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Review

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Between the Electrodes of a Supercapacitor: An Update on Electrolytes

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Abstract: Performance, in particular power capabilities and stability, of a supercapacitor critically depend on the electrolyte: the ionically conducting phase between the electrodes of a supercapacitor. This review provides an overview with particular attention to possible practical perspectives and promising developments. It addresses all studied or suggested electrolyte systems, mentions relevant properties and highlights details possibly important for practical use or posing likely problems.

Keywords: Electrolytes; Electrolyte solutions; Solid electrolytes; Gel electrolytes; Ionic liquids; Deep eutectic solvents; Supercapacitors

1. Introduction and a first overview

1.1 Fundamentals of capacitive energy storage

In a capacitor, electric energy is stored by separating electric charges. The amount of separated charges Q and the difference in electric potential ΔE between both charges (the capacitor cell voltage U) define the stored energy W assuming that cell voltage upon discharge will decrease to zero according to

$$W = \frac{1}{2} \cdot Q \cdot U \qquad (1)$$

In case discharge of a supercapacitor has to stop at a certain minimum voltage $U_{\min}$ (e.g. lithium-ion capacitor must not discharge to a cell voltage where delithiation of the negative electrode proceeds) eq. 1 is modified into

$$W = \frac{1}{2} \cdot Q \cdot \left(U - U_{\min}\right) \qquad (2)$$

Taking the relationship between voltage, charge and capacitance C (the characteristic property of a capacitor) yields

$$W = \frac{1}{2} \cdot C \cdot U^2 \qquad (3)$$

Energy density (gravimetric and volumetric) can be obtained by dividing W with the weight or volume of a device or its active components only. The latter option already indicates possible confusion and poor comparability of published data.

Capacitance in turn is related to the mechanical and physical properties of the capacitor:

$$C = \frac{\varepsilon}{d} A = \frac{\varepsilon_0 \varepsilon_r}{d} A \qquad (4)$$

with the distance d between the two electrodes, their area A, and ε_0 the absolute and ε_r the relative permittivity's. In the conventional capacitor composed of two electrodes (e.g. metal foils with area A) separated by an insulating dielectric material (e.g. a polymer foil with thickness d and ε_r) stored energy is limited by the practically possible capacitances even though voltages may go up to several hundred volts. Capacitance in turn depends on d (smaller, i.e. thinner, causes an increase), area (larger areas carry larger capacity) and ε_r (larger values again cause larger capacity). However, there are practical limits making conventional capacitors hardly suitable for large scale energy storage. Nonetheless, capacitors as a storage option have a major advantage making their use highly attractive nevertheless: No energy conversion step makes them extremely fast (high current) during charge and discharge and very long-term stable. Beyond smooth metal foils and insulating foils of the smallest thickness still suitable for mechanical handling rough surfaces like in electrolytic capacitors with extremely thin coatings of metal oxide as dielectric have already resulted in major improvements[1]. Schematically this transition is shown in **Fig. 1**.

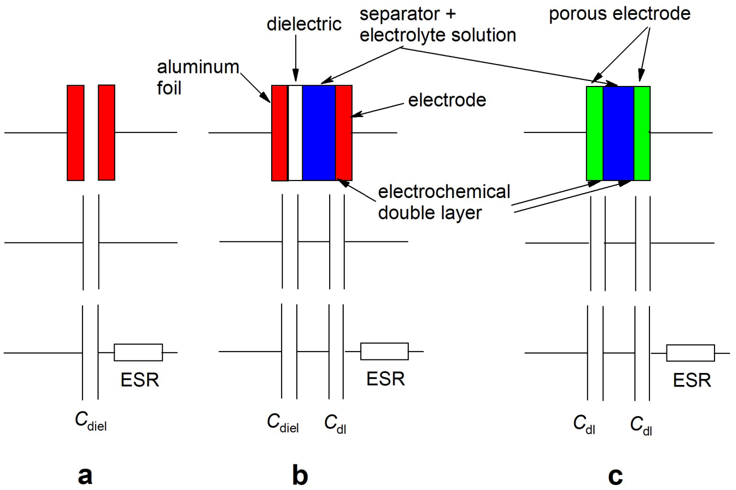


Fig. 1. Schematic cross sections, simplified and extended equivalent circuits of (a) dielectric capacitor, (b) electrolytic capacitor; (c) electrochemical double layer capacitor. Inductive contributions/elements are not shown, they are of minor importance in most supercapacitor applications, C_{diel}: capacitance established between two metallic electrodes separated by a dielectric medium, C_{DL}: capacitance of the electrochemical double layer, ESR: electric series resistance.

1.2 Fundamentals of supercapacitors

A further major increase was achieved by using the capacitive property of the electrochemical double layer itself as described elsewhere[2]. Two electrodes with their respective double layer capacities C_{DL} must be combined, thus the actual capacitance will be

$$\frac{1}{C} = \frac{1}{C_{DL1}} + \frac{1}{C_{DL2}} \qquad (5)$$

The actual device with two electrodes made from some highly porous material contains an ionically conducting but electronically insulating phase between them: the electrolyte or electrolyte solution. The device is called an electrochemical double layer capacitor EDLC. Because both electrodes are essentially the same (during operation electrochemical processes may change the surface chemistry slightly, see[3]) the device may be called symmetric. In case the materials differ (e.g. one electrode made of activated carbon and one made of graphene) the device may be called asymmetric. Because charge accumulation and storage proceed only at the interface and the maximum voltage applicable to the cell is limited by decomposition of electrodes, electrolytes and electrolyte solutions the amount of stored energy is limited and still substantially lower than that in a secondary battery. Utilization of sufficiently fast mostly superficial and/or near surface redox processes may increase charge storage capabilities by up to 100-fold[4]. Active materials used so far are metal oxides[5], mixed metal oxides[6], intrinsically conducting polymers ICPs[7-9] and their composites[10-12]. Sometimes the response of electrodes and cells to changes of applied potential/voltage/current appears capacitor-like, this is called pseudocapacitive behavior [13]. The device may be called redox-capacitor; the term pseudocapacitor sometimes encountered in reports simply does not make sense. The electrode potentials of both electrodes are now given by the redox potentials of the employed materials, different from the EDLC wherein the electrode potentials are simply determined by the accumulated charge. Obviously the electrodes are of different materials, thus the devices are almost always asymmetric. Details have been discussed elsewhere[14], for an overview see[15]. Sometimes electrodes of the redox- and the EDLC-type are combined, this combination may be called hybrid. A class of systems somewhat surprisingly not called supercapacitors but nevertheless frequently discussed in their context are metal-ion capacitors. They are hybrid systems combining a negative battery electrode like a carbonaceous host material for alkali metal ions and a positive EDLC-electrode[9]. More recently terminology appears to be changing, names like metal-ion supercapacitors are popping up. Confusion regarding the use of the terms hybrid and asymmetric seems to stay. In this report a device with the same electrode material and operating principle at both electrodes will be called (when needed at all) a symmetric device (example: two activated carbon electrodes in an EDLC-supercapacitor). One with different materials but still the same operating principle will be called asymmetric (example: graphene-based electrode and activated carbon electrode in an EDLC-supercapacitor). A device with two electrodes with different operating principles will be called a hybrid device (example: MnO_2-electrode and activated carbon electrode, more on this in[16,17]). Further distinctions presumably not helpful anyway will not be pursued nor will be hybrid and asymmetric mixed up as in[18].

Considerations concerning electrolytes are similar for the various types of supercapacitors, no particular sections dealing with them separately are provided below. Theoretical approaches towards the electrochemical double layer, charge storage therein and capacitive energy storage have been reviewed[19].

Between the two electrodes an ionically conducting and electronically insulating third phase is placed: the electrolyte. Actually this denomination is incorrect, at least incomplete. According to textbook definition an electrolyte is a material either composed of ions or capable of forming ions by a chemical reaction. The former case is called true electrolyte, the latter potential electrolyte[20]. Typical examples of the former are NaCl or KOH, of the latter HCl. In both cases, there is no ionic conductivity. NaCl and KOH may become conductive only by melting, HCl by dissolution in water and associated dissociation. Thus, it is more precise to distinguish electrolytes and electrolyte solutions - the popular usage instead suggests that both terms are synonyms. For simplicity in this report, the ionically conducting phase between the electrodes will simply be called electrolyte, when appropriate further distinctions will be added.

Beyond providing ionic conductance between the electrodes there are further tasks for the electrolyte depending on the type of supercapacitor as summarized in **Table 1**.

Table 1. Tasks of species in the ionically conducting phase

Task	Acting species	Example
Ionic conduction	ions	K^+, OH^-
Charge storage	ions	Ions in EDLC device
Reactant in surface redox reaction	H_2O	$MnO_2 + H_2O + e^- \leftrightarrows MnOOH + OH^-$
Counterion in redox reaction	ClO_4^-	$PANI + ClO_4^- \leftrightarrows PANIClO_4 + e^-$
Redox reactant in solution	I^-	$3\,I^- \rightleftarrows I_3^- + 2e^-$

The materials making up the ionically conducting phase between the electrodes of a supercapacitor can be classified for better understanding and oversight, a corresponding taxonomy is displayed in **Fig. 2**. Given the ever closer relationship between supercapacitors of the redox-type and secondary batteries (see e.g.[12, 17, 16]) similarities with a corresponding taxonomy of battery electrolytes are obvious[9]. Because of these close connections, some reports primarily addressing secondary batteries contain information pertaining also to supercapacitors (specifically redox-supercapacitors), they are included below.

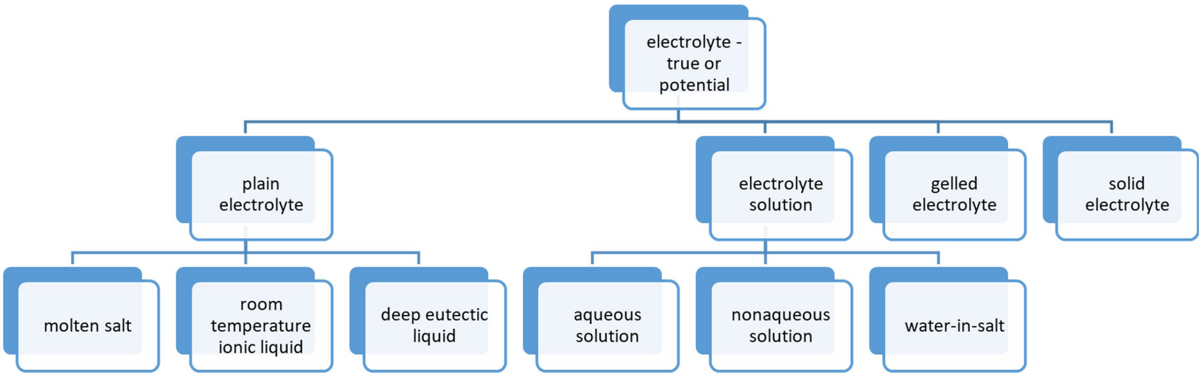


Fig. 2. Taxonomy of supercapacitor electrolytes

Before discussing representative examples of the various options summarized in the bottom line of **Fig. 2** some general considerations indicating pros and cons are collected in **Table 2**.

