

Practical and theoretical limits for electrochemical double-layer capacitors

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Abstract

Two types of double-layer capacitors, based on carbon materials, were analysed: (1) an imaginary nano-capacitor assembled from single graphene sheets, separated by electrolyte layers (thickness of nanometers) and (2) a capacitor based on porous carbons. It has been shown that the maximum specific surface of a porous carbon material which may be used for the construction of a capacitor is ca. $2600 \text{ m}^2 \text{ g}^{-1}$. The maximum energy density of an imaginary double-layer ‘nano-capacitor’, is close to 10 kJ kg^{-1} at a voltage of $U = 1 \text{ V}$ (aqueous electrolyte) of ca. $40\text{--}45 \text{ kJ kg}^{-1}$ at $U \approx 2.3\text{--}2.5 \text{ V}$ (organic electrolytes), and at the order of 100 kJ kg^{-1} at voltages close to 4 V (ionic liquids as electrolytes). The real device consists of porous electrodes and a separator, both soaked with the electrolyte, as well as current collectors. Consequently, the maximum electric capacity expressed versus the mass of the device (ca. $20\text{--}30 \text{ F g}^{-1}$), is much smaller than the corresponding value expressed versus the mass of the carbon material (ca. 300 F g^{-1}). In order to obtain the energy density of the device at a level of 100 kJ kg^{-1} (characteristic for the lead-acid battery), the capacitor with porous carbon electrodes should operate at voltages of ca. 4 V (ionic liquids as electrolytes). However, the specific power density of such a capacitor having an acceptable energy density (ca. 100 kJ kg^{-1}) is relatively low (ca. 1 kW kg^{-1}).

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1. Introduction

Electrochemical double-layer capacitors [EDLCs] (also called supercapacitors) have received much attention over the last decade due to their possible application as high-power energy-storage devices. EDLCs, based on high surface area activated carbons and aqueous, non-aqueous or polymer electrolytes, have been developed with promising results [1–3]. Batteries have higher energy density, but they suffer from low power density and low cyclability (usually <1000). EDLCs are characterised not only by higher power density but also by a much higher number of charge–discharge cycles (even 100 000).

Energy E stored in a capacitor is proportional to its capacity, C , as well as to the voltage U applied in the second power:

$$E = \frac{1}{2}CU^2 \quad (1)$$

while the maximum power P (energy delivered during time t) is independent of the capacity:

$$P_{\max} = \frac{E}{t} = \frac{U^2}{4R_s} \quad (2)$$

The resistance R_s which appears in Eq. (2) is mainly due to the resistance of the electrolyte contained both in the carbon material as well as in the separator. The electrolyte applied in lead-acid batteries (30 wt.% aqueous H_2SO_4) shows a conductivity at a level of ca. 730 mS cm^{-1} [4], while the conductivity of aqueous KOH (29.4 wt.%) solution, applied in alkaline batteries, is 540 mS cm^{-1} [4]. Non-aqueous solutions show much lower conductivity; for example, Et_4NBF_4 solution in acetonitrile, for application in double-layer capacitors, is characterised by a conductivity of ca. $50\text{--}60 \text{ mS cm}^{-1}$ [5]. The conductivity of a solution of LiPF_6 (1 mol dm^{-3}) in a mixture of ethylene carbonate with 1,2-dimethoxyethane (EC + DME), for the use in lithium-ion batteries, is 16.6 mS cm^{-1} [4]. The corresponding value for ionic liquids is in the range of $1\text{--}20 \text{ mS cm}^{-1}$ [6]. For example, the conductivity of $[\text{EtMeIm}][\text{BF}_4]$ is 14 mS cm^{-1} , while its 2 mol/dm^3 solution in acetonitrile shows a conductivity of 47 mS cm^{-1} [5].

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EDLCs are promising devices for managing energy supply or recuperation where short but high-power pulses are required [7,8]. Especially in the case of urban vehicles, the power demand shows high peaks during acceleration and braking. A hybrid battery-EDLC energy accumulator seems to be a potential solution to the problem of power and energy management [9]. The EDLC technology has been developed to create a new type of energy accumulator, having an energy density close to that characteristic of batteries and much higher power density. The literature shows that most attempts to obtain this goal are focused on the optimisation of carbon materials, as well as electrolytes [1–3]. The general aim of the present paper is to describe the theoretical and practical limitations of EDLCs' performance, associated with all aspects of the device construction, such as carbon porosity, separator, current collector and electrolyte.

