



Review

Review on supercapacitors: Technologies and performance evaluation

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ABSTRACT

The development of electrochemical capacitors (i.e. supercapacitors) have attracted a lot of attention in recent years because of the increasing demand for efficient, high-power energy storage. Electrochemical capacitors (ECs) are particularly attractive for transportation and renewable energy generation applications, taking advantage of their superior power capability and outstanding cycle life. Over the past decade, various advanced electrode materials and cell design are being studied to improve the energy density of ECs. Hybrid Li-ion capacitors and pseudo-capacitors that utilize fast surface redox reactions of metal oxide and doped polymers are the prime candidates being considered. This paper is concerned with the metrics being used to describe the performance of ECs and how the metrics are evaluated by testing devices and how the data from the testing are best interpreted. Emphasize is on relating testing of advanced ECs using materials more complex than activated carbons to testing electric double-layer capacitors (EDLCs) using carbon in both electrodes. A second focus of the paper is projecting the potential of the advanced materials and ionic liquid electrolytes for the development of complete EC cells having an energy density more than a factor of ten greater the energy density of the EDLC devices currently on the market. This potential was evaluated by calculating the performance (energy and power) of a series of ECs that utilize the advanced materials that have been studied by electrochemists over the past 10–15 years. The capacitance and resistance of the advanced ECs were calculated utilizing specific capacitance (F/g or F/cm³) and porosity data for the electrode materials and ionic conductivity of the electrolytes. It was concluded that hybrid ECs can be developed with energy densities of at least 50 Wh/kg, 70 Wh/L with efficient power greater than 3 kW/kg. Continued research on micro-porous carbons with specific capacitance of 200F/g and greater is needed to achieve these EC performance goals.

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Contents

1. Introduction	277
2. How do ECs store energy: past-present-future?	277
3. Performance evaluation and test procedures for ECs	281
3.1. Performance evaluation for carbon/carbon double layer capacitors	282
3.1.1. Capacitance	282
3.1.2. Resistance	282
3.1.3. Energy density	284
3.1.4. Power capability	284
3.2. Performance evaluation for hybrid capacitors	285
3.2.1. Capacitance/charge capacity	286
3.2.2. Resistance	286
3.2.3. Energy density	286
3.2.4. Power capability and cycle life	286
4. Analysis of the performance of cells using advanced materials	286

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4.1.	Cell design description and modeling of the cell performance	287
4.2.	Performance calculations for selected ECs.	289
5.	Applications	289
5.1.	Green transportation.	289
5.2.	Industrial applications.	289
5.3.	Renewable electricity generation and smart grid	290
5.4.	Backup power and UPS.	290
6.	Conclusions and future perspectives.	290
	Declaration of Competing Interest	291
	Acknowledgment.	291
	References	291



Jingyuan Zhao was an international Ph.D. student at the Institute of Transportation Studies, University of California Davis working with Prof. Burke. After that, he completed postdoctoral research at the computer science and technology, Shenzhen Institutes of Advanced Technology (SIAT), Chinese Academy of Sciences (CAS). His research interests focus on the electrochemical energy storage systems (EES) and their state-of-the-art applications. At ITS-UC Davis, he did extensive experiments and computational modeling in the Vehicle Power System Laboratory (VPSL) with Dr. Burke in order to investigate the actual performance of electrochemical systems from conventional carbon-based EDLCs to hybrid systems and ultimately to batteries. The concentrated interest in these studies is driven by the renewable and green applications in transportation and industry.



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1. Introduction

Electrochemical capacitors (ECs) are currently being used in some innovative application scenarios for both on-board and stationary applications [1–3]. ECs play an important role as energy storage devices in the case that vehicle accelerating or regenerative braking energy recovery in the particular driving cycles implemented under the programmed control strategy [4]. Although batteries can accomplish the transient energy storage and propulsion, the power requirements are increasing remarkably and exceed their pulse power capability. A promising way is using a reasonable alternative solution such as ECs. During the past decades, huge efforts have been made to improve the performance characteristics of the ECs using advanced electrode materials and novel architectures to shorten ion diffusion path length and increase the interfacial area. Accordingly, ECs have greatly improved, as a wide variety of advanced materials and new cell design. However, presently ECs still have a low energy density of about 8–30 Wh/L compared to about 500 Wh/L for lithium batteries. If high power is required of the battery as in a hybrid vehicle, the battery must be oversized to meet the power and cycle life demand. In this case, it can make sense to combine batteries with capacitors as an optimum solution [5,6]. The use of ECs will be greatly enhanced if the energy density of ECs can be significantly increased. Advanced ECs have been designed by a number of researchers and manufacturers including proto-type devices and early commercial products with limited improvements in energy density [7,8]. Further improvements are needed and appear to be possible based on materials research data available in the literature. Performance testing of the commercial batteries and ECs for vehicle and industry applications is generally done using DC test approaches [8–11]. Meaningful comparisons of the useable power capability of batteries and ECs are needed if combinations of batteries into energy storage systems are to be

considered. However, there is great confusion and inconsistencies in the performance of ECs resulted from the lack of a commonly accepted core group of performance metrics and evaluation method [12]. This uncertainty and confusion seriously impedes the use of ECs in large energy storage systems. These issues need to be resolved as part of efforts to better understand metrics for EC performance.

This paper is concerned with evaluating the present and projected future characteristics of ECs in terms appropriate metrics and the test procedures to obtain the metrics for advanced ECs using advanced materials. The structure of this paper is as follows: Section 2 briefly presents the classification of materials and charge storage mechanisms of ECs as well as the future prospects. In section 3, performance evaluation and test standards currently being used by various organizations are summarized. This section aims to identify the differences in the test methods and how that has/can cause inconsistencies and confusion in data interpretation and claimed device performance. A method is included in the section 4 that uses the research data to determine inputs to a calculation of complete cell performance in terms energy density, power density, and pulsed power capability based on cell voltage and resistance. In order to better to solve the issues concerning global warming, fossil-fuel crisis and environmental contamination, the innovative application scenarios that ECs can be as a promising role are briefly summarized in section 5. Finally, section 6 is trying to give our conclusions and perspective for the development of high-performance ECs.

2. How do ECs store energy: past-present-future?

The concept of the double-layer architecture was established when the phenomenon of electrostatic attraction and osmotic repulsion as charged electrodes immersed in electrolyte solutions.

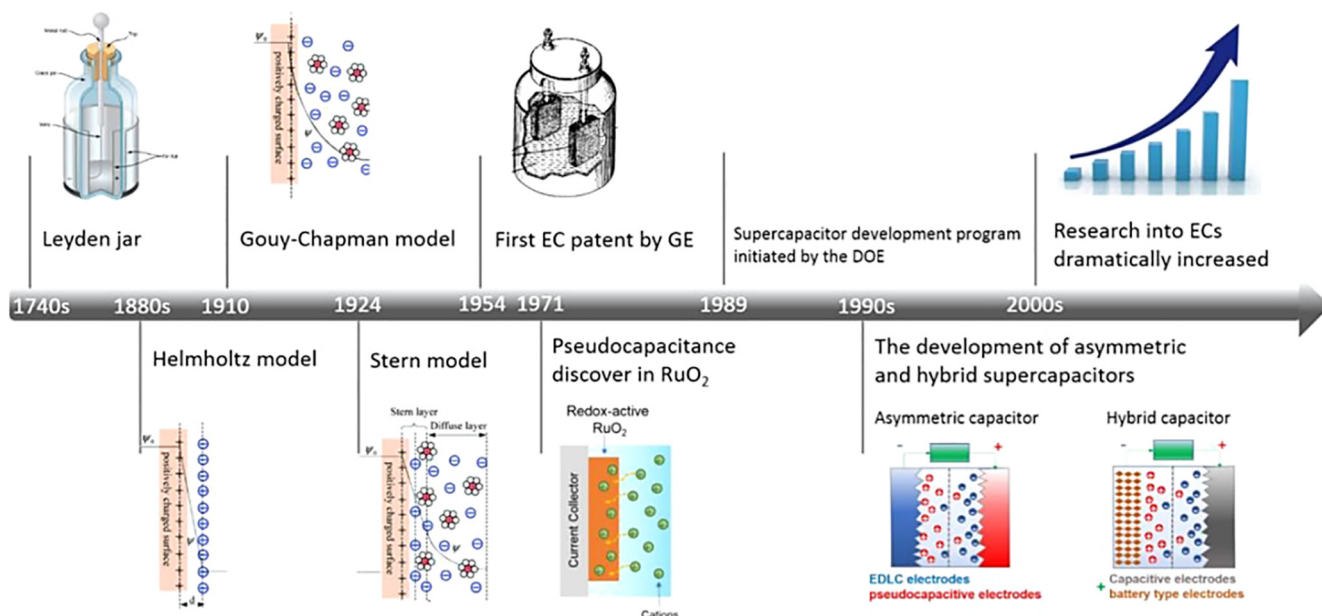


Fig. 1. Timeline: The crucial evolutionary steps that provided the primary impetus for the development of ECs energy storage technologies. Reproduced with permission from (a) ref [17], copyright 2018, American Chemical Society.

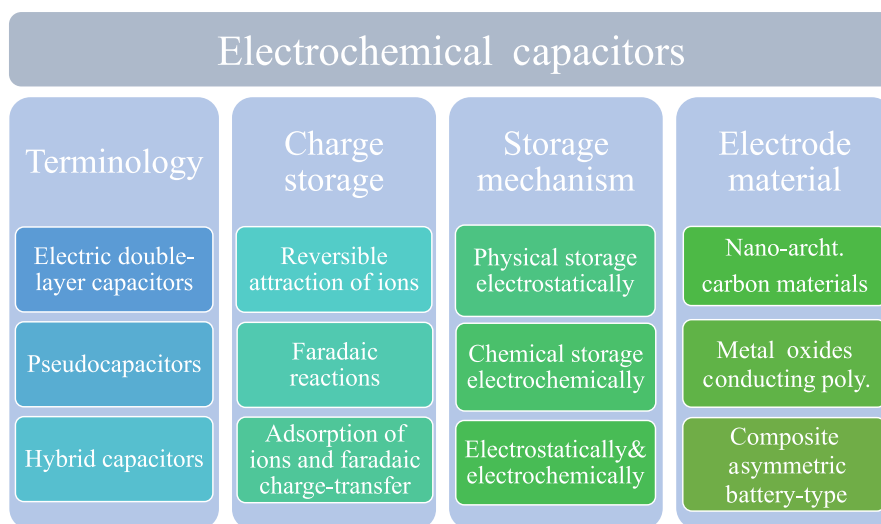


Fig. 2. The classification of EC technologies and energy storage mechanisms.

