Unusual energy enhancement in carbon-based electrochemical capacitors

Krzysztof Fic, Elzbieta Frackowiak and François Béguin*

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Electrochemical capacitors – also called supercapacitors – represent a relatively new electricity storage system applied for harvesting energy and delivering high power pulses for short periods. The main developed technology is based on charging an electrical double-layer (EDL) at the electrode–electrolyte interface of high surface area carbons. The main disadvantages of the latter are a relatively low energy density and safety issues related to the use of organic electrolytes. This paper describes alternative solutions where pseudocapacitive contributions play together with the EDL capacitance in a protic aqueous electrolyte, giving rise to a possible enhancement of energy density. It first reviews traditional solutions by using materials that are able to undergo fast faradic redox reactions, e.g. oxides and electrically conducting polymers (ECPs). Since the surface of materials essentially plays in this case, the realized capacitance values are much lower than theoretically expected; additionally the working voltage is generally lower than 1 V and the stability of some of these materials, e.g. ECPs, is relatively low. The realization of composites with carbon nanotubes which play as three-dimensional conductive supports contributes to the enhancement of performance of oxides and ECPs. A new source of pseudocapacitance involving a redox electrolyte is demonstrated by high surface area carbons. The latter is based on the interface formed by species with a large variety of oxidation states, e.g. iodine, bromine and vanadium, and gives rise to capacitance values as high as 250 F g\(^{-1}\) at 1 A g\(^{-1}\) for 1 mol L\(^{-1}\) KI aqueous solution. The last pseudocapacitive phenomenon involves electrochemical hydrogen storage in the negative electrode of carbon–carbon capacitors in neutral aqueous electrolytes, e.g. alkali sulphates. The voltage (and consequently the energy density) is considerably enhanced by comparison with systems in basic or acidic electrolytes owing to an important overpotential for di-hydrogen evolution at the negative electrode; besides a pseudocapacitive contribution related to hydrogen storage appears at the highest voltage values.

1. Introduction

Energy is one of the most often indicated keywords in the scientific papers appearing presently. At the origin of such a situation is certainly the dramatic increase in demand for novel types of energy/power delivery systems. Hence, there is a well-founded reason to develop new materials devoted for them.

Carbon is widely recognized as a unique element, because of its universal character resulting in various applications. Among the diverse forms of this element, activated carbons with well-developed surface area and porosity became interesting and useful materials in energy conversion and storage systems such as electrochemical capacitors.\(^1,2\) Obviously, other forms of carbon such as carbon nanotubes (CNTs)\(^3\) or graphene nanosheets,\(^4\) which have received much attention recently, can also serve as capacitors but, due to their moderate surface area and porosity, they are better suited as additives, enhancing the conductivity or providing additional porosity to the main electrode material.\(^5,9\)

The performance of electrochemical capacitors is closely related to an electrostatic interaction in the electrode–electrolyte interface, so-called electrical double-layer (EDL), where the oppositely charged species (electrode and ions from the electrolyte) are attracted to each other. As can be assumed, the amount of charge accumulated in the EDL is directly proportional to the surface area of the discussed interface. Hence, a well-developed surface area of carbons seems to be a crucial parameter for efficient energy storage. On the other hand, the
specific surface area is closely connected with the porosity of carbons and the type of pores plays an important role in charge accumulation. Ions from the electrolyte can be effectively adsorbed only in the smallest pores (micropores) with a diameter below 2 nm, whereas mesopores (with diameter in the range 2–50 nm) usually adopt the role of transporting channels for the ions which can be adsorbed in micropores. However, even if the total charge accumulated in the electrode–electrolyte interface depends intuitively on the surface area, there is no direct dependence between the specific surface area (determined by nitrogen or carbon dioxide adsorption) and the capacitance values achieved. It clearly suggests that apart from the well-developed surface area, the porosity with an appropriate micro/mesopores ratio (reported in ref. 15 to be 20–50%) is necessary to enhance the capacitance values. Pore diameter should also perfectly fit the dimensions of the attracted ions to preserve favourable conditions for fast and effective electrostatic interactions.

From this point of view, the development of novel carbon materials with suitable and easily accessible porosity seems to be the most reasonable way to improve the performance of electrochemical capacitors.