Table 2. Advantages and disadvantages of electrolyte systems

Type	Advantages	Disadvantages	Section
Aqueous solution	Cheap, sustainable, low tox-icity, highly conducting, good interaction with electrode	Limited cell voltage window of operation	2.1
Nonaqueous solution	Wider cell voltage window of operation, good interaction with electrode	Expensive, flammable, toxic, lower conductivity	2.2
Ionic liquids	Wider cell voltage window of operation, good interaction with electrode	Expensive, low conductivity	3.
Gelled electrolyte	No leakage, can be used also as separator	Interface with electrodes problematic, lower conductivity values in between liquid and solid electrolytes	4.
Solid electrolytes	No leakage, can be used also as separator	Interface with electrodes problematic, low conductivity	5.

Some general aspects as well as topics of supercapacitors ranging from fundamentals to numerous applications are covered in reviews and monographs[9,21-52]. A comparison of organic electrolytes for application in an optical modulator with capacitive properties has been reported; best performance in terms of specific capacitance was found with a gel electrolyte, in terms of optical performance with a polymeric solid electrolyte[53]. Actually said solid electrolyte is a mixture of polyvinylidene fluoride with an ionic liquid.

Although the focus of research activities related to supercapacitors in research reports, reviews and overviews appears to be focused on active electrode materials, to a lesser extent on auxiliary electrode components like binders, conducting additives and current collectors/electrode supports electrolytes have attracted less interest. Some partial overviews, selective reviews, and collections of such contributions on electrolytes are available[18, 28, 54-59]. Reports claiming to provide considerations applicable to electrolyte selection are available[60,61]. Unfortunately, they turn out to be of rather limited helping value; instead, they contain disturbing claims regarding e.g. the recent discovery of the influence of the pH of an aqueous solution on water electrolysis – which has been established knowledge for many decades actually. Specific advantages and disadvantages of electrolytes summarily collected in **Table 2** are addressed in the following sections with respect to specific materials. Thus, only some general considerations following the tasks of an electrolyte summarized in **Table 1** are provided as an introduction.

In a supercapacitor of the EDLC-type the ions in the electrolyte/electrolyte solution are needed for charge compensation during charging for balancing the corresponding charge of opposite polarity in the electronically conducting phase, the electrode. Aqueous electrolyte solutions are cheapest and enable high ionic concentration providing high ionic conductivities resulting in lowest internal resistances (electrical series resistance ESR) of the device. Highest conductivities are offered by strongly acidic and alkaline solutions; unfortunately these solutions tend to be chemically aggressive and corrosive. In addition the cell voltage is limited by the electrolytic decomposition of the solvent water. Although the thermodynamic value at standard conditions is 1.229 V, reported and frequently stated limits vary wildly. Possibly authors suggesting limits as low as 0.6 V want to avoid any decomposition at all costs whereas other authors suggesting values much above the thermodynamic limit apparently trust in kinetic effects, i.e. slow decomposition and associated gas evolution, caused by large electrode overpotentials. Depending on the type of carbonaceous material, composition, pH, and purity of the electrolyte solution cell voltage values above this limit may be acceptable, but possibly self-discharge[62] and ageing[3] may be accelerated. Progress in terms of higher cell voltage and thus higher energy (for the correlation between cell voltage and stored energy see eq. 2) was achieved by moving to various other electrolyte systems with much higher decomposition voltages. The expected and sometimes even achieved major improvements are accompanied by several flaws and drawbacks discussed in detail below.

A common flaw of all liquid electrolyte system is leakage and spilling when the cell container is damaged. Gel or solid electrolytes provide a way to avoid this problem. Again certain drawbacks are associated as reported in the following respective sections.

A fundamentally different mode of charge storage proposed as a way towards much increased charge storage capabilities is the use of redox-active electrode materials already briefly mentioned above. Now the electrolyte has to be at least compatible with the electrode material, it may even be necessary to consider participation of the constituents of the electrolyte solution in these redox reactions. These considerations have to be added to those already specified above for EDLC-devices. Another option is the addition of redox-active components to the electrolyte solution enabling further charge storage as also discussed below in sect. 2.4. Addition of redox systems to the electrolyte may result in further demands on the electrolyte as also indicated below.

An overview on electrolytes for flexible supercapacitors highlighting good and weak aspects of the numerous possible materials is available[63].

Summing up the aspects briefly discussed above a "wish list" for electrolytes quite in analogy to respective lists for electrode materials can be assembled:

- wide electrode potential window
- high ionic conductivity (including various related electrolyte properties like viscosity etc.)
- sufficient chemical and electrochemical stability
- thermal stability
- compatibility with electrode and separator materials
- low volatility and flammability
- environmental compatibility
- low price
- sustainable resources

These requests are related to device properties. **Fig. 3** attempts to indicate relationships between these desired material properties and supercapacitor performance in terms of several of its performance parameters.

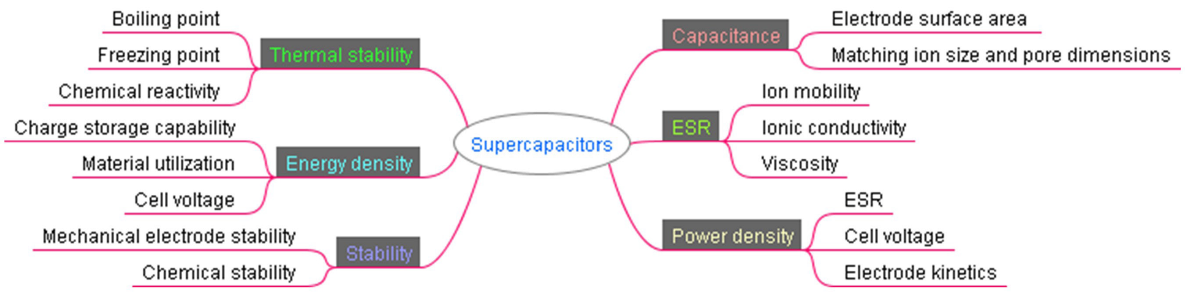


Fig. 3. Relationships between supercapacitor performance, device properties and materials properties.

The electric power P of a device depends on its capacitance C, the cell voltage U and the equivalent series resistance ESR according to

$$P = \frac{1}{4 \cdot \mathrm{ESR}} U^2 \tag{6}$$

Power density (gravimetric and volumetric) can be obtained by dividing P with the weight or volume of a device or its active components only (for details see[18]) . The latter options are an obvious source of confusion and poor comparability of published data.

Whether the separator is the most important component in a supercapacitor as claimed in [64] or not - it should be considered whenever possible together with the electrolyte or should be combined with it as described below for gel and solid electrolytes.

Although the interactions between electrolyte(s) and electrode(s) are in the focus of attention in research and reports further interactions between electrolyte(s) and other device components (binder, current collector, cell case) should be kept in mind. Relevant details are addressed in the following sections.

In the recent decade overviews and reviews covered some subtopics of electrolytes with particular attention to promising details in the most recent publications. A full overview covering the whole field without attempting to present every single research paper but instead helping researchers to find an access to the field is provided here.

2. Electrolyte solutions

2.1 Aqueous electrolyte solutions

First reports related to charge storage in the electrochemical double layer starting the development of supercapacitors[65,66] specify various aqueous electrolyte solutions. Given the vast bulk of experimental evidence regarding the electrochemical double layer with aqueous electrolyte solutions this comes as no surprise. The knowledge on such solutions has been comprehensively collected in[67-69]. Later reports generously ignore these works and rehash some content in detail, for an example see[60].

The ions solvated in the aqueous electrolyte solution provide charge carriers for ionic conduction between the electrodes in addition to their task of providing charge compensation at the electrode/solution interface. As described in detail in[67] there is a maximum conductivity for an electrolyte (salt) as a result of the conductivity-enhancing effect of growing salt and thus ion concentration and the decrease of ion mobility with growing concentration, incomplete solvation and dissociation, ion pair formation etc. A practically reasonable concentration of electrolyte will always be at or below this maximum. The corresponding minimum value of ESR will contribute to optimum power delivery of the supercapacitor, and given the dependence of capacitance on current density (capacitance retention) for a given device, a lower ESR will also result in higher specific capacitance in particular at high currents. Obviously, ESR should not interfere with charge storage capability at first glance; this can be verified by measuring specific capacitance at zero current. This is practically impossible, but values can be approached by extrapolations as discussed before[2]. Unfortunately this extrapolation is rarely performed, this results in a large number of hardly comparable data as criticized before [2,70]. As an obvious consequence of the interplay between conductivity and measured capacitance as derived from instationary measurements (cyclic voltammetry CV and galvanostatic charge/discharge measurements GCD) the better conducting acidic and alkaline electrolyte solutions provide higher specific capacitances. Since neutral electrolyte solutions permit a wider cell voltage variation energy densities of supercapacitors are generally larger with these solutions in particular because of the quadratic dependence of W on U (eq. 3).

Selection of cations and anions supporting both maximum specific capacitance and current capabilities is a further concern. In EDLC-devices various types of carbonaceous materials are used. Their large specific surface area is mostly located inside a more or less highly developed porous structure. This internal surface area can only be utilized when this surface is accessible for the electrolyte solution, is wetted and can participate in double layer formation[71]. Thus, any surface inside pores with openings smaller than the size of ions, which need to get inside, will not be used. This rather simple approach has been verified with e.g. tailored carbide-derived carbons with well-defined pore opening diameters and a variation of electrolytes with a common cation and different anions or vice versa. Because at the negative electrode cations need to be assembled at the interface whereas at the positive electrode cations are accumulated both ions of an electrolyte require attention. In an anion-related study with aqueous solutions of 6 M KOH, 2 M KCl, 1 M KNO_3 and 0.5 M K_2SO_4 with calcium-carbide-derived activated carbon electrodes specific capacitances decreased in this sequence[72]. Values were derived from CV; no attempt was made to obtain extrapolated values at zero scan rate in order to remove the already addressed dynamic effects due to the interplay between concentration (which significantly differed in this study), ionic conductivity and current. The synthesis procedure of the used activated carbon resulted in a well-defined pore size distribution which in turn enables a comparison between pore sizes (not size of the pore opening) and the anion sizes. Without any evidence of desolvation values of the hydrated anions would be used; numbers are collected in **Table 3**[73-78]. The values correlate strongly with the sequence of specific capacitances suggesting that more of the smaller hydroxyl cations fit into a pore than of the other anions resulting in more charge stored. Keeping in mind the limitations of this approach, in particular the insufficient removal of kinetic or dynamic influences on results, specific capacitance should also decrease from K^+ to Na^+ to Li^+. Using their sulfates such a study has been reported with the aim of finding relationships between identity of the electrolyte and water decomposition cell voltages[79]. In a comparison of 1 M aqueous solutions of Li_2SO_4, Na_2SO_4, and K_2SO_4, cyclic voltammetry at $dE/dt = 10$ mV•s^{-1} yielded specific capacitances significantly decreasing in the order $Li_2SO_4 > Na_2SO_4 > K_2SO_4$, this sequence is maintained up to $dE/dt = 100$ mV•s^{-1}. Galvanostatic charge/discharge measurements confirmed this observation in a wide range of current densities $0.2 < j < 50$ A•g^{-1}. Unfortunately the lowest value of j is still far away from equilibrium, i.e. $j = 0$ A•g^{-1}, where kinetic effects on the observed specific capacitances can be presumed to be absent. Extrapolation to this limiting value following the approach discussed elsewhere [2, 80] was not attempted. Even within the range of reported observations no correlation between limiting equivalent conductivity growing from Li^+ to K^+ and the specific capacitance decreasing from Li^+ to K^+ can be inferred. A look at solvated ion sizes with respect to pore opening sizes of the activated carbon used in[79] fails to yield any insights. The reported bimodal pore size distribution does not suggest that the actually only slightly larger lithium ions penetrate into pores better than the smaller potassium ions.