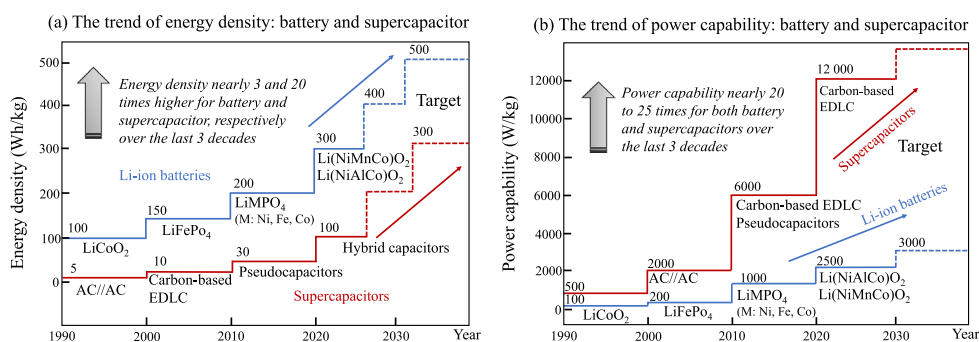


Fig. 3. The energy and power performance of Li-ion batteries and ECs. (a) The trend of energy density. (b) The trend of power capability.

Table 1

Evaluation protocols/standards and test procedures for ECs on the performance of capacitance and resistance.

Organization	Charge/discharge current	Hold time	Resistance determination	Min. voltage
DOE/USABC [26,27]	$I = \frac{\Delta V \cdot C_r}{720}$, $C = \frac{Q}{V_{\max} - V_{\min}}$	Rest 10 s (current = 0)	10 current pulses from 0 to 90% depth of discharge nominal at 10% increments	V_{\min}
IEC [28–30]	IEC 62391: $C = \frac{I_{\text{ch}}(t_2 - t_1)}{0.8V_r - 0.4V_r}$ IEC 62576: $I_{\text{ch}} = \frac{V_r}{38R}$, $I_{\text{dch}} = \frac{V_r}{40R}$ $C = \frac{I_{\text{dch}}(t_2 - t_1)}{0.9V_r - 0.7V_r}$ for ideal SCs; $C = \frac{2E}{(0.9V_r)^2 - (0.7V_r)^2}$ for unideal SCs.	Constant voltage holds at V_r for 5 min	Resistance and power capability using the hybrid power test profile Linear extrapolation to $t = 0$ to get IR drop (EDR) IEC 62,391 for use in electric and electronic equipment IEC 62,576 for use in hybrid electric vehicles	0.1 V
SII NWIP [31]	$C = \frac{2E}{V_1^2 - V_2^2}$. Calculate the capacitance according to the energy in the discharge process and the voltages at the end of the rest steps.	Same to IEC	Repeat the protocol for different currents. Measure voltage drop (dV) and current drop (dI). Using the dV/dI graph slope to calculate the R	N/A
Chinese standard [32]	Energy type capacitors: $I = \frac{\Delta V \cdot C_r}{720}$ Power type capacitors: $I = \frac{\Delta V \cdot C_r}{90}$ $C = \frac{\sum_{i=1}^3 I t_i (0.8V_r - V_{\min})}{3}$	Constant voltage hold at V_r for 30 min	The value in the 3th cycle as the internal resistance R_m based on the voltage drop at 10 ms into a discharge (Charge current at 1C rate for resistance and energy test)	V_{\min}
UC-Davis [8–11]	$I_{\text{test}} = n \frac{V_r C_r}{60}$ ($n = 0.5, 1, 2, 4, 8, \dots$) $C = \frac{I_{\text{test}} \cdot t_{\text{rest}}}{V_r - V_{\text{cut-off}}}$	Constant voltage charge at V_r for 60 s	A set of charge and discharge current pulse Current initiation and interrupt methods.	EDLCs: $\frac{1}{2}V_r$ Hybrid SCs: $V_{\text{cut-off}}$
Maxwell [33]	$I = 100\text{mA}/F \cdot C_r C = \frac{I \cdot \Delta t}{V_{\text{measure_end}} - V_{\text{measure_start}}}$	Rest 15 s (current = 0)	Bounce back at end of charge/discharge (5 s)	0.1 V
Nesscap [34]	For cell: $I = 10\text{mA}/F \cdot C_r$ For module: $I = 4 \cdot C_r V_r$ [mA] $C = \frac{I \cdot (t_2 - t_1)}{0.8V_r - 0.4V_r}$ 1 mA/F and $V_1 = 0.7V_r$, $V_2 = 0.3V_r$ are used in the early test procedures (2008)	Constant voltage charge at V_r for 5 min And 30 min in the test procedures of 2008	Resistance is calculated from the measured voltage drop at 10 ms into a discharge	0.1 V
Ioxus [35]	$I = \frac{4V_r C_r}{1000}$ for capacitance $I = \frac{4V_r C_r}{100}$ for resistance $C = \frac{I \cdot (t_2 - t_1)}{0.8V_r - 0.4V_r}$	Constant voltage charge at V_r for 10 min	Resistance is calculated from the measured voltage drop at 10 ms into a discharge and linear extrapolation to $t = 0$ to get IR drop	0.1 V
Skeleton [36]	$I_{\text{test}} = C \cdot 10\text{mA}/FC = \frac{I \cdot (t_2 - t_1)}{V_r - 0.5V_r}$	0	Resistance is calculated from the spontaneous rise in voltage after a current-cut period of 10 ms and 1 second.	$\frac{1}{2}V_r$
Yunasko [37]	$I = 0.2I_{\text{test}}$ $I_{\text{test}}, I_{\text{test}} \leq 100\text{ AC} = \frac{I_{\text{test}} \cdot \Delta t}{0.9(V_r - V_{\text{drop}}) - 0.7(V_r - V_{\text{drop}})}$	IEC 62,391	Bounce back at end of charge/discharge (5 s) or calculating from the voltage drop at 10 ms and linear extrapolation to $t = 0$ to get IR drop Bounce back after a current-cut in the middle of charge/discharge (5 s)	EDLCs: 0 Hybrid SCs: $\frac{1}{2}V_r$
Sech SA [38]	$I = C \cdot 75\text{mA}/F$, $I \leq 100\text{ AC} = \frac{I \cdot (t_2 - t_1)}{V_r - V_{\text{IR drop}} - 0.5V_r}$	0		0
MuRate [39]	$I_{\text{ch}} = 500\text{mA}$ $I_{\text{dch}} = 100\text{mA}$ $C = \frac{I \cdot (t_2 - t_1)}{0.8V_r - 0.4V_r}$	Constant voltage charge at V_r for 30 min	ESR are measured by EIS 1 kHz method	0

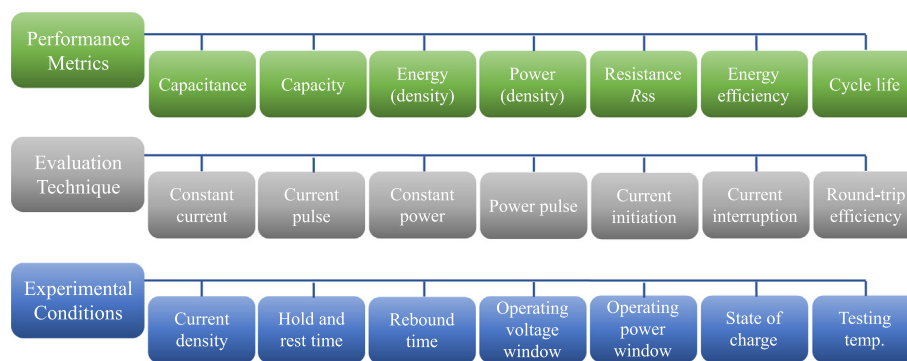


Fig. 4. A schematic representation of performance metrics and evaluation techniques for ECs.

This concept was discovered by the German physicist, Hermann von Helmholtz in 1853 [13]. He postulated the charge storage mechanism of the electrical double layer, which generated an electrical potential across the layer. The electric field in a double layer forces the diffusion of ions into the micro-porous electrodes. This kinetic behavior gives rise to a high-rate ion transfer in the thin double layer. The charge/discharge of the EDLC exhibits a quasi-triangular galvanostatic (GCD) profile and a near rectangular-shaped cyclic voltammogram (CV) due to the fundamental nature of the electric double-layer charge storage mechanism. One hundred years later, double-layer capacitance and the charging/discharging mechanism was demonstrated in a cell and patented by H. I. Becker at General Electric Company in 1957 [14].

The earliest commercial EDLC was developed by the Standard Oil Company of Ohio who licensed the technology to a Japanese Corporation NEC in 1971 for computer memory applications [15]. NEC marketed the devices under the name “supercapacitor”, and accordingly this term is utilized commonly in Asian area. In North America, the EDLC is often referred to as an “ultracapacitor” following the Pinnacle Research Institute (PRI) who coined the brand-name “PRI ultracapacitor” to highlight the high-power performance of the EC devices developed in 1982 [16]. This device, referred to as a pseudo-capacitor, utilized ruthenium oxide in the electrodes. The development history of ECs is shown in Fig. 1. (Note: Although the term “supercapacitor” and “ultracapacitor” are widely used in the literature, they are not referred to an electrochemical energy storage technology. Part of the reason why they appear frequently in the scientific literature is the purpose of keeping in line with the majority of the current literature. But these terms are generally referred to by the term “ECs”).

Over the past decade, most of the research on ECs has been directed toward increasing their energy density [18–23]. In general, this research has involved developing electrode materials

with high specific capacitance (F/g) and increased cell voltage approaching 4 V. These materials utilize pseudo-capacitance in transition metal oxides or doped conductive polymers to achieve large improvements in specific capacitance compared to the activated carbon used in EDLCs. Large increases in the cell voltage will probably require the use of ionic liquid electrolytes. Another approach to achieving higher voltage is the hybrid-structured capacitor, which consists of one electrode using a pseudo-capacitive or Faradaic material, and one electrode using activated carbon. The increased cell voltage results from the higher voltage at the Faradaic material electrode. Presently, there are a wide range of materials being studied for use in ECs. The classification of these materials based on their storage mechanism are shown in Fig. 2. Obviously, the challenges of reliably evaluating the performance of various advanced devices that have still need to be cleared up for establishing more sophisticated criteria for electrochemical energy storage devices.

