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Review Article

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Self-discharge in supercapacitors: Causes, effects and therapies: An overview**

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Abstract: Self-discharge as an omnipresent and unwelcome feature of electrochemical storage devices driven by fundamental forces is briefly introduced and put into perspective. Causes and observed effects as well as possible consequences and modifications in support of a therapy of these effects are described. Care is taken to consider observed phenomena with respect to different types of supercapacitors and different classes of electrode materials and additives inside a cell. Modeling and further theoretical approaches are presented. Recommendations for reporting and data presentation are provided.

Keywords: supercapacitors, self-discharge, energy storage, modeling, leakage currents, corrosion

1 Introduction

Self-discharge[1] is the unintended loss of energy stored in an electrochemical energy storage and conversion device by parasitic processes. To identify self-discharge as a voltage loss appears to be an oversimplification [1] although it is frequently suggested as a synonym. It seems to be an almost natural process because the driving force of the chemical energy stored in such device in the positive and negative masses is always present as long as the device is charged and not yet completely discharged (at which point this driving force simply disappears). Once this unwelcome effect was noticed as a phenomenon – there appears to be no record of a publication addressing specifically self-discharge of a primary or secondary battery for the first time – researchers have tried to understand the underlying causes and to use this knowledge to develop means and therapies to keep self-discharge at bay. More recently methods of theoretical and computational chemistry have helped in this endeavor.

Depending on the actual type of storage system numerous processes are responsible for self-discharge. They range from corrosion of the negative metal electrode in a lead-acid or alkaline-manganese battery yielding dissolved metal ions and hydrogen gas, oxidation of the added carbon in the positive electrode of a lithium-ion battery in particular at high states of charge to the (slow) hydrogen oxidation at the positive nickel oxide electrode in a hydrogen/nickel oxide secondary battery [2]. Many of these processes causing self-discharge are electrochemical processes without an external flow of current. In this context the term leakage current requires attention with respect both to batteries and also to capacitors [3]. Commonly leakage current designates the flow of current and associated consumption of charge in non-Faradaic and definitely not welcome processes during charging of a capacitor (and a battery) and the flow of electric current (and consumption of charge) later with the charged device either at open circuit or during discharge bypassing the intended consumer; this can certainly also happen with secondary batteries. Such leakage in the second meaning can be caused by even only poorly conducting electric pathways between the terminals of the storage device inside or outside the device, but this term also appears to collect all other unintended flows of current resulting in a loss of stored energy.

Attempts to limit and suppress these processes are presumably as numerous and variable as the processes themselves. They range from the almost trivial (avoid too high electrode potentials of the positive electrode to limit oxidation of added acetylene black, and too negative electrode

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** Dedicated on the occasion of his 65th birthday to H. Lang – a chemist with a strong affinity to electrochemistry and a friend.

[1] The meaning of the term “self-discharging” used most fortunately only by very few authors can only be guessed.

potential possibly causing hydrogen evolution or lithium deposition) to the rather brutal (add mercury ions to the electrolyte solution of zinc-carbon and alkaline-manganese batteries to inhibit hydrogen evolution by acidic corrosion) and to the more sophisticated (use highly purified solvents and electrolytes with small added amounts of organic corrosion inhibitors for primary zinc batteries resulting in spectacular improvements). Care should be exercised when making the distinction between self-discharge and loss of energy efficiency. The user in both cases may simply notice that s/he gets back less energy than s/he put into the device, but the loss of efficiency caused by overcharge and associated gas-evolution with products that cannot be utilized later during discharge does not qualify as self-discharge. But because the dioxygen formed during such overcharge might in turn convert part of the chemical inventory of the cell causing a respective loss of energy which could be used otherwise this process at least is somewhat connected with self-discharge. In any case following the term self-discharge will be used in this broader sense.

A list of reported self-discharge rates provided elsewhere puts the observations into perspective (Table 1).

Table 1: Self-discharge rates at room temperature [4]

	System	self-discharge
primary	Alkali-manganese cell	0.5% per month
	Leclanché cell	0.5% per month
	Lithium	0.5% per month
secondary	Lithium-ion	4% per month
	NiMH	25% per month
	LSD-NiMH[2]	4% per month
	NiCd	20% per month
	RAM[3]	0.5% per month
supercapacitor	EDLC[4]	1.8% per day

In case of rechargeable devices (initially secondary batteries, now also supercapacitors) application of a usually relatively small current needed to maintain the achieved state of charge balancing self-discharge is frequently applied. This is called floating charge and floating current, respectively [4]. In case the state of charge is exactly kept this current will be equivalent to the leakage current, accordingly an experimental method can be established (see below).

In supercapacitors self-discharge is also omnipresent despite the fact that at least in the electrochemical double EDLC type Faradaic processes are carefully avoided and at first are hardly conceivable as reasons of self-discharge. The term self-discharge has been applied with supercapacitors in a simple adaptation of this term from secondary battery despite the fact, that at least cell voltage changes in supercapacitors are not always due to the same reasons effective in batteries. Redistribution of charged species in supercapacitors hardly relevant in batteries is one of the reasons for changes of cell voltage with time (sometimes even increases) not relevant in batteries. Thus it has been suggested to use the term self-discharge more carefully [5, 6].

Supercapacitors of this type were around for quite some time [7], despite of their high price (Goldcap, Panasonic 1978) they were welcome substitutes for NiCd-accumulators in high-end electronic devices needing a power source for electronic memory maintenance. One first reported study addressing the topic and discussing ways to reduce self-discharge has been published only in 1982 and appeared in a source presumably a bit away from electrochemists attention [8]. After a hiatus of several more years the number and presumably awareness of the problems how self-discharge may adversely affect supercapacitor application and their widespread use started to rise significantly.

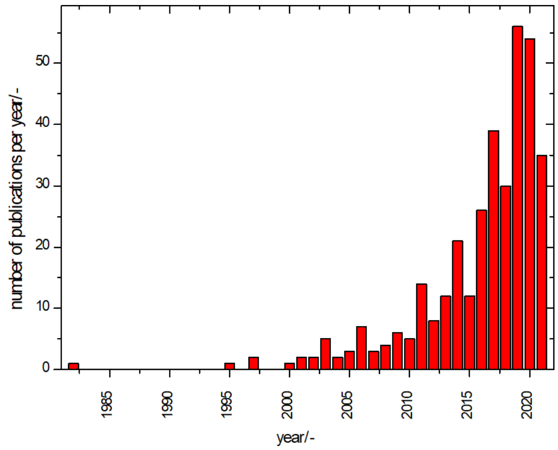

Figure 1: Annual publication numbers of reports with "self-discharge" and " supercapacitor" anywhere in the title, keywords or abstract (Data from Scopus® retrieved on May 31st, 2021). Further publications addressing this topic somewhere in the text could not be counted; when noticed and considered relevant in the present context they were evaluated below. The very few publications on "electrochemical capacitors" or "double layer capacitors" instead of "supercapacitors" were included, the associated confusion suggests once more systematic use of technical terms. The same argument applies to the slightly awkward spelling "self discharge".

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[2] LSD: Low self-discharge rechargeable alkaline-manganese

[3] RAM: Rechargeable alkaline-manganese

[4] EDLC: electrochemical double layer capacitor

Given the considerable importance that self-discharge of both batteries and supercapacitors already has and the growing effect this phenomenon will have in electric devices of all sizes depending exclusively on these storage systems it surprises somewhat that self-discharge has not been reviewed except for a first attempt dealing with some aspects of the subject published when this report was under preparation [9] and an earlier introductory overview on electrochemical capacitors[5] [10, 11] addressing some of the topics presented here in detail. But Conway already examined this phenomenon in detail with particular focus on redox-active (pseudocapacitive) materials [12]. In overviews and reviews self-discharge is addressed in passing without discussing the various aspects treated below [13, 14].

Various mechanisms and related causes (driving forces) were established for supercapacitor self-discharge starting at earlier discoveries related to primary and secondary batteries [2, 12]:

1. Consumption of species generated during overcharge (e.g. reduction of dioxygen formed at the positive electrode and reduction of hydrogen at the negative electrode) without external flow of useful current.
2. Electrochemical reactions at the positive and/or negative electrode with dissolved impurities contained in the electrolyte solution or in the electrode.
3. Consumption of charge stored in reversibly oxidized/reduced surface functional groups of carbon materials used in EDLC-supercaps or as additive in battery electrodes by their chemical reaction with other constituents of the cell inventory.
4. Ohmic leakage current caused by electronic connections inside or outside the cell between electrodes of their terminals as described above.
5. In supercapacitors of the EDLC-type redistribution of electrolyte ions accumulated during charging at the electrodes. Whether ion desorption should be considered as a synonym of self-discharge as suggested in [15] seems to be an open question.

Taking into account this first overview remedies are obvious in several cases:

Ad 1 Avoid overcharge by carefully limiting applied cell voltage. This is commonly done using more or less complex electronic circuitry. This mode will also decay with consumption of this species, and it should cease once the nominal cell voltage has reached. Given the generally poor electrocatalytic properties of most carbonaceous materials consumption of the gas will be slow, thus gas generation during overcharge may not affect self-discharge but will negatively affect energy efficiency of the device. In case electroreduction of dioxygen proceeds at the negative electrode (this may also be related to dioxygen left in the electrode material during manufacturing because of insufficient outgassing) peroxide species may be formed causing former damage to the electrode material [16], in addition a redox shuttle-mechanism between positive and negative electrodes may be established [12].

Ad 2 Highly purified materials should diminish this effect; in any case it should become inoperative once the impurities were consumed. In experimental studies self-discharge should decrease with cycle number. The importance of impurities has been addressed in general terms only in a previous review on supercapacitor technology [17].

Ad 3 At least for EDLC-type supercapacitors electrode materials with minimum amounts of functional groups shall be preferred. Because these groups add to the charge storage capability of the material their exclusion may result in a reduction of this extra storage option, i.e. of this technically most relevant parameter charge storage capability.

Ad 4 Careful construction and maintenance of the supercapacitor will reduce such currents to a minimum.

Ad 5 No straightforward countermeasure against this natural phenomenon is known. Attempts to slow down diffusion will increase the internal cell resistance because these measures will also slow down ionic motion needed for the flow of current inside the cell. Finally power capability of the supercapacitor will decrease.

In all observed causes temperature plays a role because of the well-established temperature-dependency of chemical reaction rates as well as of transport by e.g. diffusion. Accordingly lower operating temperatures tend to slow down self-discharge; this appears to be an option particular during storage of e.g. batteries before use.

2 Experimental methods

Discussion and understanding of self-discharge require experimental data obtained by suitably set-up experiments capable of separating the phenomenon under investigation from the general operation of a supercapacitor [1, 12, 18]. From the previous considerations it follows that self-

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[5] Reasons for the rare use of this term meaning in practically all identified cases supercapacitors remains unclear, the use is hardly helpful.

discharge may result in a change of electrode potential in a single-electrode experiment or the reduction of cell voltage in a full-cell measurement. Accordingly measurements of cell voltages in a two-electrode full cell setup or of electrode potentials in a three-electrode arrangement as a function of time may provide some first impression. It should be kept in mind that authors have stated that cell voltage and its change are not representing the energetic state of a supercapacitor [19].

Criteria helping in the distinction of the various self-discharge mechanisms presented above were established [20], and were applied in a study of carbon-cloth electrodes [21]. Because of the presumably small current associated with self-discharge (any discharge process can be expressed as a current, frequently called the leakage current) careful selection of suitable instrumentation is highly important. Determination of the floating current both for a full cell making up for the leakage current and a single electrode are also possible to establish a rate of self-discharge. Because the floating current or the presumably equivalent leakage current are recorded under completely different conditions (at fixed electrode potential or cell voltage) than self-discharge measurements as chronopotentiometric recording, care should be exercised when comparing results and drawing conclusions regarding underlying processes. Complementarity of data obtained from potential decay and floating current has been stressed [22]. When using a battery cycler determination of the amount of charge recovered during discharge after different times may provide access to self-discharge rates, too. For distinction or truly capacitive and pseudocapacitive contribution to overall charge storage careful inspection of cyclic voltammograms at selected scan rates was recommended [23], the used terminology can be found in [24]. A report claiming to deal with methods for the determination of leakage currents surprisingly describes only the procedure to measure the floating current [25], in addition voltage decay measurements are introduced. With growing temperature the observed “leakage current” rises, and the lowest value for the particular devices was found around $T = 0°\mathrm{C}$, for a used device the value was $T = -10°\mathrm{C}$.

Impedance measurements as a tool to determine the state of charge of lithium ion batteries and supercapacitors during long-term self-discharge were proposed [26]. Suitability of impedance measurements in particular for the determination of the leakage resistance (for equivalent circuits see below) was examined [27]. In a report claiming to examine electrochemical impedance measurements for different types of supercapacitors self-discharge was just mentioned in the abstract, and in the report data for EDLC-devices of possibly different numerical capacitances seem to be mixed up without any further evidence regarding self-discharge [28]. A fast instrument for quality assurance measurements of supercapacitors including details on self-discharge was developed [29].

A procedure enabling extraction of self-discharge rates from cyclic voltammograms was developed and successfully tested by comparing rates obtained with this method and results from electrode potential decay [30]. A potentiostatic method to determine the value of the leakage resistance (called in this report the resistance of self-discharge) was described and applied to EDLC-type electrodes made from activated carbon with fly-ash as binder [31].

