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A comparative study of Li-ion battery, supercapacitor and nonaqueous asymmetric hybrid devices for automotive applications

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Abstract

The specific energy, specific power, fast-charge capability, low temperature operation, cycle-life and self-discharge of five energy storage devices was compared. The group included a conventional carbon–carbon supercapacitor, Li-ion battery and three types of asymmetric hybrid supercapacitors. Asymmetric hybrid supercapacitors use a nanostructured $Li_4Ti_5O_{12}$ anode, and an acetonitrile electrolyte containing a lithium salt. Their cathode was activated carbon, $LiCoO_2$, or $LiMn_2O_4$. All devices were built using common plastic Li-ion technology developed by Telcordia Technologies.

Keywords: Supercapacitor; Asymmetric hybrid; Li-ion; Automotive

1. Introduction

Technological advances in the automotive industry have placed a renewed pressure on battery manufacturers to provide OEM batteries that will meet the design challenges of improving fuel efficiency while meeting the demands of power hungry applications. New components such as the integrated starter generator (ISG) that can save gas by shutting off the engine at stoplights and use regenerative braking energy to recharge the battery are driving the transition to 42 V systems. The cumulative current draw of many added safety and fuel efficiency options coming off the drawing board such as brake-by-wire, steer-by-wire, active suspension, electric valve timing, and catalytic preheater exceed that which can be provided by the conventional 12 V battery and Lundel alternator. Advanced hybrid electric vehicles being introduced in the marketplace such as the Honda Prius, Civic, and Toyota Insight offer attractive fuel savings, and have already demonstrated a fuel efficiency of up to 70 miles per gallon. The ultimate elusive goal of the all-electric vehicle is still limited by the current battery technologies and costs. For all these applications, what is required of the battery are: (I) low cost. This is the primary driving force in the automotive industry. (II) High cycle-life. Ideal case is that they last the life of the vehicle, especially if they are expensive to replace. (III) High power delivery and fast recharge capability. The ability to accept a full recharge in a very short time is very desirable in energy sources for automotive applications. There are two reasons for this: (1) if high energy density batteries could be recharged in the time it takes to refill a gas tank, such as 5–10 min, then adoption of electric vehicles would not require any major changes in consumer behavior, even if their cruising range was still lower than gas automobiles; and (2) design features to promote energy efficiency, such as regenerative braking require fast charging ability to recover the large amount of energy released in a very short time.

Each battery technology has its own advantages and drawbacks. For example, Lead-acid is the cheapest to produce, but has low cycle-life and energy density, NiMH has good power capability, but lower energy and lower cycle-life than Li-ion. Supercapacitor and Li-ion devices are interesting because they stand at two ends of the spectrum: Li-ion has the highest energy density of all systems, which can vary from 120 to 200 Wh/kg. Supercapacitors have the highest power density, that can range from 2 to 5 kW/kg or more, combined with the highest cycle-life, on the order of hundreds of thousands to million cycles. But their energy density is low, from 2 to 5 Wh/kg. Recently, Telcordia Technologies [1] has been developing a new device named nonaqueous asymmetric hybrid (Fig. 1). It aims at integrating the advantages of Li-ion batteries and supercapacitors, e.g. combining high energy density, high power capability

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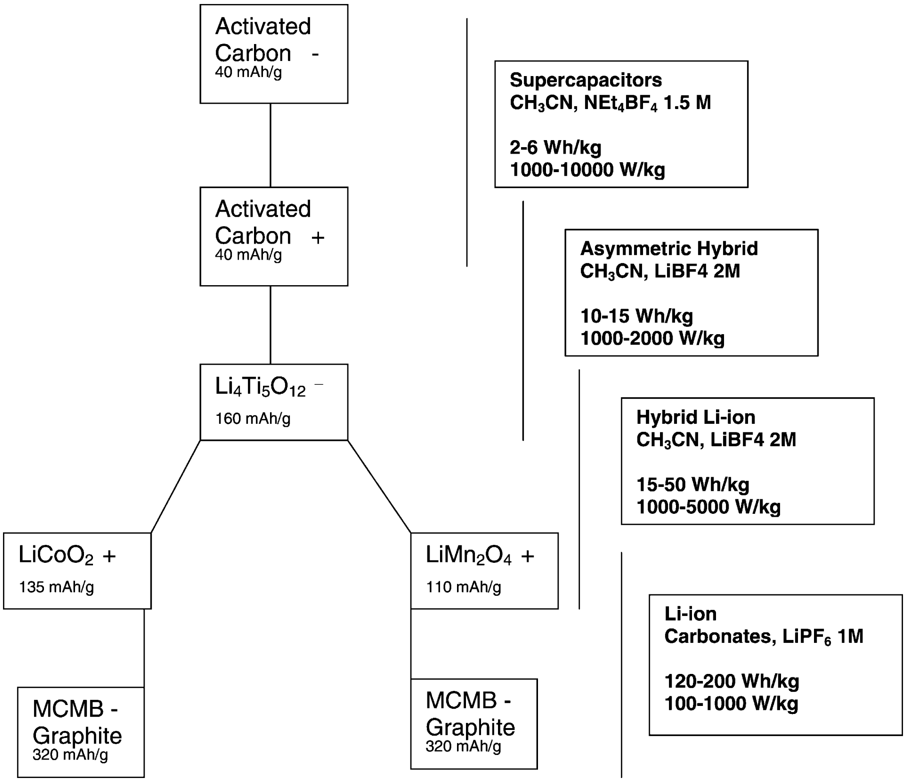