As discussed above, ECs have been extensively studied using advanced electrode materials and cell structures. Significant improvements have been made by researchers and scientists in increasing the energy storage performance, especially in terms of energy density and power capability. The trend of energy content and power performance for rechargeable batteries (Li-ion) and ECs are illustrated in Fig. 3. It can be seen that the energy and power performance of both batteries and ECs in value have greatly improved from early 1990. It should also be noted that when improving the energy level of electrochemical energy storage systems, it usually comes at the cost of losses in power performance. As a result, electrochemical energy storage systems with higher energy densities often exhibit a relatively low power capability. Furthermore, outstanding performance (F/g) reported for electrode materials not hold up an excellent energy and power performance (Wh/kg, W/kg) after fully packing at the device level because the

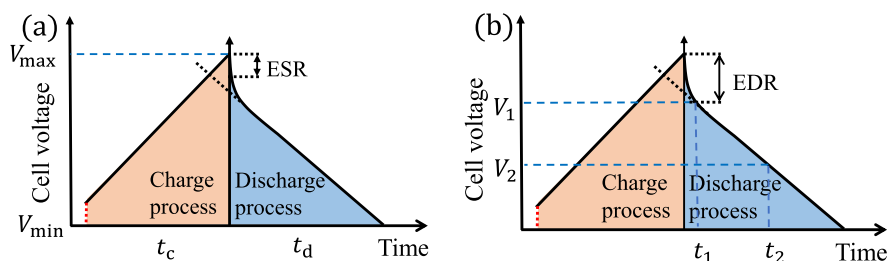


Fig. 5. Schematic representation of constant current profile for a typical capacitive EDLC device in which (a) the equivalent series resistance (ESR) resulted from the effect of IR drop and (b) the equivalent distributed resistance (EDR) determined according to IEC Test procedure [28,29] are illustrated (Note: IEC Test procedure: a. The voltage–time profile is measured under galvanostatic charge–discharge (GCD); b. The straight-line approximation to the voltage drop at the initiation of the discharge is determined based on the start voltage $0.9(V_T - V_{IR})$ and the end voltage $0.7(V_T - V_{IR})$, which is applied with the use of the least square method.

Table 2

Comparison of the capacitance of EDLCs determined using different operating voltage window.

Device	Nominal capacitance (F) ^a	Capacitance (F) 0.9V _r – 0.7V _r	Capacitance (F) V _r – 0.5V _r	Capacitance (F) V _r – 0
Skeleton	3200	3217	3202	3176
Nesscap	3000	3198	3176	3150
Maxwell	3000	3186	3151	2998
DAE-China	1400	1435	1421	1403
Yunasko(16 V module)	200 (1200F*6 S) ^b	201	198	188

^a Capacitance is acquired at 60C (60 s) discharge rate;^b The module comprises 6 cells connected in series.

mass loading, thickness and density of the electrode active materials and other cell components need to be taken into account. Only when proper performance metrics and evaluation methods are used is there an actual performance for practical applications.

The energy density shown in the plots are determined using the constant power test at 60C (1-min) for ECs and at 150 W/kg for batteries. The power capability is determined using the efficient power calculation at 95% energy efficiency for ECs, as given in Equation (11) and at 90% energy efficiency for batteries, as given in Equation (10). The performance parameters are for commercial devices and fully packaged laboratory proto-type cells. For more detailed information of various electrochemical energy storage systems/cells, some literatures reporting on the actual device performance by the authors may need to be revisited [8,9,24,25].

3. Performance evaluation and test procedures for ECs

In order to reliably evaluate the performance of electrochemical energy storage devices, a series of criteria are developed to characterize and test ECs worldwide. The test procedures are primarily for large commercial devices and utilize the DC charge/discharge approach to testing. Test procedures are summarized in Table 1 for the DOE/USABC (United States Advanced Battery Consortium) Test Procedure [26,27], IEC (International Electrochemical Commission) Test methods [28–30], SII NWIP (the standards institution of Israel) [31], the Chinese official testing method on Ultracapacitor for electric vehicles [32], ITS-UC Davis (Institute of Transportation Institute, the University of California-Davis, USA) [8–11] and several capacitor developers [33–39]. For the most part, these procedures were developed to test electric double-layer capacitors

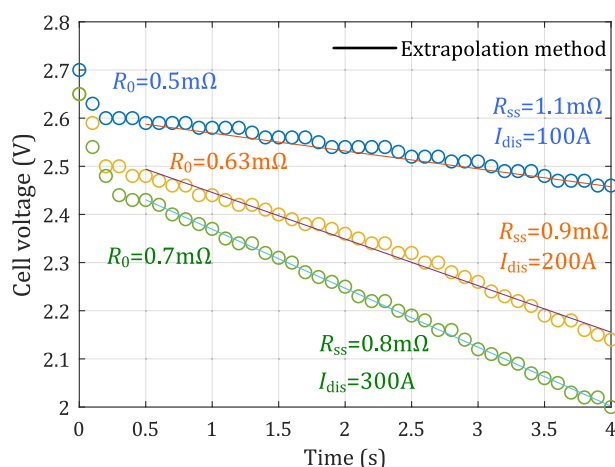


Fig. 6. Schematic illustration of the determination of resistance R_0 (equivalent to the resistance measured using USABC pulse characterization cycle, which is fully discussed in the supercapacitor book [11], that may be revisited) and R_{ss} for Nesscap EDLC/2.7 V/3000F at 100% SOC using current initiation method in a constant discharge process.

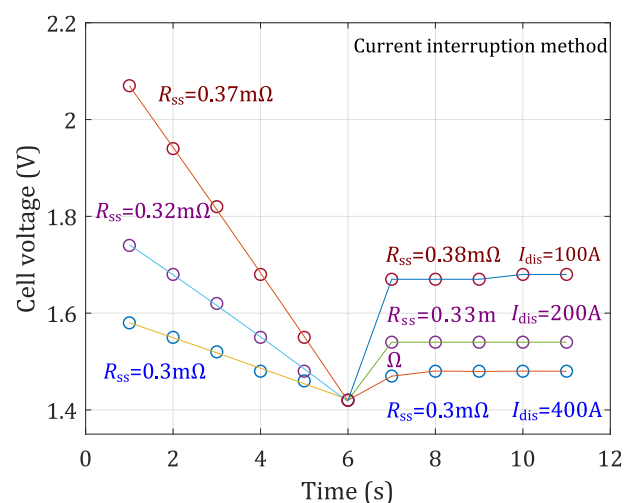


Fig. 7. Schematic illustration of the determination of resistance R_{ss} using current interruption method for Ioxus EDLC/2.85 V/3000F at 60% SOC in a constant discharge process.

(EDLC) using activated carbon and they are used to test relatively large devices currently being marketed. Little consideration to date has been given to adapting these procedures to testing hybrid capacitors. The present test procedures are intended to yield single values for the capacitance, resistance, energy and power characteristics of the device and little information on how these metrics change with test conditions. There is a need for standard methods for testing ECs over a range of test conditions and for testing devices that are still under development.

In many cases, the energy stored in an EDLC device is obtained based on the expression $E = 1/2 CV^2$ and the power density of the cell/module is based on the expression $V^2/4R$ [2,10,11]. These simple relationships in general overstate the performance of EDLCs. The test procedures in Table 1 will in general yield a more realistic evaluation of the performance of EDLCs, but there can be significant differences in the performance inferred using different test procedures. Hence it can be important to know what test procedure was used to obtain the results shown on a specification sheet for a device. Hence, there is a need to standardize the evaluation procedures for determining the capacitance and resistance of devices and their energy density and power capability.

In this paper, the test procedures developed in the Vehicle Power Systems Laboratory at ITS-UC Davis are utilized. It is customary to utilize constant current and constant power discharge tests and pulse tests over a range of currents and powers. For ECs, charging is done using a constant current to the rated voltage of the device. From the constant current tests, the fundamental parameters C and R for the device are determined as a function of current. The discharge is usually terminated at one-half the rated voltage in the case of EDLCs. The Wh/kg vs. W/kg and Wh/L vs. W/L (Ragone curves) are determined from the constant

power tests. For EDLC devices, resistance R_{ss} , termed the state-state resistance, is determined from the constant current discharge data for times after the micro-pores are fully engaged. A second resistance R_0 is determined from the pulse tests from the voltage step at $t = 0$ after the pulse is initiated. The difference between R_0 and R_{ss} is due to charge redistribution in the micro-pores. The general philosophy of the performance evaluation is to reliably evaluate the performance of ECs in terms of capacitance, resistance, energy and power performance based on the voltage and temperature limits set by the cell developers or the device manufacturer. A schematic illustration of the performance metrics and characterization techniques that are developed at UC Davis are shown in Fig. 4.

3.1. Performance evaluation for carbon/carbon double layer capacitors

This section of the paper will focus on testing capacitive EDLC devices. The charge/discharge of these devices is the simplest to understand and to interpret the test data. A glance at Table 1 will reveal that there are variations in the test procedures used by various groups, but in general, the effect of the differences on the measured device metrics are not large. In some cases, these differences will be noted in the following discussions of test data.

3.1.1. Capacitance

The charge storage mechanism in the carbon-based EDLC is based on the accumulation of static charge within the double layer. The capacitance varies only slightly with voltage due to the operating voltage of capacitive EDLC changes linearly with time during the charge/discharge process. The cell capacitance can be expressed as (Fig. 5a):

$$C = \frac{\Delta Q}{\Delta V} = \frac{I \Delta t}{V_{\max} - V_{\min} - IR} \quad (1)$$

in which, $V_{\max} - V_{\min}$ is the operating voltage window of the device. For a typical carbon/carbon capacitor based on the capacitive non-Faradaic charge storage, it can be fully discharged to zero. However, for a hybrid capacitor showing a Faradaic charge/discharge behaviour, the operating voltage window will have a great effect on the performance values as well as the cycle life of the device. As an alternative, C can be calculated from the following general expression (Fig. 5b).

$$C = \frac{I \Delta t}{\Delta V} = \frac{I(t_2 - t_1)}{V_1 - V_2} \quad (2)$$

It can be seen from Table 1, there is no commonly accepted methods for setting the current density and operating voltage window to obtain the effective capacitance C_m of the device. The effect of the voltage limits on the capacitance is relatively small as shown by the data presented in Table 2. For most carbon/carbon capacitors, it was found that the results are consistent with the trend shown in the Table 2.