2. Carbon electrodes

The specific capacity of the double layer formed at the electrode/electrolyte interface is of the order of $10 \mu\text{F cm}^{-2}$ [3,10]. Materials of a specific surface of the order of $1000 \text{ m}^2 \text{ g}^{-1}$ are necessary to obtain an electrode of high electric capacity. The specific capacity expressed versus the active material mass, is of the order of $10 \mu\text{F cm}^{-2} \times 1000 \text{ m}^2 \text{ g}^{-1} = 100 \text{ F g}^{-1}$. In principle, the only material of such properties is activated carbon (AC). Such materials have been developed in various systems: powders, fabrics, tissues or aerogels. The carbon electrode is usually well polarisable, but its resistance strongly depends on the way of its preparation. Resistivity of activated carbon powders, as well as of carbon fabrics, is usually in the range of $0.5\text{--}1.5 \Omega \text{ cm}$ (see for example [11]). However, the addition of an electronically conducting carbon material, such as carbon black (CB) or graphite (G), may sufficiently reduce the resistivity of the electrode. In a powder form, activated carbons are usually mixed with a polymer binder.

3. Maximum specific surface of a carbon material

Both graphite, as well as nanotubes (which can be considered as rolled graphene sheets) may be applied as carbon materials for EDLC. Usually the EDLC electrode is prepared from different types of activated carbon. The limitation of a carbon material specific surface is determined by the thickness and density of a carbon wall, the thicker consisting of a single layer of carbon atoms. Let us assume a graphene sheet (single plain of graphite) with a dimension of $1 \text{ cm} \times 1 \text{ cm}$ and a thickness of atomic size. In graphite, consisting of graphene sheets, each carbon atom possesses an sp^2 hybridisation (the π electrons are delocalized across the hexagonal carbon sheets). Each carbon atom is covalently bound to the three surrounding carbon atoms in the sheet. The sheet layers are connected together by weak van der Waals forces, with an interlayer spacing of ca. 335 pm. Therefore, the van der Waals diameter of graphite carbon is 0.335 nm. The total surface of the sheet is 2 cm^2 (both sides) and the volume is $V_C = 1 \text{ cm}^2 \times 0.335 \text{ nm} = 3.35 \times 10^{-8} \text{ cm}^3$. Assuming the density of the carbon material equal to that characteristic for graphite ($d_C = 2.267 \text{ g cm}^{-3}$) leads to the mass of the sheet $m_C = d_C$

$V_C = (2.267 \text{ g cm}^{-3}) \times (3.35 \times 10^{-8} \text{ cm}^3) = 7.59 \times 10^{-8} \text{ g}$. Therefore, the maximum theoretical specific surface of the carbon material is $A_{\text{sp}}^c = (2 \text{ cm}^2)/(7.59 \times 10^{-8} \text{ g}) \approx 2600 \text{ m}^2 \text{ g}^{-1}$.

4. Nano-capacitor

The maximum power and energy density of a double-layer capacitor may be deduced from the analysis of an imaginary 'nano-capacitor' (or a 'molecular capacitor'), assembled from graphene sheets as electrodes, separated by electrolyte layers. The carbon electrode surface of 1 cm^2 has the mass $m_{\text{electrode}} = (1 \text{ cm}^2) \times (0.335 \times 10^{-7} \text{ cm}) \times (2.267 \text{ g cm}^{-3}) = 0.759 \times 10^{-7} \text{ g}$. Assuming the electrolyte layer thickness for example at a level of $l = 2 \text{ nm}$, the mass of the electrolyte is $m_{\text{electrolyte}} = (1 \text{ cm}^2) \times (2 \times 10^{-7} \text{ cm}) \times (1 \text{ g cm}^{-3}) = 2 \times 10^{-7} \text{ g}$. The capacitor with a mass of $3.518 \times 10^{-7} \text{ g}$ and the thickness of 2.355 nm (two carbon electrodes and the electrolyte layer), has a surface of 1 cm^2 . Assuming the specific capacity of the carbon/electrolyte interface of $10 \mu\text{F cm}^{-1}$, the capacity of the device is $5 \mu\text{F}$ (as $1/C = 2/C_{\text{electrode}}$), while the specific capacity of the device is $(5 \mu\text{F})/(3.518 \times 10^{-7} \text{ g}) \approx 14.2 \text{ F g}^{-1}$. This leads to the specific energy density at a voltage of $U = 1 \text{ V}$ (aqueous electrolyte) of ca. $E = 7 \text{ kJ kg}^{-1}$. For organic electrolytes, at $U \approx 2.3\text{--}2.5 \text{ V}$, the maximum energy density is between ca. 40 and 45 kJ kg^{-1} . If the carbon electrodes are separated by an ionic liquid, higher voltages may be applied (3–4 V), which leads to energy densities in a range of $65\text{--}115 \text{ kJ kg}^{-1}$. Usually, the specific capacity, as well as the specific energy, are expressed versus the mass of carbon. Taking into account the maximum surface of the graphene sheet, the maximum capacity of the double layer is $(10 \mu\text{F cm}^{-2}) \times (2600 \text{ m}^2 \text{ g}^{-1}) \approx 260 \text{ F g}^{-1}$ of carbon.