Some selected data on ions in aqueous electrolyte solutions are collected in **Table 3**.

Table 3. Selected data on ions in aqueous electrolyte solutions at $T = 25$ °C sorted according to solvated ion diameter (based on data in[73-78]).

Ion	Ion diameter/ pm	solvated ion diameter/pm	limiting molar ionic conductivity/ S•cm^2•mol^{-1}
H^+	115	280	350.1
K^+	133	331	73.5
NH_4^+	148	331	73.7
Na^+	95	358	50.11
Li^+	59	382	38.69
Ba^{2+}	135	404	127.8
Ca^{2+}	100	412	119
Mg^{2+}	72	428	106.12
OH^-	176	300	198
Cl^-	181	332	76.31
NO_3^-	264	335	71.42
ClO_4^-	292	338	67.3
PO_4^{3-}	223	339	207
SO_4^{2+}	290	379	160.0
CO_3^{2-}	266	394	138.6

As already discussed before [81,82] determination of the listed values in this table is fraught with possible sources of errors. There are various approaches to the ionic radius; determination of the solvated ion radius is even more complicated. These uncertainties should be stated or at least properly addressed in respective data collections, without such annotation the completely unfounded impression is created, that listed numbers are exact beyond any doubt as e.g. in [54]. In **Table 3** ionic radii refer to the smallest coordination number. Hydration number related to size of the solvate ion has similar challenges. In a representative example hydration number is defined as the number of water molecules assumed to be necessary to explain the apparent molecular weight of the moiety as determined with a size exclusion columns[76]. Hydration of alkali metal ions has been studied with large angle X-ray scattering and double difference infrared spectroscopy[78]. Except for lithium ions, hydration is weak with only a single sphere of water molecules. Lithium ions are hydrated more with possibly a second shell. This may help in understanding differences in behavior between lithium salts and the rest. The remarkable differences between crystal, Stokes and hydrated radii of a wide selection of ions has been highlighted before[74]. A link between specific capacitance of activated carbon and ionic conductivity claimed in[28] is not at all supported by the quoted references; the problems related to proper data reporting and the insufficient separation of various factors contributing to specific capacitance and energy density addressed elsewhere in the present report[2, 70] may have contributed to the erroneous claim. It may also simply be a confusion between correlation, perhaps just coincidental, and a causal relationship. A similar impression is left by a study of the capacitance behavior[83]. Any rationale behind selection of the electrolytes (KOH, H_2SO_4, KCl, KNO_3, Na_2SO_4) and the employed concentrations is not communicated. Instead, attention was apparently focused on surface area and pore size distribution of the used mesocarbon microbeads. Actually observed pore size distributions were highly similar, specific surface areas varied between 853 and 1104 $m^2 \cdot g^{-1}$ when CO_2 adsorption was used whereas it ranged from 2759 to 1065 $m^2 \cdot g^{-1}$ when N_2 was used. Highest specific capacitance was observed with the best-conducting electrolyte solution 6 M KOH and the carbon material showing the highest BET-surface area. The authors suggested another material with about half the surface area as most promising. Beyond this somewhat confusing conclusion this study is limited to data only derived from galvanostatic cycling (whatever that means) without displaying results and the mode of evaluation. A shown plot of specific capacitance vs. solution conductivity confirms concerns regarding this evaluation stated elsewhere in this report[2, 70]. Any causal relationship between ion properties, carbon properties and observed capacitance remained elusive. A further study of the effect of salt concentration on energy density found a strong dependence[84]. As a cause, the insufficient supply of ions needed for charge compensation at the electrochemical double layer has been stated. The range of studied concentrations not specified in the text can be derived from displayed results. For the studied system tetraethylammonium tetrafluoroborate in propylene carbonate the stated dependence vanishes at concentrations above 2 M. The stored energy also showed a strong correlation with discharge current, with increasing current the amount of stored energy decreases significantly. This was attributed to iR-drop, i.e. the voltage drop across the ionically conducting phase. Because measurements were performed with flowing current and not at equilibrium, the depth of penetration of the current into the porous body and into the pores will decrease with growing current, in a separate study of material utilization of supercapacitor electrodes this has been confirmed[80]. This correlation, i.e. a drop in specific capacitance and thus stored energy, will become more obvious with poorer conducting solutions and a higher fraction of EASA located in micropores. Similar studies with other organic electrolyte systems are not available; the same applies to aqueous systems. Thus, it can be tentatively speculated only, that in aqueous solutions with electrolytes providing a degree of dissociation α close to unity and with salt concentrations in the range $c > 0.5$ M the depletion effects observed in[84] will be absent. As evident from the reports briefly discussed above connections between identity and concentration of electrolyte salts and properties of the carbonaceous materials commonly used in EDLC-type supercapacitors there appears no clear cause-and-effect correlation or connection between any of these facts. In addition the already addressed poor or even absent standards in rational reporting of data [2, 70] compound the quite obvious challenge of finding an optimum material combination based on a rational choice of materials. In the study of concentration effects[84] the authors state in passing the significant influence of an iR-drop on obtained energy values. According to the brief summary of fundamentals in the introduction above the charge storage capability of an EDLC-type electrode is given by the electrochemically active surface area EASA (for an extended discussion see[85,86] provided that sufficient ions are available for charge compensation. The stored energy depends only on the device voltage, which in turn for an EDLC-device is defined by the state of charge in the absence of any electrode-potential defining redox processes. Unfortunately, an experimental verification by a simple measurement of stored charge and effective voltage not affected by any other experimental variable is difficult. Any measurement of stored or retrieved charge is performed as a measurement of current with associated electrode potential or cell voltage. Once such a non-stationary approach is pursued, kinetic effects like iR-drop come into play. Beyond the drop in the bulk of the electrolyte solution between the electrodes, also the drop inside the porous electrode, even inside the pores of the carbonaceous material, plays a role growing with current/current density. Whether the suggested extrapolations[2, 70] based on earlier investigations[87] really provide equilibrium values of capacitance free from said influences may still be an open question, at least they highlight the need for careful consideration of experimental results and for more attention to maintaining comparability of experimental approaches and setups.

Although the water decomposition voltage does not depend on the pH-value the practically possible values may change with pH because the gas evolution kinetics for both hydrogen and oxygen evolution strongly depend on pH[88]. At neutral pH kinetics are slowest. When tolerating some water decomposition below the level of actual gas evolution cell voltages between 1 and 2.2 V are reported (with the latter value being a rare exception[79]), whereas with acidic solution values up to 1.2 V are stated and with alkaline solution up to 1 V are common. Finally, the extraordinary cell voltage up to 2.2 V was attributed to strong solvation of sulfate ions (which were also present in the other electrolyte solutions without causing such remarkable effect) and of lithium ions – which were reported to have a solvated ion radius hardly larger than those of the other alkali metal cations. The relatively low ionic mobility of lithium ions may indeed suggest stronger solvation – but this would contradict to some extent the higher specific capacitance derived from instationary measurements. In a comparative study of neutral, acidic and alkaline electrolyte solutions (unfortunately all conceivable parameters like identity of ions and concentration were generously varied prohibiting any ion-specific conclusions) with structurally modified activated carbons again the neutral yielded the highest energy density because of the largest possible cell voltage. At higher current densities, capacitance retention with the neutral solution is poorer since micropores contribute less to storage because of the slightly lower ionic conductivity. At large cell voltages corrosion of the current collector may become a problem; this should be considered also, when comparing experimental results possibly obtained with different material, e.g. gold vs. stainless steel. Limited solubility of salts in particular at low temperatures may provide another challenge when using neutral solutions.

In redox-supercapacitors solvent molecules and the ions of the electrolyte solution serve further purposes beyond those outlined for EDLC-devices discussed in the preceding section. They may participate in redox reactions:

$$MnO_2 + H_2O + e^- \rightleftarrows MnOOH + OH^- \qquad (7)$$

$$MgCo_2O_4 + H_2O \rightleftarrows MgO + 2\,CoOOH \qquad (8)$$

$$2\,CoOOH + 2\,H_2O + 2\,e^- \rightleftarrows 2\,Co(OH)_2 + 2\,OH^- \qquad (9)$$

Unwanted dissolution of active material in its various states of oxidation and corresponding chemical composition may be slowed down by additives to the electrolyte solution resulting in the formation of insoluble coatings on the active material. For examples see[89]. Ionic conductivity of these coatings must be considered in order to avoid passivating layers. Another option is the use of composites with ICPs reviewed elsewhere[10-12] wherein the ICP coating of the chalcogenides prevents dissolution. In addition to solubility considerations which may limit the selection of electrolytes to neutral or more or less alkaline ones concentrations of the participating ions of the electrolyte (being consumed and/or being created) may vary during operating with associated effects on ionic conductivity.

A further example is the positive electrode of the lead-acid accumulator. The popular elec-trode reaction (simplified) with sulfuric acid electrolyte is

$$PbO_2 + 2\,H^+ + 2\,e^- + H_2SO_4 \rightleftarrows PbSO_4 + 2\,H_2O \qquad (10)$$

With an aqueous solution of e.g. methanesulfonic acid no precipitation proceeds, the reaction changes into [90]:

$$PbO_2 + 4\,H^+ + 2\,e^- \rightleftarrows Pb^{2+} + 2\,H_2O \qquad (11)$$

To accelerate electrode reaction kinetics of the positive electrode, but mostly because of safety concerns regarding methanesulfonic acid other acids like perchloric acid, tetrafluoroboric and hexafluoric acid have been tested[90]. Research has apparently not been continued despite of earlier interest in a soluble lead-acid accumulator[91, 92]. Elsewhere the lead dioxide electrode in its conventional mode of operation combined with a negative EDLC-type electrode is successfully employed with a silica-gelled aqueous sulfuric acid electrolyte solution in a hybrid supercapacitor[93].

Use of a redox-active material instead of an EDLC-device material (a simple electronically conducting material acting only as charge sink/source) has been suggested[94] with hydroquinone wrapped around (actually and more realistic: decorated on) MnO_2.

In this example, the added organic compound added slightly to the storage capability leaving device and behavior otherwise unchanged.