As the energy released by these devices is related to capacitance and voltage, according to the following formula:

\[
E = \frac{1}{2} C U^2 \quad (1)
\]

where \(C\) stands for capacitance (F) and \(U\) is the operational voltage (V), the energy enhancement can be realized by two different approaches – through capacitance increase or by extending the voltage. Since the voltage of a capacitor is related mainly to the applied electrolyte, the latter should be characterised by a wide electrochemical stability and – due to power demand – high electrical conductivity. On the one hand, organic electrolytes (based on acetonitrile, propylene carbonate or ionic liquids) with electrochemical stability up to 4 V\(^{18,19}\) allow us to reach high energy values, but they are characterized by moderate or even poor conductivity which significantly deteriorates the power characteristics. Hence, the choice of electrolyte should rather be dictated either by the power or energy demand.

According to formula (1), energy can be also enhanced by a capacitance increase, related mainly to the electrode material; this paper is devoted mainly to this issue.

2. Towards capacitance enhancement – pseudocapacitive electrode materials

Considering the electrochemically available surface area of activated carbons and the charge amount which could be accumulated in the electrical double-layer, the capacitance values reported do not exceed 150 F g\(^{-1}\).

As was mentioned, the electrostatic attraction of ions occurring in the electrode–electrolyte interface is closely related to their properties, in particular diameter and mobility, but also with the properties of the electrode, such as the electrochemically available surface area (but not directly calculated from the adsorption isotherm) and pore structure. If the pure electrostatic capacitance of an electrochemical capacitor is described by the formula for traditional capacitors, the total charge accumulated on the interface for a given potential can be expressed by:

\[
\frac{1}{C_d} = x e e_0 + \frac{1}{kT} \left(\frac{2e_0z^2e^2}{kT}\right)^{\frac{1}{2}} \cosh \left(\frac{ze\Psi_S}{2kT}\right) \quad (2)
\]

where \(C_d\) is the capacitance for the electrical double-layer, \(x\) the length of the Helmholtz layer (inner and outer), \(\varepsilon\) and \(\varepsilon_0\) the electric permittivity for the considered electrolyte and vacuum, \(z\) the ion charge, \(e\) the ion concentration, \(e\) the exponential factor, \(k\) the Boltzmann constant, \(T\) the absolute temperature and \(\Psi_S\) the Stern potential. This equation clearly suggests a strong dependence between the capacitance and the surface area of the electrode–electrolyte interface.

The theoretical capacitance values which can be calculated from eqn (2) are in good accordance with the experimental ones and do not exceed 140–150 F g\(^{-1}\) in aqueous medium within a potential range of 0.8 V. Additionally, for aqueous electrolytic solutions at 25°C, eqn (2) can be expressed as:

\[
\frac{1}{C_d} = 1.4389 \times 10^7 x + \frac{1}{228z(\varepsilon^2)\cosh(19.5z\varepsilon\Psi_S)} \quad (3)
\]

and gives capacitance values in good agreement with those obtained experimentally. Obviously, there are many models describing the capacitance of the electrical double-layer, but only a few of them are applicable for activated carbons. One of the most interesting models is proposed in ref. 21, where the authors suggest that counterions approach the walls of mesopores to form electric double-cylinder capacitors (EDCC), whereas they line up along the axis of micropores to form wire-in-cylinder capacitors (EWCC).

Accordingly, the values obtained from pure double-layer charging/discharging result in a rather moderate energy density reported, especially in aqueous medium, with the voltage limited by water decomposition.

Apart from typical electrostatic interactions in the electrical double-layer, redox reactions with electron transfer on the electrode–electrolyte interface can greatly contribute in the charge storage process and energy enhancement. However, the typical faradic origin of these processes is associated with slow kinetics of the heterogeneous reaction (limited mainly by the diffusion of the involved electrochemical species) and with a moderate cycle life (connected with changes of the material structure undergoing the oxidation or reduction process).

These issues will be discussed in more detail further in the manuscript.