Table 3
Power performance for the cylindrical-type Maxwell EDLC/2.7 V/3000 F^a.

Power (W) ^b	W/kg	Time (s)	Wh	Wh/kg	C _{eff}
63	115	135.3	2.349	4.27	3092
102	186	82.7	2.332	4.24	3070
201	365	40.8	0.2.278	4.14	2998
301	547	26.5	2.216	4.03	2917
400	727	19.4	2.156	3.92	2838
500	909	15.1	2.097	3.81	2760

^a Weight of device: 0.55 kg;

^b The operating voltage window is from 2.7 to 1.35 V.

3.1.2. Resistance

Resistance of an electrochemical energy storage device is an important parameter, which symbolize the speed at which the device can be charged or discharged. This is one reason why EDLC often exhibit high rate/power capabilities, whereas pseudocapacitive and battery-type materials typically suffer from high internal resistance, often result in a low power performance. Currently, a number of metrics and characterization techniques are widely used worldwide, including cyclic voltammetry (CV), constant current charge/discharge (i.e. galvanostatic charge/discharge) and electrochemical impedance spectroscopy (EIS). In the case of ECs at the device level, the constant and pulse current test has a particular advantage in determining the resistance of the device, especially for the calculation of power performance of the EC. One effective method proposed by ITS-UC Davis is using the voltage drop of the $v \sim t$ curve at the initial of the discharge. This approach yields a resistance value close to EDR based on the IEC test procedures, which can be referred to as the steady-state resistance R_{ss} after the device in its fully steady state to gain reliable information. The determination of R_{ss} can be based on machine learning using linear regression analysis of the $v \sim t$ data. The least square estimation technique can be given by:

$$\Phi(A, B) = \sum_{i=1}^n (y_i - A - Bx_i)^2 \quad (3)$$

Setting the initial values of partial derivatives involving parameter A and B equal to zero:

$$\frac{\partial \Phi}{\partial A} = 2 \sum_{i=1}^n (y_i - A - Bx_i) = 0 \quad (4)$$

$$\frac{\partial \Phi}{\partial B} = 2 \sum_{i=1}^n (y_i - A - Bx_i)x_i = 0 \quad (5)$$

where parameter A and B can be determined using the $v \sim t$ data points under a sampling period of 0.1 by the expressions shown in the Equation (4) and (5). One example using this method is illustrated in the Fig. 6, in which the resistance R_{ss} can be obtained by

$$R_{ss} = \frac{V_r - A}{I_{dch}} \quad (6)$$

The resistance of an EC can also be determined using the $v \sim t$ data at the end of a charge or discharge current pulse at when the electric current flows through the device is zero (Fig. 7). The current interruption is an effective approach in this case. However, it can be seen from Fig. 7 that the voltage of the cell does not react immediately, which in general takes some seconds to reach a steady-state condition ($I = 0$). Experience has shown that the resistance determined using the test data at about 2 s after the current interruption will be consistent with the value that determined using the current initiation method. The expression of current interruption method can be given by:

Table 4Power performance for the prismatic-type Skeleton Tech. EDLC/3.4 V/3200 F^a.

Power (W)	W/kg ^b	Time (s)	Wh	Wh/kg	Wh/L	C _{eff}
106	265	123.1	3.62	9.05	12.8	2996
201	503	64.9	3.62	9.05	12.8	2996
301	753	42.4	3.55	8.88	12.5	2938
400	1000	31.1	3.46	8.65	12.2	2863
500	1250	24.3	3.38	8.45	11.9	2797
600	1500	19.8	3.3	8.25	11.6	2731

^a The operating voltage window is from 3.4 V to 1.7 V, cell weight: 0.4 kg;^b (W/kg)_{95%}=1730, (W/L)_{95%}=2436 based on the Equation (11).**Table 5**Capacitance, energy and power performance the pouch-type Yunasko EDLC/ 2.75 V/1200 F^a.

Current ^b (A)	Time (s)	Capacitance (F)	Steady-state R (mOhm)	Power (W) ^b	Power density (W/ kg)	Time (s)	Stored Energy (Wh)	Energy density (Wh/ kg)	C _{eff} (F) ^c
30	57.3	1273	-	102	464	35.6	1.01	4.59	1269
60	29.1	1293	-	152	690	24.0	1.01	4.59	1280
100	17.8	1290	-	200	909	18.1	1.01	4.59	1270
150	12.0	1281	0.10	250	1136	14.5	1.01	4.59	1274
250	7.15	1276	0.08	300	1364	12.0	1.00	4.55	1268
300	5.8	1261	0.10	350	1591	10.3	1.00	4.55	1272
350	5.0	1268	0.11	400	1818	9.0	1.00	4.55	1272

^a Weight of the device: 220 g as tested;^b The operating voltage window is from 2.75 to 1.375 V;^c C_{eff} = 2(W-sec)/((2.75-IR)² -(1.375)²).**Table 6**

Comparison of the power characteristics for a number of high-power batteries and ECs.

Devices	Capacity/Capacitance	Matched impedance	USABC method	PowerEF = 95%
Lithium batteries 60% SOC				
Kokam NCM	30 Ah	2893	2502	550
Enerdel HEV NCM	15 Ah	5491	4750	1044
Enerdel EV NCM	15 Ah	2988	2584	568
EIG NCM	20 Ah	2688	2325	511
EIG FePhosph.	15 Ah	2415	2035	458
Alaimano LiTiO	11 Ah	2088	1750	350
Alaimano LiTiO	3.8 Ah	5225	4385	992
ECs V ₀ = 3/4V _{rated}				
Maxwell	2890F	8836	4413	994
Nesscap	3100F	8730	4360	982
Batscap	2700F	18,224	9102	2050
ApowerCap	450F	22,838	11,406	2569
LSCable	3200F	12,446	4609	1038
JSR	2000F	9228	6216	1400

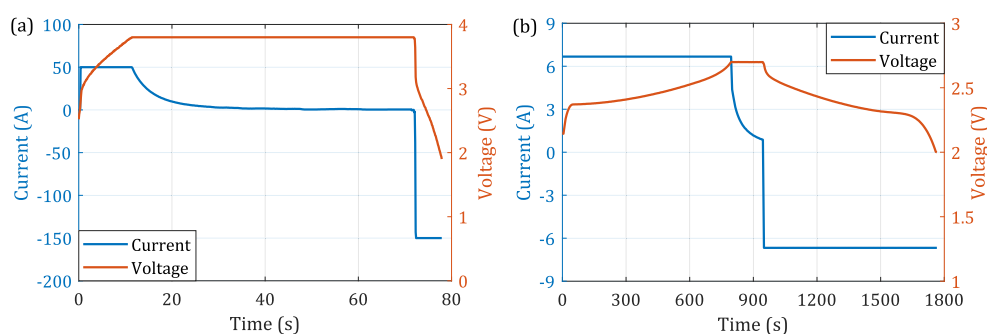


Fig. 8. Cell voltage as a function of the current in a typical constant current charge/discharge process. (a) An asymmetric EC using composite electrode (activated carbon with graphite for lithium intercalation) in one electrode (DAE-China/3.8 V/900F). (b) A hybrid EC using composite electrode (activated carbon mixed with metal oxides) in both electrodes (Yunasko/2.75 V/8000F).

$$R_{\text{reb}} = \frac{(V_{\text{reb}} - V_{\text{I=0}})}{I_{\text{dc}}} \quad (8)$$

3.1.3. Energy density

The stored energy E_{cap} in a capacitor is related to the work conducted to charge up the capacitor with a charge Q . The expression for this reaction can be given by:

$$E_{\text{cap}} = \int V dq = \int_0^Q \frac{Q}{C} dq = \frac{Q^2}{2C} = \frac{1}{2} CV^2 = \frac{1}{2} QV \quad (8)$$

in which V is the voltage between the positive and negative terminal of the capacitor in volts, Q is the stored charge flows through the capacitor in Coulombs, C is the capacitance in Farads. This expression is also useful to calculate the energy of an EC. For a typical EDLC, the resulting value using Equation (8) is equivalent to the maximum energy that can be stored in the cell. But from a practical point of view, the voltage of the device drops quickly during the discharge process due to the absence of discharge voltage plateau that evidenced with a relatively constant voltage in charge–discharge profiles for a typical rechargeable battery. As a result, once the voltage drops below 50%, the remaining energy in the cell that amounts to 25% of the total energy is essentially unusable. Thus, the energy density of the device can be generally represented as:

$$\begin{aligned} \text{Energy Density} &= \frac{1}{2} C_{\text{eff}} V_r^2 \left(1 - \frac{V_{\text{min}}^2}{V_r^2} \right) \cdot \frac{1}{\text{Wt. or Vol.}} \\ &= \frac{3}{8} C_{\text{eff}} V_r^2 \cdot \frac{1}{\text{Wt. or Vol.}} \end{aligned} \quad (9)$$

where wt./vol. is the mass/volume of the device. This expression is an effective approach to evaluating the energy density of ECs. Unfortunately, it is an accurate way only for a relatively low current and power densities. For some high-power applications, it will overestimate the energy that an EC stores/delivers. In this regard, the only reliable method to precisely determine the energy storage of an EC is to conduct a set of constant power experiments over a range of power densities. In general, power densities in the tests between 100 and 1000 W/kg are reasonable range. Typical experimental data for capacitive EDLCs are shown in Table 3 and 4. Experience has shown that the Equation (8) will overestimate the stored energy of an EDLC by at least 10% for operation of the device at high power applications, equivalent to a power density of 100–200 W/kg.

As shown in Table 3 and 4, the effective capacitance C_{eff} of an EDLC decreases as the current density or power density increases. The EDLC cell from Skeleton Technologies exhibits outstanding power capabilities with no sacrifice in energy density. It achieves an energy density of 9 Wh/kg with a power capability of 1730 W/kg at 95% efficiency (matched impedance power: 15.4 kW/kg). The excellent energy and power performance can be attributed to the fabrication of carbon/graphene electrode with

an enhanced capacitance and improved cell voltage from 2.7 V to 3.4 V.