In case of ICPs ions from the electrolyte, move in and out of the highly porous ICP for charge compensation. Because most ICPs can be oxidized for charge storage and subsequently are reduced during discharge (i.e. they are used as the positive electrode of a supercapacitor) following polypyrrole PPy (**Fig. 4**) is considered as an example:

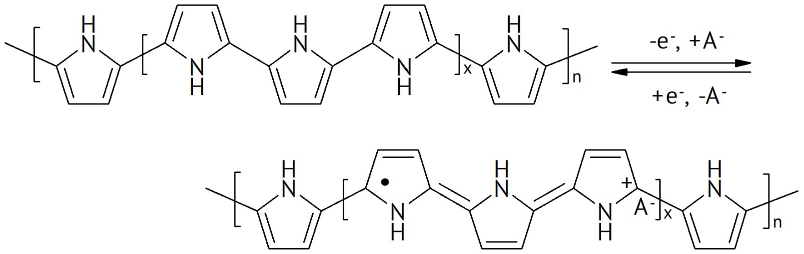


Fig. 4. Redox processes of PPy with A^-: ClO_4^-,Cl^-,SO_4^{2-}

Different anions may result already during formation of the ICP by chemical or electrochemical polymerization in different properties as extensively discussed before[81,82,95,96]. These differences as evidenced with e.g. cyclic voltammetry may include differences in charge storage capability (charge density). Cations play a role only when they are inserted upon reduction of the oxidized ICP – a rather unlikely proposition. Nevertheless, a study of cations effects with a composite of chemically polymerized PPy and graphene has been performed [97]. With HCl the highest specific capacitance was observed, differences between values reported with Na^+, K^+, and Li^+ were significant, but not overwhelming. The influence of pH (when moving between a 1 M acidic solution and 1 M neutral solutions) was as carefully ignored as the rich literature on ICPs. The reported values of specific capacitance were less than half the values reported before[98]; as they have been derived from CVs the reported correlation between capacitance and ionic mobility comes as no surprise.

Specific capacitances with aqueous electrolyte solutions are almost always much larger than corresponding values with nonaqueous solutions. In the absence of rigorous experimental verification, there are numerous conceivable reasons: The lower conductivities of the latter result in smaller currents in CVs frequently used for determination, the wetting behavior may differ [71], contributions from redox functionalities may differ. The steady mix-up of stationary and instationary values and methods (for an illustration see[55]) adds to the ongoing confusion. The new insights into the operating voltage of aqueous supercapacitors promised by the title are presumably buried in a flow of errors and misunderstandings[99].

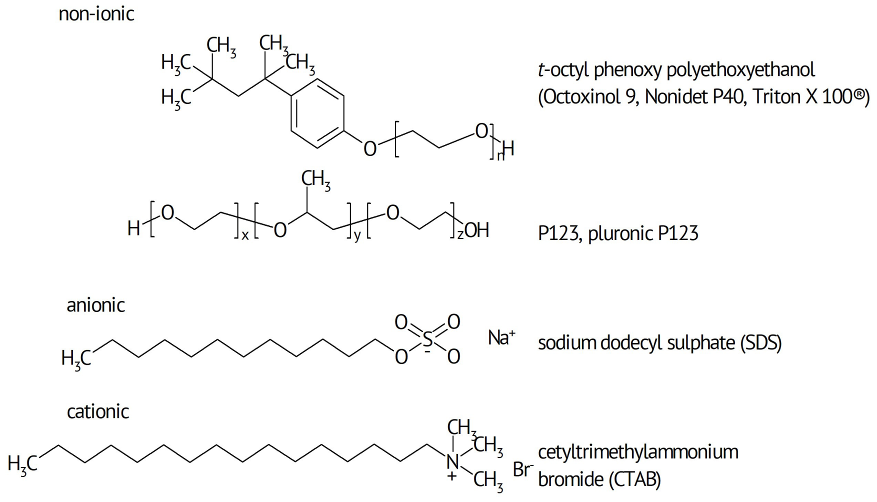


Fig. 5. Molecular formulas, systematical names, trade names and acronyms of representative surfactants.

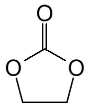
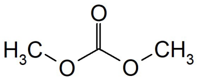
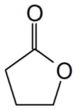
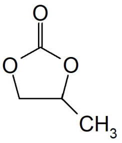
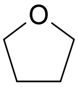
The addition of mM concentrations of surfactants (for examples see **Fig. 5**) to aqueous electrolyte solutions of both EDLX-devices and redox supercapacitors have resulted in improved performance in terms of longer lifetime and better capacitance retention with growing current density [100].

2.2 Nonaqueous electrolyte solutions

The major advantage of organic solvents in electrolyte solutions is their much higher stability versus electrochemical decomposition (electrolysis) resulting in a much wider window of electrochemical stability, i.e. a higher cell voltage (for critical reconsiderations see[101], also[102], for an ab initio approach see[103,104]). Given the mentioned relationship between cell voltage and energy content of a supercapacitor, (see eq. 2 and 3) this increase is highly welcome and valuable. As well-known from lithium ion batteries, wherein such electrolyte solutions are industry standard for decades already because of the incompatibility of a lithium or lithium-graphite electrode with an aqueous electrolyte solution, this major advantage comes with several flaws: These solutions generally show lower ionic conductivities related to poorer solvation capabilities and degrees of dissociation well below 1, the solvents and most of the electrolyte salts are more expensive, the solvents are more volatile than water resulting in evaporation with associated fire and other risks in case of cell leakage, they are sometimes flammable adding a further risk in case of cell leakage or cell destruction. Most of them are also toxic, but this applies also to many aqueous electrolyte solutions. Another practical advantage in comparison to aqueous electrolyte solutions is the possibility to use lighter and cheaper materials like aluminum as current collector and for packaging and other auxiliary purposes instead of e.g. stainless steel.

Carbonates (ethylene carbonate, propylene carbonate, dimethyl carbonate and their mixtures) and acetonitrile are popular solvents. For improved performance in terms of e.g. wider range of operating temperatures, mixtures of solvents are used. Some examples of common solvents are collected in **Table 4**, extended data collections are available[77]

Table 4. Selected organic solvents

Solvent	Acronym	Structural formula	ε_r	η/cp
Acetonitrile	AN	$H_3C{-}C{\equiv}N$	36,6	0.3
Ethylene carbonate	EC		89.8	1.93
Dimethyl carbonate	DMC		3.1	0.625
γ-Butyrolactone	GBL		39.0	1.7
Propylene carbonate	PC		66.1	2.5
Tetrahydrofurane	THF		7.5	0.49

Salts like tetrabutylammonium hexafluorophosphate ($TBAPF_6$), lithium hexafluorophosphate ($LiPF_6$), tetraethylammonium tetrafluoroborate ($TEABF_4$) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) are popular electrolyte salts. Because of environmental concerns and the formation of highly corrosive HF in the presence of traces of water in a device fluor-containing salts are not preferred. They all have relatively large ion sizes taking care at least to some extent of the poorer solvation capabilities of the solvents when compared with water. The low viscosity of AN (0.3 cP) as compared to e.g. 2.5 cP for PC results in better conducting electrolytes solutions and lower ESR values. Contrary to an erroneous claim in [28] the dielectric constant of AN ($\varepsilon_r = 36$) is not larger than that of PC ($\varepsilon_r = 65$), the donor number also relevant for solvation behavior is practically the same for both. Unfortunately AN is a health hazard, its use is limited or prohibited in some countries (e.g. Japan, Sweden). Maximum cell voltages possible with particular solvent/salt combinations are not listed above because of considerable uncertainties (see e.g. [18]): Sometimes reduction/oxidation potentials are reported with electrode materials (e.g. gold, platinum or glassy carbon) not relevant for practical applications. In addition, the terms reduction/oxidation potential are not practically defined. Thus a potential difference $E_{\text{ox}} - E_{\text{red}} = 6.6$ V has been stated for propylene carbonate, for acetonitrile the value is 6.1 V [18]. Actual cell voltages are around 2.7 V in both cases. Generally, the feasible cell voltages depend on both solvent and salts different from aqueous solutions where always water decomposition sets the limits.

Basically the same considerations regarding solvated ion size and pore size already discussed for aqueous electrolytes apply to organic solvent-based electrolyte solutions, too, when searching for the optimum combination of solvent, salt, and electrode material morphology (porosity, pore size distribution etc.). Because of the generally poorer solvation capabilities of organic solvents desolvation, i.e. stripping of some or possibly even all molecules making up the solvent shell of a solvated ion is more likely. Thus ions might get into pores with openings too small for the solvated ions. Evidence of at least partial desolvation with organic solvents has been reported[105-107]. Relationships between ion and pore size based on classical density functional theory have been examined for electrolytes based on organic solvents and ILs[108]. The poorer solvation capabilities with degrees of dissociation significantly lower than unity may also result in an insufficient supply of ions for charge compensation in the electrochemical double layer of an EDLC-device as illustrated in[84]. This possibility should be kept in mind when evaluating and combining said options.

2.3 Water-in-salt electrolytes

The cell voltage of devices with aqueous electrolyte solutions is limited by its electrolytic decomposition, mostly the decomposition of water. The rich supply of water (55.5 mol per liter) makes any attempt to inhibit its decomposition by limiting its supply a rather unlikely concept at first glance at least. With increasing concentration of the dissolved amount of salt in the electrolyte solution the fraction of water molecules not bound in the solvation shells of the ions becomes smaller and smaller. This consideration and the different properties of solutions with widely varying salt concentrations have resulted in the classification of salt-in-water (SIW) with the primary solvation shells of the ions completed, salt-water (SW) with only the primary solvation shells of the ions completed and water-in-salt (WIS or WiS) with the primary solvation shells of the ions incomplete because of insufficient supply of water[102] possibly also related to reduced water activity[109]. In addition to the limited availability of water molecules for electrolytic decomposition formation of coatings of electrolyte decomposition products on electrode surface have been suggested as causes of hindered water decomposition [110]. The widening of the “electrochemical window of stability” can thus be attributed to a thermodynamic (diminished activity) and a kinetic cause (reactionin-hibiting coatings) (for overviews see[111,112]). For consideration of a salt to form a WIS sufficient solubility is required. Alkali metal acetates are another promising choice[113]. Within this comparison cesium acetate showed the largest decomposition voltage enabling a wider cell voltage variation (up to 1.7 V) providing finally the largest energy density stable along 10000 cycles. Compared with cell voltages possible with nonaqueous solvents this is only a small achievement; however the complaint about an “inferior value” in[114] appears to be excessive. A cell voltage of 2.3 V could be reached with a 17 m solution of $NaClO_4$[115]. (Unfortunately, symbols for molal concentration (molality) m and molar concentration (molarity) M are sometimes confused in published reports). How such a high concentration of a salt elsewhere known as a major ingredient for explosive devices is called a contribution to safety remains mysterious, the claim for superior safety of the device is presumably misleading. In a study of this WIS (the acronym WISE used by these authors appears to be a misleading exception rarely found elsewhere[116]) yields promising data regarding a significant increase in cell voltage by 50 % when going from $T = 25$ °C to $T = -10$ °C, the capacitance decreased by 20 % [117]. The claim regarding non-flammability again applies to the liquid state only, but is as unrealistic once spilled liquid dries up as in the preceding report. In early reports on WIS the rather expensive lithium bis(tri-fluoromethane-sulfonyl)imide (LiTFSI) has been used in particular because of its high solubility. More recent studies of highly concentrated aqueous solutions of this salt have revealed, that two different forms of cation solvation appear enabling fast lithium ion transport[118]. For comparison and in the search for a more economical alternative $LiNO_3$ has been studied[119]. A 20 m solution of this salt showed lower viscosity and much higher ionic conductivity that 21 m LiTFSI. The cell voltage could be as high as 2.2 V. Superior safety of the system was claimed with reference to UN38.3 not further specified except for a publication by the same authors to a report with a 1 M Na_2SO_4 electrolyte solution [120]. In the latter report UN38.3 is associated with some impact test. The authors did not address the difference between 1 M Na_2SO_4 and 20 m $LiNO_3$, possibly the authors are not aware of the use of nitrates in gunpowder and fireworks. Replacement of LiTFSI because of cost and availability considerations has been tried with NaTFSI[121]. In addition to a lower molality (8 m) needed to get the desired extension of the possible cell voltage addition of KI (see also sect. 2.4) further increased the finally available capacitance staying stable for at least 100000 cycles.