The most often used materials as a pseudocapacitance source are transition metal oxides. The highest theoretical capacitance values are reported for ruthenium oxide, RuO\(_2\), i.e. ca. 1400 F g\(^{-1}\). However, a satisfying electrochemical activity of this compound is obtained only in protic medium.

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MnO$_2$ pseudocapacitance, well-defined the theoretical capacitance is 3750 F g$^{-1}$ and a theoretical capacitance value reported to be about 3560 F g$^{-1}$ and in a narrow potential range; this suggests that the latter are rather battery-like materials, not useful in high-power application. For real systems being – indeed – two-electrode cells, the values obtained are not so spectacular.

Electrochemically conducting polymers (ECPs) can also give an additional charge when applied as electrode materials for supercapacitors. Their faradic contribution consists of electron-involved doping/dedoping. Very high theoretical capacitance values i.e. 1000 F g$^{-1}$ are reported and are possible to reach at mild current regimes and in three-electrode experiments. Khomenko et al. proved that ECPs composites with carbon nanotubes (CNTs) as conductive support can even give 1100 F g$^{-1}$ for one electrode, in a selected potential range. However, in two-electrode configuration, the capacitance fades dramatically to 360 F g$^{-1}$ for the most promising composite. The most often applied polymers are polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh) and poly(3,4-ethylendioxythiophene) (PEDOT) for the positive and negative electrodes, respectively. According to the voltage value, the energy density of such an asymmetric capacitor at moderate discharging current is found to be 13 W h kg$^{-1}$, which is about ten times more than that for a symmetric capacitor based only on PEDOT and operating in neutral medium. Frackowiak et al. reported a similar voltage value for capacitors with ECPs/CNTs composites as electrode materials, giving also high capacitance values, ranging from 100 to 330 F g$^{-1}$.

Because of some oxygenated or/nitrogenated functionalities on its surface, carbon can also give a pseudo-capacitive contribution to the total capacitance in protic electrolytic media. In the case of oxygen-based functionality, the quinone/hydroquinone redox couple is the most often reported, giving rather moderate capacitance values, unfortunately. Nitrogen enriched carbons reveal a faradic response in acidic/alkaline medium because of the presence of protons that are able to interact with free electrons on nitrogen atoms.

C*=N + 2e$^-$ + 2H$^+$ $\leftrightarrow$ C*H–NH$_2$ (8)

C*–NH$_2$ + 2e$^-$ + 2H$^+$ $\leftrightarrow$ C*–NH$_3$ + H$_2$O (9)
These reactions can be presented as in Fig. 1.

The electrochemical activity of carbon functionalities is rather unstable during cycling and can be easily deteriorated, e.g., by capacitor overloading.

3. A new strategy to enhance capacitance through redox-active electrolytes

All the previously mentioned issues are closely related to the electrode material. Presently, there is a new trend in pseudocapacitance phenomena exploitation where the electrolyte stays at the origin of additional charge accumulated.

For the first time, the system applying the iodide/iodine redox couple was reported. The electrochemical activity of the electrolyte is based on eqn (10)–(13):

$$2I_2 \rightarrow I_2 + 2e^-\quad (10)$$

$$3I_2 \rightarrow I_3^- + 2e^-\quad (11)$$

$$2I_3^- \rightarrow 3I_2 + 2e^-\quad (12)$$

$$I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-\quad (13)$$

These reactions occur on the electrode–electrolyte interface and, from this point of view, a suitable porosity is a crucial factor. Cyclic voltammetry (Fig. 2) was applied to evaluate the capacitance of the carbon electrode and revealed an intriguing dependence on the type of alkali counter-ion. It suggests that the porosity significantly contributes to the active transport of ions to/from the electrode–electrolyte interface. Additionally, the ion properties such as mobility and diffusion coefficient strongly affect their electrochemical behaviour.

