

## Batteries

ACME Faculty, EHVE course  
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Leszek Niedzicki, PhD, DSc, Eng.

**Future of electrochemical cells.  
Modern cell chemistries.**

## Beyond Li-ion cells

So-called 'beyond Li-ion' are prototype (usually) cells, experimental and all (in a current realization phase) that concept of appeared after 1990. In reality, they are all in the research phase, some are just a little closer than the others from application or commercialization. Some are already produced on small scale for tests and niche applications (like Na-ion). However, it is still a challenge to keep them stable and give them long life (above 100 cycles). Due to the long time remaining to their application (and some doubts as to IF it will happen), detailed information on magnesium, calcium and aluminum based cells were omitted here.

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## Beyond Li-ion cells

In practice, it can be narrowed down to few real competitors for being closest to application:

- Na-ion
- Li-air
- Zn-air
- Li-S
- Na-air

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## Sodium-ion (Na-ion) cells

Na-ion cell design and principle of operation is basically the same as for Li-ion cells. The main difference (using sodium cation instead of a lithium one) should result in a lower manufacturing cost. Sodium is several times cheaper than lithium and is widely and evenly available in the world. However, energy density, even theoretical one, is significantly lower than that of Li-ion. It does not prevent it from applications in the anticipated field (at least not in the initial phase of introduction to the market), which is grid energy storage (energy storage for balancing the power grid and/or power grid backup power, frequency or voltage regulation, and so on). It is because in such application it is the price, not the energy density, that mostly counts.

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## Sodium-ion (Na-ion) cells

Since around 2010, research on suitable electrodes rapidly accelerated. However, just recently (2015/2016) French institutes has demonstrated a factory prototype of a larger scale (18650) and in bigger amounts (which suggests repeatability of production). Cell has 90 Wh/kg energy density, which is significantly lower than that of a modern Li-ion cells, however it is only slightly lower than the first Li-ion cells in 1990s (when Li-ion were first introduced to the market). Supposedly, those cells withstand up to 2000 cycles. The main problem is a bigger sodium cation diameter (by 25%). Thus, new electrode materials had to be found and investigated instead of taking ready solutions from Li-ion cells (what was initially hoped for by some).

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## Sodium-ion (Na-ion) cells

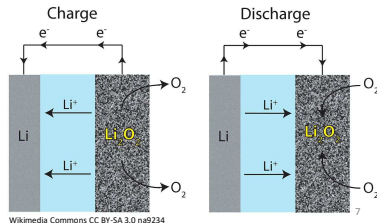
The most popular materials for components for Na-ion cells (in laboratories, not industry, yet) are:

- Anode: hard carbon, although other carbon forms are also investigated (nanotubes and other nanostructures), as well as some carbon composites with Sb and Sn;
- Electrolyte:  $\text{NaClO}_4$  in PC or  $\text{NaPF}_6$  in battery solvent mixtures (sodium versions of Li-ion and lithium cell electrolytes);
- Cathode: sodium forms of transition metal oxides similar to those in Li-ion cells, e.g.  $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ , vanadium oxides, phosphates (with Fe, Cr, Al, Co, Mn, etc.) and silicates (Fe, for instance); high hopes are set for titanium oxide ( $\text{TiO}_2$ ) doped (with lithium, for instance).

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## Lithium-air (Li-air) cells

Lithium-air cells are still an object of frustration for numerous scientists all around the world. General operation principle is relatively simple: air (particularly oxygen) is a cathode, lithium (metal) is an anode. Lithium oxidizes to cation and oxygen reduces to  $O_2^{2-}$  anion. Thus, lithium peroxide  $Li_2O_2$  is formed. Sadly, this reaction naturally runs further to the lithium oxide ( $Li_2O$ ). However, it is not possible to reverse the latter process, in which lithium oxide would be processed back to the lithium metal and pure oxygen.



## Lithium-air (Li-air) cells

In order for the reaction to stop on the peroxide step and not run to the end (to  $O^{2-}$ , to form  $Li_2O$ ), suitable catalyst is required. Unfortunately, obtaining such catalyst is a main issue. Most of catalysts direct the reaction towards oxide at least to a certain degree (or even as its main product).

Additional difficulty is electronic insulation property of  $Li_2O_2$ , so its formation at the cathode blocks cell operation quite quickly. Research is directed towards porous matrices on which peroxide would be settling in very thin layers on them. Then the thin layer of  $Li_2O_2$  would consume all available lithium.

## Lithium-air (Li-air) cells

As an alternative, some solutions consists in using additional cathode layer, carbon, for instance, in which the reaction takes place. However in such solution electrode is blocked at the surface by resulting  $Li_2O_2$ , only deposition site changes.

Apart from the  $Li_2O$  formation (instead of  $Li_2O_2$ ), other air components, such as carbon dioxide and moisture, supply their own problems, as they react with lithium on their own (producing stable, non-conducting and irreversible in cell conditions  $Li_3N$ ,  $Li_2CO_3$  and  $LiOH$ ). Thus, selective membranes have to be used so they would let only pure oxygen to the inside. Such membranes are never ideal. Thus, in reality there will be always at least small amounts of impurities reaching anode and degrading the whole cell by that.

## Lithium-air (Li-air) cells

The alternative research is focused on cells with electrolytes based on water in which the main product is  $LiOH$  instead of  $Li_2O_2$ . Here the main issue is metallic lithium reactivity with water. Thus, additional non-aqueous electrolyte is needed as a buffer, which would not let the water through. That means use of polymer or ceramic electrolytes with poor conductivity which cause worse power density. Presence of such additional component also causes worse energy density. So both decreases undo main Li-air advantages.

## Lithium-air (Li-air) cells

Use of the solution based on aqueous electrolytes increase cycle efficiency, as it approach 70% in non-aqueous electrolytes, and ca. 90% in aqueous ones. It is a result of lack of side reactions that would lead to oxide formation. Thanks to use of water as an electrolyte, side reactions leading to nitride and carbonate formation are also significantly limited. Hydroxide forming as a main product is also permeable for ions and does not block further reaction. Unfortunately, just like peroxide, lithium hydroxide is not conducting electronically.