Fig. 1. Overview of the components used in the family of electrochemical storage devices developed by Telcordia Technologies since 1994.

and long cycle-life. To this end, it uses a nanostructured $Li_4Ti_5O_{12}$ anode (LTO hereafter) that allows high power capability and outstanding cycle-life [2]. Such an anode permits Li-ion intercalation without the risk of Li plating, without creation of an SEI layer, and also allows the use of highly conductive acetonitrile-based electrolytes similar to those used in carbon–carbon supercapacitors. This anode is coupled with activated carbons, resulting in a truly double-layer capacitance at the positive electrode. Thus, the device has the charge storage mechanism of a Li-ion battery at the negative electrode, and that of a supercapacitor at the positive electrode. The LTO anode can also be coupled with intercalation cathodes, such as $LiCoO_2$ or $LiMn_2O_4$, resulting in a high-power hybrid Li-ion battery. In the present study, we have compared the energy density, power capability, fast-recharge capability, self-discharge and cycle-life of five different systems: commercial Li-ion cells engineered for high-power capability; carbon–carbon supercapacitors; $Li_4Ti_5O_{12}$–activated carbon; $Li_4Ti_5O_{12}$–$LiCoO_2$; and $Li_4Ti_5O_{12}$–$LiMn_2O_4$ (respectively, LTO/C, LTO/LCO, and LTO/LMO hereafter). All the devices were of the plastic prismatic construction type, e.g. electrodes bonded to the separator and multifoil laminate packaging.

2. Experimental

All the devices studied were in-house made laboratory prototypes, except for the Li-ion cell, which was from commercial source (Kokam Co.). The laboratory prototypes were built using plastic lithium ion technology developed by Telcordia Technologies that incorporates microporous polyolefin separators [3], propylene carbonate plasticized electrodes [4] and multifoil Al laminate housing. The Telcordia's carbon–carbon supercapacitors have been described elsewhere [5], as well as the nanostructured $Li_4Ti_5O_{12}$–activated carbon hybrid device [6]. Both used the same activated carbon electrode (same composition, same carbon, same thickness). A modified Li-ion was also added to the study: the LTO/LCO and LTO/LMO devices. Those are 3 V Li-ion cells using an acetonitrile, $LiBF_4$ 2 M electrolyte and the same nanostructured LTO anode. The cathodes were either LCO (SEIMI Co.) or LMO (Mitsubishi Co.). The construction of the devices was, in all cases, the bi-cell structure, sharing a central Al foil and external Al grids. All electrochemical tests were performed between 1 and 3 V, except for the Li-ion cell, which was tested between 2.8 and 4.2 V. The devices had a 2 in × 3 in footprint, and thickness ranging between 2 and 3 mm. Their physical and electrochemical characteristics are listed in Table 1.

2.1. Energy and power capabilities

The voltage profiles of the devices at slow discharge rate (200 W/kg) are shown in Fig. 2. This illustrates the advantages of hybrid devices, which have a flatter voltage profile than C/C supercapacitors and, therefore, posses higher specific energy. Furthermore, the density of the active

Table 1
Physical and electrochemical characteristics of the devices

	C/C	LTO/C	LTO/LCO	LTO/LMO	Li-ion
Weight (g)	8.8	11.7	9.9	9.5	3.6
Volume (ml)	10.3	11.01	7.06	7.18	1.92
ESR at 1000 Hz (Ω)	0.0225	0.033	0.039	0.032	0.090
ESR (Ω cm^2)	1.74	5.10	6.03	4.95	N/A
Capacity (mA h)	26	56	208	170	147
(mAh/cm^2)	0.33	0.36	1.34	1.09	N/A

