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# Perspective We may be underestimating the power capabilities of lithium-ion capacitors



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# HIGHLIGHTS

- · Commercial lithium-ion capacitors include lithiated graphite and activated carbon.
- · Power capabilities of lithium-ion capacitors are often understated in literature.
- · Arguably, power densities of lithium-ion capacitors may be superior to those of supercapacitors.
- · A slow charge of lithium-ion capacitors may increase power characteristics further.

# ARTICLE INFO

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# ABSTRACT

In this Perspective, we express our opinion on the specific power and power density of lithium-ion capacitors. These cells are state-of-the-art commercially available high voltage hybrid capacitors, notable for combining high energy and high power in one cell. However, the power characteristics of these electrochemical cells are not always well understood in the scientific community and there is a substantial amount of conflicting information in the available literature. It appears that their power characteristics are often understated, undermining the appropriate recognition of these cells. Therefore, we present the evaluation of the power capabilities of lithium-ion capacitors on the basis of key literature results and targeted laboratory measurements in our group. From our analysis, power densities superior to those in electrochemical supercapacitors are usually achievable in lithium-ion capacitors. Consequently, these cells may be recognised as superior alternatives to supercapacitors not only in terms of their energy densities but also in terms of power densities (or, in gravimetric terms, specific powers). The discussion points provided in this Perspective should stimulate better understanding of lithium-ion capacitors as innovative cells for high power applications.

### 1. Introduction

Aerospace, automotive and consumer electronics applications are increasingly supported by compact and rechargeable energy storage solutions in the form of lithium-ion batteries and electrochemical supercapacitors. Equipped with enviable gravimetric energy density (up to 250 W h kg<sup>-1</sup>) [1], lithium-ion batteries are an advanced type of secondary battery and are used when the supply of electricity is required for an extended period of time [2]. However, they are not equally well equipped to provide large power pulses on demand (power density of up to only 315 W kg<sup>-1</sup>) [1]. For such applications, supercapacitors (energy density of up to 15 W h kg<sup>-1</sup> and power density of as high as 10 kW kg<sup>-1</sup>) [1], also known as electric double-layer capacitors

(EDLCs), are commonly employed. As it follows, the available energy storage cells have been traditionally split into two distinct classes : (i) cells with high energy density but low power density for high-energy applications (lithium-ion batteries) and (ii) cells with high power density but low energy density for the uses where high-power capability is required (supercapacitors). It is of course desirable to develop the energy storage cells utilising the best characteristics of lithium-ion batteries and supercapacitors simultaneously, and thus possessing both high energy and high power. Recently, lithium-ion capacitors (LICs) have emerged as such devices. They are composed of a lithium-ion battery negative electrode and a capacitor-type positive electrode in a lithium-ion battery electrolyte, a design conceived by Amatucci and co-workers in 2001 [3].

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Due to the combination of a battery-type electrode and a capacitive electrode in one cell, LICs can be classified as hybrid capacitors, and their design is indeed partially parallel to the design of previously known aqueous hybrid supercapacitors with nickel oxide or hydroxide positive electrodes [4]. While Amatucci et al. initially used  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as a battery-type negative electrode in the original concept of a LIC, the commercialisation of this novel device only gained traction once graphite was introduced as a negative electrode material [5,6], improving the energy density and voltage of the cell. The optimised LICs with prelithiated graphite and activated carbon electrodes are capable of attaining the gravimetric energy density of up to 100 W h kg<sup>-1</sup> [1], and the LICs of this type are already available for purchase internationally, e.g. from Musashi Energy Solutions and Taiyo Yuden (Japan), VINATech (South Korea) and LICAP Technologies (USA/China).

Despite the commercialisation success and a large pool of available research literature (including a number of review articles) [1,7-26], there are significant discrepancies in the community's understanding of the rate capability and power characteristics of LICs. For the purposes of easy visualisation, Ragone plots are widely used to highlight the energy and power characteristics of electrochemical cells. These plots are usually presented in the logarithmic scale; gravimetric (specific power) or volumetric power density of devices is plotted on the horizontal axis, and their gravimetric (specific energy) or volumetric energy density is plotted on the vertical axis. The positions of lithium-ion batteries and supercapacitors are firmly established on Ragone plots and represent a consensus view. As batteries have a high energy density and a low power density, they are located towards the upper-left side of the graph. In turn, supercapacitors (with a high power density but a low energy density) are positioned towards the bottom-right side of the graph. Bizarrely enough, our analysis of industry presentations and 20 review articles reveals that the positions of LICs on Ragone plots vary immensely in the literature. For example, LICs are depicted to have a comparable power density with supercapacitors [7,22], an inferior power density to supercapacitors [1] and a superior power density to supercapacitors [27]. Concurrently, the dominant narrative in the textual descriptions of LICs, which seems constant from manuscript to manuscript, is that the power density of LICs should be intermediate between lithium-ion batteries and supercapacitors due to their special design combining a battery-type graphitic electrode (intercalation process) and a non-Faradaic capacitive activated carbon electrode. Based on our own analysis and data, we have obtained evidence to the contrary, which will be discussed in this article. Overall, it is clear that very different views on the power capabilities are expressed by various practitioners in the field, and the device behaviour of LICs remains partially misunderstood, complicating their adoption in applications. Thus, it is timely and important to contribute this Perspective and stimulate the discussion on the power characteristics of LICs and the behaviour of these hybrid capacitors.

