List of Figures

Figure 1. An illustration of key performance metrics, test methods, major affecting factors for the evaluation of SCs.

Figure 2. An illustration of a typical CV test result.
Figure 3. An illustration of CCCD test result with linear potential change over time.

Figure 4. An illustration of CCCD test result with nonlinear potential change over time.
Figure 5. Schematic illustrations and equivalent circuits for different experimental setups.

Figure 6. a) Effect of mass loading and b) electrode thickness on the resulting $C_S$: yellow squares, green circles and purple triangles represent crumpled graphene balls, wrinkled graphene sheets, and flat graphene sheets as electrodes; and red solid squares indicate carbide-derived carbons (CDCs) as electrodes [85, 150].
Figure 7. Cyclic voltammograms of liquid-mediated graphene materials with increasing electrode density from 0.13 to 1.33 g/cm$^3$ following the dashed red arrow [60].

Figure 8. The series RC circuit for supercapacitors.
Figure 9. The Nyquist plot of 2.7V/1F Maxwell SC with $R_{ES}$ determination methods marked in red.
Figure 10. CCCD result of 2.7V/1F Maxwell SC tested at different dwelling time from 0 – 30 min: (a) overall CCCD plots of one cycle; (b) averaged $R_{ES}$ values from first six cycles; enlarged upper region of the CCCD plots at dwelling time of (c) 0 min and (d) 1 min.

Figure 11. (a) A typical CCCD plot for large SCs with $IR$ drop and steady-state voltage drop marked as $\Delta V_1$ and $\Delta V_2$, and (b) a real case illustration of the discharge part via Skeleton Tech 1600F SC.

Figure 12. An illustration of $V_o$ determination methods using (a) CV and (b) CCCD tests.
Figure 13. Dependence of real and imaginary capacitances over frequency for 2.7V/1F Maxwell SC with the relaxation time constant $\tau_o$ pointed.

Figure 14. An illustration of the power and energy densities for several EES devices via Ragone plot. The plot is based on data from Ref. [114, 119-122].
Figure 15. Representative working diagram from CCCD test for EDLCs (a), and PCs (b).

Figure 16. An illustration of Peukert’s curve for batteries with the use of $\frac{1}{2}C$ marked by dashed lines.
Figure 17. An illustration of Peukert’s curves for a 1450F EDLC (a) and for a 2000F hybrid SC (b) with the use of 60C marked by dashed lines.

Supercapacitors Performance Evaluation
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Abstract

The performance of a supercapacitor can be characterized by a series of key parameters, including for instance the cell capacitance, operating voltage, equivalent series resistance, power density, energy density, and time constant. To accurately measure these parameters, a variety of methods have been proposed and used among academia and industry. As a result, some confusion has been caused due to the inconsistencies between different evaluation methods and practices. Such confusion hinders effective communication of new research findings, and creates a hurdle in transferring novel supercapacitor technologies from research lab to commercial applications.

Based on public sources, this review article is an attempt to inventory, critique and hopefully streamline the commonly used instruments, key performance metrics, calculation methods, and major affecting factors for supercapacitor performance evaluation. Thereafter the primary sources of inconsistencies are identified and the possible solutions are suggested correspondingly, with emphasis on device performance vs. material property and the rate dependency of supercapacitors. We hope, by using reliable, intrinsic and comparable
parameters produced, the existing inconsistencies and confusion can be largely eliminated so as to facilitate further progress in the field.
Table of Contents

1. Introduction

1.1. General power storage cells
1.2. Supercapacitors and the charge storage mechanisms
1.3. Performance evaluation for supercapacitors

2. Instruments and measurements of key metrics

2.1. Instruments
2.2. Capacitance
2.3. Equivalent series resistance
2.4. Operating voltage
2.5. Time constant
2.6. Power and energy densities
2.7. Leakage and maximum peak currents
2.8. Cycle life

3. Inconsistencies in evaluation of supercapacitors

3.1. Causes for the inconsistencies
3.2. Device performance vs. material property
3.3. Rate dependency

4. Summary and recommendations
Acknowledgements

References
1. **Introduction**

1.1. **General power storage cells**

The detrimental long-term effects of greenhouse gas emission into atmosphere and the finite supply of fossil fuels underscore the urgency of exploring renewable energy resources and the related energy generation, storage, and conservation technologies. A major hurdle, in general, lies in the dependence on the power line for electricity supply. The proposed wireless power supply [1, 2] is still largely at exploration stage and unlikely to play significant role in foreseeable future. The pending obstacle for use of renewable energy from wind and solar is the stability and quality of the produced electricity [3]. Driven by such need for power storage, rectification, transport and supply at various scales, sustained and extensive research and exploration have been conducted, and a number of electrical energy storage (EES) technologies have been developed so far; some have been serving very close to our daily life such as batteries and fuel cells, and others are more for industrial applications including pumped hydro, flywheel, compressed air, superconducting magnetic, and supercapacitors [4].

Of these EES technologies, batteries have been widely used at various scales, and have been continuously studied due to their outstanding performance. Based on the specific battery chemistry, they can be rechargeable or non-rechargeable. Both of them produce electricity from chemical energy via redox reactions at anode and cathode. For rechargeable batteries, they can reverse this process for certain times [5-7]. Starting in 20th century, batteries have been successfully penetrating into our daily life. However, there are certain areas where batteries revealed their shortcomings or failed to meet the needs, including:

- **Low power density:** This issue has severely hindered its applications where high power discharge and/or recharge rate is demanded;
• Safety issue: Many electrolytes used in batteries are corrosive, flammable, or both, and many electrodes are environmentally unfriendly or poisonous;

• Heat generation: The redox reactions in batteries may lead to Joule heating and thermochemical heating during their operation [8]. Such heat if not dissipated effectively will result in overheating, thermal runaway and even fire;

• Limited cycle life: The cycle lives of batteries are normally limited due to the nature of the redox reactions.

Because of the issues listed above, batteries alone are unable to provide the full solution for electricity storage. A durable and safe electricity storage device, with high power and/or energy performance, will undoubtedly transform the landscape of electric energy generation, distribution and utility. Besides, as consumer, industry and military require more compact and reliable electrical power systems, development of such devices continues to be one of the major thrusts in the area [9-11].

1.2. Supercapacitors and the charge storage mechanisms

Supercapacitors (SCs), often referred to as ultracapacitors or electrochemical capacitors, demonstrate outstanding power performance, excellent reversibility, very long cycle life (>1,000,000 cycles), simple mode of operation and ease of integration into electronics [12-20]. In addition, they generate less thermochemical heat because of the simpler charge storage mechanisms associated [21]. Therefore, they have been widely used in consumer electronics, memory back-up systems, and industrial power and energy management [5, 12] and will be found in more niche markets in the near future [22].
1.2.1. Charge storage mechanisms

It is generally accepted that there are three major charge storage mechanisms involved in the operation of SCs: (a) electric double layer in electric double layer capacitors (EDLCs); (b) highly reversible surface redox system, and (c) fast electrolyte ions intercalation, both occurring in pseudocapacitors (PCs).

a. Electrical double layer (EDL)

Electrical double layer (EDL) refers to the two charged layers formed at electrode/electrolyte interfaces [23]. The earliest model of EDL is usually attributed to Helmholtz [24, 25] and thus EDL is also termed as Helmholtz double-layers. Later on, Gouy-Chapman model and Gouy-Chapman-Stern model were developed to more accurately describe the detailed structure of EDLs [23, 26].