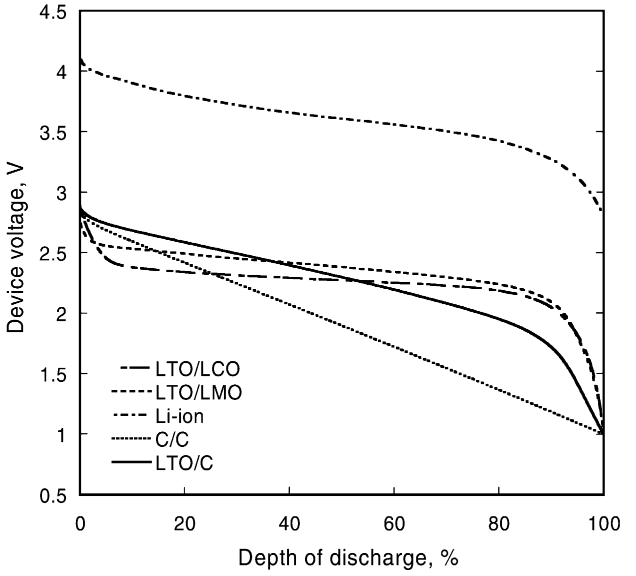

Fig. 2. Voltage profiles (discharge at 200 W/kg) of all the devices studied.

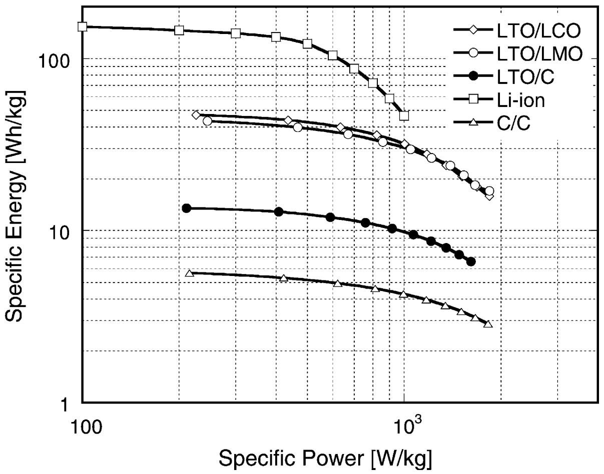

Fig. 3. Room-temperature Ragone plots of the devices, with voltage limits of 3–1 V for supercapacitor and asymmetric hybrid, 4.2–2.8 V for Li-ion.

materials is higher than that of activated carbon, which results in greater volumetric energy. The higher energy density of the Li-ion battery is due to its higher voltage (lower voltage of the graphite anode), as well as the higher specific capacity of the anode (320 mAh/g). The devices using activated carbon electrodes have a slopping voltage profile, due to the capacitive nature of the energy storage mechanism ($CdV = idt$). When an LTO anode is used (LTO/C), the intercalation reaction at the anode flattens the voltage profile of the device. When two intercalation electrodes are used (LTO/LCO, LTO/LMO and Li-ion), the voltage profile is quasi flat for the device.

Fig. 3 is a constant current Ragone plot of all the devices, plotted in W/kg and Wh/kg of their total weight (including package). Maximum energy densities were measured at a 200 W/kg discharge rate. The specific powers at 80 and 50% efficiencies are experimental values extracted from the Ragone plots (Table 2). It must be noted that in the case of C/C supercapacitors, higher specific power is achievable at the expense of specific energy by tailoring the thickness of the electrodes. In the interest of making a fair comparison between test devices, we chose to use activated carbon electrodes of the same thickness as those used in the LTO/C asymmetric hybrid device.

2.2. *Fast recharge capability*

We have performed a fast-charge study on the Li-ion, supercapacitors and hybrid devices. They were charged at constant current values of 1, 2, 4, 6, 8, 10, 20, 40, 60 and

Table 2
Specific energies and powers of all the devices

	C/C	LTO/C	LTO/LCO	LTO/LMO	Li-ion
Wh/kg maximum	5.6	11	47	43	144
Wh/l maximum	4.8	11.6	64.5	56.9	270
W/kg at 80% efficiency	900	1000	750	760	540
W/kg at 50% efficiency	1850	2100	1360	1500	800