The capacitance of the electrode increases with the van der Waals radius of the alkali ion as follows: 300 F g$^{-1}$ for LiI, 492 F g$^{-1}$ for NaI, 1078 F g$^{-1}$ for KI and reaching 2272 F g$^{-1}$ for RbI. However, for the caesium ion, which has the biggest radius, the capacitance decreases to 373 F g$^{-1}$. A detailed analysis of the alkali cation properties indicated that this curious phenomenon is in perfect accordance with the ion–solvent and solvent–solvent interactions measured in the form of potential energy as well as cation mobility values and diffusion coefficients tendencies. Taking into account the values of water diffusion coefficient in alkali iodides, it seems that the most similar parameters such as ion mobility, diffusion coefficient and energy of ion–ion, ion–solvent interactions are observed in RbI solution. It suggests that the movement of both cations and anions is not disturbed by any additional interaction and they can easily penetrate the porous structure of the carbon electrode. Moreover, the iodide anions have the smallest value of ion–water potential, which might suggest that they are rather active in water solution and preferably desolvated. It means that, besides the faradic reactions, they can be adsorbed in the micropores, giving a typical electrostatic response. However, due to the rather strong faradic character and the relatively narrow potential range of the positive electrode, the discharge capacitance of real systems (i.e., two electrode cells) does not exceed 280 F g$^{-1}$ at 1 A g$^{-1}$.

Given the fact that only the positive electrode exhibits an exceptional capacitance in the iodide-based systems, enhancing the capacitance of the negative one has been tentatively undertaken. To preserve the redox-active electrolyte idea, the vanadium/vanadyl redox couple was employed. Hence, a 1 mol L$^{-1}$ KI aqueous solution was applied as electrolyte for the positive electrode and 1 mol L$^{-1}$ VO(SO$_4$)$_2$ for the negative one. The reported values are about 1200 F g$^{-1}$ and 670 F g$^{-1}$ for the positive and negative electrodes, respectively. The relatively high capacitance values of the negative electrode could be explained considering the following multi-electron reactions:

$$\text{VOH}^2+ + H^+ + e^- \rightarrow \text{V}^{2+} + H_2O\quad (14)$$

$$[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+} + 54\text{H}^+ + 30e^- \leftrightarrow 10\text{V}^{2+} + 28\text{H}_2\text{O}\quad (15)$$

$$[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4+} + 44\text{H}^+ + 20e^- \leftrightarrow 10\text{VOH}^{2+} + 18\text{H}_2\text{O}\quad (16)$$

$$\text{HV}_2\text{O}_3^{3+} + 13\text{H}^+ + 10e^- \rightarrow 2\text{V} + 7\text{H}_2\text{O}\quad (17)$$

$$\text{HV}_2\text{O}_3^{3+} + 9\text{H}^+ + 6e^- \leftrightarrow 2\text{VO} + 5\text{H}_2\text{O}\quad (18)$$

Obviously, for the total system, the values are lower, as the two-electrode system operates like two capacitors connected in series. However, the energy density for this system, utilizing aqueous electrolytes, operating in a 1.0 V voltage range is reported to be at the level of 19 W h kg$^{-1}$. Cyclic voltammograms for this device recorded at various scan rates are presented in Fig. 3.

It is also worth noting that the carbon surface plays an important role in the
faradic response of this system because the redox vanadyl transformation occurs with the contribution of the carbon functionality. The VO$_2^+$ ions can be transported from the bulk of the electrolyte to the electrode–electrolyte interface where a proton exchange from the oxygenated functional groups takes place, leading to bonding of vanadyl groups onto the electrode surface. Additionally, electrons can be transferred from VO$_2^+$ to the electrode along the −COOVO+ bond with VO$_2^+$ formation, and then VO$_2^+$ can diffuse into the electrolyte bulk. This process is presented in Fig. 4.

Apart from iodine-based redox couples, some work from Ishikawa et al. reports the activity of bromide species utilizing a non-aqueous redox active electrolyte composed of 1 mol L$^{-1}$ of 1-ethyl-3-methylimidazolium bromide dissolved in 1-ethyl-3-methylimidazolium tetrafluoro-borate. Activated carbon fibre cloth serves as electrodes. Although such a charge storage concept should usually be useless due to inevitable, undesirable reactions, e.g. shuttle reaction or migration of active redox species between the electrodes, much-enhanced capacitance with an excellent reversibility and energy density limited by the diffusion process is obtained. Moreover, the coulombic efficiency of such a type of cell is quite high, approaching 100%. The redox species such as Br$_2$ or Br$_3^-$ being the source of reversible charge do not diffuse from the positive electrode into the electrolyte, which might suggest some kind of insertion phenomena, which is still not confirmed. Additionally, an excellent cyclability of at least 10 000 cycles was reported.