Electricity storage and delivery via EDL was first proposed by Becker in 1957 (U.S. Patent 2,800,616), and the resulting SCs is then named electric double layer capacitors (EDLCs). High-surface-area activated carbon (AC) is normally used in the system as the working medium. Owing to the huge surface area, EDLCs can store much more electricity, and are usually evaluated in Farads (F), whereas conventional dielectric and electrolytic capacitors are in picofarads (pF) and microfarads (µF).

b. Surface redox system

The second charge storage mechanism in SC was introduced by Trasatti [27], attributed to the highly reversible surface redox reaction, during which partial charge transfer between electrode and electrolyte occurs [28]. Normally during charging, the redox-active electrode
materials, i.e. RuO$_2$ or MnO$_2$, reduced to lower oxidation state coupled with adsorption of cations from the electrolyte. Upon discharge, the process can be almost fully reversed [29, 30]. Unlike EDLCs where the electrical charge storage is statically in the Helmholtz double-layers without any faradic charge transfer, such pseudocapacitors (PCs) do have partial faradic charge transfer at the interface between the electrode and electrolyte.

c. Ion intercalation

Another pseudocapacitive (PC) charge storage mechanism is a diffusion controlled intercalation process in which electrolyte ions migrate in and out of the atomic layers of electrode materials during charging and discharging [31]. This nevertheless differs from that of lithium-ion batteries by: 1) its excellent reversibility upon recharging [30]; 2) its state-of-charge dependent potential [32]. Various materials, e.g. molybdenum nitrides, niobium pentoxides and titanium carbides [33-35], have been examined for this purpose.

1.2.2. Overall charge storage ability and hybrid supercapacitors

In practice, the overall charge ability of a SC is enabled by two or three such charge storage mechanisms. They coexist in SCs and contribute in different proportions. For example, the charge storage of AC-based EDLCs is dominated by the formation of EDLs, but the oxygen-containing groups on AC surface might induce some surface-redox reactions.

Furthermore, hybrid or asymmetric capacitors by combining different electrodes of EDLCs and PCs, or even of batteries have been reported so as to improve the energy performance while maintaining their intrinsic high power performance [36]. The most widely acknowledged hybrid system is the Li-ion capacitor (LIC), normally produced by using
Li$_4$Ti$_5$O$_{12}$ nanocrystals [37-39] or advanced graphite materials [40] as positive electrode, and AC as negative electrode. Another one is called “ultrabattery” based on the combination of lead-acid battery and EDLC [41-44]. Indeed combination of high energy density of batteries with long cycle life and short charging times of supercapacitors is considered the likely future direction [45].

1.3. Performance evaluation for supercapacitors

To evaluate SCs performance, three essential parameters, cell (total) capacitance $C_T$, operating voltage $V_o$ and equivalent series resistance $R_{ES}$, are often used to assess their energy and power performance, and usually are sufficient for commercial products where the materials, fabrication and cell design are all fixed. However in the research arena of constant probing for novel materials, more advanced manufacturing processes and new cell design, some other factors become indispensable. In fact, there is a rather large group of important factors necessary to paint the whole picture for supercapacitors, and a glance of the complex inter-relationship between the different performance metrics, the major affecting factors and the corresponding test methods is presented in Fig. 1. Several color schemes are employed in the figure: the three core parameters are highlighted in yellow; the power and energy densities in dark blue; time constant and cycling stability in light orange; all the important affecting factors in light purple; and the corresponding test methods in white. Note that the chart is more for illustration purpose and is by no means exclusive in presenting all the factors or detailing the complex multifaceted connections between them. For example, the evaluation method for $V_o$ and the influence of electrolyte materials on specific capacitance are not explicitly presented.
Giving such multiple performance metrics, test methods, affecting factors shown in the figure, and the multifaceted relationships among them, *inconsistencies* become inevitable in the test results for the same cell measured in different labs, using different methods, and between academia and industry. To understand the causes for such *inconsistencies*, some important issues have to be addressed, including material property vs. device performance, and the rate dependency of supercapacitor performance.

Many attempts have been carried out to standardize the evaluation methods for SC devices. Some national and international bodies including DOD (US Department of Defense), DOE (US Department of Energy), IEC (International Electrochemical Commission), and SAE (Society of Automotive Engineers) have worked intensively on this matter. The resulting documents are summarized in Table 1 chronologically.

<table>
<thead>
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<th>Year</th>
<th>Organization</th>
<th>Title</th>
<th>Document ID</th>
</tr>
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<td>1986</td>
<td>DOD</td>
<td>Capacitors, fixed, electrolytic, double layer, carbon (metric), general specifications</td>
<td>DOD-C-29501</td>
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<td>1994</td>
<td>DOE</td>
<td>Electric vehicle capacitor test procedures manual</td>
<td>DOE/ID-10491</td>
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<tr>
<td>2004</td>
<td>DOE</td>
<td>FreedomCAR ultracapacitor test manual</td>
<td>DOE/NE-ID-11173</td>
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<td>2006</td>
<td>IEC</td>
<td>Fixed electric double layer capacitor for use in electronic equipment</td>
<td>IEC 62391</td>
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<td>2009</td>
<td>IEC</td>
<td>Electric double layer capacitors for use in hybrid electric vehicles – Test methods for electrical characteristics</td>
<td>IEC 62576</td>
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<tr>
<td>2012</td>
<td>IEC</td>
<td>Railway applications – Rolling stock equipment – Capacitors for power electronics – Part 3: Electric double-layer capacitors</td>
<td>IEC 61881-3</td>
</tr>
<tr>
<td>2013</td>
<td>SAE</td>
<td>Capacitive energy storage device requirements for automotive propulsion applications</td>
<td>J3051</td>
</tr>
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</table>

Apparently, such efforts are mainly for specific applications oriented for industry, and there is still lacking a general understanding and knowledge collected/derived from the most recent cutting edge research so as to guide a more accurate and effective practice for performance evaluation of SCs. This prompts our intension to write this article.

In view of the urgent need for more reliable test methods called for by the drastic pace in searching for new energy storage solutions, and the complexities involved, this paper represents an attempt in clarifying and streamlining the existing evaluation methods, in the hope to eliminate/alleviate such *inconsistencies* and facilitate more effective communication in the field.

2. **Instruments and measurements of key metrics**

2.1. **Instruments**
Various instruments or test modes have been developed and applied to characterize the electrochemical performance of SCs. Cyclic voltammetric (CV), constant current charge/discharge (CCCD) and electrochemical impedance spectroscopic (EIS) tests are the commonly used ones. In essence, all such instruments can be used to measure the three fundamental parameters: voltage, current and time, and then other metrics, including the capacitance, equivalent series resistance, operating voltage and subsequently time constant, energy and power performance of SCs, can be derived from them. However, each of the instruments has its own focus and the targeted parameters by design, and their applications and limits are hence discussed below.

In addition, the three test modes can all be used to examine not only SC materials, i.e. the electricity storage media including electrode materials and electrolyte materials, but also SC devices, i.e. the whole package of SCs. Clear differentiation between a property measured for the cell or just for its active material has to be made when reporting a test result - a clearly logical practice yet often ignored. Also some technical differences exist when testing SC devices versus SC materials, and we will therefore stress this in our discussion.