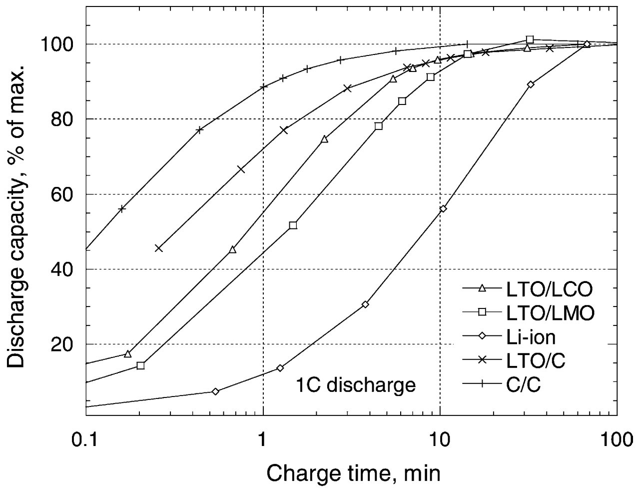

Fig. 4. Percentage of maximum discharge capacity as function of charging time for all the devices studied.

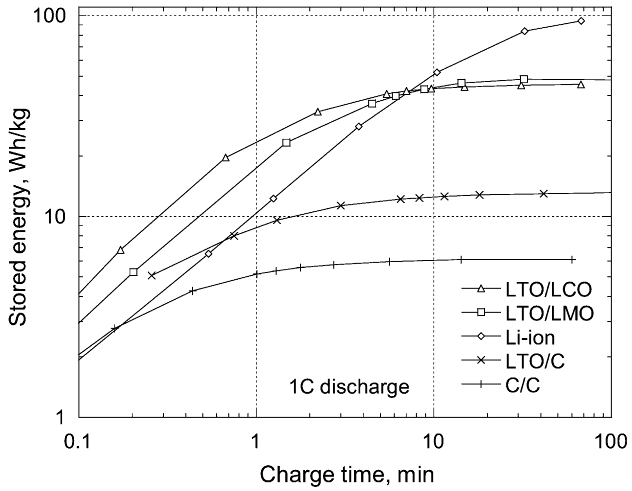

Fig. 5. Specific energy stored as function of charging time for all the devices studied.

120 C (e.g. 60, 30, 15, 10, 7.5, 6, 3, 1.5, 1 and 0.5 min), and discharged at 1 C. The percentage of maximum discharge capacity recovered as a function of charging time is shown in (Fig. 4). The data suggest that acetonitrile-based devices can be charged faster than carbonates-based ones, and that devices with intercalation electrodes are slower than devices with double-layer electrodes. Also, Li-ion batteries are handicapped for very fast charge, because Ohmic drop at the anode will result in Li plating, causing safety risk and performance degradation.

For some applications, what matters is the specific energy (how many W h/kg per unit of time) the device can accept. The results of such a plot are very interesting. For instance, Fig. 5 shows that although C/C supercapacitors have much faster charge kinetics than Li-ion batteries, it is only at charging times smaller than 0.2 min (12 s) that they become advantageous, by storing more Wh/kg than Li-ion batteries. The results also show that over the same time frame, all three hybrid systems store more Wh/kg than both C/C and Li-ion devices. Also, for a charging time of 7.5 min, all the systems based on two intercalation electrodes (Li-ion, LTO/LCO, and LTO/LCO) can store comparable energy (42 Wh/kg).

2.3. Low-temperature capability

For automotive applications, it is important that the battery system do not suffer from a high loss of performance at low temperature. Since a vehicle may be subjected to temperatures of −20 °C or below, both the power delivery and recharge capability of the battery should be preserved at these temperatures. The low-temperature capability of a battery is mostly a function of the electrolyte freezing point, and in this regard, acetonitrile-based electrolytes are in an advantageous position compared to other electrolytes. To study the low-temperature capability of the devices, we ran a Ragone test at room temperature (24 °C). Then the devices were cooled down to −20 °C in a thermostatic chamber. The currents were the same as room temperature, and the recharge was also performed at −20 °C. This provided experimental data on the recharge capability and the power capability at low temperature. The results (Fig. 6), observed at 1000 W/kg, are tabulated in Table 3.

We observe that even at −20 °C, the specific energy of the LTO/C device is higher than that of the C/C device at room temperature. Also, note that the Li-ion cell was unable to be recharged at −20 °C.