To highlight the power capabilities of LICs, we corroborate the data from the existing literature and company presentations with laboratory measurements. It is important to note that the discussion here is concentrated on the standard commercialised design of a LIC with prelithiated graphite and activated carbon electrodes [28]. Other experimental LICs have been described in the literature but remain the topic of laboratory prototyping only [29,30]. We do not apply the discussion here to those cells. We begin by recapping an early comparative assessment of power capabilities in LIC cells, with graphite and activated carbon electrodes, and supercapacitors published in 2008 by Khomenko, Raymundo-Piñero and Béguin [31]. While this initial assessment was conducted before the subsequent commercialisation of LICs by industry, the availability of a range of commercial cells today allows us to revisit these early assumptions. We therefore continue this Analysis article by assessing commercially available LICs in the cylindrical and laminar formats with respect to comparable commercial supercapacitors, and by identifying that the power densities (or specific power) of LICs are superior. Finally, we reproduce the same trends

in power characteristics in laboratory-fabricated LICs and supercapacitors. On the basis of both existing outside information and laboratory measurements, we present an educated opinion on the relative power densities of LICs and supercapacitors that is useful for the community.

#### 2. Experimental

When possible, the discussion in this Perspective uses literature data. However, to illustrate specific points, laboratory measurements were required.

#### 2.1. Testing of cylindrical capacitors

LICs (Taiyo Yuden and VINATech, 2.2–3.8 V, both 100 F) and supercapacitors (Rubycon, 0–2.5 V, 50 F; AVX, 0–2.7 V, 50 F) were subjected to galvanostatic charge–discharge using LAND D340 A battery cyclers using currents between 0.05 and 30 A (LICs) or 0.05 and 20 A (EDLCs). In order to apply currents in access of 10 A (single channel limit), multiple channels were parallelled for measurements. Energy density (Wh L<sup>-1</sup>) was calculated by integrating the discharge voltage profile and dividing by the volume of the cell. The average power density (W L<sup>-1</sup>) was then obtained by dividing the calculated energy density by the discharge time. All capacitors had identical dimensions — 18 mm (diameter) and 40 mm (length).

#### 2.2. Testing of laboratory-fabricated capacitors

Full cell LICs and supercapacitors were fabricated using 1:1 mass ratio of positive to negative electrodes. The LIC negative electrodes were fabricated with a component mass ratio of 90 : 5 : 5 (graphite : conductive carbon : binder). The LIC positive electrodes (or supercapacitor electrodes) were fabricated with a component mass ratio of 80:15:5 (activated carbon : conductive carbon : binder). Materials used amongst the electrodes were Imerys KS6 graphite, Kuraray YP-50F activated carbon, Ketjen Black EC 600-JD conductive carbon and an aqueous binder of sodium carboxy-methyl cellulose (Sigma Aldrich, product number 419281). The material loading for LICs' electrodes was  $3.3 \text{ mg cm}^{-2}$  and the material loading for supercapacitor electrodes was 3.5 mg cm<sup>-2</sup>. The electrolyte used was 1M LiPF<sub>6</sub> in ethylene carbonate and dimethyl carbonate (1:1 by volume). The cells were three-way Swagelok cells with an additional Li metal reference electrode. Prior to the assembly of LICs, their graphite electrodes were electrochemically prelithiated in three-way Swagelok cells and subsequently repacked to fabricate full cell LICs. This is done by replacing lithium metal counter-electrode with an activated carbon electrode. Prior to repacking, the graphite electrodes were cycled five times at a C/20 (19 mA/g) current rate. On the sixth and final cycle, the graphite electrodes were pre-lithiated to a capacity level of 270-320 mAh/g and the cell cycling was stopped. Supercapacitors were fabricated in the same format of Swagelok-type cells. The cells were subjected to galvanostatic charge-discharge using a Bio-Logic VMP-3 potentiostat-galvanostat.

Gravimetric energy densities (Wh kg<sup>-1</sup>) were calculated by integrating the discharge voltage profiles, and average power densities (W kg<sup>-1</sup>) were obtained by dividing the calculated energy density by the discharge time.