Supercapacitors are frequently combined with various types of batteries, possibly with photovoltaic panels or other sources of renewable energy, into electrical energy storage systems (EES). Experimental studies of such EES sometimes yield data on the incorporated supercapacitors on e.g. self-discharge [32]. Limitations of energy storage devices including supercapacitors proposed for energy harvesting were discussed [33].

3 Electrodes and systems

Following below published reports dealing both with electrodes for supercapacitors as with complete devices of various types and operating principles will be presented with respect to the various aspects of the subject of this report. Because sometimes assignment of a report to any of the following categories and sections cannot be done straightforwardly, the interested reader e.g. looking for options to suppress self-discharge in a supercapacitor with EDLC-type electrodes and redox-active substances added to the electrolyte with some further gelling agent might have to look more closely. Adding to the confusion about terminology is strictly avoided. The term “pseudocapacitor” lacking a logical foundation is not used, instead the term redox capacitor is used when needed for clarification. Data on self-discharge are quoted when provided in the reports to enable the reader an assessment of own results, when causes or at least possible reasons of self-discharge are reported they are also quoted. Unfortunately, in several cases most important parts of reported research was shifted in an apparent misunderstanding of the term and purpose into the “Supplementary Information” section difficult or even impossible to access with several publishers. All reasonable attempts were made to retrieve even these items.

3.1 Electrodes

Most studies of a material or a storage concept start with a single electrode examined in a three-electrode setup. Nevertheless, it should be kept in mind that with respect to practically relevant data actual cells with two electrodes are preferable [34]. Consequently in the following sections dealing with single electrodes sometimes contain further observations obtained with full cells. General studies not limited to a specific electrode or device are available. The influence of diffusion of self-discharge in particular was examined extensively [35].

3.1.1 EDLC-type electrodes

From the start of the rise of supercapacitors to major contributors to electrochemical energy technology, charge storage in the electrochemical double layer with associated ion accumulation was the major operating principle [3, 7]. Given the importance and charge accumulation and the possibility, that a distribution established during charging or discharging may change after turning off the current, charge redistribution may be relevant for the observed cell voltage and possibly noticed changes interpreted as self-discharge. Recorded time-dependent electrode potential variations were evaluated, a noticeable similarity with such dependencies caused by activation-controlled processes was found [36]. Inside the porous electrodes studied here charge redistribution proceeded much slower than assumed; effects of pore shapes on such observations were examined [37].

Observed losses of stored charge in the first hours after charging were attributed to a diffusion-controlled reaction possible involving traces of water in the organic solvent-based electrolyte solution [38]. Later self-discharge could not be simply attributed to a parasitic leakage current only. An essential connection between capacity losses during cycling (capacitance retention), self-discharge and leakage current was claimed but not been substantiated [39]. Various samples of the KOH-activated carbons showed very different values of leakage current and self-discharge, and no explanation is provided. Carbons with low densities of surface functional groups showed low leakage currents, this subject was addressed elsewhere [40]. Using l-glutamic acid as a precursor with $ZnCl_2$ as an activating agent a highly microporous carbon showing low self-discharge (from 1 V to 0.63 V after 24 h) in a symmetric EDLC supercapacitor with aqueous 6 **M** KOH electrolyte solution was obtained [41]. Activated carbons obtained from sulfur-containing polymer precursors yielded electrode materials showing less self-discharge [23]. The fraction of pseudocapacitive charge storage associated with redox-active surface functional groups was found to be strongly correlated with self-discharge. The influence of surface functional groups on self-discharge with single walled carbon nanotubes was noticed [11]. Self-discharge of an EDLC-device used in a setup connected with an organic solar cell and an electrochromic display in an ambient light harvester circuit was examined, and influences of both charging and discharging conditions relevant for this particular application were noticed [42]. In an attempt to utilize selected surface functional groups without risking self-discharge selective functionalization of carbon paper with cyclic ethers was tested [43]. Various modes of preparation were tried, the one yielding in plane functionalization showed lowest self-discharge presumably because these functionalities acted like tiny micropores for charge storage.

Reduction of the number of oxygen-containing surface functional groups caused e.g. by treatment of activated carbon with hydrogen was noticed [44], and at the same time this treatment increased the capacitance of the material. Starting from the advantages of using graphene instead of activated carbon self-discharge of graphene-based electrodes was examined closely [45]. In the studied example self-discharge was found to be a combination of Ohmic leakage and diffusion-controlled charge redistribution. In a displayed CV of studied supercapacitors a voltage range of ± 2.5 V was covered, and in GCD measurements only 0 to 2.25 V. The former range implies potential inversion which most likely has very negative effects on the electrodes. A feature rarely addressed is voltage recovery, i.e. the slow change of device voltage after e.g. complete discharge [3]. In the studied device it was found to increase with growing charge/discharge current. Possible relations between surface functional groups, increased capacitance and self-discharge with graphene were mentioned [46]. Electrodes prepared from di- and triamine-functionalized graphene networks showed lower self-discharge [47]. Changed interactions between the modified graphene and the electrolyte solution influencing ion mobility may be responsible. Low self-discharge of an electrode based on graphene prepared by a modified molten salt method (as compared to graphene prepared by thermal reduction) was stated [48], but an explanation has not been provided. Low self-discharge (stated without numerical values or comparisons) was claimed for hierarchical porous carbons prepared with a surfactant-template method in an otherwise barely comprehensible report [49]. For a supercapacitor with electrodes prepared with nitrogen-doped porous graphene with an ionic liquid as electrolyte, low self-discharge was claimed without providing any explanation [50]. The displayed voltage vs.

time curves not discussed by the authors showed faster discharge when the cells were charged to higher voltages suggesting contributions from decomposition reactions at large cell voltages. More precise electrode potential control helping to suppress unwanted parasitic electrode reactions causing self-discharge was claimed with *o*-benzenediol (catechol) grafted onto N-doped carbon nanosheets [51]. Because the same material was applied for both the positive and the negative electrodes, the actual mode of operation remains a bit open as well as the question, how the redox reaction of the phenolic groups can contribute to charge storage at both electrodes showing significantly different electrode potentials.

Effects of different electrolytes in aqueous solutions on self-discharge and leakage current were noticed, and self-discharge in terms of decreasing cell voltage was highest with a solution of 0.5 **M** H_2SO_4 [52]. No attempt was made to explain this significantly different behavior in a rather unintelligible article. Connections between oxidation of carbon and self-discharge for carbon electrodes in contact with aqueous electrolyte solutions were examined [53], a positive correlation was established. Consequently removal of oxygen-functionalities at the positive electrode is recommended for reduced self-discharge. This can be achieved by hydrogen thermal reduction without negatively affection electrode porosity [54]. Extending these investigations to reduced graphene rGO oxide was tried In addition it was attempted to separate carbon oxidation and redistribution of ions as contributors to self-discharge [55]. Charge redistribution was identified as main self-discharge mechanism. Further reduction of self-discharge can be achieved by oxidizing, i.e. charging more fully the positive rGO electrode.

Activated carbon prepared from dried coffee shells with $ZnCl_2$ as pore-forming agent yielded electrodes with relatively slowest self-discharge at a large excess of $ZnCl_2$ (20:1) [56]. The rather incomplete experimental data enable no assignment of this conclusion to materials properties. Carbons prepared via various activation and reactivation procedures were compared; lower self-discharge was speculatively attributed to a lower surface concentration of oxygen-containing functional groups [57]. Lower self-discharge of a non-activated carbon aerogel in an aqueous electrolyte solution was attributed tentatively to the absence of sharp edges possibly causing high local electric fields supporting dissociation reactions yielding products subsequently engaged in shuttle reactions [58]. Self-discharge behavior of carbon aerogel materials was examined [59], results are discussed with respect to functional groups on the material's surface. Incorporation of nitrogen into carbonaceous materials like multiwalled carbon nanotubes by thermal treatment (e.g. ammoxidation) resulted in lower self-discharge [60]. The influence pH of electrolyte solution on the pseudocapacitive contributions of surface functional groups on electrochemically modified graphite was studied [61]. Slight variations of self-discharge at different pH-values were rationalized with respect to the pH-dependent redox processes of the surface functionalities.

Zhang et al. have studied self-discharge of activated carbon-fabric electrodes in contact with non-aqueous electrolyte solutions of different compositions [62] with particular attention to charging current and temperature. Self-discharge in such system may be driven by electric potential gradients in front of the electrode and by concentration gradients regarding the spatial distribution of the counter-ion assembled for charge compensation in front of the electrode. The former mechanism should result in an electrode potential decay of $\ln E \propto t$ whereas the latter should show $E \propto t^{1/2}$. Self-discharge due to other mechanisms and causes as outlined above was minimized by careful experimental design and execution. The electrolyte solution of $TEABF_4$ in propylene carbonate yielded much slower self-discharge with the diffusion controlled mechanism. The influence of the charging current on self-discharge was explained by invoking different ion distributions in front of the electrode. At high currents the assembled ion excess extends farther into the electrolyte solution than after low current charge. Consequently in the latter case an energy barrier is established in the more compact layer in front of the electrode slowing down ion dissipation and thus self-discharge. But because with lower charge currents and thus smaller IR-drop higher electrode potentials will be reached after charging resulting in an initially faster self-discharge until diffusion control takes over. Not surprisingly the authors conclude that electrolyte solution systems with lower ion mobility and diffusion-controlled ion self-discharge will show higher charge retention. This approach was extended by Zhang et al. to surface-functionalized single-walled carbon nanotubes (SWCNTs as electrode material [63]. The influence of surface functional groups on the SWCNTs on the established potential at the electrode/solution interface was elucidated yielding a divided potential model describing the self-discharge. These findings were later confirmed with free-standing film electrodes made of SWCNTs [64].

Coating of carbon electrode material with a blocking layer of electrochemically deposited poly-(*p*-phenylene ox-

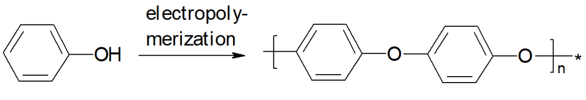

Figure 2: Electrodeposition of poly-(*p*-phenylene oxide)

ide, Figure 2) was suggested as a mode to reduce self-discharge [65].

In addition to reduced self-discharge a major increase of the Ohmic electrode resistance suggesting a corresponding loss of current capability of the electrode (this property was not studied) and a significant loss of capacitance were noticed. A specific mode of action (what is actually blocked?) has not been suggested. The authors applied modeling and simulation to this approach later [66]. A similar "coating activity" of some surfactants added to the electrolyte solution was suggested as reason for reduced self-discharge [67]. The use of atomic layer deposition ALD in materials coating for LIB [68] may be of interest for getting supercapacitor electrode materials with lower self-discharge. Based entirely on simulation and without any experimental verification the use of a layer as described before should result in a reduction of "Faradic reaction rate" by 17% and of the leakage current by 77.73% at a loss of double layer capacitance of 45.35% and an estimated voltage drop of about 50% [69]. These rather dismal conclusions may be reevaluated in the light of the report in [68]. ALD of activated carbon with alumina (Al_2O_3) primarily done to increase possible cell voltage resulted also in much slower self-discharge [70]. The latter observation was attributed to inhibited redox reactions between surface functionalities and unspecified ions, presumably of the electrolyte solution.

In a review on nanostructured carbon materials some of the reasons for self-discharge already suggested earlier were listed [71], further general remarks can be found elsewhere [72].

Purely capacitive behavior and low self-discharge were noticed for TiN-nanostructured materials [73] and for porous boron-doped diamond film electrodes [74].

3.1.2 EDLC-type electrodes with added redox system in the solution

Pore size, its distribution and further structural features of carbonaceous materials were investigated with respect to electrode performance [75]. Self-discharge could be related to pore sizes and the employed redox system. Carbons with very narrow pores showed lowest self-discharge suggesting effective trapping of redox system components. Utilization of the iodine/triiodide at the positive carbon electrode (with a zinc negative electrode) was suggested [76]. Specific adsorption (a well-known feature of halide ions growing in intensity from chloride to iodide ions) and nanoconfinement of the iodine contribute to lower self-discharge. Fast redox kinetics and optimized pore structure contribute to attractive high power performance. Immobilization of polyiodide species by entrapment in the positive carbon electrode without further halide species in the aqueous electrolyte solution prevented shuttling and associated self-discharge [77]. Solid iodine electrodeposited in nanoporous carbon showed redox contribution to charge storage without self-discharge caused by ion shuttling [78]. Electrochemically activated CNTs with the redox couple $[Fe(CN)_6^{3-}]/[Fe(CN)_6^{4-}]$ tethered to them were suggested as positive electrodes. How simple soaking of the CNTs in a solution of $K_3Fe(CN)_6$ resulted in a tethering of any kind is not explained, this obviously important question is not even mentioned. In a plot of Coulombic efficiency vs. resting time denoted as self-discharge rate in the figure caption, results of a highly unique and unusual experimental procedure are presented suggesting a much lower self-discharge of the electrode made with the activated CNTs.

Addition of *p*-nitroaniline to an alkaline electrolyte solution with a nanoporous carbon electrode has yielded improved capacitance values [79]. The relation between this additive and possible electrode reactions of electrolyte solution constituents addressed in passing in the abstract is unfortunately not discussed in the following report.