3.1.4. Power capability

There is much confusion and uncertainty regarding the power performance of electrochemical energy storage devices, which makes their comparisons for practical applications difficult. The definition and determination of the pulse power performance are not as straightforward as the case of constant power capability. This is because the pulse power performance depends heavily on the state of charge (SOC) during the current or power pulse. The voltage change is a reflection of the energy efficiency of the pulse ($EF = V_{\text{pulse}}/V_{\text{oc}}$). In the case of an EDLC capacitor, the voltage would vary during the charge/discharge process due its capacitance even if the resistance of the device was zero. This makes direct measurement of the efficiency of a power pulse for a capacitor difficult and uncertain. Hence it is more reliable to calculate the power capability from the expression:

$$P_{\text{density, bat}} = EF(1 - EF) \cdot \frac{V_r^2}{R} \cdot \frac{1}{\text{Wt. or Vol.}} \quad (10)$$

in which, EF is the energy pulse efficiency in the charge storage process. If the power pulse of the capacitor is at $3/4 V_r$, Equation (10) becomes:

$$P_{\text{density, EC}} = \frac{9}{16} \cdot (1 - EF) \cdot \frac{V_r^2}{R} \cdot \frac{1}{\text{Wt. or Vol.}} \quad (11)$$

From a practical point of view, the power capabilities of rechargeable batteries and ECs should be compared on a normalized basis, which is at the same energy efficiency. The power capabilities of batteries and EDLCs are often quoted based on their matched impedance power ($P_{\text{MI}} = V_0^2/4R$). In this case, P_{MI} amounts to the power for an efficiency of only 50% and thus is not of much practical interest in most applications.

The pulse efficiency of the energy storage system is particularly important for high power-delivery requirements in industrial and transportation (vehicle) applications. For these cases, the useable power capability for an EC can be calculated from Equation (11). Hence high power devices must have a very low resistance. The power density (W/kg) is also proportional to (Wh/kg)/RC so a high power device will have a time constant of less than 1 s. Hence the RC time constant is another important metric for ECs. For discharge time durations of several RC time constants, the response of carbon-based EDLC devices can be described by a basic R-C circuit model. For pulses much shorter than the RC time constant, an equivalent circuit of multiple R-C ladders may be needed.

Test data for a very high power EDLC device are given in Table 5. This EC has a very low resistance (0.11 mΩ) and hence achieves a power capability of 8791 W/kg at 95% EF compared with about 1000–2000 W/kg for most capacitive EDLC devices. The time constant of the Yunasko device is 0.14 s.

Over the past decade, a variety of advanced ECs and high-power lithium batteries have been developed. The pulse power density

Table 7
Capacitance and energy density for JSR Micro /3.8 V/2000F hybrid capacitor^a.

Current (A)	Time (s)	Resistance (mohm)	Capacitance (F)	Power (W) ^b	Time (s)	Energy (Wh)	Energy density (Wh/kg)	Energy density (Wh/L)	C_{eff}^c
30	102.2	-	2004	102	88.3	2.5	12.1	18.9	1874
50	58.1	-	1950	151	56	2.35	11.4	17.8	1763
80	34.1	-	1908	200	40	2.22	10.8	16.9	1665
130	19.1	2.0	1835	300	24.6	2.05	10.0	15.7	1538
200	11.1	1.9	1850	400	17	1.89	9.2	14.4	1418
250	8.2	1.84	1694	500	12.5	1.74	8.5	13.3	1305

^a Cell weight and volume 206 g, 132 cm³;

^b $P_{\text{EF}} = 9/16 \times 0.05 \times (3.8)^2 / 0.0019 = 214 \text{ W}$. 1038 W/kg. $R_{\text{ss}} = 1.9 \text{ m}\Omega$;

^c $C_{\text{eff}} = 2(W \cdot s) / ((3.8)^2 - (2.2)^2) \text{ F}$.

Table 8
Capacitance and energy density for DAE-China/3.8 V/900F hybrid capacitor^a.

Current (A) ^b	Time (s)	Capacity (Ah)	Capacity (As)	Capacitance (F)	Power (W) ^b	Time (s)	Energy (Wh)	Energy density (Wh/kg)	C _{eff}
15	104.6	0.44	1569	867	40	80.3	1.08	12.38	718
30	47.3	0.39	1419	802	80	44.3	0.98	11.32	652
50	26.2	0.36	1310	749	120	28	0.93	10.73	618
75	15.8	0.33	1185	765	175	18.6	0.90	10.39	598
100	10.5	0.29	1050	738	250	11.8	0.82	9.42	545
150	6.2	0.26	930	705	350	7	0.68	7.82	452

^a Laminated pouch cell weight 87 g;

^b Constant discharge from 3.8 V to 1.9 V.

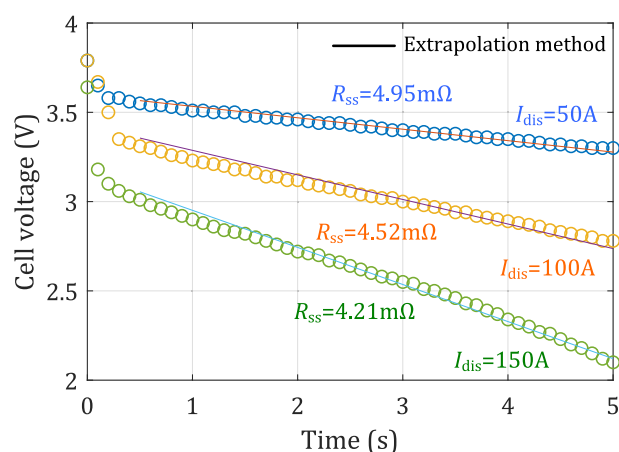


Fig. 9. Schematic illustration of the determination of R_{ss} using current initiation method for the DAE/3.8 V/900F hybrid capacitor at 100% SOC (Note: It can be seen that about 4 to 5 s test data are used in the determination of R_{ss} using linear regression analysis shown in the Fig. 6. and Fig. 9. Experience has shown that 4 to 5 s in the linear regression analysis in the determination of the steady-state resistance is a good indicator. This is because the R_{ss} is not very sensitive to the range of time, especially for electrochemical capacitors (EC). Generally, the resistance for various ECs is at the level of milliohm. Thus, the deviation between the values calculated from 4 and 5 s is negligible, especially for capacitive EDLC devices).

(W/kg)_{95%} for the batteries can be determined from Equation (10) and for the capacitors from Equation (11). The power capabilities of the batteries and ECs are compared in Table 6. Most of the capacitors have higher power than the batteries by a factor of 2–3, but only very low resistance capacitors like the Yunasko cell have power capability that is even 10 times higher than that of lithium batteries.

3.2. Performance evaluation for hybrid capacitors

The performance evaluation for carbon-based EDLC is discussed in the previous section. The charge storage mechanisms for those

carbon/carbon capacitors are based on the capacitive non-Faradaic charge storage (CNFS), exhibiting quasi-triangular and galvanostatic charge/discharge profiles and the voltage of the capacitor will change linearly with time. The test data demonstrate that the capacitances of those capacitive EDLC devices are insensitive to the increasing current density (Tables 3–5). This is because capacitive EDLC cells always have fast kinetics of electrode processes, showing a high rate capability and high power capability. In this section, test procedures in the performance evaluation will be considered for hybrid capacitors which use intercalation, pseudo-capacitive or battery-like electrode materials in one or both electrodes. The chemical and physical processes responsible for the reversibility of the electrode reactions for a hybrid capacitor are often complex. Nonlinear $v \sim t$ profiles for hybrid devices generally exhibit obvious potential plateaus, evidenced with the characteristics of rechargeable batteries (Fig. 8). Despite the remarkable progress made in the development of advanced electrode materials and in the understanding of the energy storage mechanisms of various electrochemical energy storage systems, their molecular and kinetic aspects remain mostly unknown. Accordingly, performance evaluation for hybrid devices with Faradaic behavior will be more complex than those for capacitive EDLCs. Hybrid capacitors with asymmetric electrode materials would have a minimum discharging voltage below which little charge/energy is transferred.

The voltage output of some devices using pseudo-capacitive electrode materials (i.e. metal oxides) increases and decreases linearly as current flows (Fig. 8a), while some other pseudocapacitive materials, as well as hybrid systems (battery-type materials), exhibit nonlinear charge and discharge profile (Fig. 8b) with tiny sloping voltage plateau regions (remains relatively constant) in a particular potential window. These differences and characteristics will be discussed in this section with emphasis on how they influence performance metrics and test procedures. The characterization techniques and test procedures for evaluating the electrochemical characteristics of hybrid and pseudo-capacitive cells are basically the same as for capacitive EDLC ones. That is constant current, pulse current and constant power charge/discharge

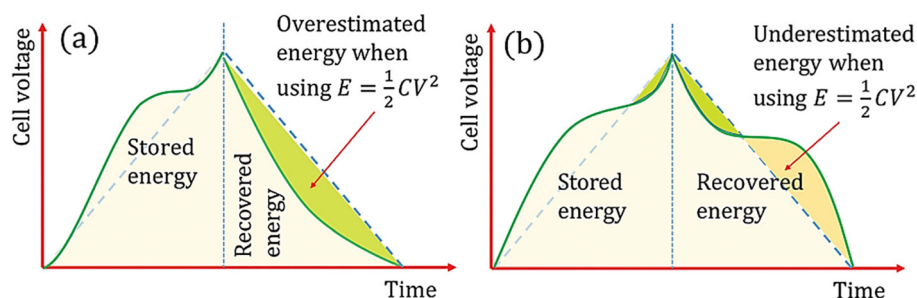


Fig. 10. Schematic illustration of galvanostatic charge/discharge profiles of a typical hybrid capacitor with capacitive Faradaic charge storage (CFS) and non-capacitive Faradaic charge storage (NCFS) processes. (a) The total energy of the cell will be underestimated if using the sample expression $E = \frac{1}{2}CV^2$. (b) The total energy will be overestimated if using the expression. Reproduced with permission from ref.[41], copyright 2019, The Royal Society of chemistry.

tests performed over a series of currents and powers. The current and power tests will be done in a way similar to that for EDLC devices, but the resulting data on the capacitance, resistance, energy and power performance of cells may vary significantly.