# 2.3. Notes on the calculation of energy and power densities

For both commercial cylindrical cells and laboratory-made cells energy (*E*) and power densities (*P*) were thus calculated according to the Eqs. (1) and (2) respectively, where *I* is the constant current applied during discharge, V(t) is the full cell voltage over time and cell discharge occurred between times  $t_0$  and  $t_1$ . All energy and power densities of laboratory-fabricated cells in this Perspective are reported per kilogramme of active material for laboratory-fabricated cells (that is, the current I in Eq. (1) is set in terms of the current's value per mass



**Fig. 1.** The first assessment of the energy and power parameters of LICs in open literature: (a) relative energy and power densities for a fabricated LIC device as a function of the mass ratio of positive (activated carbon) to negative (graphite) electrodes, (b) Ragone plot for fabricated LIC and EDLC devices, using ( $\Delta$ ) 1M LiPF<sub>6</sub> in EC/DMC for the LIC, and (**D**) 1M LiPF<sub>6</sub> in EC/DMC and (**O**) 1M Et<sub>4</sub>NBF<sub>4</sub> in AN for the EDLCs.

Source: Adapted with permission from [31].

unit of the active materials in both electrodes). All energy and power densities of commercial cylindrical cells are calculated per L of total cell volume for these cells (that is, the testing current is set in absolute terms (actual current's value in A) and the energy of cell is divided by the volume of the cell).

$$E = \int_{t_0}^{t_1} I \cdot V(t) dt \tag{1}$$

$$P = \frac{E}{t_1 - t_0} \tag{2}$$

#### 3. An early assessment of the power capabilities of LICs (2008)

The state-of-the-art, commercially deployed LICs involve two dissimilar electrodes, a negative electrode containing graphite as an active phase and a positive electrode containing activated carbon. The use of graphite enables a high practical voltage for these cells (typically, 3.8 V), as realised in the products from Taiyo Yuden, JSR Micro (now Musashi Energy Solutions), VINATech and LICAP Technologies [32– 34]. In contrast, more conventional electrochemical supercapacitors using two activated carbon electrodes are usually limited to 2.5 or 2.7 V, and, as it is well-documented, provide a much inferior energy content to LICs [35,36]. The graphitic negative electrodes in LICs are electrochemically prelithiated in order to remove the initial Coulombic inefficiency expected with such an electrode, pre-set its electrode potential to a lower value and enable higher energy density for the resulting cell [37]. As mentioned, this is usually done via an electrochemical route (and some cells may incorporate an additional sacrificial lithium electrode to be consumed during prelithiation). Despite the abundance of commercial LICs in the form of lithiated graphite and activated carbon cells on the market, the number of publications in the research literature that analyse the behaviour and characteristics of these cells is surprisingly limited.

An early and, as yet, perhaps the most comprehensive description of a contemporary LIC has been provided in the work by Khomenko, Raymundo-Piñero and Béguin, who analysed the electrode balancing, energy and power densities in LIC cells in 2008 [31]. An optimal cell with an appropriate pairing of graphite and activated carbon electrodes was reverse engineered. The energy and power contents of this cell are assessed in this work. The integration of two electrodes with two different charge storage mechanisms in a single cell naturally gives rise to some limitations. Undeniably, the optimal energy density in the cell is achieved when the capacities of both positive and negative electrodes are fully utilised. However, the power density of such a cell is limited by the electrode with slower kinetics (ion-intercalating graphite), which is sub-optimal for a high power energy storage cell such as the LIC. As a solution to this problem, a LIC's energy and power capabilities can be optimised for its intended use by adjusting the mass ratio between positive and negative electrode materials or, in other words, by various styles of electrode mass balancing in the cell. The correlation between energy and power densities as a function of electrode mass balancing is depicted in Fig. 1(a). It can be seen that the energy density increases as the mass ratio of activated carbon to graphite increases, while the power density declines. A 1:1 mass ratio of activated carbon in the positive electrode to graphite in the negative has been found to strike an optimal balance between high energy and high power content [31], as highlighted in Fig. 1(a). While it is difficult to generalise that all commercially available LICs perform electrode balancing this way (the manufacturers are trying to maintain secrecy about such details), a recent study indeed confirms that the mass balancing of electrodes in a LIC is considerably different from that used for lithium-ion batteries and adapted for the needs of high power performance [38]. With permission from Musashi Energy Solutions, Caizán-Juanarena et al. have opened a prismatic ULTIMO LIC and analysed the cell. They note that ratio of active material between the positive and negative electrodes is selected to make only a partial use of the overall capacity of graphite, in order to optimise cyclability. Such a statement is consistent with an oversized amount of capacity in the graphite electrode relative to activated carbon, although it is not stated directly that the ratio is 1:1 by mass (describing exact masses is prohibited by the manufacturer, as disclosed in the paper). In the following sections (Sections 5 and 6), when dealing with laboratory-fabricated LICs, we decided to adhere with 1:1 electrode mass balancing between activated carbon and graphite. The electrode mass balancing in the commercial cells in Section 4 is as provided by the manufacturers.