2.1.1 CV

CV test applies a linearly changed electric potential between positive and negative electrodes for two-electrode systems, or between reference and working electrodes for three-electrode configurations. The speed of potential change in mV/s is termed as the sweep rate or scan rate, and the range of potential change is called potential window or operating potential. The instantaneous current during the cathodic and anodic sweeps is recorded to characterize the electrochemical reactions involved. The data are plotted as current (A) vs.
potential ($V$), or sometimes, current ($A$) or potential ($V$) vs. time (s) [26].

To examine the charge storage mechanisms of SC materials where EDLC and PC types are separate, CV test with the three-electrode setup is regarded as the most suitable approach [33, 34]. The test results can first be analyzed by examining the shape of the CV curves, as for EDLC materials, the resulting CV curve shape is rather rectangular, whereas for most PC materials, a sudden current surge appears to skew the curve. However, a complication in this is that there a few PC materials [35] whose CV curves also appeared rectangular. To add a further twist, the shape of the CV curves can be affected by the experimental setup [46] so that some PC materials, which ordinarily would generate skewed CV curves, can produce rectangular curves as well. Caution is hence required in the process.

Another more quantitative and reliable method in interpreting the data from a SC cell tested is to extract the contributions from EDL and PC mechanisms separately by utilizing the knowledge that the instantaneous current induced by EDL mechanism is proportional to the scan rate, while the diffusion controlled ion-intercalation by PC mechanism is to the square root of scan rate [33, 34, 47-51]. However, this approach is limited to detect the contribution from the surface-redox mechanism. Therefore, more experimental and theoretical studies are demanded to address this issue.

CV test is also particularly suitable in practice to determining the potential window (operating voltage) for SC materials by successive adjustment of the reversal potential in a three-electrode system, and the reversibility of the charge and discharge processes can also be studied at the same time [32, 33]. In addition, the specific capacitance and energy performance of the SC materials can be obtained via integration of the CV curves as discussed in detail later. Similar process can also be conducted for SC devices to obtain their
total cell capacitance and hence the amount of electricity stored.

2.1.2 CCCD

CCCD test is the most widely used method for characterization of SCs under direct current [52, 53]. It is conducted by repetitive charging and discharging the SC device or the working electrode at a constant current level with or without a dwelling period (a time period between charging and discharging while the peak voltage $V_o$ remains constant), and normally a plot of potential ($E$) vs. time (s) is the output. Choosing a proper level of the constant current is critical to produce consistent and comparable data from a CCCD test.

CCCD test is regarded as the most versatile and accurate approach in characterizing SC devices. All three core parameters of SC devices, $C_T$, $R_{ES}$ and $V_o$, can be tested from it and subsequently used to derive most of the other properties, such as the time constant, power and energy densities, and leakage and peak current. It can also be conveniently used to study the cycling stability of SC devices. Moreover, by using a three-electrode setup, the specific capacitance, reversibility and potential window for SC materials can also be obtained via CCCD test.

2.1.3 EIS

EIS test, also known as the dielectric spectroscopic test, measures the impedance of a power cell as a function of frequency by applying a low-amplitude alternative voltage (normally 5 mV) superimposed on a steady-state potential. The resulting data is normally expressed graphically in Bode plot to demonstrate the cell response between phase angle and frequency, and in Nyquist plot to show the imaginary and real parts of the cell impedances on
a complex plane [54, 55].

Besides the frequency response and impedance, EIS has also been employed to characterize the charge transfer, mass transport and charge storage mechanism, as well as to estimate the capacitance, energy and power properties [56, 57]. Different equivalent circuits and models have been developed to distinguish the contribution of individual structure component in a cell system to the total impedance [40, 58, 59]. When SC devices are tested, the real parts of the complex impedance at selected frequencies are used in literature to represent $R_{ES}$. However, one needs to keep in mind that this $R_{ES}$ from EIS test is often much smaller than that derived from the CCCD test [60], and therefore is limited in describing the power performance of SC devices.

For SC materials, EIS test can be deployed to study the impedance, specific capacitance, charge transfer, mass transport and charge storage mechanisms involved by executing similar analysis in a three-electrode system.

### 2.2. Capacitance

The total capacitance $C_T$ of a SC is a reflection of the electrical charge $\Delta Q$ stored under a given voltage change $\Delta V$:

$$C_T = \frac{\Delta Q}{\Delta V} \quad (1)$$

This is preferred when specifying the total charge storage ability of SC devices. A more intrinsic *specific* capacitance $C_S$ is defined to measure, preferably, the charge storage ability of SC materials:

$$C_S = \frac{\Delta Q}{\Delta V \times \Pi} \quad (2)$$

where $\Pi$ can be the mass, volume, surface area of the electrode or the active material, or even
the size of the electrode, and the resulting specific capacitance $C_S$ is often named correspondingly as the gravimetric capacitance (F/g), volumetric capacitance (F/ml), normalized capacitance ($\mu$F/cm$^2$) and areal capacitance (F/cm$^2$) or linear capacitance (F/cm). Sometimes, $C_S$ is also used to describe device performance, when normalized by the whole cell weight or volume [61]. Note that although $C_S$ is considered the most important parameter in comparing the charge storage ability of SC materials, it is rarely mentioned by industry, as most of the commercial SCs are activated carbon (AC) based, and its $C_S$ is generally considered a constant between 100 F/g and 70 F/cm$^3$ in organic electrolyte [62]. However, for scientists in searching for new materials, $C_S$ is the more informative way to depict the charge storage ability of a given material.

2.2.1 Evaluation of $C_T$

a. CV

The total capacitance $C_T$ of a cell in Eq. 1 can be further expressed as:

$$C_T = \frac{\Delta Q}{\Delta V} = \frac{\int_0^{2V_o/V} i dt}{2V_o} \quad (3)$$

Through the integration of the resulting CV voltammograms, the accumulated charge as a function of potential can be obtained. Normally, the whole curve is recommended to use [63-67] as shown in Eq. 3. However in practice, different segments of the curve, as depicted in Fig. 2 in distinctive colors, have been used in integration [46, 68-70], thus leading to inconsistencies in test results [46, 65, 66, 71-73]. It is worthy reminding that the potential change in Eq. 3 $\Delta V = 2V_o$ (0 to $V_o$ and back to 0), for there are mistakes made in $\Delta V$ values [74-77].
b. CCCD

Since constant current is used in a CCCD test, Eq. 1 can be converted to:

\[ C_T = \frac{I \times \Delta t}{\Delta V} \]  

(4)

where \( I \) is the constant current, \( \Delta t \) is the charging or discharging time corresponding to the specified potential change \( \Delta V \). **So the key issue now is that the correct time \( \Delta t \) and \( \Delta V \) are used in calculation.** Often the entire discharging curve is used:

\[ C_T = \frac{I_{\text{dis}} \times \Delta t_{V_o-2V_o}}{V_o} \]  

(5)

Since \( IR \) drop is inevitable in CCCD test, one can adjust \( \Delta V \) so as to exclude the \( IR \) drop for more accurate result, \( i.e., \)

\[ C_T = \frac{I_{\text{dis}} \times \Delta t_{V_o-2V_o}}{V_o - V_{IR \text{ drop}}} \]  

(6)

Similar to CV test, different segments of the CCCD plots, as illustrated in **Fig. 3**, have been used in computing the cell capacitance [66, 70, 78]. Only this time as the current remains constant, identical \( C_T \) value is obtained regardless of the segment used, so long as the voltage changes linearly with time as in **Fig. 3**.

