Hybridization of electrochemical capacitors and rechargeable batteries: An experimental analysis of the different possible approaches utilizing activated carbon, Li$_4$Ti$_5$O$_{12}$ and LiMn$_2$O$_4$

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ABSTRACT

Electrochemical hybrid energy storage devices have been developed and investigated with considerable effort in recent years. The idea is to combine the high specific energy of the battery component together with the high specific power of the capacitor component within one system. We realized laboratory scale electrochemical cells based on a capacitor material (activated carbon) and two battery materials (LiMn$_2$O$_4$ and Li$_4$Ti$_5$O$_{12}$). We investigate hybrid systems following a serial and a parallel approach with two different mass ratios of battery materials over activated carbon.

The investigated systems are compared in terms of Ragone plot and pulse performance. The results clearly show that the parallel hybridization of electrochemical capacitors and lithium-ion batteries is superior to the serial approach. Parallel hybrids provide both, high specific energy and power, and they outperform both the battery and the capacitor for pulsed applications. By contrast the serial hybrid can slightly increase the specific energy with respect to the capacitor but the specific power is comparable to the power of the battery, and it does not provide any benefit with pulsed applications.

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1. Introduction

Efficient electrochemical energy storage is an important issue in today society. Electrochemical energy storage devices such as batteries and electrochemical capacitors can be found in a large variety of applications in the fields of transportation, in particular automotive, consumer goods, and industry. The demand of portable energy sources does and will constantly increase. It is therefore likely that electrochemical energy storage devices will play an increasing role in the future society.

The area of electrochemical energy storage covers a large number of different systems. The most important are rechargeable batteries such as lead-acid, nickel-metal hydride, and lithium-ion batteries, and the electrochemical capacitors [1].

The different systems have different performance in terms of specific energy and power; rechargeable batteries are typically characterized by low specific power and high specific energy, while the opposite applies for the electrochemical capacitors. Similarly, the large number of different applications has different demands in terms of the power spectrum to be provided by the power source. It is therefore clear that a single system cannot fulfil the requirements of the different applications. High energy–high power devices being

able to fulfil the requirements of more applications are highly desirable. In this respect the goal of having high energy and high power in the same systems has been pursued in the last decades with different approaches. One of these is the hybridization of electrochemical capacitors with rechargeable batteries, with a view to combining the high specific power of the electrochemical capacitor with the high specific energy of the battery.

Electrochemical capacitors are a class of electrochemical energy storage devices characterized by an inherently high specific power, typically above 10 kW kg^{-1}, but a rather low specific energy, typically less than 10 Wh kg^{-1} [2]. The electrochemical double layer capacitor typically consists of two activated carbon based electrodes soaked with an organic electrolyte. The charging process of such device is, in the ideal case, purely electrostatic. The charge is stored in the double layer, which builds up at the electrode/electrolyte interface upon polarization. The charging process clearly involves only the surface of the active material. It is therefore fast and allows for the high power of the devices. However, the specific energy is small because the charge storage process is limited to the material's surface.

Rechargeable batteries are electrochemical energy storage systems, which are characterized by a high specific energy, and among the different systems the lithium-ion battery provides the highest one (up to 250 Wh kg^{-1} for industrial products). However, batteries are characterized by a low specific power compared to electrochemical capacitors, which typically does not exceed 1 kW kg^{-1}. A

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lithium-ion battery utilizes lithium insertion materials in both the negative and positive electrode, typically graphite in the negative electrode and $LiCoO_2$ in the positive electrode [3]. The whole volume of the active material is used for charge storage and, therefore, the specific energy of the battery is higher than that of the electrochemical capacitor. However, the rate of the charge/discharge process is typically limited by the solid state diffusion of lithium in the bulk of the active materials, which is inherently slow and therefore the specific power of batteries is significantly lower than the specific power of electrochemical capacitors [4].

Both the lithium-ion battery and the electrochemical double layer capacitor have similar technical aspects. Both systems utilize an aprotic organic electrolyte and the charging processes of the respective electrodes occur in similar potential ranges. These are important issues for the practical hybridization of the two systems.

The hybridization of electrochemical capacitors and rechargeable batteries can, in principle, be performed according to different approaches. Readily available batteries and electrochemical capacitors can be externally hard wire connected, in serial or in parallel. By analogy, the same approaches can be proposed at the internal level within one device, leading to the internal serial or the internal parallel hybrid. Between these four possible approaches only two were widely exploited in the available scientific literature.

The external parallel hybridization was discussed by several authors with the main aim to improve the high rate performance and the pulse capability of rechargeable batteries in specific applications. The use of externally parallel connected electrochemical capacitors with a rechargeable battery was discussed for internal combustion engine cranking [5–7], for hybrid or electric vehicles [8–10], and for general pulsed applications [11,12]. The main outcome of these studies is that the capacitor connected parallel to the battery allows for a better pulse capability and reduced voltage drop upon pulsing. The capacitor accepts or releases the high current pulses. Those high current pulses relieve the battery and this is supposed to reduce the thermal stress of the battery and thus increase the lifetime of the battery. Thus the service time of the battery is extended.

The behavior of an external parallel hybrid based on the external connection of state of the art lithium-ion batteries and electrochemical capacitors was simulated for both constant power application and pulsed applications [13]. It was demonstrated that the specific energy and power of the external parallel hybrid varies continuously between the battery and the capacitor end values according to the relative size of the respective devices. Thus an external parallel hybrid has a maximum specific charge greater than that of the capacitor and a maximum specific power greater than that of the battery. In addition, it was demonstrated that the external parallel hybrids provide remarkably high specific energy and power during pulsed applications, in which case they outperform both the sole battery and the sole capacitor. It was shown that the power is mainly delivered by the capacitor during the pulse while the battery recharges the capacitor in the rest period [13].

The other widely investigated approach is the internal serial hybridization. In this case a battery and a capacitor electrode are incorporated within one electrochemical cell. Several approaches towards such hybrid capacitors were proposed using different battery and carbon materials [14–16].