Continuing with their in-depth investigation, Khomenko et al. also provided an important performance comparison of LIC and EDLC cells in the form of a Ragone plot (see Fig. 1(b)). It should be noted that the LICs in this work were charged to up to 5 V (the current optimised commercial cells are usually limited to 3.8 V for practical long term stability reasons), which causes the energy density values to be somewhat unrealistically large. However, this is an important early result that allows us to form realistic expectations on the correlation between gravimetric power densities (specific power) of LICs and EDLCs. Two types of EDLCs were used as control cells, one deploying the same LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) electrolyte as used in the LIC and another utilising an optimised supercapacitor electrolyte in the form of Et<sub>4</sub>NBF<sub>4</sub> in acetonitrile (AN). The control EDLC cells, the latter especially, were designed to provide a better specific power at



Fig. 2. Comparative tests of cylindrical lithium-ion capacitors and supercapacitors: (a) a photograph of a Taiyo Yuden 100 F LIC and Rubicon and AVX 50 F supercapacitors used for the test; (b) a volumetric Ragone plot, demonstrating energy and power densities calculated from galvanostatic discharge experiments.

a cost of a reduced specific energy. It is apparent from Fig. 1(b) that the supercapacitor with an EDLC-specific electrolyte outperformed the LIC with lithium-ion battery electrolyte at high power densities (high discharge current rates), demonstrating maximum power density in excess of 32 kW kg<sup>-1</sup> (per mass of both electrodes) vs 10 kW kg<sup>-1</sup> for the LIC. However, when both the LIC and supercapacitor were tested using a lithium-ion battery-type electrolyte, the LIC performed marginally better in terms of power density than the supercapacitor.

These early results are very insightful for forming our expectations on what the power characteristics of LICs might be. It should be noted, however, that electrode mass loadings in Ref. [31] were controlled in a broad range (between 2 and 6 mg cm<sup>-2</sup>), introducing the possibility that some kinetic behaviour in this work was related to the effects of variable electrode thickness. Furthermore, many commercial cells are now available as well for tests, making the task of evaluating their parameters easier and more reproducible. Recently, our group at the Australian National University analysed a range of LICs (both commercial and laboratory-made) and observed that their power characteristics were superior to those of supercapacitors.

### 4. Comparing contemporary commercial cells

Available-for-purchase LICs currently come in a variety of formats, including cylindrical, laminate and prismatic cells. Among them, cylindrical cells (such as those from Taiyo Yuden and VINATech) are often aimed at applications in electronics in which traditional capacitors and supercapacitors are also used. The appearance of this kind of LIC mimics that of a traditional capacitor and includes a cylindrical body and wire-like contacts protruding on the top surface of the cylinder. The negative and positive electrodes, with a separator in between, inside of the casing are rolled into a cylindrical fashion. The manufacturers advocate these LICs as backup power sources for integrated sensors, memory and processors, power sources for small appliances and auxiliary power sources for energy-saving devices. The cells come in the same standard formats as supercapacitors (e.g. in the form of cylindrical cells with 18 mm diameter and 40 mm length), which makes it convenient to use these cylindrical cells for comparing volumetric power densities of LICs and supercapacitors. Identical format (with the above dimensions) lithium-ion capacitors (Taiyo Yuden and VINATech, 2.2-3.8 V, both 100 F) and supercapacitors (Rubycon, 0-2.5 V, 50 F; AVX, 0-2.7 V, 50 F) were subjected to galvanostatic charge-discharge measurements in our laboratory. As Taiyo Yuden and VINATech LICs have identical specifications, parameters of the Taiyo Yuden LIC are used in this analysis. The photographs of the cells used in the test are shown in Fig. 2(a). Fig. 2(b) represents the volumetric Ragone plot of energy and power densities of a Taiyo Yuden LIC, a Rubycon supercapacitor and an AVX supercapacitor. Multiple cells were charged

and discharged in each case to ensure representative behaviour. It is easy to see that a cylindrical LIC considerably outperforms the control cells in power density, delivering values higher than 3 kW  $L^{-1}$ . Both supercapacitors are inferior while the AVX supercapacitor shows better power characteristics among the two.

The ULTIMO LICs from JSR Micro (previous company name; currently acquired by Musashi Energy Solutions Co. Ltd) are typically manufactured in either the form of laminate or prismatic cells. The manufacturer envisages to use these cells in large- and medium-scale uninterruptable power supplies, for collection of braking energy in buses and transport, and for powering forklifts and complementing small-scale wind turbines. The assembly of cells into packs of various sizes is anticipated and is being actively trialed for many of these applications. The energy and power densities of laminate ULTIMO LICs were made public via the company's presentations and it is convenient to use this information directly to compare an ULTIMO LIC with a comparable supercapacitor (all data — JSR Micro) [27].