Whereas for PCs or hybrid SCs with nonlinear curves as seen in **Fig. 4**, the selection of different regions from the curve can make a great difference in determining \( \Delta V \), and hence \( C_T \) [79-82]. In such cases, the use of a proper or fixed region or selection of suitable potential window becomes critical and needs to be standardized. Based on Burke [53], Region 3 or a potential window from \( V_o \) to the shoulder voltage is recommended. Likewise, one can also
adjust ΔV to eliminate the IR drop to improve accuracy.

c. EIS

The conventional method of deriving capacitance from EIS test is based on the imaginary part of the complex impedance \( \text{Im}(Z) \) as shown in Eq. 7 [7, 54, 83]:

\[
C_{TF} = -\frac{1}{2\pi f \times \text{Im}(Z)} \quad (7)
\]

where \( f \) is the frequency. Normally this frequency is identified at which the phase angle reaches -45 degree [83], or simply as the lowest frequency applied [7].

Another method introduced by Simon [56] is as below:

\[
\text{Re}(C) = -\frac{\text{Im}(Z)}{\omega |Z|^2} \quad (8)
\]

\[
\text{Im}(C) = \frac{\text{Re}(Z)}{\omega |Z|^2} \quad (9)
\]

where \( Z = \sqrt{\text{Re}(Z)^2 + \text{Im}(Z)^2} \) is the overall complex impedance, \( \omega = 2\pi f \) is angular velocity, \( \text{Re}(Z) \) is the real part of the complex impedance, and \( \text{Re}(C) \) and \( \text{Im}(C) \) are the real and imaginary capacitances, respectively. \( \text{Im}(C) \) is a term related to the energy dissipation of the cell, and \( \text{Re}(C) \), calculated at the lowest-frequency applied, indicates the energy stored, thus can be used to represent \( C_T \) [56].

2.2.2 Evaluation of \( C_S \)

Once \( C_T \) is obtained, the corresponding \( C_S \) can be calculated using Eq. 4. This seemingly straightforward step is made complicated by the fact that there is no established standard procedure in determining the base value for \( \Pi \), be the mass, volume, or other quantity. A mediocre \( C_T \) value can lead to an excellent \( C_S \) if a sufficiently small \( \Pi \) is used. For this
reason, along with other possible considerations, technical or cost related, although attractive
$C_S$ results are frequently reported [74-77, 79-82], few have been successfully transferred to
commercial products. **One solution to this problem is that both $C_T$ and the
corresponding $C_S$ values, as well as the $\Pi$ value, be explicitly reported side by side.**
Besides $\Pi$, other factors as discussed in next section, including experimental setup, mass
loading and electrode thickness, and electrode density, can also alter $C_S$ value dramatically
[65, 84, 85] and therefore recommended to be reported as necessary information.

### 2.2.3 Major affecting factors

#### a. Experimental setup

Study has demonstrated that quite different $C_S$ values can be obtained for the same SC
electrode when different experimental setups are adopted [46]. The three major experimental
setups: symmetric two-electrode, asymmetric two-electrode and three-electrode
configurations, are illustrated in Fig. 5. The three-electrode one is particularly useful in
accurately determining the $C_S$ for SC materials, and the two-electrode ones are normally used
in SC device prototypes or final products. It is worth noting that it is also possible [86] to
insert a reference electrode in the two-electrode system to study the detailed potential change
in other two electrodes, but this scenario is not included here and the three-electrode
configuration mentioned in this article solely means the setup presented in Fig. 5a.

The following analysis demonstrates how different setups can lead to different results.
For brevity the gravimetric $C_S$ is used. The weight of each individual electrode in Figs. 5a
and b is assumed to be $m$, while $m_1$ and $m_2$ are for the two different Electrodes 1 and 2 in Fig.
Assigning the single electrode capacitance as $C_E$, the gravimetric $C_{Sa}$ in the three-electrode system can be calculated as [59]:
\[
C_{Sa} = \frac{C_E}{m} \quad (10)
\]

For the symmetric two-electrode system shown in Fig. 5b, the cell total capacitance $C_{Tb}$ can be obtained through:
\[
\frac{1}{C_{Tb}} = \frac{1}{C_E} + \frac{1}{C_E} \quad (11)
\]

By counting the mass for both electrodes, hence:
\[
C_{Sb} = \frac{C_{Tb}}{2m} \quad \frac{1}{4} \left( \frac{C_E}{m} \right) \quad (12)
\]

That is, even with identical SC material, the specific capacitance obtained from the three-electrode system actually quadruples that from the symmetric two-electrode system, i.e.,
\[
C_{Sa} = 4 \times C_{Sb} \quad (13)
\]

This relationship has been validated experimentally by Béguin et al [46].

For the asymmetric two-electrode system in Fig. 5c, the cell capacitance $C_{Tc}$:
\[
\frac{1}{C_{Tc}} = \frac{1}{C_{E1}} + \frac{1}{C_{E2}} \quad (14)
\]
Again by counting the mass for both electrodes, there is:

\[
C_{\text{sc}} = \frac{C_{\text{Te}}}{m_1 + m_2} = \frac{1}{m_1 + m_2} \times \frac{C_{E1} \times C_{E2}}{C_{T1} + C_{T2}} \quad (15)
\]

In this configuration, normally the electrode capacitances of the two electrodes are balanced to fully unitize the charge storage ability of the SC material, i.e., \( C_{E1} = C_{E2} = C_E \). So by employing other active material like pseudocapacitive one, it is normally accepted that the *specific* capacitance of Electrode 1 is larger. Conversely if the two electrodes achieve the same capacitance \( C_E \), then less mass is needed in Electrode 1, say at a fraction \( \alpha (0 < \alpha < 1) \) of Electrode 2, so that \( m_1 = \alpha m \), \( m_2 = m \). Substituting them into Eq. 15 yields,

\[
C_{\text{sc}} = \frac{1}{2(1 + \alpha)} \frac{C_E}{m} \quad (16)
\]

Combined with Eqs. 10 and 12, there are:

\[
C_{\text{Sa}} = 2(1 + \alpha)C_{\text{sc}} \quad (17)
\]

and

\[
C_{\text{Sb}} = \frac{(1 + \alpha)}{2} C_{\text{sc}} \quad (18)
\]

Thus the three equations show distinctive results when using setup a, b or c. For example, if the *specific* capacitance in Electrode 1 doubles that in Electrode 2, \( \alpha = 0.5 \) at the same potential window. Then there is \( C_{\text{Sa}} = 3C_{\text{Sc}} \) and \( C_{\text{Sb}} = 0.75C_{\text{Sc}} \)!