The resistance of the 'nano-device' is solely the resistance of the electrolyte layer of the thickness of a few nanometers. The device with an aqueous electrolyte of high conductivity ($\sigma \approx 700 \text{ mS cm}^{-1}$), has the highest specific power. For the analysed device ($l = 2 \text{ nm}$), the resistance of the surface of 1 cm^2 is at the level of $R_s = l/A\sigma = (2 \times 10^{-7} \text{ cm})/(0.7 \Omega^{-1} \text{ cm}^{-1})(1 \text{ cm}^2) = 2.86 \times 10^{-7} \Omega$. The maximum specific power of the imaginary nano-device reaches a very high value of the order of peta Watts: $P = 1V^2/(4 \times 2.86 \times 10^{-7} \Omega \times 3.518 \times 10^{-7} \text{ g}) \approx 2.5 \times 10^{15} \text{ W kg}^{-1}$. The maximum power for the similar device with ionic liquid as an electrolyte ($\sigma \approx 10 \text{ mS cm}^{-1}$) is still high: ca. $5.7 \times 10^{14} \text{ W kg}^{-1}$.

5. Porous carbon electrode

In practical constructions, different types of highly porous carbon materials (activated carbons) are applied. The structure of a porous carbon material is usually approximated with two models, assuming the existence of rectangular or spherical pores, of the same or similar radius (Fig. 1). The micro-texture of porous carbons is characterised by pore size distribution, usually experimentally obtained from the BET isotherm of nitrogen adsorption. Let us analyse a model porous carbon cube (regular hexahedron) with edges with a length of $a = 1 \text{ cm}$. The

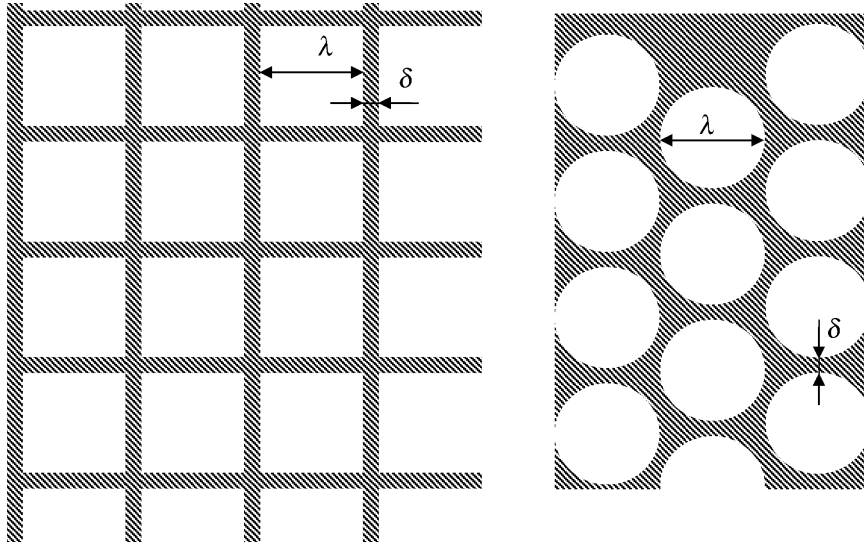


Fig. 1. Schematic representation of a porous material consisting of rectangular or tubular pores of the same size.

cube contain pores of a rectangular-shape with length a and a square base face whose sides have length λ , separated by single carbon walls with a thickness $\delta = 0.335$ nm (Fig. 1a). Therefore, the cube is constructed of N single graphene walls. The number of pores in one row is $n = a/(\lambda + \delta)$. There are n such rows and, therefore, the number of rectangular pores is: $N_{\text{rect}} = a^2/(\lambda + \delta)^2$. For example, if the pore diameter is 10 nm, the number of pores is $N_{\text{rect}} = n^2 = (1 \text{ cm}^2)/\{(10 + 0.335)^2 \times 10^{-14} \text{ cm}^2\} \approx 9.36 \times 10^{11}$. A porous carbon material may also be approximated assuming the existence of tubular pores (Fig. 1b). For the tubular pores, with diameter λ and distanced by thickness δ , their number may be somewhat higher:

$$N_{\text{tube}} = \frac{a^2}{\lambda(\lambda + \delta)} \quad (3)$$

The number of pores and their size determines the total surface of the material. Let us analyse the material with tubular pores. The total surface available inside the analysed cube with pores of diameter 10 nm is: $A \approx 10^{12} \times 1 [\text{cm}] \times \pi \times 10^{-6} [\text{cm}] = 314 \text{ m}^2$.