Another related work applying the well-known quinone/hydroquinone couple as a redox-active additive to 1 mol L$^{-1}$ of aqueous H$_2$SO$_4$ has been reported. Besides the typical electrical double-layer charging characteristic of carbon materials, galvanostatic cycling performed on each electrode confirmed a usual battery-like behaviour on the positive electrode and a pseudocapacitive hydrogen electro-sorption process on the negative one. The authors suggested that it is the consequence of an asymmetric voltage splitting between the electrodes after the incorporation of hydroquinone. A tremendous capacitance value of 5017 F g$^{-1}$ was recorded by cyclic voltammetry at 1 mV s$^{-1}$ for the positive electrode, probably due to the development of the quinoid redox reactions on the activated carbon surface. Meanwhile, the capacitance of the negative electrode also increases significantly when compared to the value obtained for the electrode operating in the electrolyte without hydroquinone (from 290 to 477 F g$^{-1}$). As a result of the combination of all these phenomena, the energy density of the hydroquinone-containing systems is significantly greater than that of the original system (30 W h kg$^{-1}$ vs. 10 W h kg$^{-1}$), accompanied by good cyclability and capacitance retention.

Even if the values of energy density as well as capacitance are slightly doubtful due to different capacitance values recorded from different methods, the idea of exploiting the quinone/hydroquinone redox couple from the electrolyte is reasonable and needs to be investigated more deeply.

4. Pseudo-capacitance related to reversible hydrogen electrosorption in nanoporous carbons

4.1. Carbon–hydrogen interactions

In the last ten years a huge number of publications dealt with di-hydrogen physisorption in nanoporous carbons. The interest for this topic was initiated by claims of high capacity values, especially

Fig. 3 Cyclic voltammograms recorded at various scan rates for a capacitor operating in iodide/vanadium conjugated redox couples as electrolyte solutions.

Fig. 4 Surface redox reactions with vanadium species.
in carbon nanotubes and carbon nanofibers. Despite many efforts to reproduce the data and to study new carbons and their composites in a wide range of conditions, the present status is that negligible amounts of di-hydrogen are stored in carbons at ambient pressure and temperature. The adsorption capacity can be enhanced by increasing gas pressure or and decreasing temperature. To date ref. 72 provides probably the most reliable data on a series of chemically activated carbons and also on other types of carbon materials, such as activated carbon fibers, carbon nanotubes and carbon nanofibers. The best values measured for the adsorption capacity at 298 K are 1.2 wt% and 2.7 wt% at 20 MPa and 50 MPa, respectively. At 77 K, the hydrogen adsorption capacity reaches 5.6 wt% at 4 MPa.

More promising hydrogen capacities, up to ca. 2 wt%, were found by electro-reduction of aqueous media on a nanoporous carbon electrode under ambient conditions.73–76 Interestingly, the electro-sorbed hydrogen can be desorbed by anodic oxidation giving rise to a potential pseudo-faradic contribution in addition to the EDL capacitance of the material.

Due to the driving force of the negative polarization, in situ produced hydrogen easily penetrates into the nanopores of carbon, where it is adsorbed. In alkaline solution, for example, water is reduced according to eqn. (19):

\[ \text{H}_2\text{O} + e^- \rightarrow \text{H} + \text{OH}^- \quad (19) \]

and the formed nascent hydrogen is adsorbed on the surface of nanopores:

\[ \langle C \rangle + x\text{H} \rightarrow \langle \text{CH}_x \rangle \quad (20) \]

where \( \langle C \rangle \) represents the carbon host, and \( \langle \text{CH}_x \rangle \) hydrogen adsorbed in the latter.