It is worth noting that for SC devices, the *total capacitances* for symmetric and asymmetric are identical under the same assumptions:

\[
C_{\text{Tb}} = C_{\text{Tc}} = \frac{1}{2} C_E \quad (19)
\]

The advantages of using asymmetric systems include first, as discussed below in 2.4.2, by using hybrid electrodes hence an asymmetric system, additional electrochemical potential
difference can be introduced so that the operating voltage of the cell can be boosted [72]. The second benefit is that for the same total capacitance, in an asymmetric system, the electrode of better PC material can cut the material use by a fraction \((1-\alpha)\) as demonstrated above. This can be significant if this PC material is so superior that \(\alpha\) is small. However so far, the symmetric SC devices still demonstrate better power performance, and consequently play a dominant role in the market, despite the intensive study on asymmetric systems [72, 80, 87-92].

b. Mass loading and electrode thickness

Mass loading is defined as the mass of active material per unit area of the electrode, and electrode thickness is the net thickness of the active material on the current collector. These two parameters reflecting the fabrication process significantly impact the resulting \(C_S\), but are often not specified. Many studies used a very small mass loading or electrode thickness in calculating the specific capacitance \(C_S\), and the resulted \(C_S\) appears outstanding in number but is often not meaningful in practice [93, 94]. In general, it is suggested [65] that the mass loading to be at least 5 mg/cm\(^2\) and the electrode thickness between 50 – 200 \(\mu\)m. Exceptions may be found for micro-supercapacitors [85, 94, 95] in special applications. Fig. 6a and b are two verifications showing the significant impact of them on \(C_S\).

c. Electrode density

The electrode density describes how densely the electrode materials are packed on current collector, and is expressed in mass/volume. Although it is related to both mass loading and electrode thickness, there is the material density involved. It is reported that the
same electrode material with different packing densities can significantly influence the resulting electrochemical performance, including \( C_s \), energy and power densities. Based on the targeted applications, there is an optimal level for the electrode density, so that the electrode is not over densely packed as to reduce the accessibility of SC materials, nor is it excessively loose to affect the volumetric performance. An example of its impact is provided in Fig. 7 by using certain graphene materials with increasing densities from 0.13 to 1.33 g/cm\(^3\) [61].

### 2.3. Equivalent series resistance

A SC is not an ideal electrical component in the sense that it has its own internal resistance, thus dissipating the energy stored. A SC cell can be simply treated as a system of a capacitor in series arrangement with a resistor \( R_{ES} \) in Fig. 8. The resistance of this resistor is usually termed as the equivalent series resistance, \( R_{ES} \), and is essential in reflecting the power performance and energy efficiency of SCs. In general, a small \( R_{ES} \) is preferred for better electrochemical performance. Note that in actual measurement, only a packed cell can give an accurate \( R_{ES} \) value. It is because of this, whenever \( R_{ES} \) is referred to in this paper, it deals with a device not the material.

#### 2.3.1 Evaluation of \( R_{ES} \)

**a. CCCD**

The most widely accepted method to evaluate \( R_{ES} \) is through the analysis of the \( IR \) drop or voltage variation at the initial stage of the discharging curve from CCCD tests. By
applying Ohm’s law to the \( IR \) drop, \( R_{ES} \) can be acquired readily:

\[
R_{ES} = \frac{\Delta V}{\Delta I} \quad (20)
\]

where \( \Delta V \) and \( \Delta I \) are the voltage and current of the \( IR \) drop, respectively.

Another less common approach is based on the voltage recovery behavior after a current interruption during a discharge process [96, 97]. This method is fundamentally the same as the \( IR \) drop method and yields matching results, and is hence not described in detail here.

b. EIS

Typically, the \( R_{ES} \) from EIS test is evaluated using the real part of the complex impedance at 1 kHz and is normally noted in Nyquist plot. Another method, via linear interpolation of the low-frequency part of Nyquist plot to \( Im(Z) = 0 \), is also used sometimes in literature. An example is provided in Fig. 9 to illustrate these two methods in EIS test, testing a typical commercial SC, 2.7V/1F Maxwell cell. Compared to the \( R_{ES} \) derived from CCCD test, the value from EIS test is normally smaller.

2.3.2 Major affecting factors

There are two major factors that affect the accuracy of \( R_{ES} \) from CCCD test: the dwelling time and the size of SC. Normally, CCCD test is carried out without dwelling at peak potential, that is, the discharging starts once the peak potential is reached. However, the practice of non-zero dwelling time is widely adopted in tests, which can greatly influence the final value of \( R_{ES} \). A couple of different dwelling time have been reported: 1 min in the procedure developed by Burke [98], 5 min in Illinois Capacitors [99], 10 min by Ioxus, [100]
etc. Another often overlooked affecting factor on \( R_{ES} \) is the size of SCs in terms of cell capacitance as defined in Table 2. The two factors are discussed in detail below.

### Table 2. Defined SC size based on total cell capacitance.

<table>
<thead>
<tr>
<th>Micro cell</th>
<th>Small cell</th>
<th>Medium cell</th>
<th>Large cell</th>
<th>Ultra-large cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_T )</td>
<td>&lt; 1 mF</td>
<td>1 mF – 10 F</td>
<td>10 F – 100 F</td>
<td>100 F – 1000 F</td>
</tr>
</tbody>
</table>

#### a. Dwelling time

To the best of our knowledge, there is no study carried out to examine the influence of dwelling time on \( R_{ES} \). Therefore, by using the same 2.7V/1F SC from Maxwell Technologies, we acquired and presented its CCCD plots with different dwelling time varying from 0 – 30 minutes in Fig. 10a. Fig. 10b demonstrated the impact of dwelling time on the resulting \( R_{ES} \).

To clearly display the variation of CCCD plots, we selected and enlarged the upper region of the plots with dwelling time of 0 min and 1 min, and showed them separately in Fig. 10c and d, with the potential and current changes marked in black and blue, respectively. If \( I \) is the constant current applied, then in the case of 0 min dwelling time, the current change is:

\[
\Delta I \approx 2I \quad (21)
\]

Whereas in the cases of > 0 min dwelling time,

\[
\Delta I \approx I \quad (22)
\]

Combined with the potential change, as charted in Fig. 10b: we have at 0 min dwelling time,
a much smaller $R_{ES} \sim 0.93$ ohms, compared to 1.47 ohms from dwelling time >0 min cases.

b. Cell size

It is still not clearly understood how the cell size affects the CCCD results. But it is generally accepted that the IR drop method works fine only for small SCs, and a steady-state voltage drop method should be used for large SCs. As shown in Fig. 11a, the steady-state voltage drop $\Delta V_2$, rather than the IR drop $\Delta V_1$, is obtained through the back extrapolation of the potential trace; it is larger than $\Delta V_1$ by almost 50%, thus leading to a nearly 50% increase in $R_{ES}$. An actual example is provide in Fig. 11b reported in Ref. [53]. Studies [53, 101] have been conducted and the results demonstrated that more accurate power performance can be estimated using $\Delta V_2$ for large cells, and it is therefore recommended.

2.4. Operating voltage $V_o$

Strictly speaking, the operating voltage $V_o$ refers to the potential applied to the system or the suitable potential window within which a cell normally operates. In this paper, the term is sometimes interchangeable to cell voltage or rated potential, which represents the maximum voltage a cell can endure.

2.4.1 Evaluation of $V_o$

Both CV and CCCD tests can be used to determine $V_o$ of either the SC materials or the devices. However actual test of this maximum potential can be risky of destroying the cell. An expedient method is normally applied, with an example given in Fig. 12 using an asymmetric MnO$_2$/AC capacitor [72], where $V_o$ can be achieved by starting with a lower
voltage applied to the cell, and then slowly increasing the voltage until a spike appears as seen in the figure.

