Attainable energy density of micro-batteries

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Recently, there is a growing interest in very small micro-batteries with footprint in the 1 mm^2 range, in particular for medical applications. For such small batteries, only the volume and not the weight matters. Generally, the practical energy density of such small cells is much lower than that of the active materials and it decreases with decreasing battery size. State-of-the-art micro-batteries have their limits when it comes to micro–sizes; their fabrication and packaging is such that the inner contact surface, wall thickness and the safety distance between anode and cathode (separator membrane) outweigh the active volume and thus significantly reduces the achievable volumetric energy density. Fig. 1 shows some characteristics of today's rechargeable lithium-based micro-batteries.

	EnFilm EFL700	stereax	medical	CP1654
	ST micro	ilika	wyon	Varta
	Thin film solid state	Thin film solid state	Coin cell	Coin cell with coil
Area [mm^2]	25.7x25.7	10x10	∅ 2 mm	∅ 12.1
Thickness [µm]	200	750	2000	5400
Capacity [µAh]	700	250	160	50000
Voltage [V]	3.9	3.5	3.7	3.7
Q_a [mAh/cm^2]	**0.13**	**0.35**	**-**	-
E_v [mWh/cm^3]	**20**	**12**	**94**	**300**
Status	prototypes	only for licensing	special product	on the market
Reference	[1]	[2]	[3]	[4]

Fig. 1: Examples of state-of-the-art rechargeable lithium-based microbatteries. Areal capacity is represented by Q_a, and volumetric energy density is represented by E_v.

Fig. 2 gives an overview of the volumetric energy densities that can be achieved with today's lithium-ion (or lithium-metal) batteries, if only the active materials of the electrodes and the separator membrane are considered. A total active material thickness of 270 µm, a separator membrane thickness of 30 µm, and a 30% and 40% porosity for electrolyte volume in anode and cathode respectively, have been considered for the calculations; the cell chemistries are presented in Table 1. The huge reduction in energy density due to the battery package can be illustrated by comparing Fig. 1 and Fig. 2. For instance, the theoretical energy density of the solid-state thin-film micro-battery is reduced from ca. 1200 Wh/l by a factor of approx. 50 in the practical devices (12 Wh/l for ilika, and 20 Wh/l for ST). This is because, the fabrication method limits the active material thickness to the range of ca. 10 µm while the total package has much larger size. For the 2 mm lithium-ion coin cell [3], the theoretical energy density is ca. 700 Wh/l and decreases down to 94 Wh/l which corresponds to a reduction factor of ca. 7. The energy density of the larger coin cell [4] is ca. half of its theoretical value, hence current collectors and housing comprises ca. 50 % of the total package (Fig. 3).

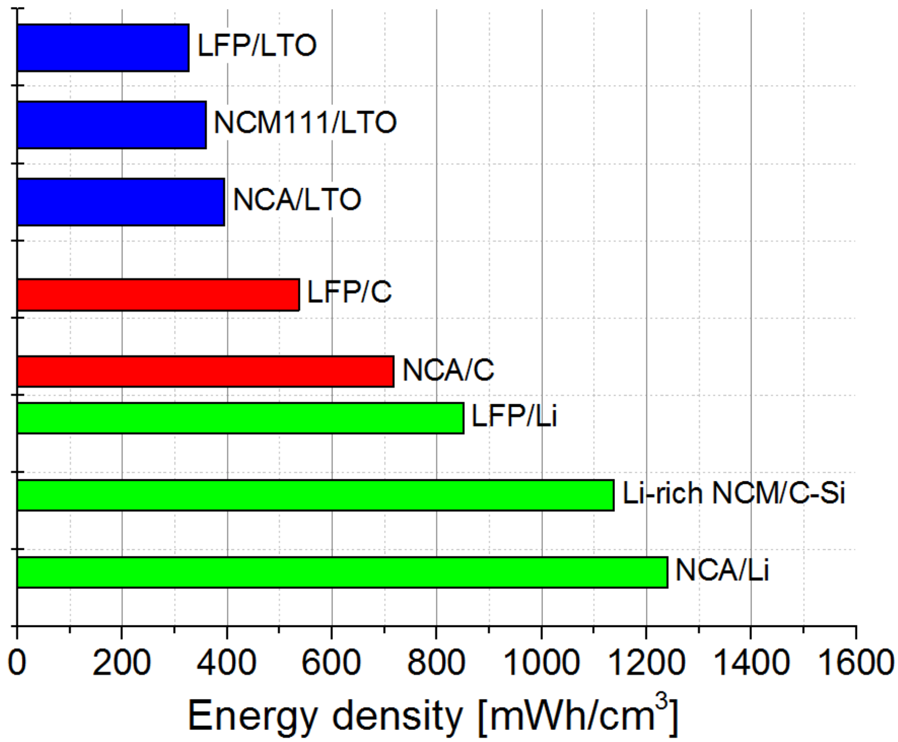

Fig. 2: Calculated energy densities for different cell chemistries.

Table 1: Considered cell chemistries, voltage and areal capacity used for calculating E_v.