2.4. Cycle-life

In order to make a fair comparison of the devices cycle-life, it was necessary to subject them to similar cycling conditions. It is well known that some systems age faster

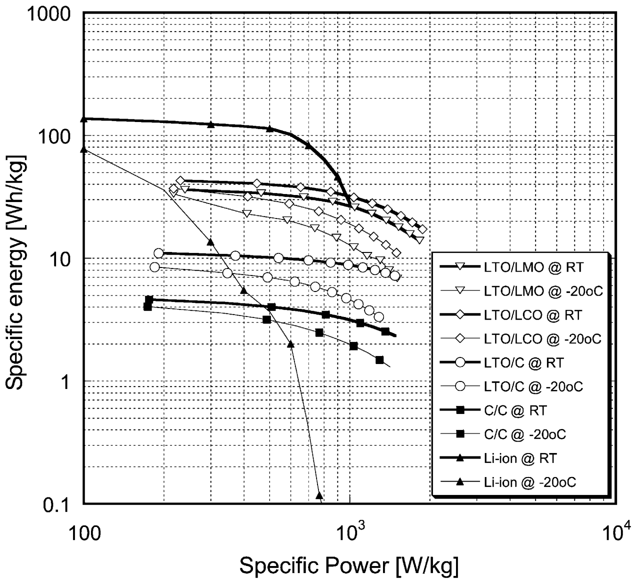

Fig. 6. Ragone plots at room temperature and −20 °C for all the devices.

Table 3
Effect of temperature on the specific energy at 1000 W/kg of all the devices

Energy at 1000 W/kg	C/C	LTO/C	LTO/LCO	LTO/LMO	Li-ion
Room temperature (Wh/kg)	4.3	8.7	32	26	28
−20 °C (Wh/kg)	2.9	4.7	19	12	N/A
Percentage energy loss	−32.5	−45.9	−40.6	−53.8	−100

when charged too fast. But as previously shown, their fast-charge capabilities are different, so we chose a charging rate of 3 C (20 min), as a compromise for all the devices, slightly fast for Li-ion, and somewhat slow for supercapacitors. For the discharge, we used a constant power discharge of 625 W/kg. This is also a discharge rate that all the devices can handle. Furthermore, it corresponds to the DOE target for PNGV 'Freedom Car' program. Thus, it is a discharge rate, which is realistic for some advanced automotive applications.

Although energy storage devices, like batteries and supercapacitors, are complementary devices that are likely to be used together to meet the transient and steady-state loads in powering systems, for a narrow overlapping power and energy range, designers may be tempted to substitute a single device to provide both the functions. For these cases, the total energy that the device is capable of delivering over its life may be as important as its cycle lifetime. For instance, 10 000 cycles for a 10 Wh/kg device are equivalent to 1000 cycles for a 100 Wh/kg device, assuming that they have the same efficiency at the power required. Thus, in addition to the classic capacity change as function of cycle number (Fig. 7), we plot change in discharge energy as function of cumulated discharge energy (Fig. 8). We also chose to test the cycle-life of the devices at their full depth of discharge, rather than performing shallow incomplete discharges. We considered end of life when the energy reached 80% of its initial value.

By using both the methods (number of cycles or cumulated energy), we find that devices using an activated carbon cathode (C/C or LTO/C) outperformed the cycle-life of devices having an intercalation cathode (LTO/LCO, LTO/LMO or Li-ion) by at least one or two orders of magnitude. In this respect, the LTO/C system is the best compromise between energy density and cycle-life (Table 4). The LTO/LCO and LTO/LMO systems are disadvantaged, because their cycle-life is similar to Li-ion in number of cycles, but specific energy is three–four times less.

2.5. Self-discharge

The self-discharge of all the devices was measured by leaving them fully charged at open circuit while recording the voltage decay and fully discharging and recharging them after 1, 10, 50, 100 and 200 h. The voltage decay is observed to follow the discharge voltage profile of the devices (Fig. 9). This to be expected, since self-discharge is nothing more than a slow discharge of the energy storage source at the rate of the leakage current [7]. Higher leakage current is expected when an activated carbon cathode is used because its large BET surface area favors oxidation of the electrolyte. This is confirmed by the higher self-discharge observed for C/C and LTO/C devices. After 200 h in open circuit, the Li-ion cell has 96.8% of its initial capacity, the LTO/LCO and LTO/LMO cells have, respectively, 93.3 and 88.8%

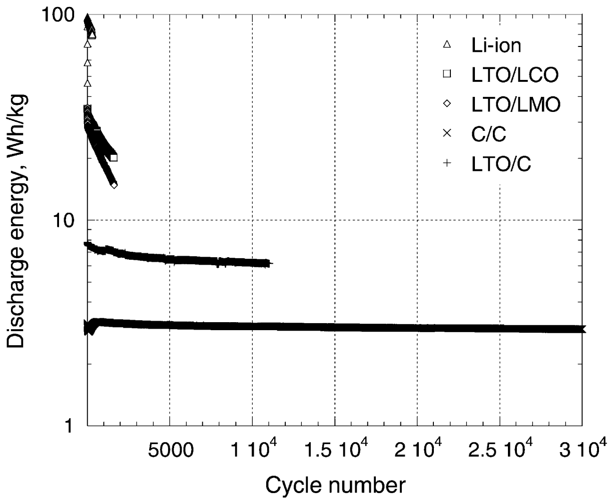

Fig. 7. Specific energy as a function of cycle number of all the devices for 3 C charges and 675 W/kg discharges.