The total volume of the tubular pores is given by:

$$V = N\pi \left(\frac{\lambda}{2}\right)^2 a = a^3 \frac{\pi}{4} \frac{\lambda}{\lambda + \delta} \quad (4)$$

The ratio $\lambda/(\lambda + \delta)$ indicates the electrode porosity X (the volume ratio of the pores in the electrode):

$$X_V^{\text{pores}} = \frac{V^{\text{pores}}}{V} = \frac{V^{\text{pores}}}{a^3} = \frac{\pi}{4} \frac{\lambda}{\lambda + \delta} \quad (5)$$

while the fraction of the carbon material in the electrode is given by: $X_V^{\text{C}} = 1 - X_V^{\text{pores}}$.

The volume of pores with a 10 nm diameter, contained in the analysed cube (the tubular pores) is 0.76 cm^3 , while the carbon volume is 0.24 cm^3 (76% porosity).

6. Mass of the electrolyte in the electrode

Very high porosity of activated carbons indicate that in contrast to batteries, the high volume fraction of the electrode is occupied by the electrolyte. Hence, the content of the carbon material in the electrode, expressed as its mass fraction, X_m^{C} , is determined by the electrode porosity:

$$X_m^{\text{C}} = \frac{m^{\text{C}}}{m^{\text{el}}} = \frac{V^{\text{C}} d^{\text{C}}}{V^{\text{C}} d^{\text{C}} + V^{\text{pores}} d^{\text{el}}} = \frac{X_V^{\text{C}} d^{\text{C}}}{X_V^{\text{C}} d^{\text{C}} + X_V^{\text{pores}} d^{\text{el}}} \quad (6)$$

For example, the mass of porous carbon under consideration (the mass of the 1 cm^3 cube with 10 nm, tubular pores) is: $m^{\text{C}} = (2.267 \text{ g cm}^{-3}) \times (0.239 \text{ cm}^3) = 0.54 \text{ g}$. Assuming the density of the electrolyte at a level of ca. 1 g cm^{-3} , one may get the following values for the electrolyte mass: $m^{\text{el}} = (1 \text{ g cm}^{-3}) \times (0.761 \text{ cm}^3) = 0.761 \text{ g}$. The simulation indicates that the highly porous electrode mainly consists of the electrolyte, and this should be taken into account in calculations of the specific energy or power density of the capacitor.

7. Porous carbon thickness and mass

From the point of view of high capacitor power, the active layer of the porous carbon on the current collector should be as thick as possible. If the device consists of n current-collector/electrode layers (Fig. 2), the contribution of the current collector to the total mass of the device increases with the decreasing thickness of the electrode. This reduces not only specific energy density but also influences the power density of the device. Moreover, carbon electrodes are separated by a separator containing the electrolyte. Consequently, the series resistance, as well as the device mass increases. The total volume of the device, V_{device} , is the sum of n volumes of: electrodes (carbon + electrolyte), 1/2 volume of the separator, and 1/2 volume of the current collector (Fig. 2):

$$V_{\text{device}} = n(2V_{\text{electrode}} + V_{\text{sep}} + V_{\text{col}}) \quad (7)$$