3.2.1. Capacitance/charge capacity

As discussed in the last section, for a capacitive EDLC system, the $v \sim t$ profiles exhibit a linear variation in voltage with time in a constant current discharge process. Thus, the capacitance of the cell can be given by:

$$C = \frac{\Delta Q}{\Delta V} = i \frac{\Delta t}{\Delta V} \quad (12)$$

However, for a pseudo-capacitive or hybrid cells, the value calculated from the capacitance definition $\Delta Q/\Delta V$ is not always the capacitance of the devices. This is because the term capacitance in Farads is not an appropriate term to characterize a hybrid or pseudo-capacitive device. In this regard, for hybrid devices and asymmetric ECs with an obvious non-linear $v \sim t$ profile, the Equation (12) should be rearranged as:

$$C = \frac{i}{dV/dt} \quad (13)$$

The capacitance of hybrid energy storage devices with Faradaic charge storage mechanisms can be derived by integrating the above relationship [40]. Thus, the capacitance of these cells can be calculated from:

$$C = \frac{2 \cdot i \cdot \int v dt}{V_i^2 - V_f^2} \quad (14)$$

The voltage (IR) drop at the initiation of discharge should be accounted for in setting the initial voltage for the calculation of C . For some hybrid capacitor devices, the $v \sim t$ profiles are highly non-linear and the voltage bounds must be taken into consideration to avoid major damage to the Faradaic electrode materials involved. In the measurement of capacitance (F) or capacity (Ah), the cut off voltage will differ for each of the electrode material components fabricated in the cell and discharge is not permitted below the minimum discharging voltage.

The electrochemical characteristics of several hybrid and pseudo-capacitance ECs are shown in Table 7 and 8. It can be seen that the energy density of the hybrid capacitors decreases much faster than capacitive EDLC cells as the current or power increases. This can be attributed to their higher resistance and slower reaction kinetics, especially if the reactions are driven at high current/power rates. This makes a set of constant power tests for hybrid capacitors particularly important.

3.2.2. Resistance

The resistance of hybrid capacitors can be measured using the same characterization technique and procedures as discussed in the section on the performance evaluation for EDLC. The steady-state resistance R_{ss} is the most appropriate metric for evaluation of pulse power characteristic of electrochemical energy storage devices. The current initiation method for determination of R_{ss} of a hybrid capacitor in constant current discharge profiles are shown in Fig. 9. It can be seen that the voltage is extrapolated to the initiation part of a discharge profile to determine the initial voltage (IR) drop and the steady-state resistance. For this hybrid cell, the resistance measured from the current interruption method are in good agreement with that from the current initiation method. In general, the resistances of the hybrid cells using Faradaic materials are higher than those for capacitive carbon/carbon capacitors of comparable capacitance.

3.2.3. Energy density

The demand for industrial and vehicle applications with elevated electrical energy and power capabilities has driven the development of pseudo-capacitive and hybrid capacitors. The energy stored in an EC with an obvious Faradaic charge storage behavior can be given by:

$$E_{\text{stored}} = \frac{1}{2} C_{\text{eff}} (V_{\text{rated}}^2 - V_{\text{min}}^2) \quad (15)$$

in which C_{eff} is the effective capacitance of the device which will vary with discharge rate. For EDLC systems, $1/2V_{\text{rated}}$ is a reasonable voltage bound for V_{min} and then C_{eff} will be essentially a constant. C_{eff} has been calculated for capacitive carbon/carbon devices in Table 3–5, and for hybrid cells in Table 7 and 8. The data shown in these tables demonstrate that the C_{eff} approximation and the basic expression $E = 1/2CV^2$ is valid to determine the energy density of the capacitive EDLC cells at low current/power densities, but not suitable for hybrid capacitors with Faradaic charge-transfer via redox reactions. As a result, the best approach to determining the energy density of hybrid capacitors is carrying out a set of tests over a wide range of power/current densities. The basic relationship ($1/2CV^2$) could result in either an overestimation or an underestimation of the energy that a hybrid capacitor stores (Fig. 10), although the former proves far more common. For capacitive EC cells, as can be seen in the Table 3–5, 7 and 8, energy density slightly decreases with increasing power density resulted from the effect of IR drop and intrinsic kinetics, but it drops much more sharply for hybrid capacitors.

3.2.4. Power capability and cycle life

The power performance of hybrid capacitors can be determined using the same expression used for capacitive EDLCs when the cell voltage and the pulse resistance of the cell are known. Hybrid capacitors based on fast redox reactions can achieve much higher capacitance, capacity and energy density than EDLCs. However, they often demonstrate a relatively low power performance and limited cycle life resulted from poor electrical conductivity and sluggish ion diffusion. In general, ECs can undergo at least thousands to millions of cycles. Thus, it seems particularly burdensome to directly determine the cycle life (below 80% of the beginning-of-life) value of ECs, especially for capacitive EDLC devices. The limited information available about the cycle life of hybrid capacitors is from the manufacturers and it demonstrates excellent cycling stability. The test data shown that JSR Micro hybrid capacitors (Table 7) achieves an excellent pulse power performance, which is as good or even better than most capacitive carbon-based capacitors and an ultra-long cycle life of 500 k to 1000 k, which is comparable to that of EDLC devices. Experience has shown that these outstanding performance and mechanical stability for a hybrid capacitor that undergoes Faradaic electron transfer reactions are an exception even for the one that fabricated with activated carbon one electrode. In the case of the Aowei Tech. hybrid capacitor cells, they claim 1000 k cycles when the operating voltage window is between 3.8 and 2.8 V, and 50 k cycles can be achieved when the operating voltage window is between 4.05 and 2.8 V [42]. The cycle life data cited above indicate it is possible to achieve cycle life in hybrid capacitors comparable to EDLCs, but third-party validation of the life cycle testing of these hybrid capacitors is clearly needed.

4. Analysis of the performance of cells using advanced materials

Much research has been done since 2010 on advanced electrode materials and nanostructure cell architectures that show the potential for greatly improving the energy density of the ECs. However, few of the advanced materials or cell designs have become

commercially available or even considered for serious development. As discussed previously, JSR Micro has marketed a hybrid Li-ion capacitor with an energy density of 10–12 Wh/kg and Yunasko has developed proto-type devices using mixtures of activated carbon and metal oxides in both electrodes. The energy density of the Yunasko devices is 25–30 Wh/kg. Skeleton Technologies has developed a cell that uses a mix of activated carbon and graphene in both electrodes. The energy density of that cell was 8–9 Wh/kg, but it was not offered for sale because of cost considerations. The characteristics of these three devices have been discussed in detail in previous sections of the paper. Nippon Chem-Con and researchers at Tokyo University of Agriculture and Technology in Japan have been developing an EC using nano-LTO in the negative electrode since 2010 [43,44], but the device has not been commercialized. The energy density of the Nippon Chem-Con cell is reported to be about 30 Wh/kg. All of these cells have energy densities significantly higher than commercially available devices.

As noted above, there has been much research on advanced materials for ECs over the past decade and there is considerable uncertainty concerning the potential improvements in energy density that could be achieved if those advanced electrode materials were used in cells developed for commercialization. As a result, this section is intended to determine the performance of the EC based on the physical dimensions (area, thickness, and porosity) of the electrodes, the properties of the material (specific capacitance, density, and electrical conductivity), the properties of the electrolyte (ionic conductivity, density, voltage windows for the materials in the electrodes), and the expected electrode operating voltages. Key of these parameters are known from tests of electrodes and cells like those discussed in earlier sections of the paper. The object of the analysis is to estimate/project whether materials, electrode, or cell characteristics determined in testing of small electrode samples and small cells can be used to design and develop advanced ECs with high energy density, high power capability, and long cycle suitable for commercialization. This section of the paper outlines the method of calculation and gives a selected set of advanced EC performance results as examples of applying the method.

4.1. Cell design description and modeling of the cell performance

As an example of cell design method, the case of a hybrid capacitor using battery-like electrode active materials is illustrated in detail. The method can be used for capacitive EDLCs and pseudo-capacitive cells using metal oxides, conducting polymers with nano-structured carbon-based materials in one or both electrodes. All the hybrid capacitor designs being taken into account in this section utilize carbon-based materials in at least one of the electrodes. The EC is designed such that the electrochemical charge transferred by separation of charge in a Helmholtz double layer and Faradaic charge-transfer via redox reactions between the electrodes during the energy storage processes is set by the charge capacity and potential change of the carbon electrode. The operating range in terms of depth of discharge (DOD) in the capacitor for the pseudo-capacitive or battery-like electrode should be taken into consideration in order to extend the cycle life such as is the situation in a battery. The cell voltage/operating voltage window of the hybrid capacitor is determined from the sum of the operating potential window of the carbon electrode and usable potential of the battery-like electrode in the electrolyte of interest. The performance estimated using the approach outlined yields an ideal estimate of the cell performance assuming all interfacial resistances between the electrode material and current collector are negligible. It is assumed that the resistance of the hybrid capacitor only is dependent on resistivity of the electrode material and the electrolyte including the mesopores in carbons.

Inputs: The properties of electrode material and physical dimensions of all device components utilized in the EC must be known. The important information for the carbon electrode is its thickness and the specific capacitance (F/g), volume density (g/cm³), and porosity (%). For the battery-like electrode, the key inputs are the specific charge capacity (mA·s/g), density (g/cm³), and electrode porosity (%). In the case of composite metal oxide and conducting polymer electrodes, the electrode characteristics will be specified by their specific capacitance as a function of A/g based on test data. The information about current collectors of the device are given in terms of their material (lead, copper, nickel, or aluminum) and thickness each side coated with electrode active material. The electrolyte is described in terms of composition (sulfuric acid, KOH, acetonitrile plus salts), volume density and specific electrical resistivity (mΩ·cm). The ion-permeable separator is described using its thickness and porosity. The initial cross-sectional area of the device can be measured on a 1 cm² basis.