The overall charge–discharge phenomenon is summarized by ref. (21):

\[ \langle C \rangle + x\text{H}_2\text{O} + xe^- \leftrightarrow \langle \text{CH}_x \rangle + x\text{OH}^- \quad (21) \]

Cyclic voltammetry is a well-adapted electrochemical technique to elucidate the mechanism and kinetics of reversible hydrogen storage.74–77 An example of voltammetry characteristics, using a microporous activated carbon in 6 mol L\(^{-1}\) KOH, is shown in Fig. 5. The minimum potential is shifted to more negative values for each cycle, i.e. towards hydrogen evolution. When the electrode potential is higher than the thermodynamic value which corresponds to water reduction (the theoretical value of the equilibrium potential in 6 mol L\(^{-1}\) KOH is –0.924 V vs. Hg|HgO), the voltammetry curves have the rectangular shape typical of charging the electrical double-layer. When the potential becomes lower than this value, both the double-layer is charged and hydrogen is adsorbed in the pores of carbon. During the anodic scan, the reactions (20) and (21) proceed in opposite directions and a peak corresponding to the electro-oxidation of sorbed hydrogen is observed. This important polarization between the cathodic and anodic processes indicates that hydrogen electrochemically stored is trapped more strongly than for a classical physisorption.77

This type of hydrogen bonding was confirmed by Thermo Programmed Desorption (TPD) on AC samples subjected to galvanostatic charge at –500 mA g\(^{-1}\) for 15 minutes or 12 hours (Fig. 6). In order to avoid any unwanted hydrogen desorption, the samples were not rinsed with water after the electrochemical charging. As a consequence they both present a peak above 400 °C which is due to the reaction of excess KOH with carbon, according to eqn (22):79

\[ 6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3 \quad (22) \]

It is the only peak observed for the sample charged for 15 minutes at –500 mA g\(^{-1}\); within this limited charging time, the Nernst potential for water reduction is not reached, and only the electrical double-layer is charged. By contrast, when charging is prolonged for 12 hours, an additional peak appears in the TPD curve at around 200 °C.77 The estimated desorption activation energy of 110 kJ mol\(^{-1}\) is characteristic of a weakly

Fig. 5 Voltammetry scans (5 mV s\(^{-1}\)) on a carbon electrode (AC) in 6 mol L\(^{-1}\) KOH with a gradual shift to negative values of potential.78

Fig. 6 TPD analysis of dihydrogen evolved from a microporous activated carbon (AC) charged at –500 mA g\(^{-1}\) in 6 mol L\(^{-1}\) KOH for (a) 12 hours and (b) 15 minutes (adapted from ref. 77).
chemisorbed state of hydrogen with the carbon surface.\textsuperscript{80,81}

The important role of active sites (dangling bonds) in hydrogen chemisorption has been proved by studying nanoporous carbons of comparable texture, but with varying amounts of surface oxygenated functionality, as estimated by TPD measurement of the CO + CO\textsubscript{2} amount desorbed at 950 °C.\textsuperscript{82} Fig. 7 shows that the hydrogen storage capacity decreases when the amount of oxygenated groups increases, i.e. when the number of available dangling bonds decreases. The formation of C(sp\textsuperscript{2})–H bonds during cathodic reduction and their dissociation during the oxidation step was confirmed by in situ Raman spectroscopy.\textsuperscript{82}

A chemical type of hydrogen bonding with the carbon surface could be confirmed by monitoring the effect of temperature on the electrochemical characteristics. The galvanostatic charge–discharge curves on the activated carbon (Fig. 8) show that the value of potential reached during the charging step is less negative when the temperature increases, because of an enhanced ionic conductivity reducing the polarization. The discharge plateau is also better defined and positioned at lower potential when temperature increases, indicating a reduction of the kinetic barrier for hydrogen extraction (oxidation) from the micropores. However, the most interesting observation from the curves is an increase of the amount of reversibly stored hydrogen, which confirms that hydrogen electroadsorption in nanoporous carbons is activated by temperature.\textsuperscript{77}

In summary, the electrochemically stored hydrogen is weakly chemisorbed, as opposed to the physisorbed state when the gas is in contact with carbon; in the latter case, the amount adsorbed decreases when temperature increases. As will be shown in the next section, this particular state of hydrogen electrochemically generated is at the origin of interesting properties when AC/AC capacitors are built in neutral aqueous electrolytes.