2.4.2 Major affecting factors

Two major factors affecting $V_o$ for SC devices include the solvent in electrolytes and the cell configuration. Normally, in aqueous systems, a cell can be charged to 1.0 V, limited by the thermodynamic decomposition potential of water at room temperature. $V_o$ in organic solvent electrolyte varies between 2.3 – 2.7 V [21, 102-106]. As both energy and power densities are proportional to $V_o^2$, much effort has been dedicated to develop novel electrolyte that can endure high voltage (>3 V). Room temperature ionic liquid (RTIL) is considered to be the most promising candidate by which high $V_o$ values between 3.0 – 6.0 V have been achieved in research labs [107, 108]. In addition, various mixtures of different RTILs, or RTIL and organic solvents, also appear to be attractive [109, 110].

The other factor influencing $V_o$ is the cell configuration. In an asymmetric system, $V_o$ can be increased by using different SC materials so as to introduce additional electrochemical potential difference [72]. This way, even in aqueous systems, $V_o$ can reach 2.0 – 2.3 V [29, 72, 111, 112], giving rise to much improved energy storage [29, 113].

In conclusion, for SC materials, all three techniques, i.e. CV, EIS and CCCD tests, can be employed with different emphases. However, for SC devices, the most effective and accurate approach is CCCD test for measuring the cell capacitance, equivalent series resistance and operating voltage [53]. Subsequently, the time constant, energy and power densities, and leakage and maximum current of SC devices can be derived based on these three core parameters.
2.5. Time constant

Time constant \( \tau \) is only for SC devices and defined as the product of \( R_{ES} \) and \( C_T \) as shown in Eq. 23 using the equivalent RC circuit for a SC in Fig. 8. A smaller \( \tau \) reflects a better responsiveness of the device, and for most of commercial SCs, \( \tau \) normally ranges from 0.5 – 3.6 s [114].

\[
\tau = R_{ES} \times C_T \quad (23)
\]

Based on the RC circuit model, the voltage of SC device changes by 36.8% at time \( t = \tau \), and by 98% at time \( t = 4\tau \), during the charge/discharge processes.

Normally \( \tau \) is fixed around a certain value for SCs produced using the same technology, for example 0.55 s from Maxwell Technologies, 1.1 s from NessCap and 3.8 s from JSR Micro, as reported in [114]. Consequently, \( C_T \) and \( R_{ES} \) for the same type of SCs are inversely proportional to each other when \( \tau \) is fixed. An example is shown in Table 3 for BCAP SCs from Maxwell Technologies, and we calculated the corresponding \( \tau \) values.

<table>
<thead>
<tr>
<th>( C_T ) (F)</th>
<th>1</th>
<th>3.3</th>
<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>310</th>
<th>350</th>
<th>650</th>
<th>1200</th>
<th>1500</th>
<th>2000</th>
<th>3000</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_{ES} ) (m( \Omega ))</td>
<td>700</td>
<td>290</td>
<td>170</td>
<td>75</td>
<td>42</td>
<td>20</td>
<td>15</td>
<td>2.2</td>
<td>3.2</td>
<td>0.8</td>
<td>0.58</td>
<td>0.47</td>
<td>0.35</td>
<td>0.29</td>
</tr>
<tr>
<td>( \tau ) (s)</td>
<td>0.7</td>
<td>0.96</td>
<td>0.85</td>
<td>0.75</td>
<td>1.05</td>
<td>1.0</td>
<td>1.5</td>
<td>0.68</td>
<td>1.12</td>
<td>0.52</td>
<td>0.7</td>
<td>0.71</td>
<td>0.7</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Attention has to be paid here not to confuse this \( \tau \) with another “relaxation time constant”,

37
\( \tau_0 \), as occurred in [77, 115, 116]. \( \tau_0 \) was proposed by Simon in [56] based on EIS test. Using the same 2.7V/1F Maxwell SC and plotting both \( \text{Re}(C) \) and \( \text{Im}(C) \) vs. frequency as in Fig. 13, \( \tau_0 \) is marked at where the imaginary part of the capacitance reaches its maximum at frequency \( f_0 \), and can be calculated by Eq. 24:

\[
\tau_0 = \frac{1}{f_0} = 3.86 \quad (24)
\]

It is much larger than \( \tau = 1.34 \text{ F} \times 1.44 \text{ \Omega} = 1.94 \text{ s} \). In fact, such difference was revealed in the same paper by Simon et al [56]: where they reported \( \tau = 0.7 \text{ s} \), but \( \tau_0 = 10 \text{ s} \) for their symmetric AC-based SC with mass loading of 15 mg/cm².

### 2.6. Power and energy densities

Of the performance metrics for all kinds of energy storage and conversion systems, power density and energy density are the most directly relevant to the end application and hence most often used parameters for performance evaluation.

They normally are evaluated gravimetrically or volumetrically in W/kg or W/L for power density to describe the efficacy in energy uptake/delivery; and in Wh/kg or Wh/L for energy density to demonstrate the amount of electrical energy stored or deliverable. For effective comparison with other EES devices, a Ragone plot [117] is shown in Fig. 14. The diagonal time line is a representative line for the so-called “characteristic time” [118], a reflection of running time of the devices at the rated power. The actual running time of EES devices varies a lot, depending on the load or discharging rate – the so-called rate dependence as discussed in 3.3 below.
Figure 14. An illustration of the power and energy densities for several EES devices via Ragone plot. The plot is based on data from Ref. [114, 119-122].

2.6.1 Power density

The outstanding power performance of SC devices is one of their major merits. The most widely used calculation method for the maximum power density is shown as:

\[ P_D = \frac{V_0^2}{4\pi R_{ES}} \]  \hspace{1cm} (25)

This maximum power delivery can only be realized when the load has the identical resistance as \( R_{ES} \), often referred to as the matched load condition.

Of course in practice, the load resistor is often not matching \( R_{ES} \). As necessary supplements, there are several other methods proposed to compute the actual power capacity. Three most widely adopted methods are DOE-FreedomCar [123], IEC 62576 [124] and the pulse energy efficiency (PEE) [114] methods, and one can refer to [70, 123, 125] for detailed discussions. Table 4 provides the resulting actual power densities with respect to the maximum \( P_D \) based on the different test procedures and the data published by Burke [70, 126]. Therefore, although the maximum value \( P_D \) is widely used for comparison, one has to keep in mind that it does NOT usually represent the actual deliverable power density, and one has to choose the proper percentage below based on the corresponding applications.

<table>
<thead>
<tr>
<th>Matched load</th>
<th>USABC</th>
<th>IEC</th>
<th>PPE</th>
</tr>
</thead>
</table>

Table 4. Power densities obtained from different methods.
In principle, a further boosted \( P_D \) value is always beneficial; but little effort has been made in this [127] given the fact that SCs already have relatively high \( P_D \).