3.1.3 Redox electrodes

As extensively reported by Conway [12] redox processes of species located on electrode surfaces safely attached to it may be used for charge storage in addition resulting in an increase of the areal charge storage capability by up to two orders of magnitude. Self-discharge of a MnO_2 film in contact with a neutral electrolyte solution (Na_2SO_4) was examined with four conceivable mechanisms (activation controlled, resistance-limited charge redistribution, diffusion-limited charge redistribution and coupled activation-controlled with charge redistribution) [80]. The influence of storage and drying conditions on the performance of electrochemically generated MnO_2 films was examined including self-discharge measurements [81]. A film deposited in two steps showed relatively lowest self-discharge. These observations were confirmed later with an optimized ratio of the first electrodeposited and subsequently heat-treated layer (5%) followed by deposition of a finally hydrous second layer (95%) [82]. The first layer shows good adherence to the current collector thus possibly contributing to stable performance. Heat-treatment seems to be related unfortunately to higher positive currents in early cycles associated with parasitic reactions and lower efficiency of the electrode reaction. Influences of both activation-controlled self-discharge and charge distribution were concluded. The self-discharge of a magnetite (Fe_3O_4) electrode in various aqueous electrolyte solutions was attributed to an unidentified Faradaic process based on chronopotentiometric measurements [83]. Lowering dioxygen content in the device significantly reduced self-discharge and improved stability. Significant self-discharge of vanadium nitride electrode was attributed to dioxygen in the electrolyte solution [84], and establishment of a mixed potential was a further detrimental effect of residual dioxygen in the electrolyte solution. 50% lost charge after 30 hours was claimed as low self-discharge property for an electrode with spherical $Co(OH)_2$ [85]. Low self-discharge of an electrode prepared from spherical $Co(OH)_2$ was claimed without providing a reason or a comparison. A $MnFe_2O_4$/carbon black electrode showed lower self-discharge than a plain carbon black electrode. At an optimized fraction of carbon black (7:3) the lowest value combined with highest charge storage capability was noted [86]. Sheet-like WSe_2 was examined as an electrode material requiring no binder when mixed with e.g. activated carbon as a storage material [87]; an improvement of "self-discharge potential" by 9% was registered (whatever that means, presumably the authors mean a slightly lower slope of the electrode potential decrease of the positive electrode). Low self-discharge not specified further was claimed for a battery-type electrode of Co_3O_4 nanowires coated with Ni_3S_4 [88]. $Fe(CN)_6^{4-}$ grafted via Co-N bonds onto Co_3O_4 was suggested as an option to enhance the limited charge storage capability of the metal oxide [89]. The modification resulted in increased storage capability and slowed-down self-discharge. Low self-discharge measured as electrode potential decay of a Co_3S_4@Ni_3S_4 electrode was attributed to the strong localization of the redox reactions of the battery-type electrode material [90]. Tetragonal $LiMn_2O_4$ was examined as electrode material [91], and it showed much slower self-discharge than an electrode made with MnO_2. Electrode potential decay of a NiCoP-electrode in an alkaline electrolyte solution was much slower than the decay observed with electrodes of NiP and CoP deposited on nickel foam [92]. A reason was not suggested. A composite of MWCNTs coated with nickel oxide used as electrode in an alkaline electrolyte solution showed low self-discharge, reasons were not provided [93].

MXenes are a class of 2D transition metal carbides, nitrides and carbonitrides of the genera formula $M_{n+1}X_nT_x$ (n = 1, 2,3) with M a transition metal, X the carbon or nitrogen and T designating a surface-terminating functional group (-O, -OH, -F) [94]. A noticeable effect of the fraction of fluorine atoms on self-discharge was found, a higher fluorine content corresponded to slower self-discharge. This was attributed to surface adsorption properties of the MXene changing with fluorine content.

Addition of surfactants [95] (for typical examples see Figure 3) to the electrolyte solution inside a supercapacitors was examined both for EDLC-materials and for redox electrode materials [96].

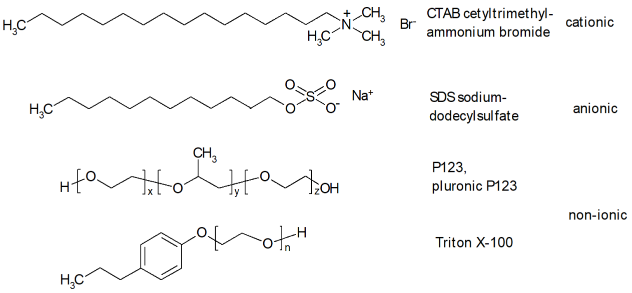

Figure 3: Structural formulas of surfactants used in supercapacitor electrode studies.

Beneficial effects in terms of stability and enhanced rate capability were observed. In a study of $MnFe_2O_4$ as an electrode material, reduced self-discharge (noticed as slower electrode potential decay) was found with both nonionic and anionic surfactants [97]. Sodium dodecyl sulphate (SDS) provided the largest effect, but an explanation was not provided. Enhanced lithium ion diffusion invoked as the cause of the improved overall performance does not seem to be related to reduced self-discharge. In a rather confusing report low self-discharge for electrodes based on PANI-coated nanowires of MnO_2 was claimed [98]; possibly this claim pertains to an all-solid-state device composed of two such electrodes with a solid electrolyte also presented in this report. For a Ni-Mn phosphate/graphene electrode measurements of self-discharge by various methods was claimed in a report containing positively no data on this aspect [99].

Intrinsically conducting polymers (ICPs) were suggested as active masses for supercapacitors [100]. Self-discharge of electrodes prepared with these materials has rarely been studied except for some reports of full cells (see below) leaving the question open which of the electrodes contributed to the observed behavior. Somewhat against the common trend away from fluorine-containing compounds in electrochemical devices visible for years already poly(5-fluoroindole) was examined as electrode material [101]. Compared with several fluorine-free polyindolines, a slightly improved self-discharge behavior was reported, but reasons were not even indicated. Oxidative vapor deposition of PEDOT:Cl on a textile substrate yielded a flexible electrode for a wearable supercapacitor with electrode potential decay (i.e. self-discharge) resulting in charge redistribution in the ICP [102]. Holding the electrode potential for some time to support this rearrangement and improving structural order by temperature control during the deposition were suggested to mitigate this decay.

2D-polymers obtained from hexaaminobenzene and pyromellitic dianhydride or phthalic anhydride showed redox electrode behavior with broad waves presumably due to electronic interactions [24] between the numerous redox centers in the 2D-layers [103]. Electrode potential decay associated with self-discharge was more severe (62% within 12 h) with the polymer obtained with phthalic anhydride (38% within 12 h), and reasons were not suggested.

A composite of CO_2-activated rice husks and poly(3,4-ethylenedioxythiophene) PEDOT was examined as electrode material [104]. CVs were displayed only for symmetrical cells with the PEDOT-electrode showing a rather pseudocapacitive response. The composite provided slower self-discharge and lower leakage current than the single materials for reasons not provided. The low self-discharge of both electrodes and a symmetrical supercapacitor with a nanocomposite of PANI and graphene prepared by a mechanochemical method was attributed without presenting data to the graphene nanoparticles [105]. A composite of small fractions of CNTs (1.5 to 5.5 wt%) and PPy obtained by chemical polymerization of pyrrole in the presence of CNTs was studied as an electrode material in aqueous 1 **M** H_2SO_4 [106]. Recorded electrode potential of the various studied composites differed somewhat, and the presence of CNTs resulted in slower self-discharge (for reasons not provided) with both 3.0 and 5.5 wt% CNTs.

A mixture of iron and PANI was coated on nickel graphene foam and carbonized subsequently [107]. The initial cell voltage of 1.7 V of a symmetric supercapacitor with two of these electrodes with an aqueous electrolyte solution of 1 **M** $NaNO_3$ dropped rapidly first below the value commonly associated with water decomposition, within 76 h it dropped to 0.85 V.

Bioderived materials possibly open an access to sustainable materials and devices with less or no metals with their known drawbacks were examined. Lignin with its rich redox-chemistry providing chemistry in particular of quinone Q and hydroquinone H_2Q groups is most prominent. Lignine hosted in a graphene structure was examined with the claim of low self-discharge provided in the abstract [108]. No experimental evidence was provided, and the report does not even contain the term again. A solid state device with H_2Q added into the PVA-KOH gel electrolyte and steam-activated coconut shell-derived electrodes was studied [109]. Self-discharge caused a voltage drop from 0.9 V to 0.48 V within 10 hours. Without H_2Q the voltage dropped to about 0.2 V within this time.

In a report on a composite of polypyrrole (PPy) with lignosulfonate a further coating with poly(*o*-aminophenol) resulted in a slower self-discharge, and reasons were not provided [110]. An electrode prepared first as a composite of lignine and PEDOT subsequently coated with electrodeposited polyanthraquinone showed lower self-discharge in terms of voltage loss after 12 h (about 30 vs. 50%) with the latter coating with the same rate of loss of potential after an initial period with high loss, and an explanation was not provided [111]. Fast self-discharge of lignin-based electrodes was deplored [112]. A mixture of reasons and reactions related to the Q and H_2Q groups was claimed as reason. Further studies of bioderived materials for supercapacitor electrodes with specific attention to self-discharge, materials purity and surface functional groups were reported [113].

Self-discharge of electrodes made from graphitic carbon nitride combined with various fractions of chemically polymerized PANI was examined [114]. Electrode potential decay of the charged electrode was similar for the studied combinations. The leakage current showed a pronounced dependency with a lowest value at an intermediate ratio of constituents, and analytical data were not provided.

Addition of redox systems to the electrolyte solution frequently results in the desired increase of storage capability at the expense of excessive self-discharge by shuttle mechanisms, this will be addressed below. Attaching or immobilizing redox systems at an electrode will help to avoid this problem since it results basically in a redox electrode as discussed above. Such modification might even enable the use of electrolyte solutions not suitable for the same redox component when dissolved (because e.g. poor solubility). This was demonstrated with anthraquinone grafted on carbon [115], for an overview see [100]. Immobilization (or whatever other name and term are used) will possibly shift the electrode operating principle to that of redox electrodes, i.e. battery electrodes, discussed above with all attached limitations, in particular with possibly reduced high current capability. Unfortunately this aspect is not addressed properly or not at all in many reports.

The concerns briefly outlined above have not kept researchers from proposing an electrode of plain nickel foam immersed in an alkaline solution of 0.5 **mM** $K_3Fe(CN)_6/K_4Fe(CN)_6$ for a supercapacitor [116]. Low self-discharge of the electrode was claimed based on the recorded single electrode (i.e. half cell) measurements. Full cells with a Nafion$^{®}$ membrane as a separator were not examined for self-discharge. Methylene blue was confined in a 3D graphene material yielding a composite electrode [117]. A symmetric device built with two of these electrodes, PVA/H_2SO_4 electrolyte and a separator was tested, but self-discharge was only mentioned in the abstract.

Biofilms of *G. sulfurreducens* showed pseudocapacitive behavior and self-discharge behavior to other supercapacitor electrodes [118].

3.1.4 Electrodes in metal ion capacitors

Self-discharge of lithium-ion capacitors was discussed with respect to the behavior of the pre-lithiated negative electrode, and recorded results were attributed to poor solid electrolyte interface formation [119].

3.2 Full cells and two-electrode systems

Although an actual supercapacitor may be considered simply as the combination of two electrodes (half-cells) into a device (full cell), their properties rarely simply add up. In addition results from full cell studies cannot be transferred straightforwardly to single electrode properties. Consequently, following observations and their interpretation obtained with full cells are presented. Terminology, in particular use of the terms asymmetric and hybrid, appears to be lacking systematic handling. In this report an asymmetric device combines two electrodes either operating on different charge storage mechanism (e.g. an EDLC electrode and a battery-type electrode) or operating on the same storage mechanism but with different reactants at the electrodes (e.g. a device with two different redox-active additives in the electrolyte solution). Sometimes the former device is also called a hybrid, on this terminology and associated confusion see also [24, 120, 121].

3.2.1 Symmetric EDLC devices

Charge redistribution inside a supercapacitor after turning off charging or discharging currents was studied in detail [5] yielding predictive possibilities helpful for users of supercapacitors in networks. Performance of a large supercapacitor considered for electric traction purposes was studied with respect to possible discharge mechanisms and their mathematical representation in particular with respect to temporal changes of the dominating self-discharge mechanism [122]. Self-discharge was mentioned in a report on an EDLC-device with activated carbon electrodes based on carbonized cellulose cloth activated for different durations [123]. Although it was claimed that the pulse-application allowed higher cell voltages without noticeable self-discharge it was later noticed that longer activation resulted in higher self-discharge. This observation was associated with the larger material surface area obtained after longer activation times. Individual and combined effects of porous electrode structure, charge redistribution and self-discharge on charge capacity of an EDLC device were studied [124]. Rather expectedly it was found that self-discharge becomes negligible at high discharge currents. Results of a study of the self-discharge of EDLC device with a neutral aqueous electrolyte solution suggest that Ohmic leakage does not describe the voltage decay correctly. Instead a process involving ion diffusion must be considered in addition [125]. A full cell prepared with two electrodes made with carbon black and 70 wt% zeolite and a neutral aqueous electrolyte solution was tested [126]. After fully charged to 1.5 V, 0.38 V was found after 24 h. Carbon paper electrodes studied as a reference provided 0.11 V, i.e. the device was practically completely discharged.

A solid state symmetric device with electrodes prepared from a mixture of CNTs and rGO aerogel with a cation exchange membrane as electrolyte providing a neutral environment was tested [127]. The rather fast self-discharge registered as a decay of cell voltage within the first minutes of a test becomes slower when the water-decomposition voltage was passed. This observation is difficult to match with the author's claim, that by "leveling potentials of oxygen and hydrogen evolution" this natural limitation can be overcome.