A battery electrode has, in first approximation, an infinite capacitance. Within this assumption, it can be demonstrated that replacing one carbon electrode with a battery electrode can double the specific energy of a regular activated carbon based electrochemical capacitor.

The other possible approaches did not find much interest so far. There are no published examples of external serial hybrids as well as of internal parallel hybrids. The internal parallel hybrids can be developed by combining a negative bi-material electrode and a positive bi-material electrode within one device. A bi-material electrode consists of an electrode where the charge is stored by two different active materials with different charging mechanisms. In particular one of the materials should mainly store charge in the double layer (i.e., an electrochemical capacitor material) and the other material should mainly store charge utilizing a Faradaic reaction (i.e., a battery material).

A few examples of devices containing one bi-material electrode can be found. The Ultrabattery[TM] developed by Lam and Lauey [17] is a system derived from the lead-acid battery where the lead based electrode was replaced by a bi-material lead-activated carbon electrode. The authors found a better rate capability, pulse capability, and cycle life of the Ultrabattery[TM] compared to a regular lead acid battery. Recently, Hu et al. proposed a device containing a $Li_4Ti_5O_{12}$ negative electrode and a positive electrode based on a mixture of $LiFePO_4$ and activated carbon [18] or $LiMn_2O_4$ and activated carbon [19]. The authors found increased specific energy compared to activated carbon based electrochemical capacitors.

Model segmented bi-material electrodes were characterized and the current sharing between the battery and the capacitor materials was addressed [20,21]. In this case an electrode based on activated carbon as capacitor material and $LiMn_2O_4$ as battery material was pulse-discharged. It was shown that the pulse current is drawn mainly from the activated carbon and that the $LiMn_2O_4$ recharges the activated carbon in the rest period [20,21].

The main aim of this work is to compare the different internal approaches to the hybridization based on three selected materials with otherwise identical experimental boundary conditions. Applying most similar conditions electrochemical cells based on the different approaches were assembled. The electrochemical characterization was focused on the specific energy and power, and on the estimation of the performance of the systems during pulsed applications.

2. Experimental

2.1. Electrode and cell preparation and characterization

The single and bi-material electrodes used in this work were prepared according to the following procedure. The commercial active materials (activated carbon YP17 – Kuraray Chemicals Japan (AC); $LiMn_2O_4$ – Honeywell Specialty Chemical GmbH, Seelze, Germany, and $Li_4Ti_5O_{12}$ – Süd-chemie AG, Moosburg, Germany) were mixed with conductive additives (Carbon black Super P and graphite KS6 both from TIMCAL SA, Bodio, Switzerland) and polytetrafluoroethylene as binder (from a 60% (w w^{-1}) aqueous dispersion, Sigma–Aldrich) and dispersed in acetone. The ratio between the different materials was: active materials 80% (w w^{-1}), carbon black 5% (w w^{-1}), graphite KS6 5% (w w^{-1}), and PTFE as binder 10% (w w^{-1}). The dispersion was then heated and vigorously stirred until a dough-like mass was obtained. This mass was then repeatedly rolled into self-supporting electrode sheets. The electrode sheets were then dried at 120 °C for at least 24 h at a pressure of 30 mbar. Diameter 12 mm electrodes were punched out of the electrode sheets and incorporated into electrochemical cells used in the characterizations. The typical thickness of the electrode is $120 \pm 20\ \mu m$ and the typical active material loading is $9 \pm 2\ mg\ cm^{-2}$.

Each electrode material is characterized by a certain electrode composition (r) defined as the relative amount of battery materials in the total active materials:

$$r = \frac{m_{BAT}}{m_{BAT} + m_{EC}}$$

where m_{BAT} and m_{EC} are the battery materials (LiMn$_2$O$_4$ or Li$_4$Ti$_5$O$_{12}$) and the electrochemical capacitor material (AC) masses in the electrode, respectively.

The specific charge of the different electrode materials was measured in a single electrode by means of galvanostatic charge discharge cycles in a three-electrode cell configuration. In this case, the counter electrode of the electrochemical cell consisted of an oversized activated carbon electrode. The use of activated carbon as quasi reference was found convenient. The immersion potential of activated carbon in organic electrolytes is sufficiently stable to be used as quasi reference [22] and it was found to be 3.05 V vs. Li/Li$^+$. However, all the single electrode potentials reported in this work are quoted after recalculation against Li/Li$^+$. Counter and working electrodes were separated by an unbound glass fibre separator (type EUJ116 from Hollingsworth & Vose, UK).

A positive electrode and a negative electrode of proper masses were incorporated in two or three electrode cells in the case of full cell characterizations. In this case carbon coated aluminium foil discs (Gaia Akkumulatorenwerke, Germany) were placed between the electrodes and the current collectors in order to improve the electrical contact. A 20 μm thick cellulose based separator (Maxwell Technologies, Switzerland) was used to separate positive and negative electrodes. An activated carbon quasi reference electrode was incorporated in the full cells in order to monitor the single electrodes potentials in the case of full cell galvanostatic cycling.

The full cell composition (R) is defined in analogy to the single electrodes with the relative amount of battery material in the cell with respect to the total mass of active materials:

$$R = \frac{M_{BAT}}{M_{BAT} + M_{EC}}$$

where M_{BAT} and M_{EC} are the battery and the electrochemical capacitor material masses in the cell. The average active material loading for the sum of both electrodes in the full cell was 18 mg cm^{-2}. In addition the electrode mass ratio (K) is defined for a full cell as:

$$K = \frac{m_{POS}}{m_{POS} + m_{NEG}}$$

where m_{POS} and m_{NEG} are the electrode masses for the positive and the negative electrode, respectively.

The electrochemical cells were assembled in air and dried at 120 °C at a pressure of 30 mbar for at least 12 h. The dried cells were then transferred into an Ar filled glovebox (H$_2$O and O$_2$ < 1 ppm). The cells were then filled with the electrolyte and hermetically sealed.

A 1 mol dm^{-3} solution of lithium perchlorate in acetonitrile was used as electrolyte which was prepared in house using dry lithium perchlorate (electrochemistry grade from Sigma–Aldrich) and anhydrous acetonitrile (Sigma–Aldrich). The water content of the electrolyte was measured with Karl Fischer titration (684 KF Coulometer from Metrohm, Switzerland, with Hydranal® Coulomat E from Sigma–Aldrich as electrolyte) and found to be less than 30 ppm.