Fig. 3 (adapted from Ref. [27]) shows the gravimetric and volumetric Ragone plots of a 2200 F ULTIMO LIC and a comparable 2300 F electric double layer supercapacitor. As it can be seen, the LIC outperforms the supercapacitor both in terms of volumetric power density and in terms of specific power (gravimetric power density). The LIC is able to achieve a power density in excess of 7 kW L<sup>-1</sup> versus only slightly beyond 1 kW L<sup>-1</sup> for the supercapacitor. The specific power of the LIC reaches 4 k W kg<sup>-1</sup> versus only about 700–800 W kg<sup>-1</sup> for the supercapacitors. Similarly to the case with commercial cylindrical LICs and supercapacitors, a laminate LIC appears to be superior to a supercapacitor in its power capabilities, according to the data from JSR Micro.

On the basis of the data sets for the cylindrical and laminate cells, the commercialised LICs appear to have much better power density metrics than those of supercapacitors. This is different from what is anticipated in the academic literature [1,7–26]. Overwhelmingly, the performance enhancement in LICs versus supercapacitors in terms of their power densities or specific power is not expected in literature; in contrast, this is clearly evident from the data that we have for the commercially available LICs and supercapacitors. In order to be more confident about such observations and to obtain additional data points with comparable behaviour, laboratory-made LICs and supercapacitors were also fabricated by us and evaluated.

# 5. Superior power characteristics in laboratory-made LICs

Full cell LICs and supercapacitors were fabricated in our laboratory using the same standard 1:1 mass ratio of positive to negative electrodes in order to compare the behaviour of LICs with that of EDLCs and to imitate the commercial design of LICs at the same time.



Fig. 3. Energy and power densities for a 2200 F laminate JSR Micro ULTIMO LIC and a comparable 2300 F supercapacitor (manufacturer's data): (a) a gravimetric Ragone plot; (b) a volumetric Ragone plot. Test conditions: charge via a constant current — constant voltage routine at 10 A to 3.8 V (for LIC) or 2.5 V (for supercapacitor) with 30 min voltage hold; constant current discharge at a particular constant current from the range of 10–480 A to 2.2 V (for LIC) and from the range of 10–200 A to 0.9 V (for supercapacitor). Source: The data are adapted from [27].



Fig. 4. Comparative behaviour of laboratory-fabricated LICs and supercapacitors: (a) a three-way Swagelok-type cell with an additional Li metal reference electrode (inserts show a top view of the cell and its internal structure containing negative, positive and reference electrodes, each in contact with a stainless steel current collector rod); (b) charge-discharge profiles recorded for both the full cell and individual positive and negative electrodes of a laboratory-made LIC; (c) Ragone plots of a laboratory-made LIC and a laboratory-made supercapacitor.

The full cells were assembled in three-way Swagelok cells with an additional Li metal reference electrode, as depicted in Fig. 4(a). An additional reference electrode allowed us to monitor both positive and negative electrodes separately to ensure the correct behaviour in all cells. Prior to the assembly of LICs, their graphite electrodes

were electrochemically prelithiated in three-way Swagelok cells and subsequently re-packed to fabricate full cell LICs. Supercapacitors were also fabricated in the format of Swagelok-type cells.

To ensure that the as-fabricated LICs behaved as expected, the cell voltages as well as negative and positive electrode potentials were monitored in the initial measurements. Fig. 4(b) shows the time-voltage profile for an assembled LIC for the first five cycles at a current rate of 253 mA g<sup>-1</sup> (current is set per mass of both electrodes). As expected, the positive electrode operates in a higher potential window and displays a triangular charge-discharge profile while the negative electrode displays a plateau upon charge and discharge at a low potential close to, but not at, 0 V vs. Li/Li+. This allows the full cell LIC to operate in the voltage window 2.2-3.8 V, typical of commercial LICs. It can be seen that the commercial LIC is successfully emulated in this laboratory LIC design. The charge and discharge currents of galvanostatic experiments were then increased to determine the gravimetric energy and power density limits of the device. The same procedure was applied to supercapacitor cells. The energy and power densities are presented per mass of both electrodes in the cell in each case.

As expected, the LIC has higher specific energy than the supercapacitor, owed to the low potential battery-type mechanism which occurs at the negative electrode. Interestingly enough and consistently with the data from commercial LIC cells, our own lab-fabricated LIC cells displayed a considerably better power performance than a similarly assembled EDLC (Fig. 4(c)). These findings are in contrast with early findings of Khomenko et al. [31]. While some extent of variability might be expected between different laboratories as a result of dissimilar graphite or activated carbon materials, electrode loadings or electrolytes, we have grounds to suggest that the power capabilities of LICs are understated in most of the previous literature. Of course, one may argue that the electrolyte used for the laboratory-made supercapacitors in this assessment is a battery-type electrolyte typical for LICs and may not be optimal for supercapacitors; however, this is certainly not the case for the commercial supercapacitor cells. Therefore, by comparing our results from laboratory-made LICs with those for commercially available cylindrical and laminate cells already described in this Perspective, we form a view that superior power metrics could be generally expected for lithiated graphite and activated carbon LICs than those available in supercapacitors. It can be suggested that the available power densities (gravimetric or volumetric) are usually superior in LICs with respect to EDLCs.