The influence of pore sizes and pore size distribution on the performance of an EDLC device with a nonaqueous electrolyte system was studied [128]. The carbon with mesopores in the range 2 to 4 nm performed best including relative slowest self-discharge. This was attributed to only moderate ionic concentration gradients inside mesopores as compared to micropores. A study of the influence of the diameter of MWCNTs on self-discharge of a symmetric device with a non-aqueous electrolyte solution suggested, that self-discharge is due to Ohmic leakage and diffusion-controlled Faradaic processes [129]. Thicker MWCNTs showed faster self-discharge which was attributed to faster ion diffusion in the larger pores of the materials made from thicker nanotubes. A symmetric supercapacitor with a nonaqueous electrolyte solution and two electrodes incorporating siloxene rGO showed lower self-discharge than devices having only one of the components in their electrodes [130]. This improvement is attributed to the 2D-heterostructures reducing Faradaic reactions and charge redistribution. Two paper electrodes coated with CNTs were assembled with a PVA/H_3PO_4 electrolyte into a supercapacitor to be combined with a triboelectric power generator [131]. Lower self-discharge and leakage currents in comparison to a device with a liquid electrolyte solution were noted.

In studies of temperature effects on cell capacitance, equivalent series resistance ESR (see also Figure 4) and self-discharge of supercapacitors with organic solvent-based electrolyte solutions a pronounced increase of the latter with operating temperature was found, and it was attributed to modifications of the electrochemical interfaces at the activated and highly porous carbon electrodes [132]. Temperature influence on self-discharge of two supercapacitors with activated carbon electrodes was examined [133]. The device for 5.5 V operating voltage at 1 F rated capacity was composed of two cells connected in series whereas the other one for 2.7 V at 10 F contained only one cell. CVs of the former device were significantly tilted suggesting a higher ESR, and this was corroborated by subsequent measurements. How this also suggests a higher equivalent parallel resistance EPR values remains unclear (see also following the Figure 4). The EPR decreased dramatically for the two-cell device at elevated temperature whereas the displayed cell voltage decay curves change dramatically for the one-cell device. This striking contradiction leaves the question open, whether some possible design or manufacturing flaw in the two-cell device may be the cause of the behavior.

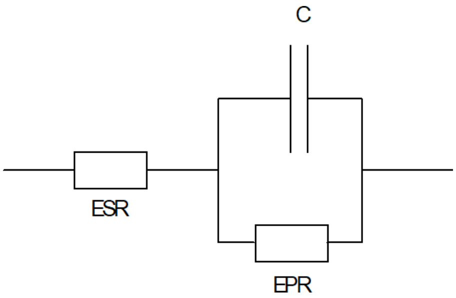

Figure 4: Most basic electrical equivalent circuit of a supercapacitor.

This equivalent circuit enables determination of the most basic device parameters from electrical measurements, and it lacks physical interpretation of the components except for the capacitance. ESR is associated with all sorts of Ohmic resistance generated by the electrode material, the current collector, wires and most importantly the electrolyte (solution) resistance. The EPR can be associated with parasitic resistances causing the flow of a current also called leakage current, details were discussed above. For the evaluation of electrochemical impedance measurements (see e.g. [3]) a slightly different and more extensive equivalent circuit (Figure 5) was suggested:

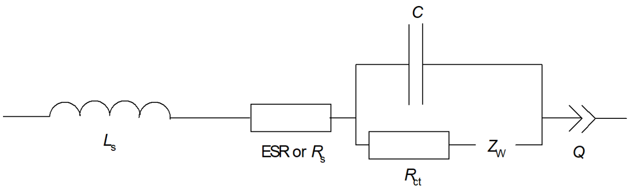

Figure 5: Extended electrical equivalent circuit for a supercapacitor used for evaluation of electrochemical impedance measurements e.g. in [134].

Unfortunately the authors do neither describe nor even identify the elements in their report. Compared with circuits discussed below as used extensively in modeling it might be assumed that *Q* elsewhere used as constant phase element or non-ideal capacitance [135] may have a similar meaning here. Further inconsistencies with equivalent circuits suggested and extensively tested elsewhere as described below still remain.

The influence of cell voltage and temperature on self-discharge of a supercapacitor with activated carbon electrodes and an aqueous electrolyte solution was examined [136]. At moderate cell voltages the negative electrode contributed mostly to self-discharge according to the observed change of electrode potential. For both electrodes a diffusion-controlled mechanism was suggested. At voltages $U > 1.6$ V (presumably beyond the electrochemical window of stability of the employed electrolyte solution) at both electrodes activation-controlled mechanisms presumably related to water and carbon oxidation at the positive electrode and water or dioxygen reduction at the negative one are operating. A symmetric supercapacitor with a “water in salt” electrolyte was inspected, and self-discharge was found to be slowest with a concentration of 15 **M** CsF [137]. This is attributed to increased viscosity and thus reduced ion mobility in the highly concentrated electrolyte solution. Tight sealing needed to keep dioxygen out of a flexible supercapacitor as a possible cause of self-discharge was stressed [138], the influence of further modifications in cell composition and assembly summarized under the term architecture are discussed beyond the leakage properties of sealing materials.

Gelation of the aqueous electrolyte solution in an EDLC supercapacitor resulted in significant reduction of self-discharge with only minor loss in current capability [139]. Similar conclusions had been reached earlier [140]. Activated carbons prepared from tree bark biomass (for a review of wood-based electrochemical energy storage devices see [141]) with a gel electrolyte yielded a symmetric device with 50% self-discharge after 15 h [142]. A micro-supercapacitor employing laser-scribed graphene electrodes and a PVA/H_2SO_4 gel electrolyte showed very low self-discharge [143]. A particularly effective suppression of self-discharge was claimed with a polyzwitterionic gel electrolyte of poly(propylsulfonate dimethylammonium propylmethacrylamide) (PPDP, Figure 6) with LiCl [144].

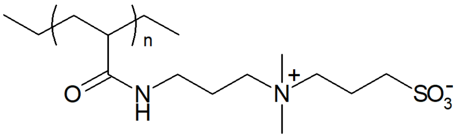

Figure 6: Poly(propylsulfonate dimethylammonium propylmethacrylamide).

The common contradiction between low self-discharge and high rate capability related to low internal supercapacitor resistance could be overcome. Compared with a corresponding gel electrolyte based on PVA, the solution resistance was reduced to less than half of the value with the latter. Self-discharge with the former gel recorded as cell voltage drop over time was reduced to half the value with PVA. Self-discharge associated with electrolyte solution decomposition (see above) was reduced because of lowered water activity, i.e. more of the charge fed into the device is stored instead of being consumed for unwanted electrolysis. A further contribution to the lower self-discharge with PPDA is attributed to ionic interactions between the zwitterions on the polymer chain and the electrolyte ions. An “interfacial wetting water based hydrogel electrolyte” (a hydrogel electrolyte) with a salt concentration much lower than observed with salt-in-water concepts (6.8 **m** instead of 21 **m**) showed significant slower self-discharge than other solid electrolyte systems [145].

A PVA-based solid electrolyte named “PVA/H_3PO_4/0.75 wt% KCl/0.3 wt% CB nanodielectric membrane” containing added carbon black for increased capacitance with two MWCNT electrodes showed 60.63% self-discharge to a residual voltage of 0.606 V after 1000 min [146]. The improvement achieved by addition of CB was attributed to their creation of “polarization with longer time constant of orientation”. A flexible supercapacitor with a neutral PVA-NaCl electrolyte and CNT array electrodes also showed low self-discharge [147].

A solid electrolyte prepared from a composite of bentonite and polyurethane soaked with an ionic liquid enabled a cell with very low self-discharge [148]. Unfortunately hardly any performance data were reported indicating the influence of this electrolyte on power capability of the cell. A solvent-free polymer composite with high ionic conductivity enabling a flexible solid supercapacitor with 88% capacitance retention after 20000 cycles and low self-discharge [149]. A microporous polymer electrolyte for EDLC-devices was prepared [150], and low self-discharge of a device constructed with this electrolyte was claimed. Modification of a microporous cellulose separator with a cationic polyelectrolyte (chemically modified polyethyleneimine) [151]. The modified separator slowed down ion diffusion driven by concentration gradients connected to self-discharge without impeding fast ion movement during charge/discharge. A separator prepared by electrospinning a mixture of dissolved polyacrylonitrile and sodium dodecylbenzene sulfonate was tested for its capability to slow down self-discharge without affecting supercapacitor performance [152]. Decreased self-discharge was ascribed to slower ion diffusion caused by the negatively charged surface of the membrane fibers. Some loss of capacitance not addressed in the report is visible in the displayed GCD curves. And the loss in power capability cannot be judged because of a lack of reported results.

Advantages of a mixed solvent of propylene carbonate and acetonitrile with tetraethylammonium tetrafluoroborate as the electrolyte seem to offer low self-discharge and leakage current with an EDLC device [153]. Carbonate-based electrolyte solutions were examined with respect to supercapacitor performance [154], and self-discharge was found to be similar to that observed with common other solvents and solutions.

Particular attention was paid to self-discharge of EDLC devices with ionic liquid electrolyte under high-temperature conditions [155]. At T = 60 °C a diffusion-controlled mechanism was found to be dominating over charge redistribution. Lower self-discharge and leakage currents (the terms are not easily separated in this report) were reported for a supercapacitor employing an ionic liquid instead of an electrolyte solution based on an organic solvent [156]. No explanation is offered. Perhaps a lower level of impurities possibly enabling the parasitic processes addressed above is part of the explanation. With specific reference to ionic liquids as electrolytes for EDLC supercapacitors detailed analysis of self-discharge was recommended for determination of suitable cell voltage limits and cell stability (instead of simple long-term cycling) [157]. The relevance of pore structure, type of anion in the ionic

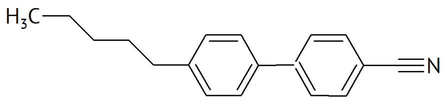

Figure 7: Schematic structure of the liquid crystal 4-n-pentyl-4-cyanobiphenyl.

liquid and purity of used carbons and their influence on the prevalent self-discharge mechanism were highlighted.

The electrorheological effect of added liquid crystal 4-n-pentyl-4-cyanobiphenyl (Figure 7) in a nonaqueous electrolyte solution was utilized for suppression of self-discharge [158].

In the charged state the electric field at the electrolyte/solution interface causes alignment of the additive resulting in increased viscosity of the liquid phase which in turn slows down diffusion processes related to self-discharge. Addition of the same liquid crystal material (2 wt%) to an aqueous electrolyte solution resulted in slower self-discharge and lower leakage current [159]. At some place in the report this was attributed to formation of an interfacial layer, and elsewhere tuned effective conductivity and slower ion diffusion were suggested. The claimed insignificant negative effect on performance, in particular on power capability, is not supported by experimental evidence. Addition of a lyotropic liquid crystal (5 vol%) into the organic electrolyte solution resulted in a decrease of self-discharge by 32% [160].

Addition of an isocyanate-based electrolytic additive 2-isocyanatoethylmethacrylate (Figure 8) to the nonaqueous electrolyte solution followed by either chemical or electrochemical polymerization resulted in a significantly slower self-discharge [161]. Chemical polymerization resulted in even lower self-discharge but slightly lower power capability of the cell, and obviously electrochemical polymerization yielded changes in the electrolyte solution providing a compromise.

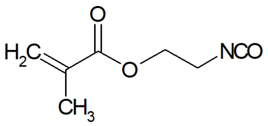

Figure 8: Molecular structure of 2-isocyanatoethylmethacrylate.

The influence of numerous operating and preparation parameters on performance of an EDLC-device was examined in a general approach [162]. Detrimental influence of high impurity concentrations and slow charging was noticed. Corrosion of stainless steel current collectors with AC electrodes in a symmetrical supercapacitor with electrolyte solutions ranging from acidic to strongly alkaline was studied [163]. Corrosion in terms of corrosion currents [164] was fastest in the acidic solution of 1 **M** H_2SO_4, and self-discharge was fastest also with this solution. This supports the participation of the dissolved corrosion products in an ion shuttle mechanism of self-discharge. Iron ions as a conceivable corrosion product or a general impurity were studied in a symmetric EDLC-device with an aqueous sulfuric acid electrolyte solution [165]. Without added iron ions (as a reference) different self-discharge profiles were observed for the positive and the negative electrode suggesting subsequent studies being performed with an additional reference electrode. At the positive electrode iron ion concentrations below 10^{-5} **M** had no detrimental effect, and at the negative electrode even 10^{-3} **M** could be tolerated. At concentrations above this level self-discharge reactions proceeded mostly on the external surface of the positive electrode. The effect of iron impurities on the performance, in particular self-discharge, of carbon electrodes in EDLC devices was examined [166]. Slightly different from observations presented above small amounts of such impurities were found to reduce self-discharge, possibly by affecting surface states and pore structure (presumably during preparation/activation of the carbon material).

A symmetric supercapacitor with electrodes prepared from PPy with K_2CO_3 as activating agent in the carbonization was examined for self-discharge [134]. Voltage decay proceeded in two steps with a rapid decay first. In this step at cell voltages above the thermodynamic stability window of aqueous electrolyte solutions, products of hydrogen and dioxygen generated by the initial “overcharge” react. In the second step self-discharge proceeding much slower is due to other diffusion-controlled processes. Experiments with a lower charge cut-off value of applied voltage confirmed this assumption.