The resistance of the cells was estimated from the voltage drop upon current application in the pulsed experiments. The delay between current application and voltage measurement was 50 ms (corresponding to 20 Hz). The resistance measured at such low frequency includes several contributions such as electrode–current collector contact resistance, electrode, electrolyte, and separator resistance. It is therefore highly related to the cell design and assembly. The resistance values estimated with this approach can be used for comparison purposes assuming that the electrode–current collector resistance, electrolyte and separator resistances do not vary significantly for the different cells and different electrode compositions.
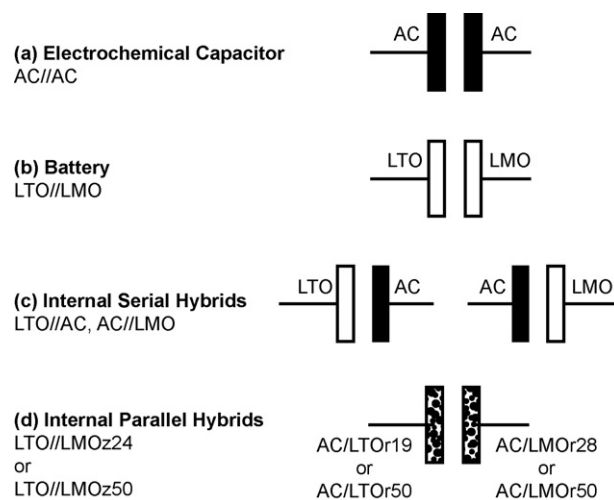

Fig. 1. Sketch of the various systems characterized in this work based on the electrode materials AC, LTO and LMO and on the different bi-material electrodes. (a) Electrochemical capacitors, (b) battery, (c) two internal serial hybrids having the battery material in the negative or in the positive electrode, respectively, and (d) internal parallel hybrids using AC/LTOr19 and AC/LMOr28, or AC/LTOr50 and AC/LMOr50 electrodes, respectively. The electrolyte is the same for all configurations.

All experiments were performed at room temperature. All reported specific values refer to the mass of active materials in the electrode or in the full cell. Energy and power densities refer to the total electrode volume in the full cell. Efforts were spent in order to apply the most similar conditions in all the experiments used in the comparisons.

All galvanostatic charge/discharge experiments discussed in this work were performed with a constant current–constant voltage protocol with a battery cycler (Astrol Electronic, Switzerland). The constant power discharge and the pulsed charge and discharge were performed with a potentiostat–galvanostat VMP3 (Biologic, France).

2.2. Electrode and cell nomenclature

Several electrode materials and cells are investigated in this work; it is therefore convenient to summarize them in Fig. 1 and Tables 1 and 2.

An electrode material is named according to the abbreviations of the constituent active materials: LMO for LiMn$_2$O$_4$, LTO for Li$_4$Ti$_5$O$_{12}$, and AC for activated carbon. The different active materials are separated by one slash ("/"). The active materials are followed by the electrode composition times 100, i.e., the percentage of battery material in the electrode.

A full cell is named according to the active material in the negative electrode followed by two slashes ("//") followed by the active material in the positive electrode. In case of internal parallel hybrids only the battery materials in the negative and positive electrodes are indicated followed by the cell composition times 100, i.e., the overall percentage of battery material in the cell.

3. Results and discussion

3.1. Single electrodes

The different electrode materials used in this work are listed in Table 1 together with the electrode composition (r) and the specific charge measured from galvanostatic discharge cycles at the $C/5$ rate. Activated carbon is used as "capacitor material" either for the positive and the negative electrode. The specific charge of the

Table 1
Description of the electrode materials used in this work.

Electrode material	Active materials	Electrode composition, r	Specific charge (mAh g^{-1})	Potential window (V vs. Li/Li$^+$)
Single material electrodes				
LMO	LiMn$_2$O$_4$	1	106 ± 4	3.3–4.3
LTO	Li$_4$Ti$_5$O$_{12}$	1	157 ± 7	3.0–1.3
AC	Activated carbon	0	36 ± 1	3.3–4.3
			62 ± 4	3.0–1.3
Bi-material electrodes				
AC/LMOr28	Activated carbon, LiMn$_2$O$_4$	0.28	49 ± 3	3.3–4.3
AC/LMOr50	Activated carbon, LiMn$_2$O$_4$	0.50	62 ± 3	3.3–4.3
AC/LTOr19	Activated carbon, Li$_4$Ti$_5$O$_{12}$	0.19	79 ± 5	3.0–1.3
AC/LTOr50	Activated carbon, Li$_4$Ti$_5$O$_{12}$	0.50	102 ± 3	3.0–1.3

Table 2
Description of the full cell systems characterized in this work.

System	Negative electrode	Positive electrode	Cell composition, R	Electrode mass ratio, K
Standard systems				
LTO//LMO	LTO	LMO	1	0.61 ± 0.04
AC//AC	AC	AC	0	0.50 ± 0.01
Internal parallel hybrid systems				
LTO//LMOz24	AC/LTOr19	AC/LMOr28	0.24	0.54 ± 0.04
LTO//LMOz50	AC/LTOr50	AC/LMOr50	0.50	0.57 ± 0.02
Internal serial hybrid systems				
LTO//AC	LTO	AC	0.24	0.76 ± 0.01
AC//LMO	AC	LMO	0.31	0.31 ± 0.01

activated carbon electrode is 36 mAh g^{-1} when positively polarized between 3.3 and 4.3 V vs. Li/Li$^+$ and 62 mAh g^{-1} when negatively polarized between 3 and 1.3 V vs. Li/Li$^+$. These specific charge values correspond to 130 F g^{-1} and 120 F g^{-1} for the positively and the negatively polarized activated carbon electrode, respectively.