4.2. Overpotential and pseudocapacitance related to electrochemical hydrogen storage in aqueous neutral medium

According to the thermodynamic stability of water, the maximum theoretical voltage of electrochemical capacitors in aqueous electrolyte is 1.23 V. In practice, for systems operating in KOH or H\textsubscript{2}SO\textsubscript{4} media, the voltage is limited to less than 1 V,\textsuperscript{83} because the potential range of the individual electrodes is not controlled and one of them might operate out of the stability limits, even though the voltage is less than 1.23 V. Consequently, for a long time, it has been accepted that the energy density of capacitors in aqueous electrolyte is much lower than in organic electrolyte.

Recently, voltage values as high as 2 V have been demonstrated for AC/AC capacitors operating in alkali sulfates, e.g., Li\textsubscript{2}SO\textsubscript{4}, Na\textsubscript{2}SO\textsubscript{4}, K\textsubscript{2}SO\textsubscript{4}.\textsuperscript{84–86} As seen on the three-electrode voltammograms of Fig. 9, the reason for these values of voltage is the high potential window of the carbon/alkali sulfate system which is roughly twice larger than in the traditional KOH and H\textsubscript{2}SO\textsubscript{4} electrolytes.\textsuperscript{84}

Actually, depending on the type of carbon, the potential window reaches 2.0 to 2.4 V in a neutral aqueous electrolyte,\textsuperscript{84–86} this is due to the high overpotential for di-hydrogen evolution, e.g., around 0.6 V. As a proof, Fig. 10 shows cyclic voltammograms, in 2 mol L\textsuperscript{−1} Li\textsubscript{2}SO\textsubscript{4}, recorded with a gradual decrease of the negative potential cut-off. At a negative potential cut-off higher than the value for water reduction (the theoretical value for di-hydrogen evolution in this electrolyte is −0.35 V vs. NHE), rectangular-shaped voltammograms, typical of the double-layer charging, are obtained. Below −0.35 V vs. NHE, water is reduced, and a pseudo-capacitive contribution related to reversible sorption of nascent hydrogen takes place together with the double-layer formation.\textsuperscript{87} The negative current increases sharply from potentials below −1.0 V vs. NHE, indicating H\textsubscript{2} gas evolution and the plausible limit for negative polarization. A noticeable hump related to the electro-oxidation of the stored hydrogen appears around 0.4 V vs. NHE during the anodic sweep.\textsuperscript{88}

The kinds of hydrogen sites were identified by following the discharge (anodic
current of +50 mA g\(^{-1}\)) profile after a galvanostatic charge (cathodic current of \(-2\) A g\(^{-1}\) for 3 hours) of AC in 0.5 mol L\(^{-1}\) \(\text{Na}_2\text{SO}_4\) at different temperatures comprised between 20 and 50 °C (Fig. 11).

The discharge curve exhibits two branches: (i) the first one at a low potential corresponds to the weakly bonded hydrogen and is not noticeably affected by temperature; (ii) the second one in the form of a plateau at a higher potential is related to the more strongly bonded hydrogen and increases with temperature.\(^{89}\) The total reversible capacity is 410 mA h g\(^{-1}\), 568 mA h g\(^{-1}\) and 646 mA h g\(^{-1}\) at 20 °C, 40 °C and 50 °C, respectively. Taking into account that 1 wt% of hydrogen corresponds to 272 mA h g\(^{-1}\), the hydrogen storage capacity at 50 °C is 2.4 wt%, whereas under such operating conditions in alkaline medium, the highest values reported are of the order of 2 wt%.\(^{76}\)

The desorption activation energy (\(E_a\)) of hydrogen was determined by Thermo Programmed Desorption (mass spectrometry detection at \(m/z = 2\)) on a powder galvanostatically charged (\(-6\) A h g\(^{-1}\)) in 0.5 mol L\(^{-1}\) \(\text{Na}_2\text{SO}_4\) at 50 °C. The curve corresponding to di-hydrogen desorption (Fig. 12) exhibits two main peaks at 125 and 430 °C,\(^{89}\) confirming two types of hydrogen bonding with the surface of AC after charging in neutral medium, whereas only one type of hydrogen, characterized by a desorption energy of 110 kJ mol\(^{-1}\), is detected in alkaline medium (see Fig. 6 (ref. 77)). Desorption energies of 110 and 205 kJ mol\(^{-1}\) were estimated at 125 and 430 °C, respectively. The part of hydrogen more strongly bonded to the AC surface corresponds to the higher potential plateau on the oxidation curve (Fig. 11).