Nitrogen-doped rGO was examined as electrode material self-discharge nowhere substantiated in the report with the lowest [167]. With electrodes composed of rGO and nitrogen-doped rGO, a symmetric supercapacitor with claimed low self-discharge caused by diffusion of charge carriers was obtained [168, 169]. For undoped rGO these authors verified diffusion-controlled processes as the main cause of self-discharge [170]. A combination of graphite and CNT was used in a symmetrical EDLC-supercapacitor with an alkaline and for comparison with a gel H_3PO_4 electrolyte [171]. Low self-discharge was claimed without a numerical reference in this report which contains further inconsistencies and erroneous claims. Inserting a bipolar electrode joining two cells, a “bipolar” device somewhat confusingly called electrochemical capacitor was created [172]. Self-discharge was not different from that observed before with a single cell.

The influence of temperature changes on a supercapacitor with electrodes made from SWCNTs was studied in a temperature range 25 to 100°C [173]. Improved room temperature performance after thermal cycling was attributed to increased electronic conductivity of the electrodes and surface modification on the SWCNT. A decrease of the resistive element in the equivalent circuit used for evaluation of the performed impedance measurements suggested a faster self-discharge after thermal cycling. Calendar aging of an EDLC-type supercapacitor was monitored [174]. Suitability of commercial EDLC devices for use in spaceflight was confirmed showing a self-discharge in terms of voltage decay of 2.5% within two days [175]. Exposure of an EDLC supercapacitor to γ-rays did not change the self-discharge behavior [176]. Stretching of a suitably designed supercapacitor did not affect self-discharge noticeably [177].

3.2.2 Devices with redox-active electrolytes

Classification of these devices is hardly straightforward, and a review on these systems is available [178]. It remains unclear why the authors of the latter report oscillate between redox-active electrolytes and redox mediator since the latter term is a well-established one with a different meaning in organic electrochemistry. Many authors start with a symmetric EDLC-type device and add a redox active component which (as it turns out subsequently) is active only at one electrode but may participate in self-discharge when allowed to move to the other electrode. Setups started from this point are subsequently classified as symmetric ones. In a few cases single electrodes in contact with an electrolyte solution containing a redox system were examined. Although no complete cells were studied these examples are discussed in the following section. For whatever reasons (possibly because many reports might suggest this) authors start with a divided cell and two distinctly different redox reactions at both electrodes. This obviously asymmetric devices are called this way below.

Addition of a redox-active component into the electrolyte solution of a supercapacitor with two EDLC-type electrodes can result in significantly increased charge storage capability [34], consequently such devices are sometimes called "redox-enhanced" or redox electrolyte-aided hybrid energy storage systems (REHES) [179]. In the absence of a separator or a similar device (semipermeable membrane) keeping the participating dissolved species from engaging in a shuttle mechanism between both electrodes rapid self-discharge is highly likely, and strategies to overcome this limitation were reviewed [34, 179, 180]. For an overview of organic molecules as possible additives see [181]. An EDLC-type supercapacitor with two added redox systems (0.75 **M** NaI at the positive and 0.5 **M** VO_SO_4 at the negative electrode) in the aqueous electrolyte solution showed fast self-discharge tentatively assigned to a redox-shuttle mechanism by the authors [182]. Furfural residues were converted into electrode materials for a symmetric device with a KOH electrolyte solution [183]. Upon addition of either 0.05 M $K_3Fe(CN)_6$ or KI reduced self-discharge was observed. The cell voltage of 1 V after charging decreased to 0.11 V with the alkaline solution only after 28 h, and after this time with $K_3Fe(CN)_6$ 0.2 V and with KI 0.23 V were noticed.

Addition of methylene blue as a redox mediator into a gelled electrolyte for an all-solid-state supercapacitor resulted in decreased electrical series resistance and significantly enhanced charge storage capability [184]. An EDLC-supercapacitor with an aqueous electrolyte solution of 1 **M** Li_2SO_4 showed significantly reduced self-discharged measured in terms of cell voltage decay upon addition of KI or LiI [185]. This was attributed to the redox activity of I^-/I_2 at the positive electrode keeping this in a narrow electrode potential range avoiding processes possible causing or supporting self-discharge.

A further development of the "salt in water" concept introduced above by creating a redox-active (Br^-/Br_3^-) hydrogel polymer electrolyte was reported [186]. Initial self-discharge of the device with added KBr was slower, and later the presence of the halide did not affect the self-discharge. Apparently the electrolyte suppressed self-discharge. Addition of tetraalkylammonium bromide during charging of a supercapacitor with added Br^-/Br_3^- redox system resulted in formation of solid polybromide subsequently suppressing self-discharge [187].

A mixed organic-aqueous electrolyte solution benefited the use of polyoxometalates as redox-active additives in the electrolyte solution by suppressing the corrosion of the aluminum current collector, shifting the hydrogen evolution electrode potential to more negative values and accelerating the redox reaction [188]. Lower self-discharge was attributed to adsorption of the polyoxometalates into the carbon pores,

3.2.2.1 Symmetric devices with redox-active electrolytes

Fast self-discharge resulting in 50% loss within 0.6 h was reported with quinone dissolved in the electrolyte solution in a device with two carbon electrodes [189]. When anthraquinone was grafted (i.e. covalently bonded) to the negative electrode the losses occurred within 6 h (see below, next section). Self-discharge in a symmetrical device with added KI was noticed during ageing tests (both cycling and floating, i.e. at a fixed cell voltage) [190]. Two hydrogel electrodes of rGO containing VO^{2+} were brought into contact with a Neosepta[6] membrane between them [191]. Leakage current was found to be lower than observed with comparable devices, and a cell voltage loss as indicator of self-discharge from 1.2 V for the charged cell to 0.57 V after 14 h was noticed.

A general reduction of self-discharge could be achieved by immobilizing the redox-active species in a polymer-like sulfonated polyaniline [192]. Addition of the polymer increased storage capability significantly but did not negatively affect rate capability at higher current densities. A device with two activated carbon electrodes and an ionic liquid-based gel polymer with incorporated CNTs and bromide added as redox reactant at the positive electrode was described and tested [193, 194]. The cell voltage of this device was much larger than the comparison without added CNTs, and the comparison with an aqueous electrolyte system performed even worse. The superiority of the first system was attributed to halide adsorption on the CNTs inhibiting their diffusion resulting in self-discharge. In an all-solid-state supercapacitor with a redox-active ionic liquid (*N*-butyl-*N*-methylpyrrolidinium bromide ($Pyr_{14}Br$)) added to the gel polymer electrolyte was described [195]. The Br^-/Br_3^- couple provides additional charge storage at the positive electrode. The voltage decay curves of the cell with/without the ionic liquid have visibly the same slope, only the cell voltage is larger with the additives. The authors conclusion regarding slower self-discharge is not apparent.

High self-discharge in supercaps with redox-active additives to the electrolyte solution was deplored in a report on a high performance energy storage device with potassium ferricyanide addition, and insertion of a cation-exchange membrane was suggested as a remedy [196]. The detrimental effect of this addition on power capability of the cell was not examined. Suppression of self-discharge of a supercapacitor with a ferrocene-modified ionic liquid electrolyte was attributed to film-formation, i.e. deposition, in case of the ferrocene-modification applied to the anion of the ionic liquid [197].

A symmetric supercapacitor with poly(dithieno[3,4-b:3',4'-d]thiophene) as both negative and positive electrodes and a gelled electrolyte lost 25% of its initially stored charge within 14 h [198]. A symmetric supercapacitor with 2-mercaptopyridine added to the gel PVA/H_2SO_4 electrolyte with two activated carbon electrodes was tested and examined for self-discharge [199].

3.2.2.2 Asymmetric devices with redox-active electrolytes

A negative electrode made from MXene $Ti_3C_2T_x$ and a positive electrode of activated carbon with KBr added into the aqueous electrolyte solution of H_2SO_4 with a fiberglass separator showed moderate self-discharge (62.9% of the initial voltage left after 2500 s) attributed to adsorption of the oxidized form of the redox additive at the positive electrode [200]. Without the added redox system only 26.5% of the initial voltage was found after the same time supporting this conclusion.

A divided cell with an anion exchange membrane inhibiting a shuttle mechanism causing self-discharge with different redox systems in both half-cell was described [201]. The novelty of this concept claimed by the authors appears to be surprising given the publication of a patent suggesting exactly this concept years earlier [202]. Self-discharge of a cell with a gel electrolyte of H_2SO_4 containing in the positive compartment added $CuCl_2$ with an unspecified separator in between was significantly reduced because of the increased viscosity of the gel (and possibly also with a contribution from the separator) [203].

Use of an anthraquinone-grafted electrode instead of a plain carbon electrode with an electrolyte solution containing quinone resulted in a decreased self-discharge still exceeding practically acceptable levels [189]. Self-discharge was attributed to redox reactions between the dissolved species and the covalently attached ones. Combination of a rGO-hydrogel/PANI electrode as anode[7] with an electrode utilizing the Cu/Cu^{2+}-redox couple at an rGO-hydrogel as cathode yielded a device with low self-discharge attributed to the deposition of metallic copper in the charged state [204].

With two activated carbon fiber cloth electrodes and an aqueous electrolyte solution of either 3.5 **M** NaBr or NaI and the positive electrode impregnated with the respective halogen was proposed [205]. Low self-discharge is only claimed in the abstract but not mentioned anywhere in the report. In a somewhat complicated discussion of observed leakage currents, which includes observations with a further electrolyte solution (sulfuric acid) it is concluded, that the claimed low leakage is due to adsorption of the halide species at the positive electrode. Given the experimental approach – measuring leakage currents by keeping the cell at the fully charged state and associated cell voltage this does not surprise, but this observation should not be confused with low self-discharge. Carbon

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[6] This is a trademark of ASTOM corporation designating a family of cation and anion exchange membranes. The authors of the present report fail to provide even basic information, but CMS suggests a cation exchange membrane.

[7] Designation of the electrodes as anode/cathode appears unlikely given the electrode potentials reported in the text.

paper electrodes modified with a PANI gel network with a redox additive, 3-(2,2,6,6-tetramethyl-piperidiynl-1-oxyl)-1-methylylimidazolium bromide (this compound is correctly called a „biredox salt“, sometimes the author use in error the term „biredox molecule“, see Figure 9) were used in a supercapacitor with a nonaqueous electrolyte solution [206].

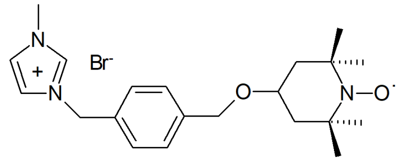

Figure 9: Structural formula of 3-(2,2,6,6-tetramethyl-piperidinyl-1-oxyl)-1-methylylimidazolium bromide.

The modification of the carbon paper resulted in a substantial increase of cell voltage and slightly slower cell voltage decay, i.e. self-discharge.

An ionic liquid with both cation and anion modified with attached redox-active groups (“biredox ionic liquid”) for use in a supercapacitor was proposed [207]. Solubility of the modified ions in an ionic liquid without modified ions was increased because of the higher charge density on the modified ions. This in turn increases the specific charge storage capability of the material. In addition the higher charge density on the modified ions helps to keep them attached to the respective carbon and inside the porous material thus reducing self-discharge usually caused by ion shuttle effects in such devices.

Insights from modeling and simulation on the effects of self-discharge on the performance of supercapacitors with redox active additives were discussed [208, 209].

3.2.3 Symmetric redox-electrode devices

The use of symmetric redox-electrodes prepared of the same ICP for use in a supercapacitor was identified as being somewhat inefficient very early [210, 211]. Polythiophene and polymers prepared from substituted thiophenes provide an exception because they are capable of undergoing both oxidation and reduction from the neutral state enabling a symmetric supercapacitor with a practically relevant cell voltage and overall performance. With optimized films of poly(3,4-ethylenedioxythiophene) (PEDOT) and an ionic liquid as the electrolyte, devices with low self-discharge could be prepared [212].

A device with two PEDOT electrodes and an agarose hydrogel electrolyte with NaCl showed self-discharge from 1.75 V to 0.67 V within 25 h [213]. A symmetric supercapacitor with both electrodes made from PEDOT deposited on carbon cloth with a nonaqueous electrolyte solution with a layer of sulfonated polystyrene placed between two layers of Celgard as separator showed reduced self-discharge because the ion exchange material trapped impurities in the electrolyte solution otherwise causing parasitic Faradaic reactions [214]. Power capability was hardly affected. Nickel oxide deposited electrochemically on CNTs yielded a mesoporous electrode material providing low self-discharge in a supercapacitor [215].

For a flexible all-solid-state symmetric supercapacitor with electrodes containing a graphene/PANI composite, a low self-discharge was noticed [216]. Similar observations were reported with CNT/PANI-electrodes used instead, and a comparison of different solid electrolytes suggests a polyacrylamide-based hydrogel as the electrolyte providing lowest self-discharge (50% loss after 10 h) [217]. Electrodes prepared with PANI-coated CNTs were combined with a gel electrolyte into a flexible solid state supercapacitor with low self-discharge: after 24 h 0.22 V of the initial cell voltage of 0.8 V were left [218]. Two electrodes of porous PANI prepared by electropolymerization on carbon paper combined with a PVA/sulfuric acid electrolyte were tested as solid state supercapacitor [219]. Self-discharge caused a voltage loss of about 50% after 24 h. Two paper-like electrodes of rGO infiltrated with PANI:PSS (polystyrene sulfonate) were combined with an electrolyte gel into a flexible all-solid-state supercapacitor showing low self-discharge [220]. Essentially the same results were obtained with PPy instead of PANI:PSS [221]. In a symmetric device with the same gel electrolyte and two rGO/PPy nanotubes paper-like electrodes these authors claimed low self-discharge (from 1 V initially to 0.22 V after 24 h) [222]. How the measured leakage indicates high stability of the supercapacitor remains unclear.