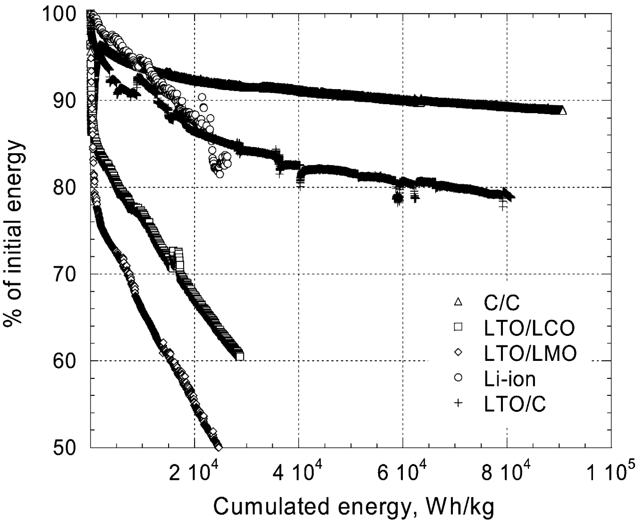

Fig. 8. Percentage of maximum specific energy as a function of cumulated specific energy for all the devices.

Table 4
Cycle-life of all the devices

	C/C	LTO/C	LTO/LCO	LTO/LMO	Li-ion
Cycles achieved[a]	30000[b]	9550	620	240	320
Cumulated energy[a] (Wh/kg)	93000[b]	69950	5300	744	24300

[a] Values at 80% of initial energy.
[b] Testing not finished yet.

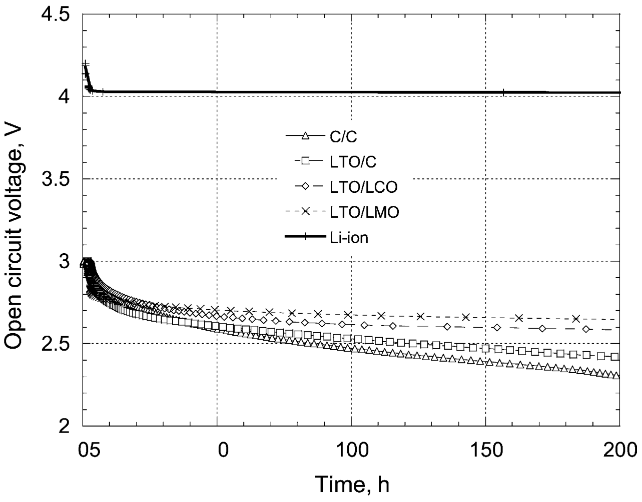

Fig. 9. Voltage decay as function of time in open circuit for all the devices.

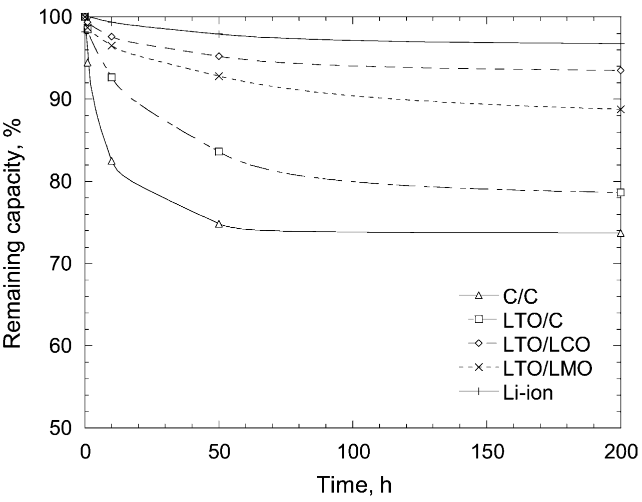

Fig. 10. Percentage of initial capacity remaining as a function of time in open circuit for all the devices.

capacity remaining, while the LTO/C and C/C cells have, respectively, 78.6 and 73.7% of their initial capacities (Fig. 10).