Nevertheless, other drawbacks like increased viscosity and thus lower ionic conductivity in addition to costs are also not welcome. The use of mixed solvents of e.g. water and ethylene glycol as suggested in[114] enables a cell voltage of 3.88 V at a moderate salt concentration of 1 molal Na_2SO_4 with a capacitance retention of 100 % after 10000 cycles. As compared to a completely nonaqueous solution, the common risks associated with them are greatly reduced with this mixture. Possibly the cause of the particular behavior of the mixed solvent is related to "molecular crowding" resulting in reduced activity of water as studied elsewhere with respect to aqueous batteries[122]. Reviews on WIS are available[123,124], with particular attention to non-lithium metal-ion capacitors in[116,125]. The reasons of the extended cell voltage, i.e. the wider window of electrochemical stability, have been addressed in[116]. An overview on highly concentrated electrolyte solutions in EES is available[126].

2.4 Electrolyte solutions with redox-active additives

To increase charge storage capability and thus energy density of a supercapacitor addition of redox systems to the electrolyte solution has been proposed as outlined in an early patent [127] picking up on an earlier report about enhanced capacitance of a supercapacitor after addition of $AgNO_3$ to the aqueous acidic electrolyte solution[128]. Terminology of the various systems thus prepared appears to be volatile and inconsistent (see e.g.[129] wherein the title calls for redox electrolytes (which is hardly correct) whereas in the text redox mediated electrolytes are named – with the meaning of mediated well-established in a quite different context with a different meaning – and finally redox additives are listed), herein the simple but certainly correct and inclusive terminology of *redox-active additives* is preferred. Redox-active electrolytes as in[28, 54] is certainly not helpful because it simply ignores the vast excess of non-active electrolyte (except for one rare example[130]): the redox-active material is always an additive only. Different claims found sometimes turn out to be incorrect (see e.g.[131]). For short overviews with lists of a few examples see[129,132-134]. An overview limited on anionic species with one more acronym coined (aqueous anionic redox liquid electrolyte (AARLE)) is available[135]. When highlighting the reasons for the author's interest in only anionic redox species (actually almost all soluble redox species studied so far have been anionic) they appear to confuse redox reactions of battery electrode materials with redox reactions of dissolved species. Self-discharge is addressed in passing only. Calling the additives or their effects pseudocapacitive resp. pseudocapacitance appears to be confusing[132, 128].

The concept is rather simple: The soluble redox system added into the electrolyte is participating in the charge/discharge reactions at the electrodes in a supercapacitor, which had been an EDLC-supercapacitor before without his addition. Numerous redox systems have been proposed and examined, and given the wide-ranging considerations applied in selecting a redox system there seems to be hardly a generally valid and accepted list of required properties of the finally suggested materials.

Both inorganic and organic materials have been examined, e.g.:

$$3\ I^- \rightleftarrows I_3^- + 2\ e^- \qquad (12)$$

$$2\ I^- \rightleftarrows I_2 + 2\ e^- \qquad (13)$$

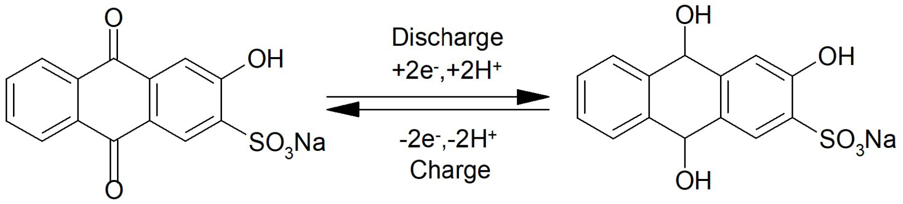
$$2\ I_3^- \rightleftarrows 3\ I_2 + 2\ e^- \qquad (14)$$

$$I_2 + 6\ H_2O \rightleftarrows 2\ IO_3^- + 12\ H^+ + 10\ e^- \qquad (15)$$

This redox system is active at the positive electrode of a system, which was simply an EDLC-device before. Actually, KI can be used as the only electrolyte also[130]. Because it does not react in any way at the negative electrode, the shuttle effect and associated self-discharge are not expected. A remarkable “cation effect” was observed in a comparative study [136]. No reason for the huge differences could be found. The striking imbalance regarding charge storage capabilities between positive and negative electrodes can be corrected in a device by increasing the active mass of the negative EDLC-type electrode. This fundamental aspect is addressed only in passing. Another option is the use of a battery-electrode material at the other electrode. This was demonstrated using Bi_2O_3 as the negative electrode in this system [137]. Capacitance retention after 1000 cycles was 72 %. Different from redox-capacitor materials, i.e. battery electrode materials, where diffusion limitations sometimes curtail currents at these electrodes, with dissolved redox system these limitations do not apply. Accordingly, large currents can be supported even at high current densities in addition to the significantly increased specific capacitance. The electrode potential of this electrode is fixed by the redox potential of the added redox system. Some of the reaction participants may be adsorbed more or less strongly on the EDLC-type electrode materials (mostly carbonaceous ones) reducing mobility and associated self-discharge[131]. They can also be trapped inside the porous electrode body with their localization supported by electrostatics: The negatively charged oxidation production of eq. 12 may thus be attached to the positive electrode. Presumably the first additive [128] involving a metal oxidation/deposition couple was

$$Ag \rightleftarrows Ag^+ + e^- \qquad (16)$$

The addition of two redox couples, one for every electrode, requires insertion of an effective separation between both half-cells. Using a cation exchange membrane and a WIS electrolyte with a cobaltocene compound in the negative and the bromine system on the positive half-cell a system with 91 % capacitance retention after 8000 cycles was realized[138]. Given the growing interest in sustainable and even renewable materials from sustainable resources [98] organic redox-active additives have been examined[139].



(17)

Fig. 6. Redox processes of a water-soluble substituted anthraquinone.

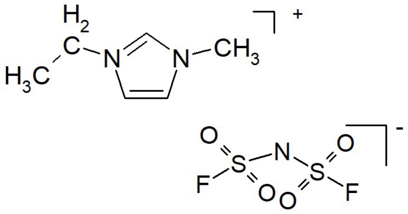
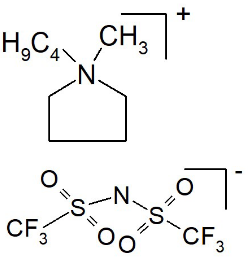
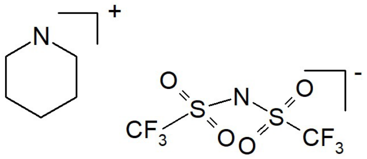
Self-discharge of supercapacitors with added redox-active substances has been a problem from the very beginning once the active species could move freely between both electrodes establishing a shuttle mechanism. For an example see[140], a review examines the topic in detail[62]. Addition of *p*-benzoquinone to a neat IL in an EDLC-device with two different carbon materials as electrodes has been studied[141]. With the carbon, having a lower specific BET surface area capacitance growth was much larger than with a high surface area carbon; the difference depended on operating conditions suggesting pore clogging and further effects. Insertion of a membrane or any other device restricting this mechanism provides a solution at the expense of an increased ESR-value and accordingly reduced power capability. Unfortunately, the gained increase of capacitance turned out to be rather unstable in terms of capacitance retention vs. cycle number. Another option is the use of hardly soluble additives, which strongly adsorb on the respective electrode or are deposited there during assembly. Such cell is actually a redox-supercapacitor, for examples see the preceding sections.

3. Plain (neat) liquid electrolytes

A molten salt is composed of only ions and does not contain any solvent; it can be truly called an electrolyte. Once the melting point is low enough (i.e. < 100 °C) the material may be called an ionic liquid (IL); materials showing an even lower melting point are called room temperature ionic liquids (RTIL) [142]. For an extended range of operating temperatures as well as for optimization of the properties mixtures of ILs as well as mixtures of IL and organic solvents are sometimes suggested (see melting temperature T_m in **Table 5**). When the composition is adjusted to a minimum melting point value the mixture may be called a eutectic mixture, this assignment should not be confused with mixtures described next.

Mixtures of solids also liquid at room temperature (or relatively low temperatures, exact specifications appear to be missing[77,143]) with composition of the mixtures adjusted to ratios yielding eutectic mixtures called deep eutectic solvents (DES) are also combined of ions only [144-146]. ILs as well as DES (for more see below) have been examined as ionically conducting phases in many technical applications (see e.g.[147-149]), this includes their use in supercapacitors[150-153]. Toxicity is less relevant with deep eutectic solvents. Structural variability enabling changes of size and geometry in particular of cations (the selection of anions appears to be much smaller [143]) can be advantageously employed when matching ion and pore size aiming at an optimal utilization of internal pore surface area, for an example with a remarkably high energy density see[154]. Correlations between ion properties and values of C_{diff} have been examined with tools of theoretical chemistry[155], this follows earlier observations of correlations between e.g. length of the alkyl chain in aliphatic alcohols and values of C_{diff}[156,157]. This was experimentally confirmed at least for one type of IL cation in 1-methyl-3-alkylimidazolium chloride[158]. The smaller cations with the shorter alkyl substituent resulted in a thinner double layer and thus a larger C_{diff} at the capacitance minimum at the E_{pzc}. The low vapor pressure of ILs strongly reduces volatility in case of a cell leak. Their low or practically absent flammability related to their pronounced chemical and thermal stability further reduces safety risks in case of leakage. As compared to aqueous electrolyte solutions their ionic conductivities are significantly lower whereas their prices are still much higher. Different from erroneous and possibly dangerous claims about their non-toxicity[159], even contradicting within one report[150], most of them are highly toxic[160].

Table 5. Typical ionic liquids

Name	Acronym	Structural formula	T_m/°C
1-Methyl-3-ethylimidazolium bis(fluorsulfonylimide)	EMI-FSI		-13
N-Butyl-N-methylpyrrolidinium-bis(trifluormethansulfonylimide)	PYR_{14}-TFSI		-6
Piperidiumbis(trifluor-methansulfonylimide)	PIP-TFSI		12

Ionic liquids have been studied as electrolytes for supercapacitors needing no further additives; for some typical examples see **Table 5**, overviews are available[159,161-163]. In a typical example neat 1-ethyl-3-methyl imidazolium bis(fluorosulfonyl)imide (EMI-FSI, see **Table 4**) has been used in an EDLC-supercapacitor keeping more than 90 % of its initial capacitance after 10000 cycles[164]. Rather general claims regarding low self-discharge have been reported, for a correct and realistic appraisal see[62]. Overviews covering many aspects of the use of ILs in supercapacitors beyond the simple substitution of electrolyte solutions are available[150,165]. Using an IL with polypyrrole (an ICP) as active electrode material in a symmetric supercapacitor may cause subtle differences between single and double charged cations of the IL[166]. The provided explanation leaves room for further discussion.

ILs can be classified into aprotic, protic and zwitterionic ones with only compounds from the first class being of practical interest for supercapacitors (and possibly alkali metal-based batteries). ILs with imidazolium-based cations have been preferred because of their low viscosity and consequently relatively high conductivity whereas ILs with piperidinium-based cations show wide windows of electrochemical stability, for further considerations and comparisons of results obtained with various theoretical approaches see[167].