Step 1: Measure the weight of the carbon electrode (W_{carbon}) and estimate the capacitance of that (C_{carbon}). On the basis of the voltage window of the electrode material (ΔV_{carbon}) and its capacitance, the charge transferred to the electrode by separation in a Helmholtz double layer during charge–discharge process can be expressed as:

$$\text{Chg} = C_{\text{carbon}} \times \Delta V_{\text{carbon}} \quad (16)$$

$$C_{\text{carbon}} = W_{\text{carbon}} \times (Fg^{-1}) \quad (17)$$

$$W_{\text{carbon}} = (th \times p \times A_{\text{cell}})_{\text{carbon}} \quad (18)$$

Step 2: An important constraint condition on the design analysis is that the charge transferred to the battery-like or pseudo-capacitive electrode must be equal to that transferred to the carbon electrode. The Faradaic electrode using battery-like materials will be matched such that to readily accommodate that charge, the change in the depth-of-discharge (DOD) of this electrode during the charge–discharge process should be smaller than 20%. The change in SOC is symbolized as $\Delta \text{SOC}_{\text{battery-like}}$. The weight of the battery-like electrode ($W_{\text{battery-like}}$) can be calculated as:

$$W_{\text{battery-like}} = \frac{\text{Chg}}{\Delta \text{SOC}_{\text{battery-like}} \times (mA \cdot sg^{-1})_{\text{battery-like}}} \quad (19)$$

Thus, the thickness of the battery-like electrode can be expressed as:

$$th_{\text{pseudoref}} = \frac{W_{\text{battery-like}}}{(p_{\text{battery-like}} \times A_{\text{cell}})} \quad (20)$$

In the case of a pseudo-capacitive electrode, the weight can be given by:

$$W_{\text{pseudoref}} = \frac{\text{Chg}}{(Fg^{-1} \times \Delta V_{\text{pseud}})} \text{for } (Ag^{-1})_{\text{ref}} \quad (21)$$

The thickness of the electrode is then calculated from:

$$th_{\text{pseud}} = \frac{W_{\text{pseud}}}{p_{\text{pseud}} \times A_{\text{cell}}} \quad (22)$$

It should be noted that the charge for the pseudo-capacitive electrode at different currents and power can be calculated using different values of specific capacitance corresponding to higher current density (A/g). In this case, charge for the cell will be set by the pseudo-capacitive electrode not the carbon electrode.

Step 3: The weight of the electrolyte involved needs to be estimated, which can be given by:

$$W_{\text{elypor}} = \sum (th \times A_{\text{cell}} \times \text{porosity} \times p_{\text{electrolyte}})_{\text{cellomp}} \quad (23)$$

Table 9

A summary of estimated energy and power performance of advanced electrode chemistries and electrolytes for EC technologies.

Electrode chemistry	Capacitance/capacity of the electrode	Electrolyte	Cell voltage	(Wh/kg) _{act}	(Wh/kg) _{cell}	(Wh/L) _{cell}	(W/kg) _{cell} 95% eff.	(kW/kg) _{act} Mat. impd.	Ohm-cm	RC
Symmetric carbon/carbon										
Activated carbon	150F/g	H ₂ SO ₄	1.0–0.5	3.9	0.9	1.9	4249	166.6	0.14	0.06
Activated Carbon	200F/g	Li ₂ SO ₄	1.6–0.8	13.3	2.21	4.8	706	37.7	1.2	0.84
Activated Carbon	80F/g	ACN	3.0–1.5	18.75	6.97	9.64	2171	51.9	2.4	0.87
Nano-carbon	210F/g	ACN	3.0–1.5	49.2	16.9	21.0	5353	138.0	1.1	0.86
3D carbon	300F/g	Ionic liquid	4.1–2.0	175	38.5	46.7	1855	75.1	7.8	4.2
3D carbon	300F/g	ACN	3.0–1.5	70.3	20.6	39.1	1950	59.2	2.5	2.8
Asymmetric graphite/hybrid										
Active carbon/Lithiate graphite	80F/g 370 mAh/g	ACN	4.0–2.0	96.8	35.6	55.1	6851	165.5	1.5	1.4
3D carbon/LTO carbon	300F/g 150 mAh/g	ACN	3.0–1.5	155.7	60.8	100.4	3962	90.3	1.5	4.2
3D carbon/Li graphite with Sic	300F/g 600 mAh/g	Ionic liquid [EMI][BF ₄]	4.1–2.0	356	74.1	157.8	4079	174.2	3.5	4.7
Asymmetric metal oxide										
Carbon CuO/Nano-graphene	950F/g 200F/g	KOH	1.6–0.8	26.5	12.2	30.1	2600	50.1	0.35	0.82
Carbon MgO/Nano-graphene	300F/g 210F/g	KOH	1.6–0.8	13.8	6.2	18.5	4171	82.6	0.26	0.26
Carbon CuO/3D carbon	950F/g 300F/g	Ionic liquid	4.0–2.0	271	83.4	316	1086	31.4	1.5	1.42
Asymmetric conducting polymer										
P-doped pMet/N-doped pMet	240F/g 180F/g	PC	3.0–1.5	65	24.1	44.6	2102	50.4	4.5	3.8
P-doped pMet/Act. carbon	240F/g 120F/g	PC	3.0–1.5	54.1	21.8	40.9	1009	22.2	0.8	1.8
Nanocarbon	800F/g 1 80F/g	Na ₂ SO ₄	1.6–0.8	53.4	15.3	29.4	1557	48.3	0.8	1.8
SnO ₂ /Activated carbon										
P-doped pMet/3D nano carbon	240F/g 300F/g	Ionic liquid	4.0–2.0	354	58.7	110.8	1866	100.1	3.6	1.88

The electrolyte weight used here is the sum of the weights of the electrolyte in each of the multi-layers of the cell component.

Step 4: The weight of the current collectors is given by:

$$W_{\text{current_collector}} = t_{\text{current_collector}} \times A_{\text{cell}} \times \rho_{\text{current_collector}} \quad (24)$$

Step 5: The cell weight is then determined using the weight of each component by simply adding up the weights of the cell components.

$$W_{\text{cell}} = W_{\text{current_collector}} + W_{\text{carbon}} + W_{\text{battery-like}} + W_{\text{electrolyte}} \quad (25)$$

Step 6: The total energy of the EC can be deduced simply from the energy stored in the carbon electrode when the voltage changes from V_{max} to $V_{\text{max}} - \Delta V_{\text{carbon}}$.

$$E_{\text{carbon}} = \frac{1}{2} C_{\text{carbon}} ((V_{\text{max}})^2 - (V_{\text{max}} - V_{\text{carbon}})^2) \quad (26)$$

A small amount of additional energy is discharged at the negative electrode due to small change there, but that energy is neglected. Thus, the energy density of the cell can be expressed as:

$$\left(\frac{Wh}{kg}\right)_{\text{cell}} = \frac{E_{\text{carbon}}}{W_{\text{cell}}} \quad (27)$$

This estimation method does not include the cell packaging weight, but it does include the weights of all the other components of the cell. The average power of the discharge can be expressed as:

$$P_{\text{avdisch}} = I_{\text{ref}} \times (V_{\text{max}} - \frac{\Delta V_{\text{carbon}}}{2}) \quad (28)$$

$$\left(\frac{W}{kg}\right)_{\text{cell}} = \frac{P_{\text{avdisch}}}{W_{\text{cell}}} \quad (29)$$

For hybrid capacitors using a pseudo-capacitive electrode, it will be the positive electrode and the carbon electrode will be the negative electrode. In this case there will be energy discharged

at both electrodes because there will significant voltage changes at each electrode. At the pseudo-capacitive electrode, the energy discharged will be:

$$E_{\text{pseud}} = \frac{1}{2} (Fg^{-1}) \times (V_{\text{max}})^2 \quad (30)$$

$$\Delta V = \Delta V_{\text{pseud}} \quad (31)$$

At the carbon electrode the energy discharged will be

$$E_{\text{carbon}} = Chg \times \Delta V_{\text{carbon}} \quad (32)$$

$$\Delta V_{\text{carbon}} = \frac{Chg}{C_{\text{carbon}}} \quad (33)$$

$$V_{\text{cellmin}} = V_{\text{max}} - \Delta V_{\text{pseud}} - \Delta V_{\text{carbon}} \quad (34)$$

The total energy discharged by the pseudo-capacitive cell can be expressed as:

$$E_{\text{totalpseud}} = E_{\text{pseud}} + E_{\text{carbon}} \quad (35)$$

$$\left(\frac{Wh}{kg}\right)_{\text{cellpseud}} = \frac{E_{\text{totalpseud}}}{W_{\text{cell}}} \quad (36)$$

$$P_{\text{avdisch}} = I_{\text{pseud}} \times (V_{\text{max}} - P_{\text{avdisch}}) = I_{\text{ref}} \times (V_{\text{max}} - \frac{\Delta V_{\text{pseud}} - \Delta V_{\text{carbonpseud}}}{2}) \quad (37)$$

$$\frac{W}{kg} = \frac{P_{\text{avdisch}}}{W_{\text{cell}}} \quad (38)$$

Step 7: The resistance of the cell can be given by:

$$R_{\text{cell}} = R_{\text{electrodes}} + R_{\text{sep}} + R_{\text{curcollector}} \quad (39)$$

The ionic resistivity of the electrolyte (Ω cm) in the porous electrodes can be calculated using the relationship:

$$R_{\text{elypor}} = (\Omega\text{cm})_{\text{electrolyte}} \times (\text{porosity})^{-1.8} \quad (40)$$

The areal resistance (Ωcm^2) of each porous electrode layer can be calculated by:

$$\Omega\text{cm}^2 = R_{\text{elypor}} \times \frac{th_{\text{electrode}}}{2} \quad (41)$$

The contribution of the solid material portions of the electrodes can be included by

$$W_{\text{cell}} = W_{\text{current_collector}} \quad (42)$$

The areal resistances of the ion-permeable separator and the current collector can be calculated in a similar way as shown for the cell resistance is then expressed as:

$$R_{\text{cell}} = \frac{(\Omega\text{cm}^2)_{\text{cell}}}{A_{\text{cell, total}}} \quad (43)$$

The total cell area would include the area of all cells overlaid in a pouch cell configuration. This method to calculate the cell resistance should be considered that of an ideal capacitor and the total resistance because it neglects all contact and the micropore resistances in the electrochemical device.

Step 8: The pulse power capability of the cell can be calculated based on the cell voltage and resistance using the relationship:

$$P_{\text{max}} = \frac{9}{16} \times (1 - EF) \times \frac{V_{\text{rated}}^2}{R_{\text{cell}}} \quad (44)$$

in which, EF is the pulse efficiency in the charge–discharge process.

Thus, the power density for the device design being analyzed is expressed as:

$$\left(\frac{W}{\text{kg}}\right)_{\text{max}} = \frac{P_{\text{max}}}{W_{\text{cell}}} \quad (45)$$

4.2. Performance calculations for selected ECs

The method has been implemented and applied to symmetric and asymmetric devices using advanced carbons, metal oxides and polymer composites in the electrodes, in terms of energy density and power characteristics of selected ECs using advanced active materials. The method can be applied to carbon/carbon EDLC and hybrid capacitors using appropriate material properties and estimated electrode voltages for each capacitor design. Note that the inputs for the calculations are based on available test data in the literatures [45–60]. Much of that data has been discussed in previous sections of this paper. All the results for the ECs analyzed are unpackaged devices, but all other weights and volumes are considered. The resistances do not include interface and micropore resistances, but all others are included. Results of the calculations for selected advanced ECs are shown in Table 9.