The LiMn$_2$O$_4$ used as positive electrode battery material exhibited a specific charge of 106 mAh g^{-1} in LiClO$_4$/AN electrolyte. The material chosen as negative electrode battery material is Li$_4$Ti$_5$O$_{12}$, which had a specific charge of 157 mAh g^{-1}.

Bi-material electrodes based on LiMn$_2$O$_4$ and activated carbon were prepared and their specific charge was measured. The chosen electrode compositions were $r = 0.50$ and $r = 0.28$. For $r = 0.28$ the charge is roughly equally shared between the battery and the capacitor materials. The measured specific charge for the AC/LMOr28 bi-material electrode is 49 mAh g^{-1} while the specific charge of the AC/LMOr50 bi-material electrode is 62 mAh g^{-1}.

The bi-material electrodes used as negative electrode are based on Li$_4$Ti$_5$O$_{12}$ and activated carbon. Again two compositions were used: $r = 0.50$ and $r = 0.19$. For $r = 0.19$ the charge is roughly equally shared between the two active materials. The bi-material electrode AC/LTOr19 has a specific charge of 79 mAh g^{-1} while the electrode AC/LTOr50 has a specific charge of 102 mAh g^{-1}.

The specific charges measured for the bi-material electrodes are close to the linear combination of the specific charges of the single active materials.

3.2. Full cell systems

The single material electrodes (AC, LMO, and LTO) and bi-material electrodes (AC/LMOr28, AC/LMOr50, AC/LTOr19, and AC/LTOr50) were used to assemble different representative systems, which are listed in Table 2.

Standard systems such as a battery and an electrochemical capacitor were assembled. The battery (LTO//LMO) uses a LTO negative electrode and a LMO positive electrode. Only battery materials are included in the battery, thus, the cell composition R is 1. The other standard system is the electrochemical capacitor AC//AC for which the cell composition R is 0.

Two internal parallel hybrid systems based on the described bi-material electrodes were assembled. The cell LTO//LMOz24 has a cell composition of 0.24 and the stored charge is roughly equally shared between the battery materials and the capacitor material. The other internal parallel hybrid assembled is the cell LTO//LMOz50 which has a cell composition of $R = 0.50$. In this case the battery materials store 0.75 of the total charge.

The other class of systems characterized in this work accounts for the internal serial hybrids. The LTO//AC and the AC//LMO systems are the internal serial hybrids considered in this work, which have a cell composition (R) of 0.24 and 0.31, respectively. In case of the internal serial hybrid the charge sharing discussed for the internal parallel hybrid cannot be applied.

All the considered systems have a maximum cell voltage of 3 V.

3.2.1. Galvanostatic charge/discharge cycling

Galvanostatic charge/discharge cycling was performed on the different systems at a low rate in order to measure the maximum specific charge. In addition the cell voltage and the single electrode potentials profiles are recorded and discussed in the following.

The cell voltage profiles and the electrode potential profiles for the different systems based on AC, LTO, and LMO electrodes reported in Table 2 are shown in Fig. 2. The charge and discharge rate was C/5.

The voltage profile for the LTO//LMO battery (Fig. 2) is characterized by a voltage plateau at 2.5 V and the specific charge is close to 60 mAh g^{-1}. The corresponding single electrode potential profiles have the expected shape (Fig. 2). The positive electrode (LMO/PTFE) has a potential plateau at ca. 4 V vs. Li/Li$^+$ and the negative electrode (LTO/PTFE) at ca. 1.5 V vs. Li/Li$^+$.

The parallel hybrids (LTO//LMOz50 and LTO//LMOz24) are characterized by a voltage plateau at ca. 2.5 V alike the battery. The course of the electrode potentials shows a potential plateau at ca. 4 V vs. Li/Li$^+$ and at ca. 1.5 V vs. Li/Li$^+$ for the positive and the negative electrode, respectively. Furthermore, the voltage profile below 2 V for the internal parallel hybrids is due to the charge or discharge of the double layer of the activated carbon in the electrodes.

The specific charges of the internal parallel hybrids are 29 and 38 mAh g^{-1} for the LTO//LMOz24 and LTO//LMOz50, respectively.
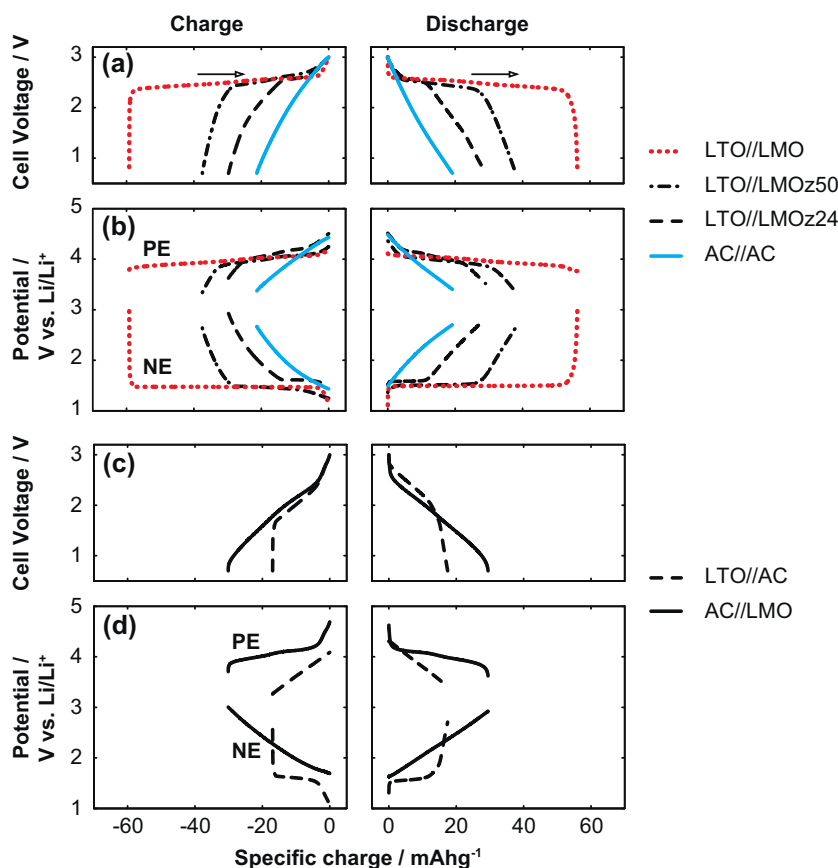
Fig. 2. Cell voltage and single electrode potential profiles for the different systems characterized in this work. The charge/discharge rate was C/5. (a) Cell voltage profiles for the systems LTO//LMO, LTO//LMOz50, LTO//LMOz24, and AC//AC. (b) Positive electrode (PE) and negative electrode (NE) potential profiles for the systems LTO//LMO, LTO//LMOz50, LTO//LMOz24, and AC//AC. (c) Cell voltage profiles for the systems LTO//AC and AC//LMO. (d) PE and NE potential profiles for the systems LTO//AC and AC//LMO.