# 6. Power enhancement in LICs upon slow charging and lithium plating prevention

While it is intriguing enough to spot that LICs may have better power densities than supercapacitors, it appears that the power capabilities of LICs can be further enhanced utilising the effect of asymmetric kinetics of lithium ion intercalation and deintercalation in graphite. This kinetic effect has previously been considered by Sivakkumar, Nerkar and Pandolfo utilising samples of graphite with different average particle sizes (12, 24, 36 and 100  $\mu$ m) [39]. The data from this work are shown in Fig. 5(a, b) and the effect in question is the most pronounced for smaller graphitic particles with sizes 12 and 24  $\mu$ m. When the lithiation in half-cells is performed at a slow current rate (intercalation at C/10), the capacity retention during delithiation (deintercalation) is remarkable up to 60 C (Fig. 5(a)). While, if the lithiation and delithiation currents are ramped up together, the capacity in graphite quickly drops, and the material is not able to sustain good capacity retention at high currents during delithiation (Fig. 5(b)) [39]. These observations are directly related to the power capabilities of LICs, as the charging process in LICs corresponds to the lithiation of graphite, and the discharging process in LICs corresponds to the delithiation from graphite.

Using these considerations as a guide, we applied the concept of slow lithiation and fast delithiation to our laboratory-fabricated LICs. Fig. 5(c) shows the comparison of the two Ragone plots for gravimetric energy and power densities (specific energy and specific power). All metrics are calculated per mass of both electrodes in the corresponding

cells. The first plot is obtained under a symmetric test regime, where the charge and discharge currents are ramped up together during the test (in other words, this is the same Ragone plot shown in 4(c)). To produce the second Ragone plot, we used a steady slow current of 250 mA g<sup>-1</sup> to charge the LIC, while the discharge current was progressively increased to 20 A g<sup>-1</sup>. Indeed, as it can be seen from Fig. 5(c), the LIC's specific power is enhanced as a result of using it in a slow charge regime. The improvement is considerable and significantly enhances LIC's power metric. By simply charging the LIC device at slow rates, the maximum discharge rate is increased and the power limits of the cell are extended. The power characteristics of LICs can be even better if an appropriate charging process is used.

When LICs are operated in practice, it is a manufacturer's recommendation that the voltage range of the cell is limited to between 2.2 and 3.8 V [40]. Using a Li metal reference electrode in a threeway Swagelok cell format, the potentials on negative and positive electrodes in LICs can be tracked in both slow charge regime and the regime involving a progressive increase of charge current and discharge current. The results of such measurements are shown in Fig. 5(d, e). The behaviour of the potential on the negative electrode sets these charging regimes apart. In a LIC with a progressively increased charge current, the potential of the negative electrode experiences significant hysteresis and shifts to the negative values versus the Li metal reference (Fig. 5(d)) during charging. As the cell is limited to the maximum cell voltage of 3.8 V, this causes a smaller available capacity in the positive electrode upon charging due to a lower limiting cut-off potential for this electrode. For example, when the charge current of 20 A is used, the potential on the negative graphite electrode of a LIC reaches -0.1 V vs Li/Li<sup>+</sup> and limits the maximum potential of the positive electrode to 3.7 V vs Li/Li<sup>+</sup>, thus reducing the available capacity. Meanwhile, as it can be seen in Fig. 5(d), nearly all accumulated capacity in a LIC can be released upon the discharge of the cell, and the power characteristics of a LIC are limited by what happens during charge. In contrast, a LIC operated under a slow charge regime (Fig. 5(e)) does not experience significant polarisation upon charge, and its graphite electrode does not undergo a shift to negative potentials, always staying above 0.067 V vs Li/Li<sup>+</sup>. As a result, larger capacities can be accumulated by a LIC cell upon charge and released at high currents during discharge, leading to a higher power density. We take the view that the difference in the power characteristics of LICs under the two charge regimes is substantially linked to the degree of potential hysteresis in the graphite electrode.

Furthermore, it is clear from these measurements that when LICs are charged in a slow charge regime the safety of the cell is improved. Indeed, the potential of the graphitic electrode stays above 0 V vs  $\text{Li/Li}^+$  at all times. In contrast, during the fast charge of a LIC, the potential of the graphitic electrode may go under 0 V vs  $\text{Li/Li}^+$  and, at very high currents, as low as -0.1 V vs  $\text{Li/Li}^+$  where the plating of lithium on the surface of graphite is possible. Lithium plating is not guaranteed in this scenario since polarisation effects at high currents shift many electrochemical reactions to lower potentials, including metal deposition. Even so, the negative potential range is commonly avoided in practice. Our results show that the slow charging mode of a LIC can deliver exactly that, combined with an increased power density in the cell. This method of improving LIC power metrics also reliably prevents lithium plating.