3. Discussion

This comparative study has shown the general pluses and minuses of each system considered. Since all the properties studied have been quantified, it is now possible to give a ranking from up to 10 (best number). This summarized in Table 5, where each property was quantified on a scale from 0 to 10. Power was compared for 80% utilization of the maximum energy. The fast-charge note was attributed from the percentage of total energy stored after 5 min of charging time. The cycle-life ranking was based on total energy cumulated after 20% loss of the initial energy. The self-discharge note was attributed from the capacity left after 200 h of self-discharge.

Table 5
Comparative ranking of all the devices by properties studied

Device type	Energy	Power	Fast charge	Cycle-life	Self-discharge
C/C	0.39	9.0	10	10	7.48
LTO/C	0.76	10	9.4	7.5	7.98
LTO/LCO	3.3	7.5	9.1	0.57	9.49
LTO/LMO	3.0	7.6	8.2	0.080	9.01
Li-ion	10	5.4	3.9	2.6	10.00

It should be emphasized, however, that this is only a rough comparison, as each system can be engineered for better power or better energy. In particular, performance tradeoffs can be driven by the effect of electrode thickness, with thinner electrodes favoring higher power capability, better low-temperature operation and cycle-life, at the expense of the energy density. For example, we made a variation of the LTO/LMO cell with thinner electrodes. The energy density was lower (25 Wh/kg), but the power density was greater (Fig. 11), along with the cycle-life (Fig. 12). Same effects are true for all the systems. Also, although LTO/LCO and LTO/LMO systems exhibited similar performance in the present study, they have some differences that we could point here: for elevated temperature operation, LTO/LMO suffers from higher capacity fade, which is mostly due to the well-known Mn dissolution issue [8] and has been addressed with better formulation [9]. We also observed that this system generates more gas (package swelling) than its LCO counterpart. On the other hand, for serial cell stacking considerations, an LMO cathode can be advantageous due to its end of charge signal, which can be used by control circuitry to prevent damage if one cell goes out of balance by overcharge. Also, the ratio of package weight to active weight differs for all these systems, and is greater for C/C than Li-ion, but will dissipate for larger cells.

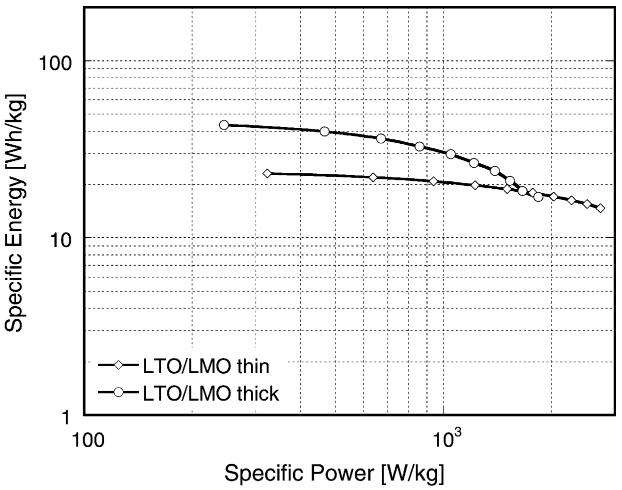

Fig. 11. Ragone plot of an LTO/LMO device made of thick or thin electrodes.

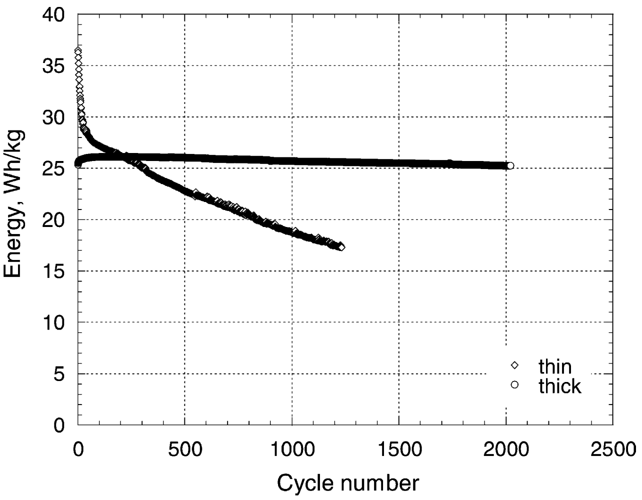

Fig. 12. Variation of energy density as function of cycle number for LTO/LMO devices made of thick or thin electrodes.