The voltage profile of the AC//AC electrochemical capacitor is a straight sloped line as expected for an electrochemical capacitor, and the single electrode potential profiles as well. The specific charge is 20 mAh g^{-1}.

The voltage profiles of the internal serial hybrids LTO//AC and AC//LMO are reported in Fig. 2c and the corresponding single electrode potentials in Fig. 2d. The voltage profiles of the two systems are similar. The voltage profiles, basically, correspond to the potential profile of the AC electrode which is shifted by the potential (with respect to the immersion potential) of the plateau of the battery material electrode. Thus, the "capacitor like" voltage profile starts above 1 V in case of the internal serial hybrid AC//LMO and above 1.5 V in case of the internal serial hybrid LTO//AC. The specific charge of the investigated hybrids is 18 and 30 mAh g^{-1} for LTO//AC and AC//LMO, respectively.

The internal parallel hybrids based on bi-material electrodes retain features of both the capacitor and the battery. A voltage profile of an internal parallel hybrid (IPH) is characterized by a plateau due to the battery materials, and a part where the charge is stored in the double layer of the activated carbon. The charging of the two materials occurs at different state of charge of the IPH. The activated carbon is typically charged at the beginning and at the end of the charge, while the battery material is typically charged in the middle. The same applies for the discharge.

The serial hybrids are characterized by a voltage profile similar to a capacitor. In contrast to the internal parallel hybrid the charging of the battery and the capacitor material occurs at the same time.

Further details about the specific charges of the different systems are reported in Table 3.

3.2.2. Energy–power relationship

The energy–power relationship is highly relevant for all electrochemical energy storage devices. Electrochemical capacitors are characterized by a low specific energy and a high specific power. The opposite applies for lithium-ion batteries which are characterized by a high specific energy but a relatively low specific power. The effect of the hybridization of batteries and capacitors has to be addressed for both the power and the energy. A hybrid device should improve the capacitor in terms of specific energy and the battery in terms of specific power.

The cell voltage profiles for the constant power charge and discharge for the systems LTO//LMO, LTO//LMOz50, LTO//LMOz24, and AC//AC are reported in Fig. 3. The battery LTO//LMO is able to accept or deliver approximately 50 mAh g^{-1} at the specific power of 0.1 kW kg^{-1} (Fig. 3a). This specific charge value drops to 15 mAh g^{-1} when the specific power is increased to 1 kW kg^{-1}. The battery cannot be charged or discharged at the specific power of 10 kW kg^{-1}.

The case of the internal parallel hybrid LTO//LMOz50 is reported in Fig. 3b. The voltage profile has the expected shape with a pronounced voltage plateau for a specific power of 0.1 kW kg^{-1}. In this case the specific charge accepted or delivered is 32 mAh g^{-1}. The potential plateau is highly distorted or absent when the specific power is increased to 1 or 10 kW kg^{-1}. This parallel hybrid is typically able to accept and deliver higher specific charge than the battery at high power. Thus, the LTO//LMOz50 outperforms the battery in terms of specific charge at high power.

The results are similar in the case of the hybrid LTO//LMOz24. The specific charge at low power is 25 mAh g^{-1} which does not significantly drop when the power is increased. The specific charge is 15 mAh g^{-1} in case of a specific power of 10 kW kg^{-1}.

Table 3
Specific charge, energy, and power, and cell resistance for the different systems characterized in this work.

| Systems	Specific charge (mAh g^{-1})	Specific energy (Wh kg^{-1})	Specific power (kW kg^{-1})	Resistance[a] (Ω cm^2)
Standard systems				
LTO//LMO	61 ± 3	130 ± 5	2.0 ± 0.3	52 ± 16
AC//AC	18 ± 2	33 ± 2	41 ± 3	7 ± 1
Internal parallel hybrid systems				
LTO//LMOz24	28 ± 2	53 ± 2	27 ± 3	5 ± 1
LTO//LMOz50	37 ± 1	71 ± 2	12 ± 2	4 ± 2
Internal serial hybrid systems				
AC//LMO	28 ± 2	45 ± 5	1.2 ± 0.1	38 ± 14
LTO//AC	20 ± 3	30 ± 2	1.3 ± 0.5	48 ± 28