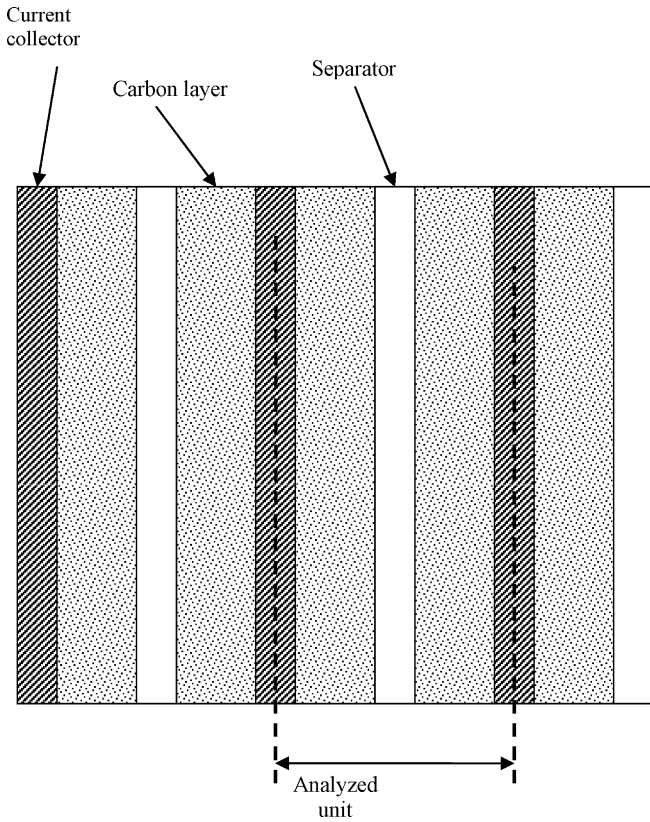


Fig. 2. Scheme of a capacitor, consisting of porous carbon electrodes deposited on metallic current collectors.

The corresponding mass of the device is:

$$m_{\text{device}} = n \{ S_{\text{electrode}} [2l_{\text{electrode}} (\nu X^C d^C + \nu X^{\text{el}} d^{\text{el}}) + l_{\text{sep}} d_{\text{sep}} + l_{\text{col}} d_{\text{col}}] \} \quad (8)$$

Finally, the mass ratio of the carbon expressed versus the total mass of the device, is given by m_C/m_{device} . Fig. 3 shows

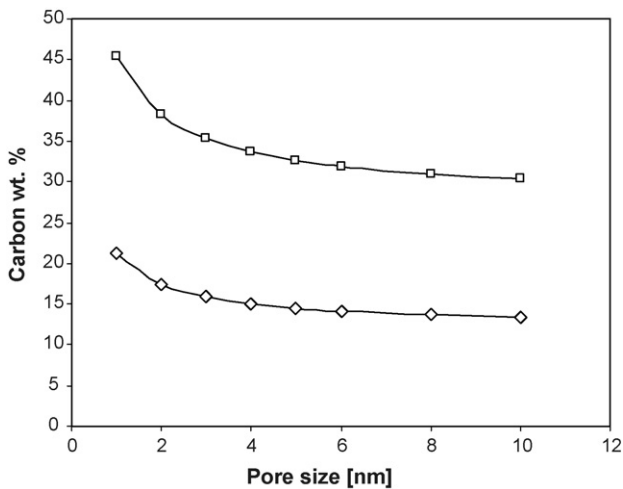


Fig. 3. Carbon content in the capacitor, as a function of carbon porosity, as well as thickness of electrode, separator and current collector. Upper curve: $l_{\text{electrode}} = 1.0 \text{ mm}$, $l_{\text{sep}} = 0.5 \text{ mm}$, $l_{\text{col}} = 0.05 \text{ mm}$, lower curve: $l_{\text{electrode}} = 0.1 \text{ mm}$, $l_{\text{sep}} = 0.1 \text{ mm}$, $l_{\text{col}} = 0.05 \text{ mm}$.

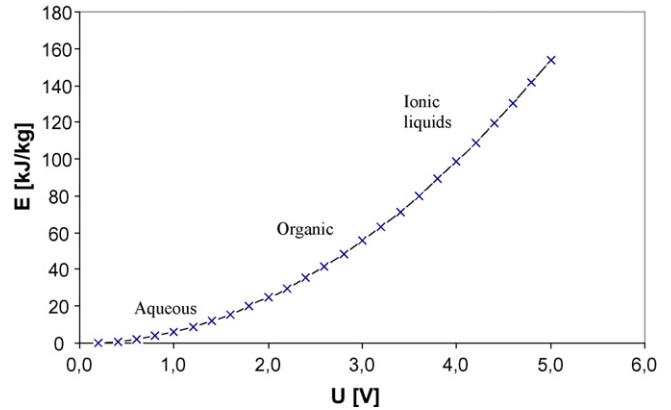


Fig. 4. Specific energy of the capacitor shown in Fig. 3, as a function of voltage applied between current collectors.

the simulation of the carbon content in the device as a function of pore diameter, for different electrode and separator thickness (the copper density was taken as the density of the current collector). It can be seen that applying a thin separator together with a thin electrode (both 0.1 mm), and the current collector of the thickness of 50 μm , leads to a low carbon content in the device, at the level of ca. 20 wt.%. With the increasing thickness of the electrode (to 1 mm), the carbon content increases twice up to ca. 40–45 wt.%, even with a separator with a conventional thickness of ca. 0.5 mm. The simulation indicates that it is difficult to construct a device with thick electrodes, characterised by high specific power and energy densities.