A symmetric supercapacitor with two composite electrodes both made from α-MnO_2 and nitrogen- and sulfur-doped rGO with an ionic liquid-based polymer electrolyte was reported [223]. Cell voltages up to 4.5 V were obtained, and the displayed GCD curves suggest significant Coulombic inefficiencies was not addressed in the text. The displayed voltage vs. time curves recorded after charging the studied devices confirm this assumption, and an immediate and sharp voltage decline from 4.5 V to about 1.5 V can be seen. The slight voltage increase in the following hours contradicts the stated rate of voltage decline provided in the text. A symmetric device with two electrodes prepared from binder-free MoS_2 on nickel foam with an unspecified, presumably aqueous, electrolyte solution was developed and tested [224]. Within a cell voltage range from 0 to 1 V (possibly stipulated by the available range of redox potentials of the employed electrode material) the cell showed rapid self-discharge to 0.2 V despite the rather limited cell voltage. Unfortunately numerous discrepancies between text and diagrams and further inconsistencies leave any conclusion rather tentative. A symmetric supercapacitor with electrodes made from branch-like MoS_2 with a solid PVA/Na_2SO_4 electrolyte showed a voltage drop from 1.5 V fully charged to 0.62 V after 2 h due to self-discharge [225]. For a symmetric device with two electrodes made of tellurium nanorods electrodeposited on carbon cloth with an unspecified electrolyte solution (according to display data presumably an aqueous one) low self-discharge was claimed [226]. Within 22000 s the device voltage decreased from 1.5 V to 0.1 V with the initial decline possibly being a mixture from Ohmic drop and overcharge.

3.2.4 Asymmetric devices with two redox-electrodes

Gong et al. have proposed a flexible device with FeOOH and polypyrrole deposited on carbon fibers as electrodes [227]. Mitigation of self-discharge could be achieved by using an ionogel electrolyte of an ionic liquid soaked into fumed silica. A supercapacitor with two electrodes based on polyaniline PANI showed 20% self-discharge after 10 h [228]. An asymmetric device combining a negative $MnFe_2O_4$ and a positive $LiMn_2O_4$ electrode showed lower self-discharge than symmetric devices using these materials or their combinations with EDLC-type electrodes [229].

In an asymmetric supercapacitor with a negative electrode of γ-FeOOH and a positive one of amorphous Ni-Mn hydroxide (both prepared by electrodeposition on carbon nanofoam paper) showed self-discharge dominated by the positive electrode [230]. At the negative electrode reduction of dioxygen was indicated as a possible cause of the self-discharge. The experimental part does not specify whether electrolyte solutions were degassed. Possibly this may have caused unwanted electrochemical activity of the still present dioxygen as part of the explanation.

An asymmetric supercapacitor with a positive electrode of 3D graphene-wrapped V_2O_5 nanospheres and a negative one of Fe_3O_4@3D graphene with an aqueous electrolyte solution of 1 **M** Na_2SO_4 was examined for self-discharge [231]. The initial sharp drop of cell voltage after disconnection from the charging circuit was attributed to decomposition of water, i.e. a result of overcharge. The subsequent decline to 1.04 V within 48 h was not discussed.

3.2.5 Asymmetric devices combining an EDLC-type electrode and a pseudocapacitive electrode

An asymmetric supercapacitor based on woven fabric coated with carbon nanofibers and subsequently with activated carbon with MnO_2 added to the positive electrode and either paper or Nafion® as separator and an aqueous electrolyte solution of Na_2SO_4 was developed [232]. Low self-discharge and low cost materials were claimed, and the use of Nafion® seems to be a contradiction. A device composed of a negative electrode of activated peanut-based carbon and a positive one made of sulfur-reduced GO loaded with MnO_2 was examined for self-discharge [233]. The rather hard to understand report seems to suggest that self-discharge was attributed to water decomposition. A nickel foam with very fine pores was proposed as substrate for electrodeposition of MnO_x [234]. Such electrodeposition results according to known literature reports in formation of MnO_2, XRD is not helpful to identify stoichiometric details suggesting MnO_x. In case the authors intended to state – without writing it – that their stoichiometry was deduced from *ex situ* XPS measurements they might have overlooked the previously addressed pitfalls of such *ex situ* experiments [235]. The material showed pseudocapacitive behavior in a neutral electrolyte solution of Na_2SO_4, and in an alkaline KOH solution weak redox peaks were superimposed on a mostly pseudocapacitive-like CV. Self-discharge of cells with carbon cloth as a negative electrode was examined with both electrolyte solutions. The cell voltage decreased from the fully charged state within 7.3 h with the neutral and 9.7 h with the alkaline electrolyte solution to 0 V. In a comparative study of combinations of α-MnO_2 and activated carbon electrodes with an optimized aqueous electrolyte solution of 7 M KOH were tested, and the asymmetric configuration with a negative AC and a positive α-MnO_2 electrode performed best including lowest self-discharge [236].

A device combining a negative electrode made from Ti_3C_2 MXene and a positive one made from α-MnO_2 in a potassium acetate-based water-in-salt electrolyte showed lower self-discharge than a device made with a positive electrode of activated carbon YP-50 [237]. Also using a negative MXene $Ti_3C_2T_z$ electrode and a mixture of Mn_3O_4 and MnOOH as the positive with a saturated aqueous LiCl solution/14 **M**) a device with 34% self-discharge after 54 h was built [238].

An asymmetric supercapacitor with a negative electrode of activated carbon and a positive prepared from hierarchically structured $NiCo_2O_4$ (for reasons not provided called a batter-supercapacitor hybrid) was integrated with solar cells and LED illumination and tested for performance [239]. Self-discharge was low with a small initial voltage drop after disconnection from the solar cell with the voltage subsequently stable for 24 h.

3.2.6 Asymmetric devices combining an EDLC-type electrode and a battery-type electrode

Self-discharge as one of the properties of an asymmetric supercapacitor of the type discussed in this section was examined in general terms [240], and the risk of overcharging the electrode showing lower self-discharge and associated effects were stressed. A composite of nanosheets of MnO_2 and Ni,Mn layered double hydroxide used as positive electrode (with activated carbon as negative electrode when combined into a full cell) showed lower self-discharge than a simple mixture of the two components [241]. With an alkaline electrolyte solution the positive electrode behaved battery-electrode-like, and with a neutral solution of 0.5 **M** Na_2SO_4 a pseudocapacitive behavior was evident in the presented CVs. A positive electrode made of a composite of rGO and ultrathin NiAl layered double hydroxide combined with a negative electrode of activated carbon and an alkaline electrolyte solution yielded a supercapacitor showing a self-discharge from 1.5 V to 0.5 V within 12 h [242]. A device with a negative electrode of activated carbon, a gel PVA/KOH electrolyte and a positive electrode of mixed Ni,Co-hydroxides offered 20% voltage loss during 24 h attributed to self-discharge [243].

Various morphologies of $CoFe_2O_4$ were prepared on nickel foam and coated with PEDOT as a positive electrode combined with a CNT negative electrode for a supercapacitor and presumably an aqueous electrolyte solution [244]. One third of the cell voltage recorded after charging was lost after 10000 s. A device with a positive electrode of a $NiCo_2O_4$@$Ni_{4.5}Co_{4.5}S_8$ composite combined with a negative activated carbon electrode in a 3 **M** KOH aqueous electrolyte solution lost half of its cell voltage during 26.62 h [245]. A device combing cobalt phosphate on nickel foam as positive electrode and activated carbon on nickel foam as negative one in an aqueous electrolyte solution of 3 M KOH was proposed as storage for implantable medical devices utilizing energy harvesting from piezoelectric sources [246]. Self-discharge was found to be low enough (79.4% of the fully charged voltage left after 237 s) for application in cardiac emergencies.

An asymmetric supercapacitor with a negative electrode of $Ni(OH)_2$ deposited on carbon cloth and a positive one of CNTs grown on such substrate with a solid PVA/H_2SO_4 showed a voltage decay from almost 2 V in the charged state to about 0.5 V within less than 90 min [247]. Two devices connected in parallel showed a complete loss of cell voltage even faster. A nickel hydroxide film deposited electrochemically on CNTs and thermally treated at an optimized temperature of 250 °C combined with a negative CNT electrode in a KOH electrolyte solution yielded a device providing lower self-discharge than a symmetric device with two CNT electrodes [248].

An asymmetric supercapacitor with a positive electrode of PANI and heteroatom-doped activated carbon as negative electrode in an aqueous sulfuric acid electrolyte solution was examined. A fast loss of about 50% of the initial voltage was followed by a slower decay, and no explanation was provided [249]. A negative activated carbon and a positive PANI electrode combined in a sulfuric acid electrolyte solution yielded a device with a self-discharge much lower than that of a symmetric EDLC device [250].

Gao et al. combined a composite of $MgCo_2O_4$@PPy (PPy: polypyrrole) as positive and activated carbon as negative electrode into an all-solid-state supercapacitor with a gel electrolyte of KOH in PVA [251]. The noticed low self-discharge is presumably due to the limited ion mobility in the gel electrolyte. Use of an aqueous polymer gel electrolyte in an asymmetric device activated carbon/$LiMn_2O_4$ was demonstrated [252], the claimed high ionic conductance is not supported by a comparison with data for non-gel solutions, and influence of the gelation on internal cell resistance and rate capability was not examined. An asymmetric “ultracapacitor” (NiOOH/AC) was combined with a lead-acid battery into a hybrid arrangement [253]. Self-discharge of the hybrid was smaller than of the supercapacitor alone, presumably the battery took care of the leakage current of the supercapacitor.

Low self-discharge was claimed for an asymmetric supercapacitor with a negative electrode of nitrogen-doped rGO and a positive electrode based on $NiCo_2S_4$ without providing a comparison or any explanation [254]. A positive electrode of sulfur-doped nickel zinc hydroxyl carbonate combined with a negative activated carbon electrode into an all-solid-state supercapacitor with a gel electrolyte lost 0.7 V of its initial cell voltage of 1.7 V within 4 h [255]. VO_2 deposited on rGO as a negative electrode and activated carbon on carbon cloth were combined with a non-aqueous electrolyte solution into a device showing self-discharge leaving 70% of its initial voltage after 100 h [256].

As a further development of devices considered in this section an “Ultrabattery”® (see Figure 10) combining a positive PbO_2-electrode with a negative electrode composed in part of a lead and in part of an activated carbon capacitor electrode was proposed [257]. Low self-discharge meeting or even exceeding technical standards was noticed. An update on further performance characteristics can be found in [258].

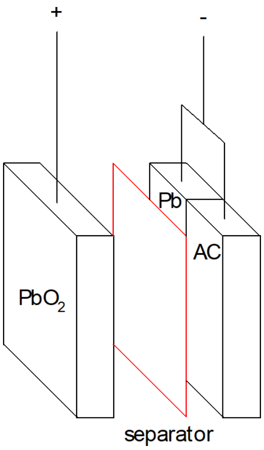

Figure 10: Schematic concept of the Ultrabattery®

In case manganese or titanium ions were present in such device their participation in a shuttle mechanism causing self-discharge was confirmed [259], and similar observations were made with iron ions instead [260].

A similar device with a non-aqueous electrolyte solution containing a negative electrode of $Li_4Ti_5O_{12}$ and a positive electrode combining $LiFePO_4$ and activated carbon AC showed promising low self-discharge [261].

A device called "rocking-chair"-type metal hybrid supercapacitor combining a negative metal and a positive activated carbon electrode with suitable nonaqueous electrolytes was suggested [262]. Its lower self-discharge was attributed to the fact, that the positive carbon electrode had its electrode potential fixed to its potential of zero charge by the cell operating mechanism.

3.2.7 Asymmetric devices combining an EDLC-type electrode and a metal-ion battery-type electrode

Devices of this type are commonly called metal-ion capacitors. Because they are mostly discussed separately from the asymmetric devices treated in the previous section they are discussed in their own section here, too. Leakage currents and self-discharge of a lithium-ion capacitor (LIC) was examined with constant voltage charging [263]. The claim, that self-discharge occurs mainly at the activated carbon positive electrode is hard to understand. Self-discharge pertains to a full device, and for a single electrode only electrode potential decay can be measured. No such data were provided. Increase of leakage current with growing number of charge/discharge cycles and with growing charge voltage was demonstrated. Surface modification of graphene and activated carbon with a solid ion conductor for both positive and negative electrodes in a LIC resulted in significant reduction of self-discharge [264]. Capacitance retention at higher current densities (up to 50 C) was found to be negligible.