Acronym	Materials	Cell Voltage (V)	Cell Capacity (mAh/cm^2)
LFP/LTO	$LiFePO_4/Li_4Ti_5O_{12}$	2.0	5.50
LFP/C	$LiFePO_4$/Graphite	3.3	5.14
LFP/Li	$LiFePO_4$/Lithium	3.5	7.26
NCM-111/LTO	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/Li_4Ti_5O_{12}$	2.2	5.34
NCA/LTO	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2/Li_4Ti_5O_{12}$	2.2s	5.88
NCA/C	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$/Graphite	3.6	6.36
NCA/Li	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2/Li$	3.7	9.9
Li-rich NCM/C-Si	$xLi_2MnO_3\cdot[1-x]LiNiO_2$/Graphite-Silicon composite	3.5	10.58

The smallest Li-ion batteries available today are the coin cells (Fig. 1 [3, 4]), and their fabrication with liquid electrolytes limits their applications in several micro-electronic applications. On the other hand, the solid-state microbatteries (Fig. 1 [1, 2]) are limited in capacity because of the planar configuration, and the very small amount of active material. Truly, the insufficient areal energy density from thin-film planar microbatteries has inspired the search for three-dimensional microbatteries with the use of low-cost and efficient micro- and nano-scale materials and their processing techniques [5]. To the best of our knowledge, no 3D microbattery architecture concept has been commercialized because of the complexity and challenges in the processing steps.

Unfortunately, though many concepts of printed batteries have been reported, no one shows a complete integration concept for micro-batteries; and those technologies are aiming at flexible and low-cost batteries of small lifetime [6] but not at extremely small sizes. Another aspect of such small batteries is related to their small capacity. In case of lithium-ion batteries, any percentage of water that diffuses through the package will react with lithium and thus reduce the energy density. This is not a problem for large batteries because here the capacity reduction of some microampere–hours per month is negligible but it will be crucial if the total capacity is only 100 µAh. Hence, very small batteries need a hermetic packaging. Similar aspects of hermeticity have to be considered for other cell chemistries with aqueous electrolytes like zinc batteries since dependent on the ambient condition battery dry out or swelling will occur if water permeation through the package is possible.

Current packaging of small micro-batteries mainly relies on different polymers which are volumetrically inefficient and cannot prevent the permeation of oxygen and water completely [7-9]. We therefore propose a novel substrate-integrated packaging technology based on additive manufacturing to overcome those challenges. In this case, deposition of housing and feedthrough structures will be done with a package volume fraction which is far less than 50% of the total battery size and therefore allows to obtain high volumetric energy densities even for very small micro-batteries as shown in Fig. 3.

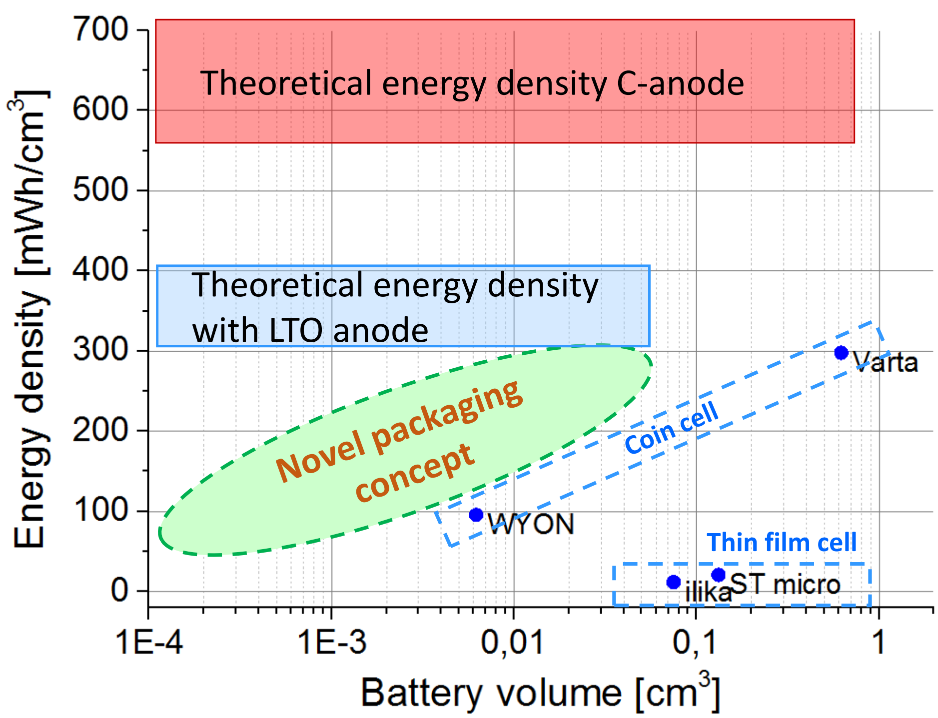

Fig. 3: Energy density as a function of battery size. Comparison of total energy density of today's products (blue dots) with theoretical energy density according to Fig. 2.

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