8. Specific energy density of a capacitor based on porous carbons

Fig. 4 shows the dependence of the energy density of the capacitor (energy stored in 1 kg of the device) as a function of the voltage U applied between current collectors, assuming the double-layer specific capacity (expressed versus the mass of the carbon) at a level of $C_{\text{sp}}^C = 10 \mu\text{F cm}^{-2}$, the classical battery technology ($l_{\text{electrode}} = 1 \text{ mm}$, $l_{\text{separator}} = 0.5 \text{ mm}$, $l_{\text{cc}} = 50 \mu\text{m}$) and the activated carbon pores with the diameter of $\lambda = 2 \text{ nm}$. The porosity of such carbon would be: $X^C = 0.683$, number of pores $N = 2.17 \times 10^{13}$, and the specific surface $A_{\text{sp}}^C = 880 \text{ m}^2 \text{ g}^{-1}$ of carbon. The electrode of the surface of 1 cm^2 contains $m^C = (0.1 \text{ cm}^3) \times (1 - 0.683) \times (2.267 \text{ g cm}^{-3}) = 71.9 \text{ mg}$ of carbon and $m^{\text{el}} = (0.1 \text{ cm}^3) \times (0.683) \times (1 \text{ g cm}^{-3}) = 68.3 \text{ mg}$ of the electrolyte ($m_{\text{electrode}} = 0.1402 \text{ g}$). The capacity of the double layer is $C_{\text{electrode}} = 880 \text{ m}^2 \text{ g}^{-1} \times 0.1402 \text{ g} \times 10 \mu\text{F cm}^{-2} = 12.33 \text{ F}$. The mass of the separator is $m_{\text{separator}} = (0.05 \text{ cm}^3) \times (1 \text{ g cm}^{-3}) = 50.0 \text{ mg}$ and the mass of the current collectors (made of copper in this example) is $m_{\text{cc}} = (0.005 \text{ cm}^3) \times (8.93 \text{ g cm}^{-3}) = 44.7 \text{ mg}$. Finally, the mass of 1 cm^2 of the device is $m = 2 m_{\text{electrode}} + m_{\text{separator}} + m_{\text{cc}} = 0.375 \text{ g}$ and the specific capacity of the device is: $C = (1/2)12.33 \text{ F} / 0.375 \text{ g} = 16.44 \text{ F g}^{-1}$ of the device. In order to obtain the energy density of the device at a level of ca. 100 kJ kg^{-1} (characteristic for the lead-acid battery), the analysed capacitor should operate at voltages of ca. 4 V.

9. Specific power density of a capacitor based on porous carbons

Assuming that the resistance of the carbon is much smaller than the electrolyte resistance, the series resistance, R_s , of the porous electrode is proportional to the ratio of the electrode thickness, l , and the electrolyte conductivity, σ [2]:

$$R_s^{\text{electrode}} = \frac{1}{3\pi(\lambda/2)^2 N \sigma} \quad (9)$$

The voltage U operates between two current collectors (Fig. 3), and hence, the series resistance is the sum of resistances of two electrodes and the separator:

$$R_s = \frac{1}{\sigma} \left[\frac{2l_{\text{electrode}}}{3\pi(\lambda/2)^2 N} + \frac{l_{\text{sep}}}{A_{\text{sep}}} \right] \quad (10)$$

where $\lambda/2$ is the average pore radius and A_{sep} is the separator area.

If the analysed device ($l_{\text{electrode}} = 1$ mm, $l_{\text{separator}} = 0.5$ mm, $l_{\text{cc}} = 50$ μm , carbon with 2 nm pores) is filled with an electrolyte of a relatively low specific conductivity (characteristic for ionic liquids), at a level of 10 mS cm⁻¹, the resistance of 1 cm² of the electrode is ca. 5 Ω and the separator resistance is ca. 5 Ω , the resistance of 1 cm² of the device is as high as ca. 15 Ω . The surface of 1 kg of the capacitor is (1000 g)/(0.375 g cm⁻²) = 2667 cm², which leads to the series resistance of the device at a level of $R_s = (15 \Omega)/(2667) = 5.6 \times 10^{-3} \Omega$. At the voltage of ca. 4 V the specific power is ca. 0.73 kW kg⁻¹. A similar capacitor working with an aqueous electrolyte (acidic, $U = 1$ V, $\sigma \approx 700$ mS cm⁻¹), is characterised by 70 times lower R_s value, but the specific power is only 4.4 times higher (ca. 3.2 kW kg⁻¹). Decreasing the electrode and the separator thickness to 0.1 mm, leads to the R_s value of ca. $7.4 \times 10^{-4} \Omega$ and the specific power of ca. 5.4 kW kg⁻¹ (for IL as an electrolyte, $\sigma \approx 10$ mS cm⁻¹).