Self-discharge of an LIC was compared with that of an EDLC-device and a lithium-ion battery (LIB). Results for the former device were found to be between the two latter ones [265]. An explanation was not attempted although it appears reasonable to suggest that low self-discharge may be due to the battery-type negative electrode and its storage mechanism. Verification would require measurements with an independent reference electrode. At temperatures above and below typical ambient values typical drawbacks of one electrode in the LIC started to dominate: at high temperature faster self-discharge, and at lower temperature increased polarization at the negative electrode. In another comparison of LIC and LIB self-discharge of 2% per month for the former and of 1% for the latter at a much shorter charging time of the former device (30% faster) and related higher power density were highlighted [266]. Lower self-discharge of an LIC in comparison to an EDLC-device employing the same electrodes was observed [267]. Low self-discharge (18% in 50 h) was noticed with a LIB employing a silicon-based negative electrode [268]. A similar result was obtained with only slightly different electrode materials was reported [269]. The claimed improvement is not supported by any comparison, experimental evidence suggesting any cause of the claimed improvement is not offered. In a study of the influence of metal-doping on the performance of LIC with a negative lithium titanate electrode examination of self-discharge was announced in the abstract but forgotten in the report [270]. An LIC with a negative electrode of a MoS_2@C nanocomposite was built and tested [271]. "Subordinate self-discharge" was claimed in the abstract, but in the report nothing on this subject can be found. An overview of early progress on LICs and related systems is available [272].

Nanocrystals of molybdenum sulfide (the material is called Mo-S mostly, but in the experimental part presumably correctly described as MoS_2) were suggested as negative electrode material for a LIC [273]. After about 350 h the initial cell voltage of 3.29 V decreased to 2.94 V.

$Li_4Ti_5O_{12}$ can act as host for both lithium and sodium ions; and a metal ion capacitor with an electrolyte solution containing both metal ion salts showed significantly lower self-discharge than cells with a single ion electrolyte [274]. In a comparison of LICs with various positive carbon electrodes including carbon onions, detonation nanodiamond and mesoporous carbon significant discharge of cells with oxidized positive electrode materials somewhat depending on the particular electrolyte solution was recorded, and porous carbons appear to have rather poor application perspectives because of low storage capabilities [275].

Basically similar observations regarding self-discharge were made with sodium ion capacitors (SICs) [276]. Onto porous carbon nanofibers first MoO_2 was deposited, this was subsequently coated with PEDOT and used as a negative electrode in a SIC [277]. Combined with a positive electrode made by coating activated carbon on the same substrate and a gelled nonaqueous electrolyte a supercapacitor was assembled showing a self-discharge of 15 $mV{\cdot}h^{-1}$. For comparison the rate for a symmetric device with two of the used activated carbon electrodes was 64 $mV{\cdot}h^{-1}$. An all-solid sodium-ion microcapacitor with a negative sodium titanate and a positive activated graphene electrode with a high-voltage ionogel electrolyte between both was prepared; it showed 40% of initial voltage loss within 44 h due to self-discharge [278].

A systematic study of operating cell voltage window and self-discharge of a zinc-ion capacitor was reported [279]. Lower self-discharge in comparison to a symmetric EDLC-device was attributed to the energy barrier, which is higher for zinc dissolution than for ion redistribution. A zinc-ion supercapacitor with a negative electrode of zinc metal and a positive electrode of layered boron/nitrogen-doped porous carbon with a gelled $ZnSO_4$ electrolyte had a leakage current curve (according to the figure caption) which is actually a voltage decay curve showing a change from 1.8 V fully charged to about 1.4 V after 24 h [280]. Low self-discharge in a zinc-ion capacitor was attributed to hierarchical pore structure and suitable surface functional groups [281].

The influence of electrolyte anions on the performance of a zinc-ion capacitor with a titanium nitride positive electrode was studied [282]. Although the text of the report leaves ample space for interpretation it appears safe to state that 16% voltage decay within 500 h suggest a modest self-discharge. This corroborates findings on slow electrode potential decay of TiN-electrodes reported elsewhere [73]. A positive electrode of MXene Ti_3C_2 and a negative zinc metal electrode were combined with an aqueous $ZnSO_4$ solution into a zinc-ion capacitor [283]. During 240 h after charging a self-discharge of 1.24 $mV{\cdot}h^{-1}$ was observed. Few-layer phosphorene obtained by exfoliation of black phosporus was used as the positive electrode, zinc metal as the negative one, and a water-in-salt electrolyte were combined into a zinc-ion capacitor with a cell voltage decay due to self-discharge from 2.2 V to 1.47 V within 300 h [284]. A symmetric device containing instead only phosphorene electrodes showed a decrease from 2.2 V to 0.96 V within 200 h.

A completely degradable zinc-ion supercapacitor with a negative electrode of zinc nanosheets deposited on Ti_3C_2 MXene and a positive one of just Ti_3C_2 with a self-discharge rate of 6.4 $mV{\cdot}h^{-1}$ much lower than previously reported values was described in a report severely suffering from frequent confusion of the terms anode and cathode [285]. The low self-discharge is attributed to the fact, that zinc atoms formed during charging of the device are anchored on the negative electrode surface. Whether this bland statement is as spectacular as the authors suggested appears to be an open question.

3.3 Miscellaneous observations

The influence of charging methods (constant current vs. constant current-constant voltage [4]) on self-discharge was examined [286]. The latter procedure resulted in slightly lower self-discharge. Consideration of self-discharge is recommended when using pre-charging strategies in supercapacitor electrode mass-balancing [287].

Claiming that self-discharge is one of the inherent disadvantages of an electrochemical double layer at the solid/liquid interface as a replacement solid/solid interfaces (desolvated interfaces) showing higher interfacial capacitance were suggested [288]. A divided supercapacitor with a membrane showing tunable ionic conductivity was proposed in order to reduce self-discharge [289]. Because of the particular response of the device during charge/discharge it was called redox transistor battery. The membrane composed of PPy:DBS (dodecylbenzenesulfonate) deposited on a porous polypropylene separator helped to reduce self-discharge to 1/10 of the value without the membrane.

In a comparative study of state-of-the-art commercial supercapacitors in 2002 self-discharge was not examined but the poor energy density of supercapacitors in comparison to LIBs combined with the suggested high rate current capabilities of the latter was named as a major challenge for supercapacitor developers [290]. In a slightly wider comparison reported briefly later the generally higher self-discharge of devices (both supercapacitors and batteries) with activated carbon in the positive electrode is attributed to the larger surface area [291]; and these devices tend to show longer cycle life. Possibly detrimental effects of electronic circuitry added to multi-cell supercapacitor modules were addressed [292]. Such additions are sometimes employed when matching supercapacitors with their inherently low operating voltage to electric circuits running on higher voltages, and they are called “balancing circuits”. A review taking into account different operating principles and effects on self-discharge of the incorporated supercapacitors is available [293]. A stochastic supercapacitor model was used for the design of balancing systems [294]. In terms of efficiency and complexity a dissipative balancing system was found to be most suitable. Degradation of a module composed of just two supercapacitor cells with and without such balancing or equalization circuitry taking into account self-discharge was examined [295]. The added circuitry basically enabled a more equal change of performance with minor differences depending on the actually employed circuit. An equalization circuit suitable for supercapacitor modules in vehicles for urban rail transport was developed and tested successfully [296]. A comparison of equalization concepts was reported [297]. A simplified equalizer circuit was developed and successfully tested on strings of supercapacitors and of LIBs [298]. During tests it was noticed that cell voltages became more similar during cycling. A suitable algorithm assuming a first-order equivalent circuit model taking into account self-discharge and cell voltage-dependent capacitance variations for online monitoring of state-of-charge and state-of-health of a supercapacitor in a vehicle application was developed and tested [299].

Supercapacitor energy delivery during constant power discharge with attention to porous electrode structure, charge redistribution and self-discharge was studied [300]. Peukert’s law [4] is applicable at power above a certain threshold; and this was confirmed in a more extensive study of its applicability and application [301].

Because self-discharge is a serious concern even in sub-mW indoor photovoltaic-power energy harvesting wireless sensor nodes a charge-based method to evaluate energy stored in a supercapacitor was proposed based on measurements of the leakage current [302]. In a comparison of supercapacitors and LIBs as storage for piezoelectric energy harvesting the former turned out to be more efficient than the latter despite of the inherently larger self-discharge [303]. Energy storage systems based on flywheel, batteries and supercapacitors for application in LEO satellite applications were compared taking into account typical application requirements and systems properties including self-discharge [304].

The use of supercapacitors as replacement of lead-acid batteries for starting vehicles was an early suggestion because of the high power capabilities of supercapacitors and the need of having the power supplied only for the usually very short period of time for cranking an internal combustion engine. Self-discharge, in particular the drop of the output of a supercapacitor bank composed of several devices, possibly within days results in a drop of output voltage below a critical value necessary to crank an engine. A voltage-booster circuit was proposed [305]. Another option combining a secondary battery with a supercapacitor and a photovoltaic panel with the latter compensating self-discharge of both storage devices was constructed and tested as an engine start module [306].

A device combining a negative silicon electrode and a positive TiO_2-electrode both prepared by respective deposition processes on vertically aligned carbon nanofibers with a gel electrolyte in between low self-discharge was recorded [307]. Why this device showing well-defined battery-type CVs of the electrodes is called a battery-supercapacitor device remains unclear. To compensate for self-discharge in an EDLC-type supercapacitor with a $ZnSO_4$-containing polymer electrolyte zinc (negative) and copper (positive electrode) foils were used as current collectors which provided as a galvanic couple small Faradaic currents compensating for self-discharge enabling longer storage times of the charged device [308]. An arrangement with an electrode shared between a solar cell and a symmetric supercapacitor with MnO_2/poly(3,4-ethylenedioxypyrrole) electrodes was called photo-supercapacitor [309]. Self-discharge (in darkness) was slowest for the device with the composite electrode, with electrodes made of one component only initial voltage loss was bigger although with the MnO_2-electrode the later rate of voltage decay was significantly smaller suggesting the whatever reaction caused self-discharge is slower on this single component electrode.

Undesired effects of the manufacturing process (coffee ring effect) causing severe self-discharge observed with printed supercapacitors were reported [310]. The effect was attributed to Ohmic leakage, and addition of graphene oxide to the polymer electrolyte resulted in a decrease of 99% of the rate of self-discharge.

Because most self-discharge measurements record cell voltage as a function of time under open circuit, i.e. at conditions away from real-world ones where a constant voltage is applied (and thus leakage current would be the more adequate approach) a test setup simulating this condition was proposed [311]. The suggested setup performs exactly such leakage current measurements without saying so.

In studies of side reactions in capacitive deionization processes self-discharge of the employed electrodes was studied, and results were interpreted in terms of models and mechanisms discussed above [312].

Self-discharge of supercapacitors and of mechanical energy storage devices (FRP) was compared [313], and the low self-discharge of the latter was stressed.

4 Modeling

Modeling is applied in supercapacitor research and development in fundamental studies of effects of pore size, pore structure, numerous materials properties as well as properties of the other ion-conducting phase trying to input these parameters into a model of the working electrode or a full, two-electrode supercapacitor describing its behavior as complete and correct as possible thus making a connection between (microscopic) properties and (macroscopic) performance. The other major field is modeling of energy harvesting and EES for various different purposes again taking into account device properties now on the cell level like leakage currents and self-discharge.

4.1 Device Modeling

A macrohomogenous model assuming constant capacitance and constant concentration of the sulfuric acid in contact with the porous carbon electrode assuming basically only water decomposition, i.e. hydrogen and dioxygen evolution, as side reactions was reported [314]. Keeping the cell voltage within the window of thermodynamic electrolyte solution stability does not exclude the side reactions entirely. The observed decrease is in agreement with the removal of surface functional groups on the carbon material enabling charge storage but also causing parasitic processes. Starting from the elsewhere also suggested charge redistribution inside a supercapacitor as a cause of voltage decay (and thus self-discharge) a model including effects of charging current and further operational parameters on self-discharge was reported [315]. From modeling an optimized charging protocol was developed. Whether a procedure suggesting a charging current as small as possible followed by a constant voltage period is practically relevant appears to be doubtful.

A 3D-model of a solid-state supercapacitor with added redox systems (the author call them mediators despite the well-known different usage established elsewhere long ago) taking into account self-discharge by shuttling of the redox mediator was developed [316].

A segmentation optimization based on a parameter identification method to establish a three-branch equivalent circuit representing self-discharge as an Ohmic resistor was developed and tested [317].

A most simple equivalent circuit just composed of a capacitance, a series resistance and a current-dependent leakage resistance in parallel to the capacitance was proposed and found to be satisfactory in reproducing recorded discharge curves [318]. Based on observations of the influence of temperature, charge voltage, charge duration and further experimental variables on self-discharge a descriptive RC-circuit-based model based on de Levie's transmission line model was developed [319] and expanded in a following work by these authors [6]. It was demonstrated as being capable to predict the influence of said parameters on device performance. The distinction between real self-discharge and the influence of ion redistribution on electrode potential and cell voltage is highlighted. A two-branch equivalent circuit addressing ion redistribution was developed [320]. Inadequate contribution of ions inside of micropores (resistance to ion movement in these micropores is four orders of magnitude larger than in the bulk solution, and this is attributed to a different mode of ion propagation) was stressed, and this seems to call for development and preparation of carbon materials with tailored porosities. An extended equivalent circuit of a supercapacitors taking into account self-discharge was proposed [321]. An equivalent circuit as depicted in Figure 11 was suggested [322]. R_{le} represents the leakage current, R_r and C_r the Faradic self-discharge reaction, R_1 and C_1 are the main branch immediately involved in charge/discharge, R_2 and C_2 represent the delayed charge/discharge processes, respectively. The latter capacity usually amounts to 1/10th or less of the former. Satisfactory agreement between measurements with several different commercial devices and simulated voltage-time curves was achieved.