An EDLC-type supercapacitor with EMI-FSI as electrolyte has been reported showing more than 90 % capacitance retention after 10000 cycles and low self-discharge (suppressed self-discharge as stated by the authors appears to be overly optimistic)[164].

Mixtures of ILs aiming at low melting points (eutectic mixtures, not to be confused with deep eutectic solvents, see below) have been proposed yielding an EDLC-type device showing stable cycling behavior during 500000 cycles at 3.5 V cell voltage[168].

Ionic liquids can also be used for preparing gel electrolytes; examples are presented in sect. 4 following. Polymeric ILs like poly(diallyldimethylammonium) bis(trifluoromethanesulfo-nyl)imide (PILTFSI) have been blended with further ILs yielding solid polymer electrolytes inspected in detail below in sect. 5[169].

Addition of redox active substances to electrolyte solutions in EDLC-type devices has been proposed as a simple towards increased energy density (see sect. 2.4). This concept has been combined with the use of ILs. To mitigate self-discharge by a shuttle effect of the mobile redox species their immobilization has been suggested. In addition to cumbersome covalent attachment of redox moieties to a polymeric IL-chain electrostatic attachment has been proposed for electrochemical energy storage EES including supercapacitors without naming a practical example of the latter type of device[170].

In addition to lower toxicity of DES in comparison to most ILs as already addressed above [171] there are further advantages of DES: They can be prepared from common materials easily available, they are significantly cheaper than ILs. A comparison of advantages and disadvantages of IL and DES can be found in[150], although the former appear to be more popular with researchers the latter seem to have more advantages in particular with respect to practical and possibly widespread application. DES are biodegradable, they can be considered as “green” solvents whereas this assignment sometimes found with ILs seems to be hardly applicable there although claimed sometimes[150]. The wide operating temperature range of choline-based DES as electrolytes in supercapacitors has been highlighted in an overview[172].

The variability of components added into a DES can result in a combination with sodium ions particularly interesting for a sodium ion capacitor. A DES composed of $NaNO_3$ and *N*-methylacetamide has been suggested[173].

4. Gel electrolytes

The fundamental flaws of liquid electrolytes and electrolyte solutions have become obvious in the preceding sections: they all share the risks associated with leakage and subsequent spill of cell content after a failure of the container by e.g. corrosion, breakage or a package becoming brittle after time as an effect of mechanical damage. Depending on the solvent further risks like volatility, flammability or environmental damage may follow. Attempts to reduce the liquid inventory have resulted in limitation of potential damage, unfortunately not more. The frequently praised fundamental advantages of solid electrolytes more closely examined in the following section 5 are theoretically correct but difficult or even impossible to achieve in a practical application. Beyond the frequently addressed limitation of insufficient ionic conductivity at ambient temperatures so far not overcome satisfactorily another problem looms: Establishment of a stable interface between electrode and electrolyte deeply penetrating into a porous electrode, even into the pores, and ensuring a sufficiently fast electrode reaction in case of a redox capacitor. Thus a gel being neither a solution nor a solid[174,175] as an electrolyte appeared as a possible option, the terms gelled electrolyte and gel electrolyte are obviously synonyms. Although the words gel and gelled should clearly be distinguished with the former designing a substance and the latter characterizing a material in the literature both terms are used as synonyms. The obvious drawback of this approach – lowered mobility of ions as the charge-carrying species – was not considered as a major hurdle. Actually gelation, i.e. the transformation of a liquid into a semi-solid state by adding a suitable gelation agent, has been studied decades ago for lead-acid batteries in an attempt to reduce problems related to the large inventory of rather concentrated sulfuric acid[176,177]. Further advantages like the development of cracks in the material enabling gas recombination were discovered subsequently. The mechanical properties of a gel support tight mechanical contact with the hard electrode materials. Since the interior of the porous electrode cannot be reached by the gel, additional steps are needed to ensure participation of the internal surface, e.g. soaking or wetting the electrodes before attachment of the gel electrolyte or by formation of the gel *in situ* after cell assembly. Description of a gel electrolyte as being semi-solid already suggests some uncertainty regarding the distinction from solid electrolytes presented in the next section. To avoid confusion in the present context all electrolytes – and only they - prepared by some gelation process, sol-gel process or similar are included in this section. Frequently polymeric materials play a role in formation of a gel electrolyte. The corresponding designation as polymer gel electrolytes makes classification difficult. In this report, they are included in this section. This challenge becomes apparent also in[178] where some further examples of gel electrolytes can be found.

The use of gel electrolytes in lithium-ion batteries has been reviewed[179]. Gels are found elsewhere in EES beyond gel electrolytes in focus here; an overview of so-called “energy gels” is available[180].

4.1 Gel electrolytes

Numerous examples of gel electrolytes based on aqueous electrolyte solutions of KOH, H_2SO_4 and various inorganic salts with polyvinyl alcohol PVA have been studied, numerous performance data have been reported (for a typical overview see[181], a review can be found [182]). Gels prepared with aqueous solutions and a gelling agent are sometimes called hydrogels, an overview has been provided by Choudhury et al.[183]. A PVA/H_2SO_4 gel electrode was found to be suitable for a microsupercapacitor. Unfortunately, the description of the experimental procedure is incomplete, but apparently, an EDLC-device was constructed on the interdigitated Au/Cu-substrate. Capacitance was stable for 11000 cycles.

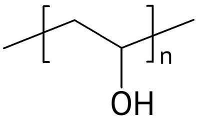


Fig. 7. Polyvinyl alcohol

Significant improvement of ionic conductivity (by a factor 3) of a PVA-based gel electrolyte by incorporation of hexagonal boron nitride nanosheets has been reported[184]. Improved conductivity was attributed to acceleration of ionic movement along the incorporated nanosheets. An EDLC-supercapacitor with this electrolyte kept 99.2 % of its initial capacitance after 5000 cycles. Based on DFT-calculations the high crystallinity of PVA-based gels causing poor ionic conductance can be disrupted by hydrogen bond formation with agarose macromolecules yielding an interpenetrated network with improved ionic conduction[185]. An EDLC-device with this electrolyte kept 90 % of its initial capacitance after 8000 cycles. The high water retention made the material flame-retardant. A fire-retardant polyethylene glycol-based gel electrolyte has been prepared, an EDLC-device prepared therewith kept 78 % of its initial capacitance after 3000 cycles[186]. A modification in the preparation procedure for a PVA-based gel electrolyte with glycerol and NaCl yields a thermoplastic and mechanically tough material[187]. An EDLC-device kept 90 % of its initial capacitance after 2500 cycles. A PVA-based gel H_3PO_4 electrolyte has been used in a flexible supercapacitor with a positive AC electrode and a negative electrode composed of MnO_2 deposited on lignin and AC keeping 97.5 % of its initial capacitance after 2000 cycles[188]. These authors again elsewhere have reported highly similar observations and results[189]. An alkaline gel electrolyte with PVA and carrageenan with KOH as ion source and cross-linking agent shows good performance at low temperatures and even under deformation[190]. A hydrogel with superior mechanical properties has been prepared by forming a double network of agarose and polyacrylamide PAM (the acronym PAAM is also used) with an aqueous electrolyte solution[191].

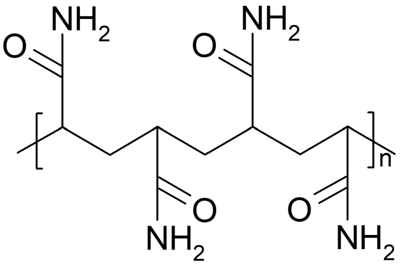


Fig. 8. Polyacrylamide

The tensile strength of a PAM-based hydrogel could be increased by using vinyl group-grafted silica nanoparticles as cross-linkers[192]. An asymmetric flexible supercapacitor with a negative MnO_2-based electrode and a positive one using PPy and this electrolyte kept 85 % of its initial capacitance after 5000 cycles. Using the same approach towards an improved gel electrolyte a material showing high stretchability and remarkable self-healing capabilities was developed[193], see also for a further study[194]. The helpfully large water-binding capability of PAM combined with xanthan enabling formation of hydrogen bonds between the amide groups of PAM and the hydroxyl groups of xanthan yields a gel electrolyte when combined with an aqueous solution of lithium acetate which in addition is very flame-retardant[195]. A flexible EDLC-type solid state supercapacitor kept 82 % of its initial capacitance after 10000 cycles. Another PAM-based aligned polymer hydrogel containing polyampholytes had particularly good adhesion to the carbon electrodes in an EDLC-device enabling particularly high capacitances and complete capacitance retention after 10000 cycles[196].

Given the still deplorable absence of unified and generally accepted standards in measuring and reporting data[2, 70] reported values vary widely and are impossible to compare. A most suitable combination with best performance does not emerge; this includes the highly desirable stability. This slightly disappointing observation includes gel electrolytes based on ionic liquids with perfluorinated polymers and water-based systems with added redox systems. Further examples of gel electrolytes based on ionic liquids (sometimes also called ionogels) can be found in [161], for a review with particular attention to flexible supercapacitors see[197]. Emulsion gels with polymerizable ionic liquids have been reported as an option towards gel electrolytes[198]. The influence of various IL and PIL[1] ions in gel electrolytes on supercapacitor behavior has been compared[199].

A photothermal supercapacitor of the EDLC-type with a gel electrolyte suitable for a very wide range of operating temperatures has been proposed[200]. To keep the device operating at very low temperatures the photothermal packaging converted incoming sunlight into heat.

A flexible EDLC-supercapacitor with a polyelectrolyte-based gel electrolyte obtained via a simple polymerization process serving also as a separator has been reported[201]. After 10000 cycles, 95 % of the initial capacitance was retained. An EDLC-type supercapacitor assembled with a flexible gel electrolyte obtained with PVA, an ionic liquid and Li_2SO_4 kept 88 % of the initial capacitance after 1000 cycles of 135 ° bending[202].

A gelled electrolyte was prepared by filling samples of carbon nanofiber mats prepared by electrospinning with a mix of a sol-gel silica precursor and an ionic liquid[203]. Subsequent drying resulted in formation of a gelled electrolyte (see also[204, 205]) yielding finally a flexible device operating within a 3.5 V cell voltage window. Performance data suggest high penetration of the electrolyte into the fiber network.

