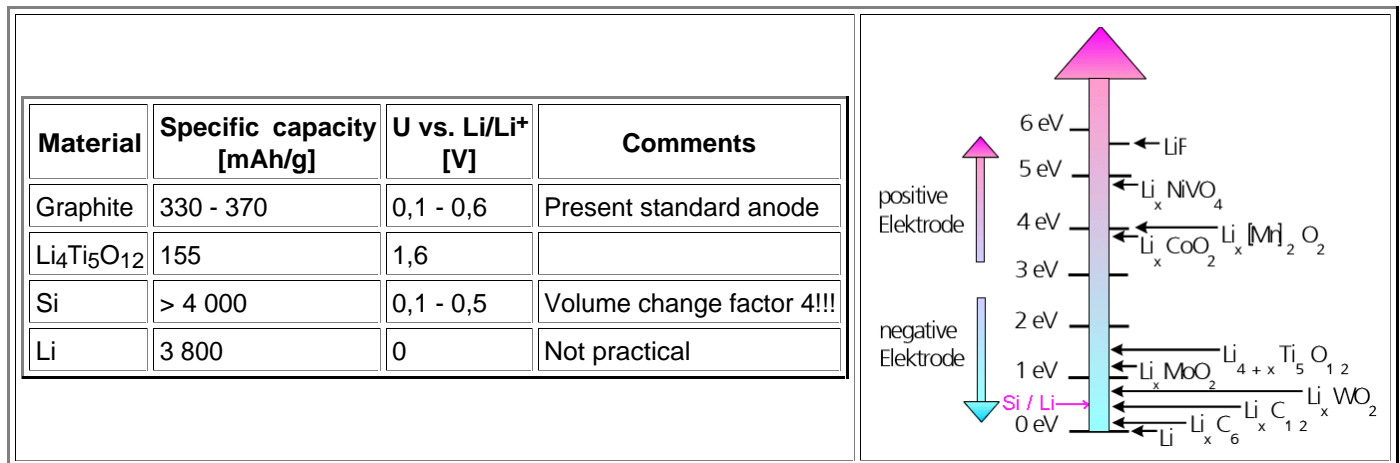
▶ What determines the capacity of a given **Li** ion battery? Easy. We first do a quiz to get some ideas.

Quiz 4
Battery capacity

- ▶ What we see is that about **90 g** of **Li** would be enough for a capacity of **1 kWh**. But the [diagram above](#) shows that presently we need at least **5.000 g** for that. How can that be?
 - Well - besides the **Li**, you need the two electrodes that contain it, an electrolyte, current collectors, and a housing; not to mention security features.
 - If we want to improve the gravimetric energy density by at least a factor of **5** [as we must](#), we realize that there is a lot of work out there for enterprising Material Scientists. What we have to work at are the electrodes (and everything else). The crucial question is: What is the specific capacity (in **mAh/g**) of an electrode. In other words: How much **Li** (in **g**) can I incorporate into **1 g** of the electrode material.

- The reference would be metallic **Li**, where one obviously can have "**1 g Li in 1 g Li**" with a specific capacity of **3 800 mAh/g**. It also takes a voltage of **0 V** to get **Li** "out", i.e. to drive the reaction **Li/Li⁺** because we use that as the zero point of the potential scale.
- The relevant voltages are shown for various reactions in the figure. The difference between the high end and the low end is what you get as the battery voltage. With a **Si/Li** anode and a **Li_xCoO₂** standard cathode, you should obtain around **3.5 V**.

Let's look what else we have



Now you should be a bit surprised. How can you have more **Li** in **Si** than in **Li** itself?

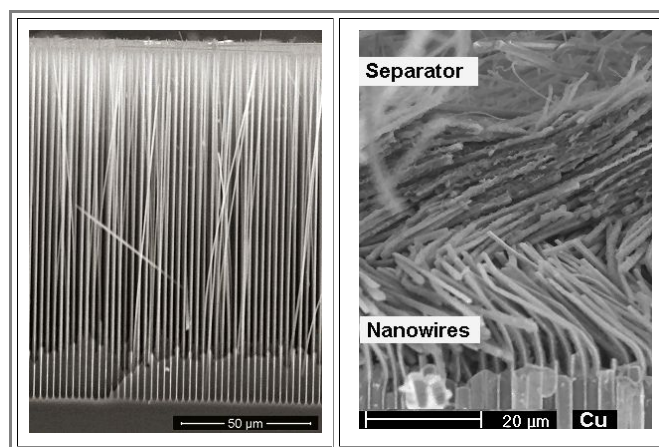
- Yes - you can. By forming alloys like **LiSi**, **Li₁₂Si₇**, **Li₇Si₃**, **Li₁₃Si₄** and **Li₂₂Si₅**.

So why don't we have **Si** anodes as a matter of course in our **Li** ion batteries?

- Because the volume of the **Si** expands by a factor of **4** when **Li** in high concentrations is incorporated. What that means is that your piece of **Si** anode will have fractured to fine dust if you load it just once with **Li**. This is obviously not practical.
- Nevertheless it can be done. The keyword are "**nanowires**". Overcoming that problem by using **Si** nanowires instead of bulk **Si** is not only a story in itself but brings you to the heart of "hot" research in materials science and engineering as it is going on right now (Oct. **2009**).

The Si Nanowire Anode

The pictures below show **Si** nanowire anodes. On the left we have a **Si** nanowire array as made by anodic pore etching and chemical over-etching: On the right we see a **Si** nanowire anode with a **Cu** backing after it has been used in a few charge and discharge cycles in a battery.



- It works! No destruction of the **Si** nanowires is visible.
- If you want to know more about this, refer to these two short papers:
 - The [Stanford paper](#) that started it all in **Jan 2008**.
 - The [Kiel paper](#) that makes it practical (and was co-authored by a student presently (fall term **2009/10**) taking this course).