Industry data demonstrate that LICs can also exhibit high stability for many cycles at high discharge rates. For example, laminate 1100F Ultimo LICs can maintain 95% of initial capacitance after 200 000 cycles, with minimal changes in the IR drop, at a high discharge current of 100 A [27]. Overall, this information suggests that LICs should be perceived as innovative hybrid cells combining long cyclic life and high power capabilities. As we show in this Perspective, their power characteristics (power density or specific power) may be superior to electrochemical supercapacitors.



Fig. 5. Intercalation-deintercalation kinetics in graphite electrodes and the power density of LICs: (a) deintercalation capacity of graphite electrodes evaluated in Li half cells under the conditions of intercalation at C/10 rate and deintercalation at various C-rates; (b) deintercalation capacity under conditions with intercalation and deintercalation at the same C-rate. Adapted with permission from [39]; (c) Ragone plots for laboratory-made LICs tested under the slow charge regime (250 mA  $g^{-1}$ ) and standard conditions (identical charge and discharge currents); (d, e) positive and negative electrode potentials in a LIC tested under standard test conditions and in a slow charge regime, respectively.

# 7. Conclusion

The literature analysis reveals that very conflicting views on the power performance of LIC are presented in various review manuscripts and other publications. Some of the existing sources indicate that the gravimetric and volumetric power densities of LICs are inferior to supercapacitors, some publications indicate similar power-related metrics between the two types of energy storage cells and a limited volume of literature argues that the power densities of LICs are superior. This lack of consensus in the literature is very confusing.

In this Perspective, we attempted to provide analysis points aimed at stimulating the debate in this space. The power characteristics of LICs and those of supercapacitors were compared through the consideration of both commercially available (cylindrical and laminate cell types) and laboratory-made cells. All data sets pointed to the superiority of the volumetric power density and gravimetric power density of LICs with respect to those of comparable supercapacitors. We also discussed the opportunity to push the limits of power density in LICs by employing a slow charge regime and, in doing so, exploiting the asymmetric kinetics of lithium intercalation and deintercalation in graphite. It should be noted that the paper does not necessarily recommend the slow charging protocol to be used with LICs. However, it was interesting and important to point out that the power capabilities of LICs increase even further if a slow charging routine is applied. Even with fast charging, the power capabilities of LICs appear superior to supercapacitors in our data sets (Section 4 and Section 5). Overall, the aim of the manuscript was to stimulate the discussion in the field; suggesting precise charging protocols was not intended. To conclude all the discussions in this manuscript, we understand that conflicting views on the power characteristics of LICs currently exist in the field and we hope that this Perspective will stimulate the discussion around this matter.

### CRediT authorship contribution statement

Chiara Cementon: Conceptualization, Investigation, Writing. Thrinathreddy Ramireddy: Conceptualization, Methodology. Daniel Dewar: Methodology, Investigation. Michael Brennan: Investigation. Alexey M. Glushenkov: Conceptualisation, Methodology, Writing, Supervision.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### References

- [1] B. Babu, P. Simon, A. Balducci, Adv. Energy Mater. 10 (29) (2020) 2001128.
- [2] R. Korthauer, M. Wuest, Lithium-Ion Batteries, Basics and Applications, Springer Nature, 2018.
- [3] G.G. Amatucci, F. Badway, A. Du Pasquier, T. Zheng, J. Electrochem. Soc. 148 (8) (2001) A930.
- [4] A. Brisse, P. Stevens, G. Toussaint, O. Crosnier, T. Brousse, Materials (Basel, Switzerland) 11 (7) (2018) 1178.
- [5] H. Tanizaki, N. Ando, Y. Hatou, Lithium-ion capacitor. US Patent US7848081B, 2010.
- [6] K.P. Gadkaree, R.S. Kadam, A.F. Husted, Anode for lithium ion capacitor. US. Patent US20160225540A1, 2017.
- [7] V. Aravindan, J. Gnanaraj, Y. Lee, S. Madhavi, Chem. Rev. 114 (23) (2014) 11619–11635.
- [8] J. Ding, W. Hu, E. Paek, D. Mitlin, Chem. Rev. 118 (14) (2018) 6457-6498.
- [9] E. Frackowiak, F. Béguin, Carbon 39 (6) (2001) 937–950.
- [10] H. Gu, Y. Zhu, J. Yang, J. Wei, Z. Zhou, ChemNanoMat 2 (7) (2016) 578-587.
- [11] D. Han, J. Zhang, Z. Weng, D. Kong, Y. Tao, F. Ding, D. Ruan, Q. Yang, Mater. Today Energy 11 (2019) 30–45.
- [12] P. Han, G. Xu, X. Han, J. Zhao, X. Zhou, G. Cui, Adv. Energy Mater. 8 (26) (2018) 1801243.
- [13] F. Holtstiege, P. Bärmann, R. Nölle, M. Winter, T. Placke, Batteries 4 (1) (2018).
- [14] A. Jagadale, X. Zhou, R. Xiong, D.P. Dubal, J. Xu, S. Yang, Energy Storage Mater. 19 (2019) 314–329.
- [15] L. Jin, C. Shen, A. Shellikeri, Q. Wu, J. Zheng, P. Andrei, J. Zhang, J.P. Zheng, Energy Environ. Sci. 13 (8) (2020) 2341–2362.
- [16] L. Jin, J. Yuan, A. Shellikeri, R. Naderi, N. Qin, Y. Lu, R. Fan, Q. Wu, J. Zheng, C. Zhang, J.P. Zheng, Batteries Supercaps 4 (5) (2021) 749–757.
- [17] J.J. Lamb, O.S. Burheim, Energies 14 (4) (2021) 979.