A gel with an ionic component, e.g. an IL, may be called more specifically an ionogel, for examples see[161, 196, 206]. It is generally observed that a higher content of IL results in higher conductivity but lower mechanical stability. Improved conductivity

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[1] The commonly accepted meaning of PIL is protic ionic liquid [142]; the present authors prefer their special definition: poly(ionic liquid)!

could be achieved by adding fibrous cellulose filler to an ionogel[207]. In the report, it is claimed that the functional groups of the added fiber enhanced directed ionic movement, i.e. conduction, along thus formed ion channels. An EDLC-type supercapacitor with this electrolyte retained 91 % of its initial capacitance after 3500 cycles. Phosphorylated microcrystalline cellulose has been processes with an IL-mixture into a ionogel with high conductivity in a wide temperature range keeping 93 % of its initial capacitance in an EDLC-device after 10000 cycles[208]. Polyacrylamide and the ionic liquid 1-vinyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide were combined into an ionogel electrolyte[209]. An ionogel electrolyte was prepared from a mixture of an IL and an organic solvent with dissolved chitosan and nano-SiO_2 as gelling agents[210]. An ionogel piezopolymer electrolyte for a self-charging supercapacitor has been studied[211]. Incorporation of cellulose as a renewable, bio based polymer into a gel electrode with a solvent composed of a “superbase” (1,1,3,3-tetramethyl guanidine or 1,8-diazabicyclo[5.4.0]undec-7-ene), dimethylsulfoxide, and CO_2 with PVA and an ionic liquid has been demonstrated[212]. An EDLC-supercapacitor showed stable performance for 8000 cycles. A phase change from crystalline to amorphous with an increase of temperature from 25 °C to 45 °C associated with an increase of conductivity by about five orders of magnitude has been observed for an ionogel of 1-ethyl-3-methylimidazolium nitrate[213]. The specific capacitance grows from 0.02 to 37.35 $F{\bullet}g^{-1}$. At the lower temperature self-discharge is significantly decreased, this matches with the extremely reduced ionic mobility in the crystalline phase. Accordingly, the authors have suggested operating such supercapacitor in the storage (low temperature) and in the operating mode (high temperature). Aligned ionogel nanocomposites with various inorganic constituents have been found to be particularly suitable at elevated operating temperatures[214]. An ionogel with pores aligned by incorporation of TiO_2 nanoparticles showed improved mechanical properties and enhanced ionic conductivity[215]. A zwitterionic ionogel electrolyte for a graphene-based EDLC device showing superior capacitance retention with increasing current load indicative of favorable ion transport properties has been prepared[216].

A symmetric supercapacitor with two poly(3,4-ethylenedioxythiophene)/carbon cloth electrodes and 93 % capacitance retention after 3000 cycles was prepared. Given the frequently discussed inherent drawbacks of symmetric redox supercapacitors[11] further improvements may be achieved by moving towards a more suitable asymmetric setup. Incorporation of ionic liquid-based ionogels into commercial porous membranes yielding components for supercapacitors serving both as separator and electrolyte has been studied[217]. Although incorporation lowered specific conductivities by an order of magnitude, the materials reached the practical application level. Capacitance retentions up to 97 % after 10000 cycles were noted suggesting a promising approach to cell components suitable for roll-to-roll processing.

Hybrid polymer gels composed of a polymer gel and a second constituent like nanoparticles of metals or carbons yielding a hybrid material have been reviewed[218]; their application in supercapacitors is addressed.

The particular suitability of gel electrolytes in wearable devices has been discussed in[219], further examples of gel electrolytes can be found in[220]. A review highlighting current flaws and limitations for polymer gel electrolytes in flexible supercapacitors is available[181], for further examples see[221]. A mechanically tough and self-healing gel electrolyte composed of an ionic liquid, hydroxyethyl methacrylate, chitosan and water has been described[222]. In a supercapacitor with this electrolyte the presence of water in the mixture resulted in a much higher specific capacitance than observed without water. A similar combination with cross-linked chitosan for improved mechanical stability has been described elsewhere[223].

Inclusion of renewable materials in particular from natural resources enjoys growing interest. With a gel electrolyte prepared with a cross-linked soybean protein isolate and an aqueous electrolyte solution of 1 **M** Li_2SO_4 an EDLC-supercapacitor has been built[224]. The observed specific capacitance was larger than that of a comparison using the same electrolyte solution and a conventional separator. An unknown cycling retention close to 100 % was noted after 5000 cycles. From displayed GCD-data after this number of cycles an ESR more than double the initial value and a specific capacitance reduced by more than 10 % can be deduced. A very similar concept with the same ingredients but without the crosslinking has been reported by the same authors[225]. A gel electrolyte was prepared from waste materials of egg and rice production and an aqueous NaCl-solution[226]. A sealed EDLC-device kept 94.5 % of its initial capacitance after 6000 cycles. A combination of various different ILs and chitosan yielded a solid electrolyte, not a gel[227]. The various examined combinations were time-stable for more than two years. A seaweed-based lithium alginate/lithium acetate gel electrolyte showed high ionic conductivity and also flame-retardant properties[228]. In addition to preparing electrolytes from natural raw and sustainable materials, biocompatibility may become relevant once the useful life of a device is over. A biodegradable agarose gel with aqueous NaCl solution has been proposed for a flexible supercapacitor[229]. An overview of further biodegradable biogels is available[230].

Safety aspects with gel electrolytes of various types, i.e. with various gelling agents, have been discussed in[231].

Incorporating a gel electrolyte into porous material results in a material acting as both separator and electrolyte in a supercapacitor. Provided it combines sufficient ionic conductivity and mechanical strength it may simplify roll-to-roll production of devices. An example of such material starting with a porous sulfonated poly(ether ether ketone)/polysulfone film prepared by electrospinning combined with PVA and sulfuric acid has been described[232]. The prepared EDLC-type supercapacitor kept 97 % of its initial capacitance after 1500 cycles. Mechanical robustness (stiffness) is a weak point of many gel electrolytes. In addition to the option described before the preparation of a semi-interpenetrating network of a polyacrylamide and PVP with phosphoric acid yielded an electrolyte with good flexibility, stretchability and ionic conductance even at low temperatures[233].

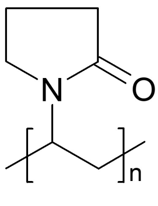

Fig. 9. Polyvinylpyyrolidone

A procedure to handle gel electrolytes in EDLC-supercapacitors by injection with encouraging results has been developed[234].

4.2 Gel electrolytes with redox-active additives

Addition of redox-active compounds to the electrolyte solution has been suggested as an option for increased storage capability of an EDLC-device. The conceivable mobility of redox species may result in undesired self-discharge by establishing a shuttle mechanism between the electrodes[62]. Several options to mitigate this flaw are conceivable, unfortunately some of them like using a membrane as a separator result in power performance losses. Using a gel electrolyte may reduce self-discharge by lowering mobility of the redox species, i.e. by keeping them near the electrode where they participate in charge storage. Adding alizarin red S as redox-active component into a gel of polyvinyl alcohol PVA and sulphuric acid with two activate carbon EDLC-type electrode yielded a flexible supercapacitor with significant increase of capacitance due to the added dye[235]. Rather surprisingly self-discharge is not even mentioned in the report.

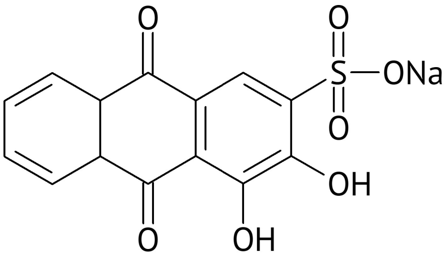

Fig. 10. Structure of alizarin red S.

Addition of phloroglucinol (trihydroxybenzene) as a redox-active component (10 %wt.) in a gel electrolyte of PVA and $LiClO_4$ has been suggested[236]. Some increase of capacitance and 94 % capacitance retention after 5000 cycles were reported.

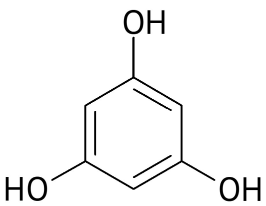

Fig. 11. Structure of phloroglucinol (trihydroxybenzene).

Further examples of devices with added redox systems can be found in[161, 196]. A PVA-based flexible hydrogel electrolyte containing the bromide redox couple operating according to

$$2\,Br^- \leftrightarrows Br_2 \text{ and } Br_2 + Br^- \leftrightarrows Br_3^- \qquad (18)$$

at the positive electrode has been prepared and studied in a supercapacitor[237]. 93.4 % of the initial capacitance were still present after 10000 cycles. Self-discharge was limited by inserting a Nafion®-membrane. This membrane also separated the two different electrolytes at the positive and negative electrode. Unfortunately, this arrangement resulted in inferior capacitance retention with growing current density.

A multifunctional flexible and self-healing gel electrolyte with a hydroquinone redox system has been developed[238].

5. Solid electrolytes

Solid electrolytes as employed in electrochemical devices for energy storage and conversion like primary and secondary batteries can be inorganic or organic crystalline or polymeric materials[239]. Presumably, only the latter materials should be called polymer electrolytes whereas porous polymer films soaked with some electrolyte solution should be considered as separators. The sometimes prevailing opinion that anything, which is not liquid, should be called a solid may be an oversimplification, definitely, it is confusing. Nevertheless, terminology has been confused and remains confusing, for examples see[240,241], reported examples are mentioned in this section consequently. A particular confusing example can be found in a report wherein a mixture of polyvinylidene fluoride with an ionic liquid has been called a solid electrolyte[53]. Another example of confusion can be found in[161] wherein e.g. an “ionic-liquid-embedded polymer electrolyte” is introduced. This is simply an ionogel as already stated above. A helpful, unfortunately not commonly accepted, designation of materials as “solid-like electrolytes” has been suggested[242].

First studies of polymeric solid electrolytes for EES devices started with poly(ethylene oxide) (PEO, (-CH_2O-)$_n$), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA) and some other heteroatom-containing polymers. Their ionic conductivity at common operating temperatures was too low for practical application[243], thus further materials like polymers with ionogenic functional groups (carboxylates or sulfonates) or the starting polymers with electrolyte dissolved into them have been developed[239]. The acronym SPE (solid polymer electrolyte) was coined, nowadays mostly naming polymers acting as cation exchange membranes (CEM, Nafion®, Flemion®) in electrolyzers and fuel cells. An application of the latter class of ion conductors has been reported with an EDLC-supercapacitor with a Nafion-membrane as solid electrolyte[244]. Drawbacks – beyond the high price – of the use of CEM related to the acidic character of this membrane have been known for a long time in fuel cell research. With respect to supercapacitors interest in alkaline ion exchange membranes has resulted in achievements reviewed together with those of alkaline (OH^--conducting) solid polymer electrolytes[245]. Polymers like polyvinylidene fluoride, itself an insulator and more popular as a binder for electrode materials and as a material for porous separators in lithium ion-batteries, and its copolymers can be dissolved and mixed with e.g. ILs to yield solid electrolytes[246].

To overcome the already addressed problem of poor electrolyte/electrode contact Nafion® ionomer was mixed into the RuO_2 electrode preparation materials. A similar approach with activated carbon as electrode material yielding an EDLC-device has been described[247,248]. Another approach towards improved interfacial contact by forming an ionogel *in situ* during device preparation has been proposed[249]. Poly(vinylidenefluoride-co-hexafluoropropylene) dissolved in DMF with an added IL and $Al(Tf)_3$ yielded a gel-like solid electrolyte[250]. An EDLC-device prepared with the electrodes soaked first with the polymer solution before assembly showed a very stable capacitance for 50000 cycles.

An EDLC-supercapacitor prepared with a freestanding film of a mixed polymer subsequently soaked with an acetonitrile-based electrolyte solution kept 85 % of its initial capacitance after 5000 cycles[251]. With some of the polymer used for film preparation dissolved in the electrolyte solution an even better performing device was obtained; solvent evaporation was significantly diminished at an only slightly reduced capacitance.