### 2.6.2 Energy density

The electricity stored in or released from SCs can be evaluated through the integration of the working diagrams as illustrated in Fig. 15 corresponding to ECLCs and PCs, where the difference in shape is caused again by their distinct charge storage mechanisms. In either case, the stored electric energy can be obtained from the charging curve, and the deliverable energy from the discharging curve. The ratio of the two is termed the energy efficiency of the cell, an indicator of the difference between the two parts of the curve. Calculations for the stored electricity are illustrated below.

**a.** For EDLCs or any other SCs with linear charge/discharge curves, the integration of the working diagram turns into the calculation of triangle area as shown in Fig. 15a, therefore:

\[
E_D = \int_0^Q V_o dq = \frac{1}{2}V_o Q \quad (26)
\]

Substituting Eq. 2 into Eq. 26 yields,

\[
E_D = \frac{1}{2\Pi} C_r V_o^2 \quad (27)
\]

Dividing by 3600 converts \( E_D \) in Joule/\( \Pi \) to watt hour/\( \Pi \):
It is worth mentioning that by combining Eqs. 23, 25 and 27, the relationship between \( P_D \) and \( E_D \) for EDLCs is given below:

\[
\frac{E_D}{P_D} = 2R_{ES} \times C_T = 2\tau \quad (29)
\]

This equation indicates that the energy and maximum power densities are closely coupled by the cell time constant \( \tau = R_{ES} \times C_T \). Although \( E_D \) can be increased in Eq. 27 by improving either the capacitance or operating voltage, raising the capacitance alone will simultaneously increase the time constant \( \tau \), leading to a less responsive cell, assuming \( R_{ES} \) unchanged. Whereas boosting the voltage can considerably enlarge both \( P_D \) and \( E_D \), while still maintaining the same \( \tau \) value. Also even though increasing \( E_D \) is the major stride for SC community, extra attention is required at the same time for the associated possible changes in \( \tau \) or \( P_D \).

b. However, for PCs or hybrid SCs with nonlinear charge/discharge curves as shown in Fig. 15b, the integration of the diagram has no simple solution, depending on the specific shape of the curve, so that:

\[
E_D = \int_0^Q Vdq = \int_0^{tQ} V \times dt \quad (30)
\]

Dividing by 3600 and \( \Pi \), one can still obtain the energy density in watt hour/\( \Pi \):

\[
E_D = \int_0^Q Vdq = \frac{\int_0^{tQ} V \times dt}{3600 \times \Pi} \quad (31)
\]
That is, Eq. 28 is **NOT** valid for PCs with nonlinear charge/discharge curves, and for them Eq. 31 has to be used.

### 2.7. Leakage and maximum peak currents

For SC devices, an additional yet useful parameter is the leakage current, widely used in industry to evaluate the capability of SCs to maintain the rated potential when not in use. Normally, it is recorded as the compensating current that applied to hold a fully charged SC after 72 hours.

Another similar device parameter is the maximum peak current, normally appearing in the specifications for commercial SCs. It is evaluated by discharging a fully charged SC device from $V_o$ to $\frac{1}{2} V_o$ in 1 s, and calculated as:

$$I_{\text{max}@1s} = \frac{\frac{1}{2} C_T V_o}{C_T R_{ES} + 1}$$

(32)

### 2.8. Cycle life and capacitance retention rate

Long cycle life of SC devices is one of their major merits and leads to the so-called “fit-and-forget” benefits, highly desirable for certain applications. But this extremely long cycle life (>1,000,000 cycles) also makes it difficult to directly measure it. Another term, the capacitance retention rate is therefore used to indirectly estimate the cycle life of SCs. It is easily obtained in CCCD test by comparing the capacitance after given thousands of cycles with that of the first cycle. One attempt [128] was made recently by continuously test SCs for 3.8 years, and the results showed that the capacitance retention rate is decreasing almost linearly with the square root of the number of cycles. Further validations are needed to
establish this relationship, but it does give us a glimpse on the time demanding nature of the direct measurement of cycle life.

3. Inconsistencies in evaluation of SCs

3.1. Causes for the inconsistencies

For any comparison to be meaningful, the same or consistent metrics and test methods have to be used. As demonstrated and discussed in this article so far, it is easy to see why performance evaluation of SCs has become so prevalently plagued by inconsistencies, and where such inconsistencies are originated. Herein, the common causes are listed below:

a. Different instruments or calculation method used, i.e. CV, CCCD or EIS;

b. Different experiment setups:
   - Three-electrode, and symmetric and asymmetric two-electrode configurations;

c. Differences in electrode fabrication:
   - Mass loading, electrode thickness and density;

d. Different base \( \Pi \) used:
   - Volume or mass; active material only, or combined with additives, binders; single or two electrodes; with or without electrolyte, or the whole cell;

e. Different test conditions applied (rate dependency):
   - Scan rate in CV, charge/discharge current in A/g, mA/cm\(^2\), or mA/F for CCCD tests;

The inconsistencies caused by the first three items on the list have been discussed in preceding sections. The effects of improper use of the base \( \Pi \) and with the rate dependency are examined below.
3.2. Device performance vs. material property

Although this issue has been dealt with above, the difference between device performance and material property can be huge, often overlooked, and may play a critical role in performance evaluation for any EES system. A recent paper by Gallagher et al [129] emphasizes such difference in the case of lithium-air batteries. To substantiate the discussion, some useful information from several SC manufacturers, including Maxwell Technologies, WIMA, Nesscap, and Ioxus [102-105], is collected and analyzed here. Owing to the fact that the mainstream SC material in industry is still activated carbon (AC), only AC-based SCs are considered.

For SC devices, their energy and power densities are summarized below:

- $E_D$ ranges from 1 – 6 Wh/kg or 2 – 8 Wh/L;
- $P_D$ ranges from 2 – 20 kW/kg or 4 – 30 kW/L;

The same devices but for SC materials (AC), $C_S$ between 100 F/g and 70 F/cm$^3$ [62]:

- $E_D$ ranges from 15 – 25 Wh/kg or 12 – 18 Wh/L;
- $P_D$ ranges from 20 – 120 kW/kg or 13 – 80 kW/L;

The substantial difference between device performance and material property is clearly demonstrated above. This is due to the fact that only a small portion of the weight and
volume of SC devices are composed of active electrode materials, around 5 – 20 %, even smaller for micro-SCs [85, 94, 95]. What is worrisome is that in almost all published scientific literature [55, 60, 69, 80, 86, 130-138], no distinction has been made explicitly between the device performance and material property, leaving a room for potential misinformation and confusion.

3.3. Rate dependency

The rate dependence of all EES devices is a universal, yet thorny issue [139]. For example, batteries are usually affixed with a rated energy $C_o$ in Ampere hour at a rated potential. However, in actual use, how much energy this battery can actually deliver to a load depends on the discharge/recharge rate [139]. In other words, if a load drains this battery in a shorter time period, the actual energy supplied will be $C_d < C_o$. Peukert’s law [139, 140] is usually applied to describe this phenomena as:

$$C_A = i \cdot t = \frac{C_o}{(t_o/t)^{k-1/k}}$$

(33)

And therefore the current,

$$i = \frac{C_o \cdot (t_o/t)^{k-1}}{t_o}$$

(34)

Where $t_o$ is the discharge rate or time (hrs) used to measure $C_o$, $k$ is the Peukert’s factor, usually $1.1 < k < 1.6$ for batteries. This $k$ value indicates the degree of dependency of $C_d$ on discharge rate, and a smaller value is more desirable, implying less rate independency [139].