[a] For a 200 μm thick electrodes–separator stack.
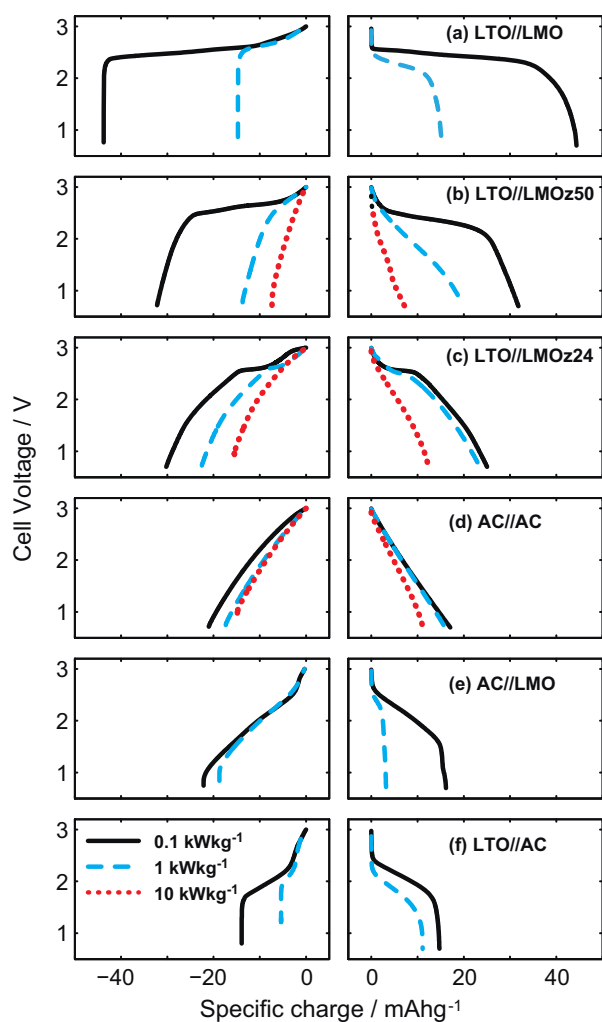
Fig. 3. Cell voltage profiles for the charge (left) and the discharge (right) of (a) LTO//LMO, (b) LTO//LMOz50, (c) LTO//LMOz24, (d) AC//AC, (e) AC//LMO, and (f) LTO//AC at the specific power of 0.1, 1, and 10 kW kg^{-1}.
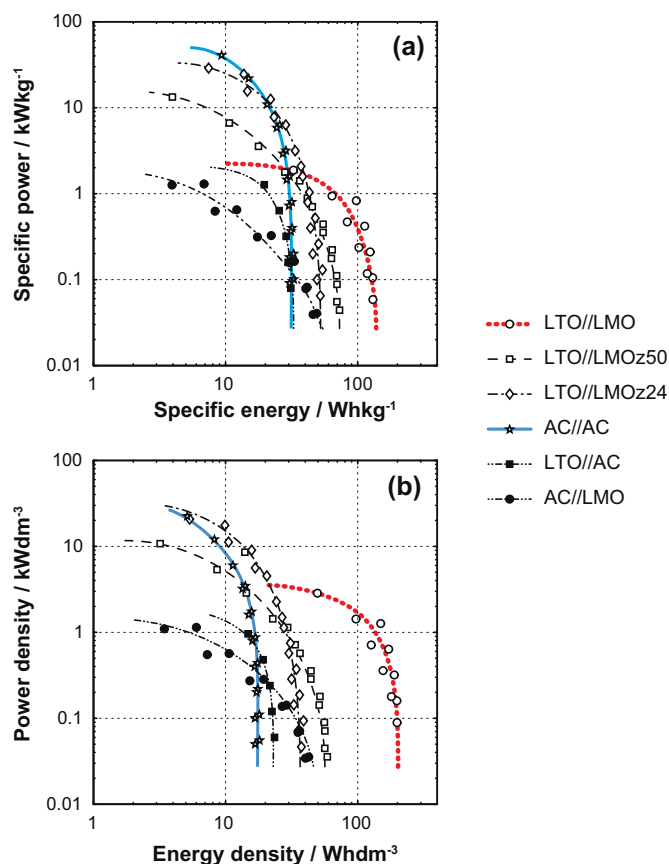

Fig. 4. Ragone plots for the different systems. (a) Ragone plot in terms of specific power against specific energy and (b) Ragone plot in terms of power density against energy density.

The capacitor is clearly the device less affected by the charge discharge conditions. Its practical specific charge stays between 12 and 19 mAh g^{-1} when the specific power is varied between 0.1 and 10 kW kg^{-1}. Both the serial hybrids present relatively low specific charge at low specific power. The specific charge is 15 and 16 mAh g^{-1} for the discharge of AC//LMO and LTO//AC, respectively. These systems are highly sensitive to the applied power and the practical specific charge drops to 4 or 11 mAh g^{-1} for AC//LMO and LTO//AC, respectively when the specific power increases to 1 kW kg^{-1}. None of the internal serial hybrid is able to be charged or discharged at a power of 10 kW kg^{-1}.

A more detailed analysis of the energy–power relationship for the systems LTO//LMO, LTO//LMOz50, LTO//LMOz24, AC//AC, AC//LMO, and LTO//AC is reported in the Ragone plots of Fig. 4. Specific energy and power are plotted in Fig. 4a. The battery LTO//LMO is the system with the highest specific energy of 130 Wh kg^{-1}. The maximum specific power of the battery is limited to 2 kW kg^{-1}. The internal parallel hybrid LTO//LMOz50 has a maximum specific energy of 71 Wh kg^{-1}, while the maximum specific power is 12 kW kg^{-1}. This system is able to roughly provide half of the specific energy of the battery but seven times higher maximum specific power.

The second considered internal parallel hybrid (LTO//LMOz24), which is close to a capacitor, has a specific energy of 53 Wh kg^{-1} with a maximum specific power of 27 kW kg^{-1}. The capacitor AC//AC has a specific energy of 33 Wh kg^{-1} and a specific power of 41 kW kg^{-1}. This set of Ragone plots shows the transition from the high energy–low power battery to the high power–low energy electrochemical capacitor for these exemplary internal parallel hybrids.
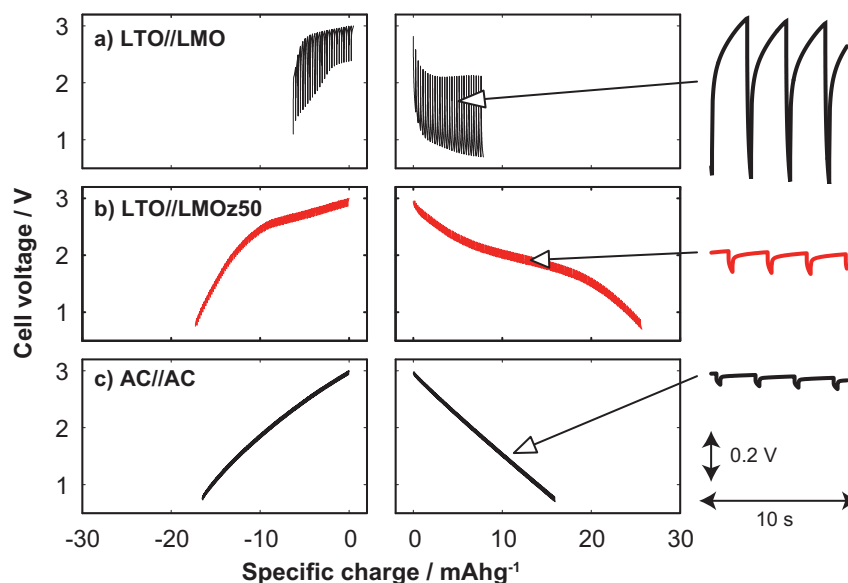
Fig. 5. Cell voltage profiles for the pulsed charge (left) and the pulsed discharge (right) for (a) LTO//LMO, (b) LTO//LMOz50, and (c) AC//AC. The applied pulsed pattern had an amplitude of 50 C and a duty cycle of 10%. 10 s of pulse discharge are enlarged on the right side of the plots.