The results for the performance of the devices are given in terms of both the weight of active material in the cell and the total weight of the cell. The characteristics of small laboratory cells described in the literature are in most cases given in terms of the weight of the active material in the electrodes which significantly overestimates the energy density and power capability potential of cells fabricated using the materials being studied. However, the present projections of the performance (Wh/kg , Wh/L , and $\text{W/kg}_{\text{EF}=95\%}$) of the cells shown in Table 9 indicate that future development of ECs should yield devices with large improvements in performance compared those presently available. As expected, the energy densities Wh/kg based only on the weight of the active material in the cell are much higher than for the complete cell. The difference factor varies greatly dependent on the electrolyte

and cell voltage, but is greater than 3 in most cases. The Wh/L for the cell is the best indicator of the energy density of the cell in practical applications for the different advanced materials and electrolytes. On that basis, the calculated results indicate that it should be possible to develop ECs with Wh/L between 50–100 using organic electrolytes and even higher using ionic liquid electrolytes. The power capability ($\text{W/kg}_{95\%}$) of the hybrid cells using organic electrolytes are projected to be high in excess of 4 kW/kg , but the ($\text{W/kg}_{95\%}$) of asymmetric cells using metal oxides and polymers in the electrodes would be lower in the range of 1–2 kW/kg . Cells using ionic liquids are projected to have the highest Wh/L , but in most cases with power capability in the lower range. The energy density of cells using aqueous electrolytes could be as high as 25–30 Wh/L using advanced carbon and metal oxide composites.

5. Applications

Renewable and green energy applications have a great need for energy storage and thus, offer great opportunities for both batteries and ECs. ECs have been applied to a multitude of projects for transportation and industrial applications. In this section of the paper, the roles of ECs in selected large-scale applications are highlighted. At the present time, most of the major markets for ECs are for small devices (less than 10F) used in consumer and industrial electronics. In those applications, the energy density (Wh/L) of the available ECs is adequate and the high-power capability and very long life of the EDLC cells is key to their practical application.

5.1. Green transportation

ECs are considered innovative for the transportation energy storage technology taking advantage of their high-power performance, excellent cycle life and good working temperature range (Fig. 11). The most impressive projects involve public transit, such as electric and hybrid buses and electric trams [61,62]. Most of the ECs used in those projects were manufactured by Maxwell and Aowei. With the high energy density Aowei supercapacitor, energy storage systems of up to 50 kWh are practical. For car, truck, and bus applications with hybrid electric powertrains, ECs have been utilized especially for stop–go city driving for the following:

- Engine Start in stop–go hybrids
- Regenerative braking
- High Power Assisted propulsion
- Cold weather engine start



Fig. 11. All-electric tram with ECs of Shanghai Aowei Technology Development Co., Ltd. The energy storage unit can provide 300 A continuous charge/discharge current and 510 A maximum charge/discharge current [63].

5.2. Industrial applications

ECs can provide potential solution for energy storage in industrial applications, turning challenges into advantages [1,3]. They provide multiple benefits for industrial applications including forklifts, excavators, straddle-carriers, harbor/construction/mining cranes and earth-moving. In these lifting and hoisting applications, the electrical systems using ECs can enhance the lifetime of the equipment and minimize the downtime and maintenance costs in addition to reducing by a significant fraction the energy needed to operate it. In most cases, the primary motivation for using ECs in industrial applications is the energy cost savings resulting from regenerative energy recovery during dynamic power demand use cycles. ECs are an excellent supplement to the energy storage units with high energy density but only modest power capability, such as fuel cells and rechargeable batteries. Further benefit can be achieved using smaller-than-normal conventional internal combustion engines (i.e. gasoline engines, diesel engines or natural gas engines), owing to the peak power demands are no longer provided by the engine, which reduces CO₂ emission from the use of fossil fuels.

5.3. Renewable electricity generation and smart grid

Due to the need to reduce CO₂ emissions from electrical power generation, there has been a strong trend towards renewable power generation technologies (i.e. solar, wind and tidal energy), which have inherent intermittent production. ECs possess a number of advantages for these particular scenarios including excellent cycle life, high energy roundtrip efficiency and high-power delivery capability. In solar photovoltaic (PV) energy storage applications, the ECs can provide the frequency regulation while the rechargeable batteries meet the slower changing demand requirement. This will lower the cost of the battery storage unit and extend its cycle life. There are a number of grid battery/EC projects worldwide in the demonstration phase at the present [64–66]. In the case of wind power generation, adjustment of the angle of the blades of the wind turbine as the wind speed varies plays an important role in wind energy generation. The high power capability and very long cycle life of ECs makes them ideal for this application, which was one of the first large scale applications of ECs. That remains the case at the present time.

Smart grid, the next generation power grid, is an interconnected network of power distribution using digital technology and sustainable energy for power generation. It requires upgrades of energy storage, electricity transmission and distribution, which delivers not only electric but also intelligent information. In the case of the integration of smart grid technology, there exist a number of challenges referring to renewable energy integration, power quality control and smoothing strategy. ECs are an attractive solution to solve these challenges. They can deliver fast, reliable and high-efficiency electrical energy in a static-synchronous-compensator system, for which injecting or absorbing active and reactive power from the power grid, and thereby mitigate the impacts of voltage perturbations on the distribution bus to improve the power quality (Fig. 12). Specifically, the operation of EC storage devices for generation applications includes:

- Spinning reserve
- Power smoothing and frequency regulation
- Peak shaving and load leveling
- Renewable energy storage

5.4. Backup power and UPS

The selection of uninterruptible power supply (UPS) with back-up power devices is an important issue of great concern in case of

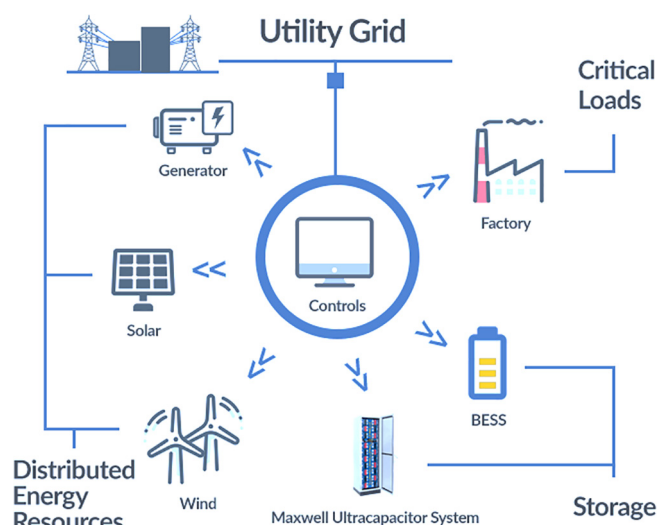


Fig. 12. Renewable generation and smart grid with battery–supercapacitor hybrid energy storage system [67].

fault conditions and emergency shutdowns [68,69]. UPS with rechargeable batteries as back-up devices are currently the primary approach to cope with grid interruption and blackout. However, batteries have limitations in terms of their long-term service time (cycle and calendar life) and pulse power capability. Hence, ECs are a promising solution to reinforce the performance of UPS system taking advantage of their high pulse power capability, high efficiency and very long service life. They can be used as a standalone backup energy source and provide power for 5 to 15 s for the situations where long periods of backup are not needed. Combined with renewable energy sources, battery-supercapacitors units can rapidly supply back-up power for seconds or hours.

6. Conclusions and future perspectives

This paper is concerned with the evaluation of ECs of all types from those presently on the market to advanced devices that could be developed in the future using advanced electrode materials and ionic liquid electrolytes. Metrics for characterizing the ECs are reviewed and their evaluation by testing available devices and by analysis for future ECs using advanced materials are considered in detail. Of particular interest are the energy density (Wh/kg and Wh/L) and the power capability (W/kg)_{95%} of present and future ECs.

Most available ECs are electric double-layer capacitors (EDLCs) using activated carbon in both electrodes and propylene carbonate or acetonitrile as the electrolyte solvent. These EDLCs have a rated voltage of 2.7–3 V and an energy density of 4–6 Wh/kg, 5–8 Wh/L and a power capability of 1–2.5 kW/kg. The variation in power capability between EDLC cells is much greater than the variation in energy density. The change in capacitance and resistance of EDLCs with discharge current (time) is not significant in most cases. Available test data indicates that by mixing graphene with the carbon the energy density can be increased to 8–9 Wh/kg with an increase in power capability. Test data in the literature for advanced microporous carbons indicate their specific capacitance can be increased to 200 or even 300 F/g, which would increase the energy density of EDLCs to 15–25 Wh/kg using acetonitrile and to 30–35 Wh/kg using an ionic liquid (IL) as the electrolyte. The power capability of the cells using IL would be lower in the range 1–1.5 kW/kg.

There are a limited number of advanced ECs on the market at the present time. They are all of the hybrid lithium-ion capacitor type using lithiated graphite in the negative electrode, activated

carbon in the positive, and an organic electrolyte. The cells operate between 3.8 and 2.0 V. The hybrid ECs available from JSR Micro have an energy density of 10–12 Wh/kg, 16–19 Wh/L and power capability of about 1.5 kW/kg. Their cycle life is over one million deep discharge cycles. The analysis of ECs using advanced materials indicate that the hybrid approach with one electrode of EDLC carbon results in the highest increase in energy density with good power capability of all the approaches available. Using advanced carbons ($F/g = 200$), energy densities of about 70 Wh/kg, 100 Wh/L with a power capability of 4 kW/kg are projected for hybrid lithium-ion capacitors. For hybrid ECs using graphene and LTO in the negative, energy densities of 40 Wh/kg, 65 Wh/L are projected. The hybrid EC with highest projected energy density used the advanced carbon in the negative and a metal oxide carbon composite in the positive with an ionic liquid electrolyte. The energy densities projected were 75 Wh/kg, 270 Wh/L, but the power capability was only about 1 kW/kg.

Testing of hybrid ECs to date indicate that their charge/discharge characteristics are predictable (voltage nearly linear vs. time for constant current) and their cycle life has been very long. It also seems clear that the development of advanced micro-porous carbons with specific capacitances of 200–300 F/g in organic and ionic liquid electrolytes is critical to success in achieving large improvements on the energy density of ECs. Recent papers in the literature offer encouragement that these carbons can be developed.

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.

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