It is now interesting to look at the potential limits of both electrodes in an AC/AC capacitor; this was done by adding a reference electrode.\(^{85}\) Fig. 13 represents the maximum potential (\(E^+\)) reached by the positive electrode and the minimum potential (\(E^-\)) reached by the negative one, for a given maximum voltage applied to the capacitor. The \(E_{OV}\) values represent the electrode potential when the voltage is set to 0 V between two successive cycles at different values of maximum voltage. For a maximum voltage of 1.8 V, the negative electrode potential reaches \(-0.81\) V vs. NHE, which is lower than the thermodynamic limit for water reduction (\(-0.35\) V vs. NHE), but still higher than the practical negative potential limit of ca. \(-1\) V vs. NHE where a noticeable \(\text{H}_2\) evolution starts to be observed. Comparing the operating range of the negative electrode in Fig. 13 with the values of potential for hydrogen desorption in Fig. 11 indicates that the weakly sorbed hydrogen can bring a pseudocapacitive contribution to the negative electrode. This situation occurs during the discharge of the capacitor when the voltage is sufficiently low to reach an oxidation potential of ca. \(-0.2\) V vs. NHE.
Fig. 14 exemplifies this pseudocapacitive effect for an AC/AC capacitor in 2 mol L\(^{-1}\) Li\(_2\)SO\(_4\). Up to 1.2–1.4 V, the curves exhibit a rectangular shape, typical for charging the electrical double-layer. Above 1.4 V, one can observe a peak which is attributed to water reduction and hydrogen storage in the negative electrode. Correspondingly, during voltage decrease, a pseudocapacitive contribution appears below ca. 0.8 V; according to Fig. 13, this value corresponds to a negative electrode potential higher than −0.2 V vs. NHE, allowing the oxidative desorption of hydrogen from the negative electrode.

From the foreword, it can be concluded that the carbon–hydrogen interactions in protic neutral medium provide two interesting effects for enhancing the energy density of supercapacitors. The important overpotential for di-hydrogen evolution at the negative electrode allows the voltage to be considerably extended by comparison with systems in basic or acidic electrolytes. The second effect related to hydrogen storage at the highest voltage values is an added pseudocapacitive contribution.

5. Conclusions

The various ways of capacitance improvement through pseudocapacitive effects have been reviewed in this paper. A large range of electrically conducting polymers (ECPs) and oxides can deliver high capacitance values but are scarcely exploited because of hindered bulk diffusion and/or doping limited redox processes. Volumetric changes of ECPs during cycling as well as semiconducting properties of oxides are additional hurdles in the practical application of these materials. Thin layers or special architectures in the form of nanorods, flakes, flowers, urchins, etc. can deliver high capacitance values but without practical application. Composites with carbon nanotubes and graphene additives could be advantageous due to high conductivity and resilient properties, but they are too expensive and they will not be able to operate during long term cycling.

A novel interesting source of pseudocapacitance is provided by electrolytic solutions containing redox active species (halides, vanadium, quinones). The redox reactions take place on carbon electrodes with a well developed specific surface area. Taking into account the size of the redox species, the micro/meso ratio of carbon pores is decisive for a good operation of a capacitor. It is noteworthy that diffusion plays an important role in this novel type of device, therefore high energy is expected, but power could be limited. Moreover, one electrode generally gives extremely high capacitance, hence, it is
crucial to equilibrate the system and select two different redox couples well separated from each other.

It has been also shown that neutral media in the form of aqueous alkali sulfates can serve as extraordinary electrolytes for hydrogen electroosorption in the presence of nanoporous carbons. The operating voltage range of capacitors can be enhanced up to ca. 2 V, significantly increasing the energy of devices.

Definitely these new concepts using redox active electrolytes and alkali sulfates in the presence of activated carbons are by far more promising than traditional materials as ECPs and oxides to develop high performance capacitors in environment-friendly aqueous media.

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