While the specific energy density of a capacitor based on porous carbon material is comparable to that characteristic for the 'nano-capacitor' shown in Fig. 1, its power density is much lower.

10. Organic electrolytes and ionic liquids

The electrolytes for application in electrochemical capacitors should be resistant to electrochemical reduction and oxidation at carbon and produce possibly high specific capacity at the carbon/electrolyte surface. The electrochemical stability of aqueous solutions is limited by the thermodynamic stability of water, corrected by the activation overpotential. Practically, the maximum operating voltage for a unit EDLC cell with the aqueous electrolyte is limited to ca. 1 V. The most popular organic electrolyte seems to be a solution of tetraethylammonium tetrafluoroborate in acetonitrile, which is characterised by both high conductivity and a relatively broad electrochemical stability window. The electrochemical stability window of tetraalkylammonium salts in organic solvents determined at glassy carbon electrodes suggests the possibility of operating voltages of ca. 3 V. However in

practical carbon/electrolyte systems this value is limited to ca. 2.3 V [2]. The energy stored at 2.3 V is still much higher than that characteristic for aqueous systems (ca. five times). Moreover, due to much lower conductivity, the power of the device with the organic electrolyte is lower in comparison to aqueous alkaline or acidic systems.

High vapour pressure of many organic solvents, including acetonitrile, is the main drawback of capacitors based on such systems, due to environmental regulations, as well as their flammability and risk of explosion at higher temperatures. Room temperature molten salts [6,12–14], often called ionic liquids, may be regarded as ideal electrolytes for application in double-layer capacitors, as they show ionic conductivity, exceptionally broad electrochemical stability window and negligible vapour pressure. Ionic liquids have been applied in capacitors, as solutions in molecular liquids [15–17], making the system similar to conventional solutions of organic salts in non-aqueous solvents as well as without any solvent [18]. Polymer electrolytes based on ionic liquids were also prepared for application in EDLCs [19–21]. Table 1 collects the specific conductivity as well as electrochemical stability of a number of representative ionic liquids. Inspection of the table shows that the electrochemical stability window of ionic liquids, generally in the range of 4–6 V, is exceptionally high. However, conductivity is poor. For example, one of the most studied ionic liquids, [EtMeIm][BF₄] is characterised by a conductivity of ca. 14 mS cm⁻¹ at 25 °C and stability at a level of 4.3 V, but on the other hand, one of the most stable ionic liquids (stability window of ca. 5.6 V), based on the piperidinium cation and imide anion, [MePrPip][N(CF₃SO₃)₂], shows poor conductivity of ca. 1.5 mS cm⁻¹ at 25 °C.

11. Temperature effect on capacitor power

Electrolyte conductivity strongly depends on the temperature, according to the Arrhenius or VTF equations. If the electrolyte conductivity is approximated by the Arrhenius equation:

$$\sigma = \sigma_0 \exp \left[\frac{-E^\#}{RT} \right] \quad (11)$$

the power of the device depends on the temperature according to the following expression:

$$P = \alpha \frac{U^2}{l} e^T \quad (12)$$

where

$$\alpha = \frac{3\pi(\lambda/2)^2 N}{2} \sigma_0 \exp \left[\frac{-E^\#}{R} \right]$$

and $E^\#$ is the activation energy for the conduction process.

For activation energies of the order of 25 kJ/mol [22], the conductivity increases by one order of magnitude with a temperature increase of ca. 90 K. Consequently, changing the temperature of a device from 25 to 115 °C, may result with power increase from ca. 0.7 kW kg⁻¹ to a level of 7 kW kg⁻¹. The heating of the capacitor to a desired temperature can easily be done in hybrid vehicles, where the combustion engine produces waste heat. The

Table 1
Electrochemical stability window (ΔU) together with conductivity (σ), for some representative salts liquid at room temperatures (ionic liquids) [6]