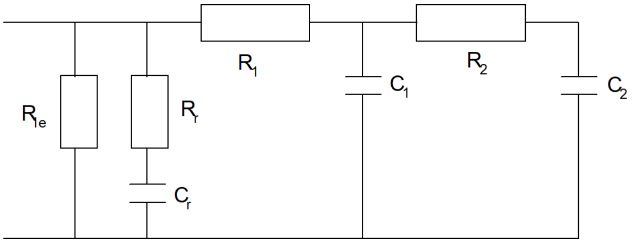

Figure 11: Equivalent circuit suggested in [322].

For better representation of the various self-discharge mechanisms discussed above an equivalent circuit with a variable leakage resistance VLR instead of a fixed one as shown above was proposed and applied with attention also to applications in e.g. sensor networks and operational details like charge redistribution between components in such network [323–330]. Changes of actual values of VLR with maximum charging voltage and temperature were discussed, and increased precision of the simulations with this modification causing no major complication was noticed. Impedance measurements at various cell voltages, i.e. states of charge, and temperatures were performed and evaluated with an equivalent circuit taking into account further components like inductivity yielding good agreement between measurement and simulation [331]. Temperature and cell voltage influence on self-discharge were represented by separate elements in addition to a leakage resistor representing long-term self-discharge. A polynominal equivalent circuit model focused on charge redistribution was developed with a slightly different equivalent circuit shown in Figure 12 [332]. The nonlinear behavior of the immediate capacitance C1 is t$_{a}$ken into account by adding a linear voltage-dependent capacitance KV×U1, $_{R}$4 $_{r}$epr$_{e}$sents the leakage resistance, the other elements are not assigned to specific phenomena. Using a commercial EDLC supercapacitor satisfactory agreement between experiment and simulation was found. This circuit was called elsewhere Zubieta model [333]. More precisely it should be called Zubieta-Bonert model [334].

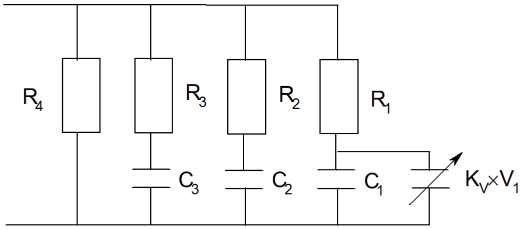

Figure 12: Equivalent circuit suggested in [332].

A slightly different two-branch equivalent circuit with a controlled current source was proposed [335] (see Figure 13).

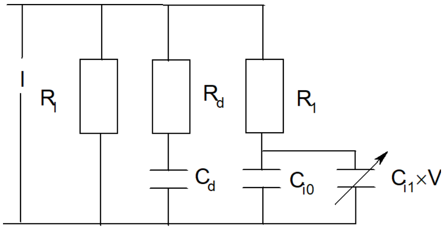

Figure 13: Equivalent circuit suggested in [335].

In comparison with a conventional two-branch circuit it was shown, that both self-discharge and dynamic behavior can be correctly modeled when the controlled current source was added.

A further comparison of the VLR and the charge redistribution model describing both self-discharge was reported, and the latter represented experimental data better [336].

A modified version of this model (Figure 14) with a variable leakage resistance was proposed [337].

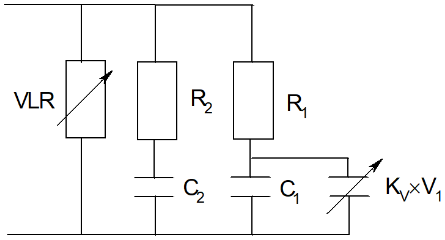

Figure 14: Equivalent circuit suggested in [337].

To the immediate capacitance including a voltage-dependent contribution (subscript 1) a delayed branch modeling charge redistribution and a variable leakage resistance representing the time-dependent self-discharge were added. In a comparison of two supercapacitor characterization methods both equivalent circuits shown above were used [338]. Self-discharge is frequently named in the report, but results or data are not shown.

Starting with an extended ladder-type equivalent circuit taking into elements for micro-, meso- and macro-pores after some simplification two parallel resistances representing self-discharge and a voltage-depending capacitance were added [339]. This circuit was simplified again leaving a simplified circuit suggested before [340]. The circuit finally proposed after addition of a controlled current source physically justified by reference to diffusion of residual charges in the electrodes during rest phases is depicted in Figure 15.

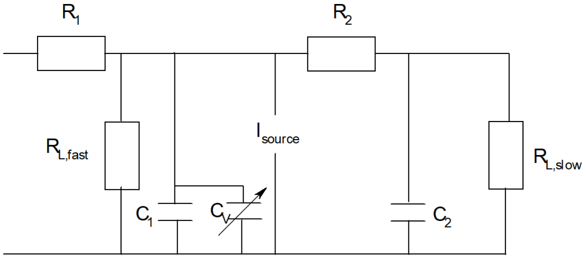

Figure 15: Equivalent circuit suggested in [339].

Voltage vs. time transients showed the predictive and descriptive capabilities of the equivalent circuit in particular during open circuit periods.

An equivalent circuit model based on a particle swarm algorithm was employed to described voltage performance and estimate the energy in a supercapacitor [341].

Dynamic simulation taking into account pore structure and self-discharge was verified with impedance measurements including parameter variation, and it enables accurate prediction of dynamic device features [342]. Thermal effects on supercapacitor behavior were included in a very simple “porous circuit equivalent model” (see Figure 16) [343].

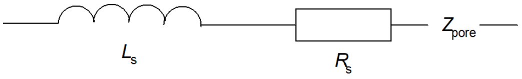

Figure 16: “Porous circuit equivalent model” suggested in [343].

The pore impedance Z_{pore} contains a resistive element related to ionic conductivity showing a temperature dependence. In addition, the non-ideal interfacial capacitance is temperature-dependent. The parameter γ describing this non-ideality also includes implicitly leakage currents and self-discharge. The non-ideality can be understood in a first simplification as a parallel resistor to the interfacial capacitance. Somewhat surprisingly and not discussed in the report is the observation in the list of simulation parameters, that non-ideality, i.e. deviation of γ from unity for the ideal behavior of the interfacial capacitance, is most pronounced at $T = 0°\mathrm{C}$, which decreases (contrary to expectation) with further growing temperature suggesting lower self-discharge and/or leakage with growing temperature. Simulated self-discharge currents show in displayed curves the expected rise with growing temperature.

A much simplified dynamic equivalent circuit model assuming several relaxation times extracted e.g. from impedance measurements taking into account self-discharge [344]. Self-discharge, i.e. cell voltage decay, was modeled with a distribution of rate constants with faster charging resulting in a wider distribution [345].

A fractional order model known for accurate frequency and time-domain representation taking into account self-discharge of a supercapacitor was developed and applied successfully [346]. Fractional order modeling of the voltage response of a supercapacitor to a given current profile was successfully performed without taking self-discharge into account [347]. An empirical model taking into account effects of charging current on self-discharge was developed and tested successfully [348]. A model paying particular attention to changes of current on capacitance-voltage relations of a supercapacitor was developed using Matlab/Simulink [349]. Self-discharge affects both the main capacitance as well the “branch capacitance” (see Figure 15). This confirms observations reported elsewhere [339]. Modeling of an equivalent circuit of a supercapacitor module in the backup of the pitch system of a wind turbine providing a lower error in calculating effects of self-discharge was described [350].

Using Pspice software for supercapacitor self-discharge modeling was discussed [351]. This approach has also been used for studies of self-discharge and leakage currents of supercapacitors used in energy harvesting from photovoltaics [352]. A module incorporating photovoltaics and a carbon dioxide sensor for indoor air quality monitoring using a supercapacitor as energy storage device was described [353]. When comparing LIBs and supercapacitors the longer lifetime/larger cycle number expectations favor the latter. Both batteries and supercapacitors were investigated as components of solar-powered airport electrification systems with attention to the vastly different self-discharge of both storage devices [354]. An arrangement with lead-acid battery was initially cheaper, but for longer lifetime with more expensive photovoltaic devices supercapacitor might be the better choice. Self-discharge is less of an issue for outdoor energy harvesting applications whereas indoor with a lower level of available light even small self-discharge may become a problem. Time-dependent change of the self-discharge rate after charging add to the complexity. Taking into account these concerns as well as further demands of electronic circuitry possibly employed in such harvesting devices a module could be developed successfully.

Two simple dynamic mathematic models using either an R-C circuit or a constant phase element were compared [355]; results were found to be the same. Imperfections including self-discharge of both secondary batteries and supercapacitors in energy harvesting systems were included in modeling [356].

Modeling of ICPS as electrode materials using equivalent circuits sometimes resulted in difficulties, a broader approach was described [357]. Self-discharge recorded as electrode potential change proceeded initially relatively faster, and this was attributed to equilibration between regions of low and high diffusivity in the polymer. The following slower process is due to dioxygen reduction.

4.2 System Modeling

Modeling of a supercapacitor directly connected to a bidirectional AC/DC-converter with an Ohmic resistor representing self-discharge in the equivalent circuit of the supercapacitor was reported [358]. A descriptive model of self-discharge in an EDLC supercapacitor taking into account system, materials properties and dynamics instead of suggesting an equivalent circuit illuminating the role of ion redistribution at various times was proposed [359]. Management of charge redistribution between the components in a supercapacitor-based wireless sensor network taking into account self-discharge was developed and tested [360]. A power management model including a supercapacitor model taking into account self-discharge and charge redistribution ensuring operation of the supercapacitor within its operational limits was developed and tested with a radar sensor network [361]. Optimization of operating parameters for an energy storage system combining LIB and supercapacitors taking into account the higher self-discharge of the latter could help improving life time of the LIB [362]. For scaling of energy management to low voltage microgrids an approach "multi-agent energy storage system aggregation" including consideration of self-discharge was proposed [363]. Design and stability of a DC microgrid with both batteries and supercapacitors were tested taking into account the possibility, that cell voltages of supercapacitors may decrease simply by self-discharge to 10% of their rated operating voltage [364]. Addressing stability of a DC-microgrid composed of a photovoltaic system with attached HESS voltage decrease of the integrated supercapacitor because of self-discharge was taken into account yielding improved performance of the controller and HESS [365, 366]. Control of a HESS fed by photovoltaics in a stand-alone micro-grid application was examined taking into account the optimized utilization of both battery and supercapacitor [367]. Self-discharge was addressed with respect to the possibility that it can decrease supercapacitor cell voltage to low values possibly causing system instabilities. In a theoretical study, stability of a stand-alone photovoltaic stability negatively affected by sudden clouds quickly decreasing the photovoltaic out put was examined when a HESS is connected [368]. Under this condition stabilization effect of a battery was much poorer than that of a supercapacitor. Unfortunately the latter decreased efficiency of the microgrid slightly because of self-discharge of the supercapacitor. Life-time depending on operation parameters and self-discharge were incorporated in an extended approach to technology selection and sizing for an energy storage system including supercapacitors [369].

Supercapacitor modeling including representation of self-discharge with particular attention to their practical application was reviewed [370].

An overview on mathematical modeling of supercapacitors also addressing self-discharge [371] was withdrawn.

Incorporation of supercapacitors in a hybrid electric energy storage system HESS (elsewhere abbreviated as HSS) with particular attention to self-discharge was developed into an algorithm for charge allocation [372, 373]. A broader comparison of component properties (including self-discharge) in HESS for various applications was reported [374, 375]. The "Minimum variability injection" approach was examined for optimal sizing of supercapacitors and batteries in a HSS [376]. Self-discharge was considered in particular with attention to its effect on system performance at various storage times for energy in the supercapacitor. Taking into account the special requirements of electrical circuits for electric energy harvesting and storage self-discharge of supercapacitors as crucial elements in such arrangements with radio frequency energy transfer a circuit model for the renewable energy cycle was developed [377].

5 Conclusions

In most studies of supercapacitors, their electrodes and ionically conducting (electrolyte) materials self-discharge is not even mentioned. In those reports where attention was paid to this topic frequently self-discharge is just registered as a more or less natural phenomenon. The obvious need to identify and understand causes of self-discharge is rarely fulfilled. When attempts to reduce self-discharge are discussed suggested modifications seem to reduce self-discharge at the expense of storage capability and other performance parameters. High current capability as the particular property most interesting with supercapacitors is frequently not even examined. Attempts to increase energy density of a device by pushing the cell operating voltage window (driving the electrode potentials apart) is mostly based on utilization of slow kinetics of overcharge reactions. Charge is delivered into the cell nevertheless, and the longer an electrode stays at extreme potentials the more chance even a slow parasitic process will have to consume charge in self-discharge. Certainly, capacitance retention is not necessarily related to self-discharge although more detailed inspection of the change of self-discharge during lifetime of a supercapacitor both in terms of cyclic and calendar aging seems to be recommended, but e.g. 90% capacitance retention after just 2000 cycles is not as spectacular for a supercapacitor as suggested by some authors. Given the number of reports and various aspects addressed there appears no simple general strategy safely reducing self-discharge. Nevertheless some general recommendations already addressed above should be summarized: When aqueous electrolyte solutions are used (this seems to be preferable for reasons already discussed) dioxygen should be excluded. Metallic impurities soluble in the electrolyte solution in all components possibly causing self-discharge by a shuttling mechanism should be avoided. Excessive cell voltages approaching the limits of electrolyte solution decomposition should not be used for increased capacitance.

Finally claims of particularly low self-discharge should be made carefully given the absence of a standard or a commonly accepted reference or benchmark. Presumably it would be helpful if authors would state rates of self-discharge in terms of cell voltage or electrode potential change per hour or per day, and leakage currents should be provided with respect to the specific state of charge/electrode potential maintained during the experiment and to the mass of electrode material(s).

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