In addition to these systems the internal serial hybrids LTO//AC and AC//LMO were characterized. Both serial hybrids have limited specific energy: 30 Wh kg^{-1} for LTO//AC and 45 Wh kg^{-1} for AC//LMO. They are also limited in maximum specific power, which is 1.3 and 1.2 kW kg^{-1} for LTO//AC, and AC//LMO, respectively. The specific power of the internal serial hybrid is lower than the specific power of the battery LTO//LMO.

Fig. 4b shows the respective Ragone plots in terms of power density against energy density. The trend is the same as discussed before. It is relevant noticing that the higher density of the bi-material electrodes with respect to AC leads to better volumetric properties for the internal parallel hybrids. In particular the system LTO//LMOz24 has the same power density like the capacitor AC//AC and an energy density more than doubled.

Specific energy and power for the different systems are reported in Table 3.

3.2.3. Pulsed applications

In order to investigate the performance of the different systems for possible pulse power applications the systems were pulse charged and discharged. The applied pulse pattern is expected to charge or discharge the cell with $n_P = 250$ pulses. The pulse amplitude is varied between 25 and 400 C and the applied duty cycles were 2%, 10%, and 50%.

An example of cell voltage for the pulsed charge and discharge of the systems LTO//LMO, LTO//LMOz50, and AC//AC is reported in Fig. 5. A very large voltage drop affects the battery LTO//LMO when the pulse current is applied. As a consequence the voltage cut-off criterion is reached after a few pulses and in total the system is able to accept or deliver only less than 10 mAh g^{-1}. The capacitor AC//AC can be clearly efficiently charged and discharged with this pulse pattern and the specific charge is close to the maximum value of 18 mAh g^{-1}. Finally, the internal parallel hybrid LTO//LMOz50 outperforms both the capacitor and the battery in terms of specific charge for both, charge and discharge. The gain during charge is limited to a few mAh g^{-1} while the gain during discharge is very high and the practical specific charge is 26 mAh g^{-1}, thus, more than three times the specific charge of the battery under the same conditions.

A detailed comparison of the performance of the different systems is reported in Fig. 6. The results are reported as specific pulse current amplitude against specific energy on logarithmic scales in "Ragone like" plots. The use of the specific current instead of the C-rate for indicating the pulse amplitude allows for a better comparison of the systems. The specific current is higher for a battery than for a capacitor for the same C-rate. Applications are typically defined by the peak current (power) demand and not by a certain C-rate.

Furthermore the specific energy intrinsically includes the effect of the voltage drop, thus, it is a better parameter than the specific charge for comparing full cell systems. The specific energy at the current amplitude of 0.1 A g^{-1} was assumed to be equal to the maximum specific energy for constant power discharge.

The performance of the parallel hybrids in pulsed charge and discharge are highly promising. In case of a duty cycle of 2% (Fig. 6a and d) the internal parallel hybrids can provide significantly greater energy than the battery for a pulse amplitude greater than 3 A g^{-1} for both charge and discharge. The specific energy of the internal parallel hybrids is always between 10 and 70 Wh kg^{-1} under these conditions. The capacitor is able to provide high pulse amplitudes in all cases; however, it is limited in specific energy when compared to the internal parallel hybrid systems. The internal parallel hybrids clearly outperform both the capacitor and the battery for pulsed applications. An increased duty cycle of 10% (Fig. 6b and e) or of 50% (Fig. 6c and f) does not significantly affect the performance of the internal parallel hybrid or the capacitor. However the battery performance drops for increased duty cycles. Thus, the gain in performance with pulse application is even more pronounced. The internal parallel hybrids outperform the battery for a pulse amplitude of 2 A g^{-1} when it is discharged with a duty cycle of 10% and in all the cases when the duty cycle is further increased to 50%. The internal parallel hybrids provide higher specific energy than the capacitor in all the cases considered.