Ionic liquids	Electrochemical stability				Conductivity	
	Cathodic limit (V)	Anodic limit (V)	ΔU (V)	Working electrode	Reference	σ at 25 °C (mS cm ⁻¹)
Imidazolium						
[EtMeIm] ⁺ [BF ₄] ⁻	-2.1	2.2	4.3	Pt	Ag/Ag ⁺ , DMSO	14
[EtMeIm] ⁺ [CF ₃ SO ₃] ⁻	-1.8	2.3	4.1	Pt	I ⁻ /I ₃ ⁻	8.6
[EtMeIm] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-2	2.1	4.1	Pt, GC	Ag	8.8
[EtMeIm] ⁺ [(CN) ₂ N] ⁻	-1.6	1.4	3.0	Pt	Ag	–
[BuMeIm] ⁺ [BF ₄] ⁻	-1.6	3	4.6	Pt	Pt	3.5
[BuMeIm] ⁺ [PF ₆] ⁻	-1.9	2.5	4.4	Pt	Ag/Ag ⁺ , DMSO	1.8
[BuMeIm] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-2	2.6	4.6	Pt	Ag/Ag ⁺ , DMSO	3.9
[PrMeMeIm] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-1.9	2.3	4.2	GC	Ag	3.0
[PrMeMeIm] ⁺ [C(CF ₃ SO ₂) ₃] ⁻		5.4	5.4	GC	Li/Li ⁺	–
Pyrrolidinium						
[<i>n</i> PrMePyrrol] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-2.5	2.8	5.3	Pt	Ag	1.4
[<i>n</i> BuMePyrrol] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-3.0	2.5	5.5	GC	Ag/Ag ⁺	2.2
[<i>n</i> BuMePyrrol] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-3.0	3.0	6.0	Graphite	Ag/Ag ⁺	–
Tetraalkylammonium						
[<i>n</i> Me ₃ BuN] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-2.0	2.0	4.0	Carbon		1.4
[<i>n</i> PrMe ₃ N] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-3.2	2.5	5.7	GC	Fc/Fc ⁺	3.3
[<i>n</i> OctEt ₃ N] ⁺ [N(CF ₃ SO ₂) ₂] ⁻			5.0	GC		0.33
[<i>n</i> OctBu ₃ N] ⁺ [N(CF ₃ SO ₂) ₂] ⁻			5.0	GC		0.13
Pyridinium						
[BuPyr] ⁺ [BF ₄] ⁻	-1	2.4	3.4	Pt	Ag/AgCl	1.9
Piperidinium						
[MePrPip] ⁺ [N(CF ₃ SO ₂) ₂] ⁻	-3.3	2.3	5.6	GC	Fc/Fc ⁺	1.5
Sulfonium						
[Et ₃ S] ⁺ [N(CF ₃ SO ₂) ₂] ⁻			4.7	GC		7.1
[<i>n</i> Bu ₃ S] ⁺ [N(CF ₃ SO ₂) ₂] ⁻			4.8	GC		1.4

problem is the boiling point of the organic electrolyte solution and the increase of the solvent pressure. If non-volatile ionic liquids are applied as electrolytes, the only limit is their thermal stability, as well as their possible reaction with the carbon material at increased temperatures.

12. Conclusions

1. The maximum specific surface of a carbon material, which may be used for the construction of a double-layer capacitor is ca. 2600 m² g⁻¹.
2. The maximum energy density of an imaginary double-layer 'nano-capacitor', assembled from single graphene sheets (0.335 nm) and separated by electrolyte layers (thickness of nanometers), is rather not higher than 10 kJ kg⁻¹ at a voltage of $U = 1$ V (aqueous electrolyte), of ca. 40–45 kJ kg⁻¹ at $U \approx 2.3$ –2.5 V (organic electrolytes), and about 100 kJ/mol at voltages close to 4 V (ionic liquids as electrolytes). The theoretical specific power of the analysed imaginary nano-device is of the order of PW kg⁻¹.
3. The specific energy density of a capacitor based on porous carbon electrodes is somewhat lower than characteristic for the reference 'nano-capacitor' (possible maximum value). The device consists of porous electrodes, a separator and a current collector. The maximum electric capacity expressed versus the mass of the device, is much smaller than the cor-

responding value expressed versus the mass of the carbon material (ca. 20–30 F g⁻¹). In order to obtain the energy density of the device at a level of 100 kJ kg⁻¹ (characteristic for the lead-acid battery), the capacitor with porous carbon electrodes should operate at voltages of ca. 4 V (ionic liquids as electrolytes). However, the specific power density is ca. 0.7 kW kg⁻¹ at 25 °C, for the capacitor having a specific energy density ca. 100 kJ kg⁻¹ (ionic liquid as electrolyte).

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