To address this issue, the $C$-rate scheme has been proposed and widely used to scale the charge and discharge current for batteries. Different batteries are rated differently, i.e., with different $k$ values, based on the kinetics of the battery chemistry involved. If a battery is rated
at \( n \) C, the discharging time will be fixed at around \( 1/n \) hours \([141]\), i.e., if rated at 2C, for example, batteries will be completely discharged in 0.5 h. By fixing the discharge or recharge time, this C-rate system tackles successfully the issue of rate dependency for batteries with little confusion. **Fig. 16** is constructed using both **Eqs. 33** and 34 to illustrate the actual energy deliverable \( C_A \) and the electric current \( i \), as functions of both discharge time and the C-rate level, where one can easily locate the \( C_A \) and \( i \) for a given pair of discharge time and C-rate level.

For SCs, similar rate dependency has been long and widely recognized \([48, 50, 51, 65, 69, 114, 142-145]\), yet poorly analyzed and understood. Also similar to the C-rate system for batteries, a **60 second discharge/recharge time is recommended for SCs**\([146]\). This 60C discharge rate or 60 s discharge/recharge time can settle the **inconsistencies** caused by the different test conditions in CCCD tests, i.e. A/g, mA/cm\(^2\), mA/cm\(^3\) or mA/F \([130, 132, 147, 148]\), and can be used as a guidance to determine the proper scan rate used in CV test: \( v = 1/60 \) V/s (\(~16.7\) mV/s) for 1 V systems; \( v = 2.3/60 \) V/s (\(~38.3\) mV/s) for 2.3 V ones; and \( v = 2.7/60 \) V/s (45 mV/s) for 2.7 V ones.

To demonstrate the rate dependency and the use of 60 s discharge/recharge time for SCs, we collected the test data of a 1450F EDLC \([11]\) and a 2000F hybrid SC \([53]\) and fitted them nicely using again both **Eqs. 33** and 34 as shown in **Fig 17**. Consequently, Peukert’s factor \( k \approx 1.02 \) is estimated for the EDLC and \( k \approx 1.06 \) for hybrid SC, reflecting the different kinetics of charge storage/release mechanism in each system.
5. **Summary and recommendations**

We identified and examined the *inconsistencies* existed in the current practice for evaluation of supercapacitors. Such *inconsistencies* are caused by some common sources including different test instruments, evaluation methods and other related factors. In summary, a fair comparison is only possible if we:

a) employ the same instruments under consistent test conditions and experimental setups;

b) derive the performance metrics using consistent calculation methods;

c) compare the comparables.

Moreover, a few more specific recommendations are proposed as followings:

1. Apply 60 seconds discharge or recharge time to address the rate dependency of supercapacitors so as to produce comparable parameters.

2. Use constant current charge/discharge (CCCD) test to determine all the three core parameters, i.e. the capacitance, equivalent series resistance and operating voltage, and subsequently the time constant, energy and power densities and leakage/maximum peak current for supercapacitor devices.

3. Use cyclic voltammetry (CV) or constant current charge/discharge (CCCD) test on a three-electrode setup to examine the operating voltage and specific capacitance of supercapacitor materials.

4. Use electrochemical impedance spectroscopic (EIS) test to study the transient impedance behavior and frequency response of supercapacitors.

5. Differentiate between the device performance and material properties, and clearly
state the mass loading, thickness, density of the electrode.

6. Pay extra attention to nonlinear charge/discharge curves when evaluating capacitance and energy performance for pseudocapacitive SCs.

7. Keep in mind the interconnections between the energy density, maximum power density and the cell time constant: they cannot be altered individually. Also note that increasing the operating voltage by using advanced electrolyte or novel cell design is the most effective way to raise both energy and power densities, while still upholding the $\tau$ value.

It is fitting to end this article by quoting from the paper by Simon et al “The prospect of developing materials with the energy density of batteries and the power density and cycle life of supercapacitors is an exciting direction that has yet to be realized. Whether to approach these goals by increasing the power density of battery materials or increasing the energy density of supercapacitors is one of the enticing features of the field. However, there needs to be clarity in the terminology used in combination with appropriate measurements and analyses. Proper evaluation of new materials and their charge storage mechanisms will facilitate progress in this important field of electrical energy storage.” [146]
Acknowledgements

This work has been supported by California Energy Commission EISG Project 57470A/12-02TE, as well as by NIFA projects CA-D*-TXC-6426-RR and CA-D*-TXC-7694-H.

References

81. Yan, J., et al., Preparation of a graphene nanosheet/polyaniline composite with high specific energy storage.


100. Representative Test Procedures for Customer Evaluations, Ioxus, Inc.


Captions for Figures

Figure 1. An illustration of key performance metrics, test methods, major affecting factors for the evaluation of SCs.

Figure 2. An illustration of a typical CV test result.

Figure 3. An illustration of CCCD test result with linear potential change over time.

Figure 4. An illustration of CCCD test result with nonlinear potential change over time.

Figure 5. Schematic illustrations and equivalent circuits for different experimental setups.

Figure 6. a) Effect of mass loading and b) electrode thickness on the resulting $C_S$: yellow squares, green circles and purple triangles represent crumpled graphene balls, wrinkled graphene sheets, and flat graphene sheets as electrodes; and red solid squares indicate carbide-derived carbons (CDCs) as electrodes [85, 149].

Figure 7. Cyclic voltammograms of liquid-mediated graphene materials with increasing electrode density following the dashed red arrow from 0.13 – 1.33 g/cm$^3$ [61].

Figure 8. The series RC circuit for supercapacitors.
Figure 9. The Nyquist plot of 2.7V/1F Maxwell SC with $R_{ES}$ determination methods marked in red.

Figure 10. CCCD result of 2.7V/1F Maxwell SC tested at different dwelling time from 0 – 30 min: (a) overall CCCD plots of one cycle; (b) averaged $R_{ES}$ values from first six cycles; enlarged upper region of the CCCD plots at dwelling time of (c) 0 min and (d) 1 min.

Figure 11. (a) A typical CCCD plot for large SCs with $IR$ drop and steady-state voltage drop marked as $\Delta V_1$ and $\Delta V_2$, and (b) a real case illustration of the discharge part via Skeleton Tech 1600F SC.

Figure 12. An illustration of $V_o$ determination methods using (a) CV and (b) CCCD tests.

Figure 13. Dependence of real and imaginary capacitances over frequency for 2.7V/1F Maxwell SC with the relaxation time constant $\tau_o$ pointed.

Figure 14. An illustration of the power and energy densities for several EES devices via Ragone plot. The plot is based on data from Ref. [114, 119-122].

Figure 15. Representative working diagram from CCCD test for EDLCs (a), and PCs (b).

Figure 16. An illustration of Peukert’s curve for batteries with the use of $\frac{1}{2}C$ marked by dashed lines.
Figure 17. An illustration of Peukert’s curves for a 1450F EDLC (a) and for a 2000F hybrid SC (b) with the use of 60C marked by dashed lines.

Captions for Tables

Table 1. A chronological review of SC evaluation standards.

Table 2. Defined cell size based on cell capacitance.

Table 3. $C_T$ and $R_{ES}$ for BCAP SCs from Maxwell Technologies.

Table 4. Power densities obtained from different methods.