The internal serial hybrids LTO//AC and AC//LMO were included in the comparison and clearly provide the worst performance in pulsed applications. The specific energy available is typically one order of magnitude lower than the practical specific energy available from the other systems at moderated low pulse amplitude. The internal serial hybridization clearly does not provide any benefit in pulsed applications.
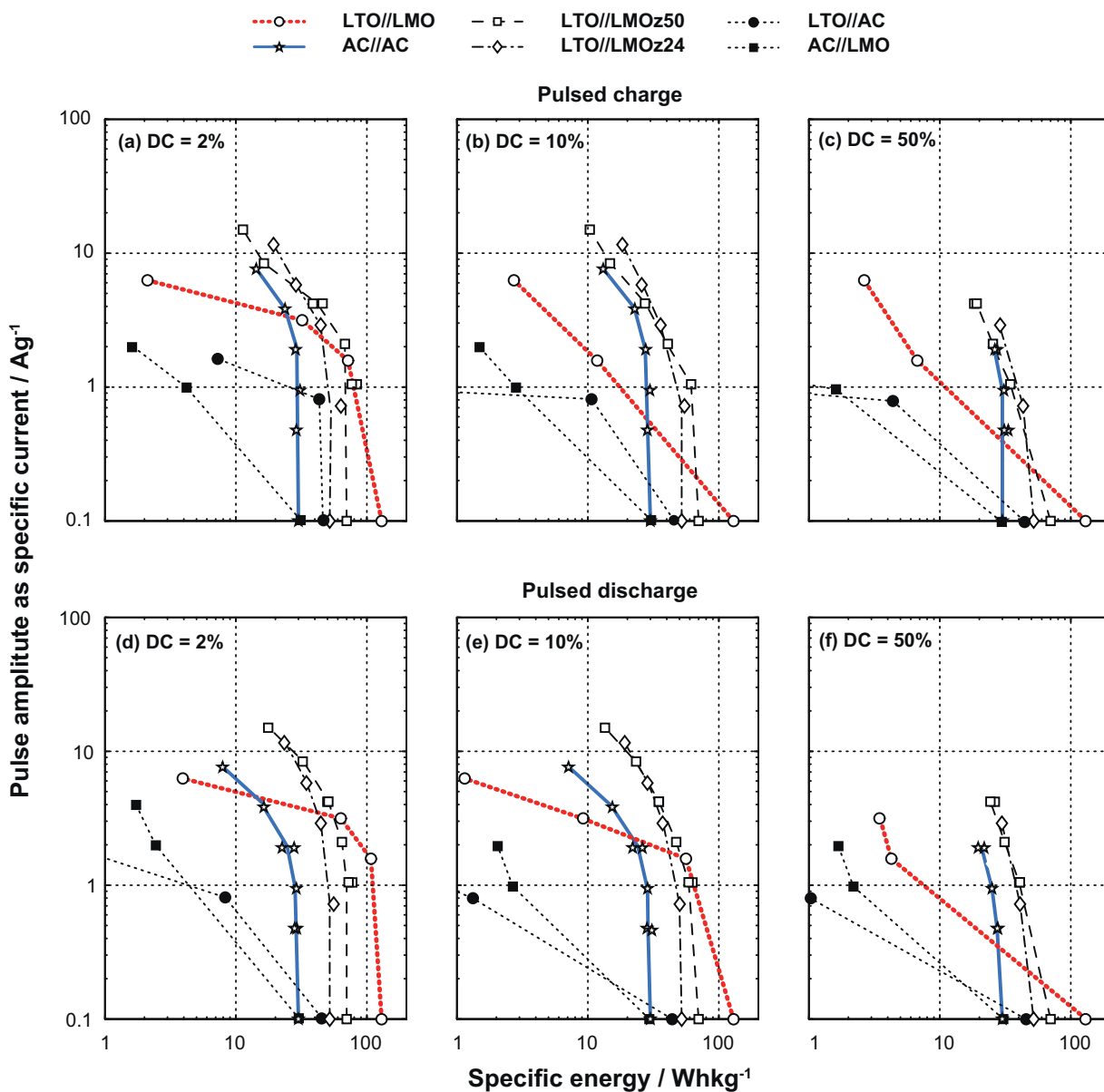
Fig. 6. "Ragone-like" plots for the pulsed charge (top) and the pulsed discharge (bottom) for the different systems. The applied pulse amplitude, expressed as specific current, is plotted against the available specific energy on logarithmic scales.

3.3. Cell resistance

The resistances of the different cells, normalized for 200 μm thick electrode–separator–electrode stacks, are summarized in Table 3. The capacitor AC//AC and the internal parallel hybrids have very comparable internal resistance between 4 and 7 Ω cm^2 while the battery LTO//LMO and the internal serial hybrid are characterized by a much higher internal resistance of 38–52 Ω cm^2, thus, one order of magnitude greater resistance than the electrochemical capacitor and the internal parallel hybrids.

The matched impedance power is inversely proportional to the cell resistance, therefore, the AC//AC capacitor and the internal parallel hybrid are expected to provide one order of magnitude greater specific power than the battery and the internal serial hybrids. The Ragone plots have shown the same trend of this estimation.

4. Conclusions

A detailed comparison of the electrochemical properties of internal serial and parallel hybrids, batteries and electrochemical capacitors was presented. All the systems were based on electrodes prepared with the same procedure, electrolyte and cell assembly. In addition the test procedure was the same for all the systems. This allowed a quantitative comparison of the systems in terms of specific energy and power, for constant current as well as pulsed current loads.

The Ragone plots measured for the different systems showed that the battery is the system, which provides the highest specific energy while it is limited in specific power. The electrochemical capacitor provides the highest specific power in the comparison, however, it is limited in specific energy.

The internal parallel hybrids provide a specific energy greater than that of the capacitor and a specific power greater than that of the battery. Thus, the internal parallel hybrids improve the capacitor in terms of specific energy and the battery in terms of specific power. Indeed, they are able to provide moderately high specific energy and power. The internal parallel hybrids do not exceed the maximum specific energy of the battery or the specific power of the capacitor.

The internal serial hybrids provide a maximum specific energy comparable to the capacitor, and a maximum specific power, which does not exceed the power of the battery. Therefore the internal serial hybrids do neither improve the battery nor the capacitor, because the specific energy is typically limited by the capacitor (AC) electrode and the specific power by the battery (LMO or LTO) electrode. On the other hand, in the parallel hybrid each electrode contains battery as well as capacitor material and is thus capable of delivering reasonably high energy and power, according to the mixing ratio.

For pulsed charge/discharge the internal parallel hybrids provide remarkable high specific energy at a current pulse amplitude where both the battery and the capacitor fail. The superior behavior of the internal parallel hybrid in pulsed applications is more pronounced for high duty cycles, thus, fast pulse repetition. This is due to the recharging of the activated carbon by the battery material. For the internal serial hybrid such recharging is impossible.

The internal serial hybrids typically provide one order of magnitude less specific energy in pulsed charge or discharge than the other considered systems.

The internal parallel hybrids and the capacitor are characterized by a significantly lower internal resistance than that of the internal serial hybrid and the battery. Therefore these systems can provide high specific power with a high energetic efficiency.

The internal parallel hybridization allows realizing high power–high energy devices.

The greatest advantages of the parallel hybridization are in pulsed applications.

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