- [18] B. Li, J. Zheng, H. Zhang, L. Jin, D. Yang, H. Lv, C. Shen, A. Shellikeri, Y. Zheng, R. Gong, J.P. Zheng, C. Zhang, Adv. Mater. 30 (17) (2018) 1705670.
- [19] G. Li, Z. Yang, Z. Yin, H. Guo, Z. Wang, G. Yan, Y. Liu, L. Li, J. Wang, J. Mater. Chem. A 7 (26) (2019) 15541–15563.
- [20] W. Liu, X. Zhang, Y. Xu, C. Li, K. Wang, X. Sun, F. Su, C. Chen, F. Liu, Z. Wu, Y. Ma, Batteries Supercaps 4 (3) (2021) 407–428.
- [21] Y. Ma, H. Chang, M. Zhang, Y. Chen, Adv. Mater. 27 (36) (2015) 5296–5308.
- [22] M. Soltani, S.H. Beheshti, J. Energy Storage 34 (2021) 102019.
- [23] H. Wang, C. Zhu, D. Chao, Q. Yan, H.J. Fan, Adv. Mater. 29 (46) (2017) 1702093.
- [24] X. Wang, L. Liu, Z. Niu, Mater. Chem. Front. 3 (7) (2019) 1265-1279.
- [25] F. Yao, D.T. Pham, Y.H. Lee, ChemSusChem 8 (14) (2015) 2284–2311.
- [26] K. Zou, P. Cai, X. Cao, G. Zou, H. Hou, X. Ji, Curr. Opin. Electrochem. 21 (2020) 31–39.
- [27] J. Banas, M. Peterson, Advances in lithium ion capacitor technology, 2012, URL https://nccavs-usergroups.avs.org/wp-content/uploads/Joint2012/ 2012, 2Peterson.pdf.
- [28] S.R. Sivakkumar, A.G. Pandolfo, Electrochim. Acta 65 (2012) 280-287.
- [29] K. Karthikeyan, V. Aravindan, S.B. Lee, I.C. Jang, H.H. Lim, G.J. Park, M. Yoshio, Y.S. Lee, J. Alloys Compd. 504 (1) (2010) 224–227.
- [30] A. Byeon, A.M. Glushenkov, B. Anasori, P. Urbankowski, J. Li, B.W. Byles, B. Blake, K.L. Van Aken, S. Kota, E. Pomerantseva, J.W. Lee, Y. Chen, Y. Gogotsi, J. Power Sources 326 (2016) 686–694.
- [31] V. Khomenko, E. Raymundo-Piñero, F. Béguin, J. Power Sources 177 (2) (2008) 643–651.
- [32] T. Yuden, Cylinder Type Lithium Ion Capacitor(High Temperature Resistance Type)[RH series] Spec Sheet. URL https://ds.yuden.co.jp/TYCOMPAS/or/detail? pn=LIC1840RH3R8107&u=M.
- [33] VINATech, Hybrid Capacitor. 10/07/2022. URL https://www.vinatech.com/eng/ product/lithium-capacitor.php.
- [34] LICAP, Lithium Ion Capacitors. 10/07/2022. URL https://www.licaptech.com/ lithium-ion-capacitor-cells.
- [35] K. AVX, SCC Series: High Capacitance Cylindrical SuperCapacitors Spec Sheet. URL https://datasheets.kyocera-avx.com/AVX-SCC.pdf.
- [36] Rubycon, Electric Double Layer Capacitor DMA/DMB Series Spec Sheet. URL https://au.mouser.com/datasheet/2/977/e\_DMA\_DMB-1601086.pdf.
- [37] M. Arnaiz, J. Ajuria, Batteries Supercaps 4 (5) (2021) 733-748.
- [38] L. Caizán-Juanarena, M. Arnaiz, E. Gucciardi, L. Oca, E. Bekaert, I. Gandiaga, J. Ajuria, Adv. Energy Mater. 11 (32) (2021) 2100912.
- [39] S.R. Sivakkumar, J.Y. Nerkar, A.G. Pandolfo, Electrochim. Acta 55 (9) (2010) 3330–3335.
- [40] T. Yuden, Cylinder type lithium ion capacitors: Product usage guide, 2019, URL https://www.yuden.co.jp/productdata/manual/en/lithosion\_ug01\_en.pdf.