Most of automotive applications require several kW of power, for duration that can range from seconds to minutes. In many cases, several chemistries can be used, and one given chemistry can be used at various rates, so there is a vast number of possible solutions to a given problem. The Ragone plots can be extremely useful for selecting the right chemistry and the rate to use it. They can be used to compute the weight (or volume) of power source needed for a given application, to determine if the power source is energy or power-limited for that application, and the optimum rate to use it. For instance, let us consider an application that requires a 10 kW pulse, and duration of 1, 10 or 100 s. And let us consider C/C, LTO/C, LTO/LCO and Li-ion chemistries. We plotted the weight needed for a 10 kW pulse for a duration of 1, 10 or 100 s, for each of these chemistries, and for various discharges rates in W/kg (Fig. 13). There are three possible cases: (1) the device is always power-limited. This is the case for the Li-ion battery, and the weight required decreases when the W/kg drawn out of the device increases. (2) The device transitions from being power-limited to being energy-limited. In this case, there is an optimum rate of utilization that minimizes the weight needed. For instance, an LTO/LCO device used for a 10 kW–100 s pulse would give optimum results at 1000 W/kg. (3) The device is energy-limited. This is the case for a C/C device used for a 10 kW–100 s pulse. In this

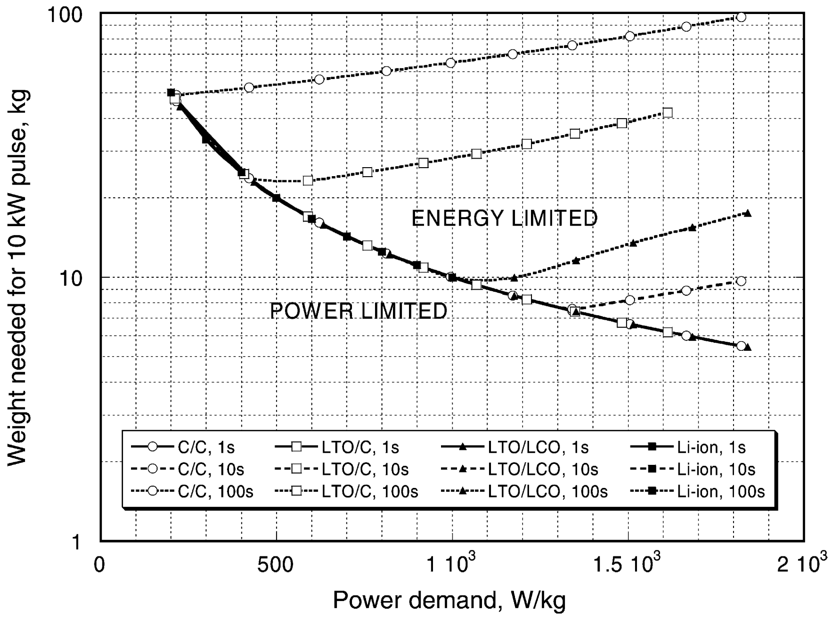

Fig. 13. Weight of power source required to provide a 10 kW pulse of various duration, as function of the chemistry considered and the power demand put on the power source.

condition, the power capability of the device is being wasted, and a more energetic chemistry should be chosen.

4. Conclusion

Objective comparison of different energy storage systems is a not a straightforward task because there are many interdependent parameters to compare and, because their absolute values, changes with experimental conditions and state of life of the device matter. It is also clear that no device satisfies all the needs of power designers, and compromises have to be made. It is ultimately the application that decides which device is most suited. The present study was made feasible because most of the devices were constructed in a similar manner (same size, same packaging, same binder, same separator, and same current collectors, etc.). But even in this case, differences naturally occur in the choice of the electrolyte, thickness of the electrodes, and voltage limits, etc. Our intention was to show the general trends and expose some important concepts for a salient comparison of devices. The results show that two components lead to highly visible performance differences between devices. The use of activated carbon cathodes (or not) impacts the length of cycle-life. The two devices using those cathodes (C/C and LTO/C) have significantly greater cycle-life than those which do not. The use of acetonitrile-based electrolyte leads to improved low-temperature capability and fast-charge capability. However, for large scale use of acetonitrile, vapor pressure and flammability may need to be reduced by additives or co-solvents. We hope that this paper will be an useful tool for application engineers in their task of selecting the right power storage source for automotive systems of the future. At the same time, we are keenly aware that the data presented here for a limited number of samples are purely technical, and do not include other very important parameters, such as cost of production, availability of the devices and safety features. Given the early stage of development of some devices, such as the hybrid, such data is not yet available.

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