

ELECTRIC ENERGY STORAGE, ENERGY POTENTIAL and ENERGY DENSITY : WHAT ABOUT THERMAL SAFETY ?

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Energy storage requires always the development of well-designed materials. It cannot be dealt with without taking into account how the stored energy will be recovered. In this frame, special attention must be paid to the maximum allowable energy recovering rate.

To recover the stored energy from a storage device, one must generally run a transformation resulting from the spontaneous lowering of the *global* potential characterizing the system. The *total* potential is the driving force of the system evolution, which can only release energy as long as this process simultaneously decreases the *total* potential of the system. Thus *the potentials are the only driving magnitudes* from which the actual physico-chemical behavior of matter can be derived.

A potential is the ratio of the energy to the mass of the matter containing it, *paying special attention to its nature and all correlated state variables*. The potential characterizes the “aggressiveness” of the contained form of energy towards the surrounding matter.

But the *commercially interesting* magnitude characterizing the energy content of matter for practical applications is the *energy density* which is expressed in units of the ratio of the energy content to the mass, *but here regardless to the nature* of the matter containing the energy.

Energy densities are additive magnitudes. To the opposite potentials are generally not additive when their effects must be compared in devices where different materials interact with each other. Each material and each state of a given material will need *its own measuring scale* for each described system, making impossible any comparison between systems without a common unit resulting from a common, easy-to-measure magnitude.

For each material, each kind of energy (thermal, electrical, mechanical, chemical, superficial etc...) will lead to a different upper limit of potential beyond which some dangerous destructive processes will take place releasing most often high amounts of thermal energy in the energy storing matter. Therefore, in order to assess the resilience of energy storing devices with regard to safety considerations, the amount of stored energy cannot simply be expressed in terms of Joules/kg, but *must* be expressed in potential-indexed Joules, that is in Joules/(kg-type of matter). Therein, the term “type of matter” must include not only the chemical composition, but also *all* information concerning *all* relevant physical properties.

For example, chemical fuels can store very high energy densities showing values up to about 33 (carbon, graphite, hydrocarbons ...) to more than 50 (methane) MJ/kg. However, they often remain stable up to remarkably high temperatures. Carbon is extremely stable far beyond 1000°C and methane is a molecule which can be heated up to nearly 800°C without undergoing noticeable thermal degradation.

To the opposite, the best available electric batteries, when charged up to their full electrical storage capacity just reach electric energy densities in the 300Wh/kg range (order of magnitude: 1 MJ/kg). They become easily explosive even at room temperature when used under heavy duty conditions.

The question arises to know the origins of such a difference in energy storing capabilities between chemical energy in fuels and electrical energy in storage batteries.

In chemical fuels, nearly half part of the energy is stored in a stable fuel (carbon, hydrocarbon, hydrogen ...). The second half is stored in the combustive agent (often oxygen) taken from atmospheric air. Thus the energy density related to elemental carbon being about 33 MJ/kg, the same energy density but related to both the mass of fuel (12 g/mol) *and* the required mass of combustive (32 g for CO₂) drops down to 9 MJ/kg. For methane these values are respectively close to 50 and 13 MJ/kg.

In electric storage cells, although the electrical energy density is much lower (generally by more than one order of magnitude) the safety aspects are quite different: instead of being separated from each other, both the fuel (cathodic reduced species) and its associated combustive (anodic, oxidized species) are present *in close vicinity*. The electrochemical oxido-reduction process is only blocked by the opening of the external electrical circuit the storage cell is intended to feed. If for any reason the charge transfer becomes internally possible through the cell active materials, the resulting energy release will locally be totally transformed into heat *on the chemical bonds* in charge of the electrical storage process.

From the safety point of view, there must be done a clear difference between the total available energy density in terms of J/kg of a storage device, which describes the maximum recoverable energy by the user, and the local, potential-induced strains resulting from thermal, electrical and mechanical energies stored in local chemical bonds. In lithium storage batteries the open circuit voltage is close to 3.7 V. Since lithium is a monovalent atom, the entire amount of energy is stored on just one chemical bond, with an average molar energy close to 370 kJ/mol. In the case of an internal self-discharge process, the local adiabatic temperature rise (ΔT_{ad}) is in the range of 10 000 to 15 000 K for a lithium (7g/mol) atom. For lead batteries, involving *a tetravalent* lead atom (207g/mol) at an open circuit voltage close to 2.3V, the same local adiabatic temperature rise (ΔT_{ad}) drops down to the 200 to 250 K range with an energy per bond close to 57 kJ/mol, that is about 6,5 times less than for lithium.

Discharging the battery at a high rate will result in local heating by Joule's effect which is a *quadratic* function of the current intensity. This results in local temperature increasing. Beyond a critical limit, local thermally induced auto-discharging phenomena will take place inside the battery by the temperature driven exponential process described by TAFEL. This phenomenon results in a runaway situation transforming most part of the stored electrical energy into heat which increases the storage device temperature. In aqueous lead-type batteries, these phenomena are not relevant because of the low electrical resistance of the aqueous electrolyte giving rise to extremely low values of the internal resistance and small local overheating due to the high heat capacity (Cp) of water. To the opposite, solid electrolytes show much higher internal resistances, giving easily rise to destructive local overheating resulting in explosive runaways in a low heat capacity environment. .

Therefore thermal stability of electrical storage cells must absolutely be studied by adapted reaction calorimetric measurements in order to define as precisely as possible the limit discharge rates compatible with safe operation at variable external storage temperatures. By better understanding of the tri-potential driven (chemical potential μ , electrical potential E, thermal potential T) runaway processes as started by a temperature rise in solid state batteries, the energy density could be substantially improved: presently, safety requirements impose the nominal charge to be kept below the half or the third of the of the theoretical expected value. Effective prevention of the runaway starting processes at atomic scale could provide means to operate lithium batteries at electrical energy densities close to 300 Wh/kg, increasing by up to 200 to 300% their present achievement close to 100 Wh/kg of commercial appliances.