The low ambient temperature conductivity of polymer electrolytes (about 1/100 or even 1/1000 of the conductivity of inorganic conductors based on glasses, ceramics or inorganic crystals) is more than compensated by their advantages, in particular the possibility of preparing very thin but mechanically still stable films for wound cell designs and their generally lower energy demands in preparation. The polar groups (in particular oxygen in e.g. PEO) interact with ions of the dissolved salt, thus SPE may be considered as solvents. Molecular architecture of the SPE, chain flexibility and further details are relevant for actually observed conductivity[242], for an overview see also[241,252]. The influence of segmental motion in polymer chains of a plasticized PEO-electrolyte on ion transport has been examined[253].

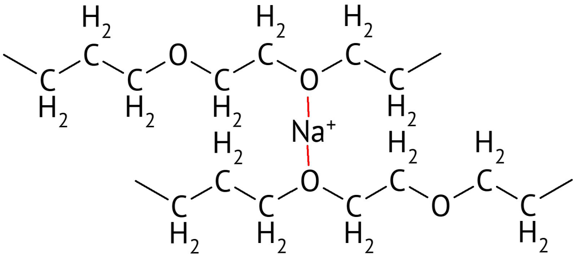

Fig. 12. Scheme of interactions between PEO and a sodium ion.

To further improve properties plasticizers can be added[241]. The result may be close to a gel electrolyte although the approach starts from a different end: In case of a gel electrolyte a liquid is "solidified" by adding a gelling agent (see sect. 4.1) whereas a plasticizer is added to a solid (hard) polymer) yielding a more or less soft substance. PEO plasticized with propylene/ethylene carbonate and nanoclay and with tetraethyl ammonium tetrafluoroborate has been used as solid electrolyte in a hybrid supercapacitor with poly(3-methylthiophene) as positive and activated carbon as negative electrode[254]. About 30 % of the initial capacitance was lost in 1000 cycles. PEO plasticized with aqueous KOH was also found to be compatible with an asymmetric supercapacitor with two different redox-active materials in the positive and the negative electrode with 97 % capacitance retention after 10000 cycles [255]. The same device showed poorer performance when a PVA-based or plain aqueous KOH-solution was used. A cross-linkable poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer shows high IL electrolyte solution uptake[256]. An EDLC-device kept 95 % of its initial capacitance after 10000 cycles. Sometimes the number of ingredients combined with PEO without providing any rational reason leaves open the question of the function of the additives and the proper assignment of the obtained electrolyte to any of the classes discussed in the present report; for an example see e.g.[257].

An example of a solid electrolyte of PAN plasticized with ethylene and/or propylene carbonate has been reported, the material was designated a plasticized gel polymer electrolyte supporting the concerns noted above[258].

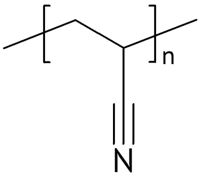

Fig. 13. Polyacrylonitrile

A solid electrolyte compatible with a redox-active electrode material based on PAN soaked (gelled) with an electrolyte solution of a mixture ethylene and propylene carbonate and $LiPF_6$ has been studied[259]. Because structural flexibility of the molecular chains is essential for conduction crystallization of the SPE should be avoided. This can be supported by making copolymers or polymer blends. Typical conductivity values around 10^{-3} S•cm^{-2} have been collected[241]. Adding further materials, in particular nanoparticular inorganic ones like TiO_2, can further enhance conductivity. Handling of materials has been reviewed[241]. Properties of supercapacitors prepared with the various polymers in gelled form have been compared[260]. Highest ionic conductivity was found with a PAN-based electrolyte, lowest with a PMMA-based one. The supercapacitor prepared with the latter electrolyte turned out to be more stable in terms of capacitance retention. A copolymer of polythyleneglycol and PAN with dimethylformamide as plasticizer and $LiClO_4$ a solid electrolyte suitable for roll-to-roll manufacturing of an EDLC-device with only little capacitance decay after 30000 cycles has been developed [261].

Solid electrolytes based on poly(methyl methacrylate) profit from several advantages of this polymer including simple synthesis, low density, mechanical stability, weak binding to ions of added electrolyte and high charge carrier mobility; they suffer from low ionic conductivity. Application of plain PMMA is difficult because its brittleness prevents good contact with an electrode. Thus, various modifications of PMMA have been examined for remediating this flaw and to improve ionic conductivity. Initial attempts including copolymerization, addition of plasticizers or organic fillers, and copolymerization did not yield significant progress. Combination with ionic liquids provide some moderate improvements. PMMA-based electrolytes have been reviewed[262].

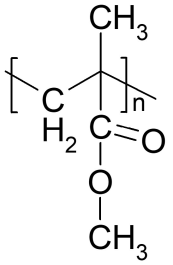

Fig. 14. Poly(methyl methacrylate)

A solid electrolyte (ormolyte) has been prepared by a sol-gel process starting with tetraethoxy orthosilicate and tetra ethylene glycol combined with various magnesium salts[263]. An EDLC-device could be cycled more than 1000 times.

A flexible copolymer film of vinyl acetate and 1-ethyl-3-vinylimidazolium cations (a polycation) with the bromide anion serving as main conductor and a vinyl chain as molecular backbone and a wide electrode potential window of electrochemical stability has been prepared[264]. The prepared EDLC-type supercapacitor kept 90 % of its initial capacitance after 5000 cycles. The performance was attributed in part to an electrolyte-electrode interface utilizing the flexibility of the electrolyte supporting fast charge transfer. Polymer electrolytes as widely employed in lithium-ion batteries are ion-conducting polymeric materials solid at room temperature[179]. Because their ionic conductivity is relatively low, they are at first glance of lower interest for supercapacitor application. Their flexibility, bendability and stretchability depending on the polymer itself and – when applicable – added further ingredients make them nevertheless candidate materials worth further examination[218], more examples of solid electrolytes as applied in flexible, wearable etc. supercapacitors can be found in[219]. The importance of flexible semi-solid or solid electrolytes has been highlighted in an overview[63]. Blends of PILTFSI with various ILs suggested as solid polymer electrolytes for EDLC-type devices have been compared[169]. Differences in terms of actual conductivity and electrochemical stability window were noticed and attributed to properties of the added IL.

A free-standing electrolyte film was prepared from a mixture of a partially fluorinated, microphase-separated comb copolymer of superhydrophobic poly(2,2,2-trifluoroethyl methacrylate) and amphiphilic crystalline poly(ethylene glycol) behenyl ether methacrylate with an ionic liquid [EMIM][TFSI] acting also as separator[265]. An EDLC-type supercapacitor outperformed a corresponding cell made with a PVA-based gel electrolyte. A similar approach with different starting materials has been reported[266].

A flexible solid-state EDLC-type supercapacitor capable of withstanding elevated temperatures (120 °C) based on a solid electrolyte of a poly(aryl ether ketone)-poly(ethylene glycol) copolymer has been reported[267]. Negligible capacitance losses after 2000 cycles were found.

Polymer electrolytes inspected so far are mixtures of various solid and/or liquid materials; to date, no single-phase single material has apparently been studied successfully as an electrolyte for a supercapacitor. In a review of polymer blend nanocomposites as applied in energy storage devices including supercapacitors nanocomposites for the latter application cannot be found[268].

A microporous polymer membrane soaked with an aqueous solution of 1 **M** $LiClO_4$ has been called a polymer electrolyte[269], the device prepared with an optimized membrane (the terminology appears to be somewhat misleading, actually the membrane serves as a separator and does not have any of the typical functions of an electrolyte) showed a slightly higher specific capacity than a device with liquid electrolyte and decreased self-discharge. The small amount of added chitosan is presumably the reason for calling the membrane a gelled electrolyte in a figure. A porous film of polybenzimidazole was soaked with an IL (1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride)[270]. The subsequent hydrolyzation of the latter resulted in the formation of an -O-Si-O-network improving the mechanical stability of the film, increase water uptake and ionic conductivity. An all solid state EDLC-supercapacitor kept 91 % of its initial capacitance after 10000 cycles.

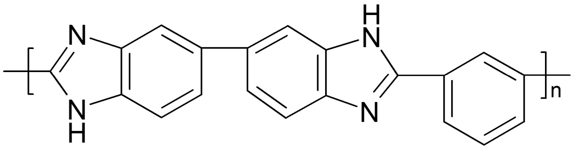

Fig. 15. Polybenzimidazole

A microporous membrane of poly(ethylene glycol)–grafted poly(arylene ether ketone) filled with a chitosan-based aqueous $LiClO_4$ gel electrolyte was examined in an EDLC-device[271]. Capacitance was stable along 5000 cycles. Polymer electrolytes based on algae polysaccharides as promising alternatives to conventional synthetic materials have been reviewed[272]. A porous lignocellulose membrane prepared from natural raw material showed remarkable uptake of aqueous KOH-solution when subsequently used as electrolyte in an EDLC-device with 92.5 % capacitance retention after 10000 cycles[273].

Flexible solid-state supercapacitors utilizing 2D-materials may require matching electrolytes, an overview has been provided[274]. Once a supercapacitor becomes a structural element and building block solid electrolytes in a supercapacitor are essential[275,276].

Inorganic solid electrolytes for supercapacitors have attracted some attention in research with limited possibly practically relevant results as reviewed in[55]. Beyond their preparation and still limited ionic conductivity, establishing an effective electrolyte/electrode interface appears as a challenge hard to meet.

The role of electrolytes has been mentioned in passing in a boisterous report on the “emerging electrochemical activation tactic”[277]. Actually, the authors discuss changes of cell constituents during operation of the cell and observed effects!

Conclusions

A comparison of achieved results and performance data even when taking into account the frequently criticized shortcomings of reporting of pertinent data yields no perfect electrolyte material. In terms of ionic conductivity, electrolyte solutions are best; they also provide the best electrolyte solution/electrode interfaces because of good wetting and penetration of the solution into the porous electrode body. The obvious drawbacks and risks of electrolyte solutions when leakage of a cell happens are hard to avoid, in case of organic solvent-based electrolyte solutions, flammability is a further safety risk. High cell voltage and associated higher energy density with the latter solutions are a another advantage. The frequently praised advantages of solid electrolytes, in particular the absence of any problems caused by leakage and flammability, are noteworthy. Unfortunately, the still disappointing ionic conductivities even with thin electrolyte layers and the poor electrolyte/electrode interfaces causing significant Ohmic resistance still limit their perspectives. Even manufacturing processes wherein electrode and electrolyte are deposited as subsequent layers will provide only partial relief once the challenge of large-scale manufacturing has been met: The electrolyte hardly penetrates into a porous electrode body.

Perspectives

Adding a few drops of an electrolyte solution to the porous body before bringing it into contact with a solid electrolyte provides significant improvements. This is already very close to a gel electrolyte. These electrolytes provide ionic conductivities sometimes rather close to those of electrolyte solutions. Their softness helps to improve the electrolyte/electrode interface resulting in lower cell resistance. In addition preparation procedures enabling considerable penetration of the gel or at least its liquid constituent into the porous electrode body have been developed. Their relative softness may leave a mechanical separator as a necessary component to keep the electrodes apart. Approaches to integrate the gel into a porous separator seem to provide a solution. Thus, it appears that gel electrolytes are the most promising direction. Because the cell voltage limitation provided by water even in a gel electrolyte remains, the combination of WIS and gelling may be a particularly promising new approach. This may also apply to “green devices”. Whether [278] helps as a guidance remains an open question.

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