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Review

Composites of Intrinsically Conducting Polymers with Carbonaceous Materials for Supercapacitors – An Update

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Abstract: Supercapacitors are an important component in the electric energy landscape with rapidly growing importance. Their energy density still does not meet growing expectations. For improvements optimization of already established materials as well as new materials in electrodes and in electrolyte (solutions) are required. To compensate or correct drawbacks and flaws of a given material – whether new or already established – combination with a second one, i.e. formation of a composite, is a helpful and popular option. Carbon in its many forms is an established supercapacitor electrode material with only limited charge storage capability; intrinsically conducting polymers show promising storage capabilities but limited stability and electronic conductivity. Adding carbons to these polymers has been a popular recipe rather early, but a systematic survey of these combinations with attention to the type of carbon, of polymer, of their relative fractions and the electrode architecture has indicated major room for improvements. This update presents representative examples, follows lines of reasoning and searches for conclusions from already available results. It ends with suggestions for further research and development.

***Keywords*:** intrinsically conducting polymer; polyaniline; polypyrrole; polythiophene; carbon; carbon nanotubes; nanostructured carbon; carbonaceous materials; composites

Nomenclature

Term	Description
CCG	chemically converted graphene
CNC	Carbon nanocage
CNT	Carbon nanotube
CSA	Camphorsulfonic acid
EDLC	Electrochemical double layer capacitor
ESR	electrical series resistance
GCD	galvanostatic charge discharge cycles
GN	Graphene
GNS	Graphene nanosheets
GO	Graphene oxide
ICP	Intrinsically conducting polymers
MWCNT	Multi-walled carbon nanotube
PANI	Polyaniline

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PEDOT	poly-3,4-ethylenedioxythiophene
PET	Polyethylene terephthalat
PPy	Polypyrrole
PSS	Polystyrene sulfonate
PTh	Polythiophene
PVA	poly(ethylene-co-vinylacetate)
rGO	reduced graphene oxide
SWCNT	Single-walled carbon nanotube

1. Introduction

In devices for electrochemical energy conversion and storage, several parameters attract the attention of researchers and engineers. Among them are – with respect to the complete device – gravimetric and volumetric energy and power density, stability, price and environmental compatibility. Broken down with respect to materials for electrodes, current collectors, electrolytes, electrolyte solutions etc. requirements become more specific. For an electrode (or electrode material) in a supercapacitor, requirements can be specified:

- high charge storage capability
- low energy consumption in winning and/or preparation of material and electrode
- long term stability under all operating conditions
- insoluble in electrolyte (solution)
- no side reactions with other cell constituents
- when redox active redox potential should be within window of electrochemical stability of electrolyte solution
- material should fully utilize window of electrochemical stability of electrolyte solution
- environmental compatibility
- sufficiently large resources

In early supercapacitors (and in the majority of the currently sold devices) carbon materials are used in the electrodes utilizing almost exclusively double layer charge storage (EDLC, electrochemical [sometimes less precise electric] double layer (storage) capacitor). Limitations of this approach – which has nevertheless resulted in most impressive results and devices – have been noticed early [1]. Utilization of surface-confined redox reactions of a wide range of electrochemically active materials has been proposed initially in [1], the further development of materials, electrodes, devices and applications has been reviewed repeatedly, see, e.g., [1, 2-25]. Particular attention to storage mechanisms has been paid in [26]. The increasing energy density on the device level addressed in passing in many of these publications has been highlighted with respect to practically relevant results in [27]. The latter aspect combined with advantages of hybrid and asymmetric designs of devices has been discussed [28], accepted terminology seems to be subject of ongoing debates.

A general aspect of electrode material investigations and materials application is the mass loading of a material on the electrode (i.e. in a rough approximation the thickness). Very thin films generally show highest specific charge storage values sometimes approaching calculated (theoretical) values because of close-to-optimum mass utilization [29, 30]. The latter report addresses the problem of calculating theoretical capacities. Because the storage capability of an electrode and implicitly of the device directly depends on the participating mass of active material high mass loadings are desirable – a striking contradiction to the previous statement. Thus, part of the research efforts is to find a compromise between these contradicting opposites. In case of composite materials, this aspect has been discussed with respect to electrodes with high mass loadings [31]. As expected and fairly obvious 3D-structures and morphologies with suitable porosities are highlighted. With composite materials containing intrinsically conducting polymers ICP, the participating dopant needed in practically all applications for charge compensation of the ICP in its oxidized form has been addressed because of the possibly structure-forming or –inducing capabilities of such anions.

Rather early it was noticed, that a supercapacitor electrode could hardly be prepared from just a single material. Addition of a binder for sufficient cohesion between particles of the active material and between them and the current collector/mechanical support as well as addition of a highly electronically conducting material for sufficient conductivity of the complete electrode were recognized as needed. Presumably, exaggerated claims of high conductivity of e.g. activated carbon repeatedly published are no contradiction, but may indicate insufficient reception of materials facts and unsuspecting copying of statements found elsewhere.

Every combination of an active mass to be used in a supercapacitor electrode with a second component when preparing an electrode may already be called a composite or a blend with the latter term used only very infrequently in this field (e.g. [32]). The term hybrid (material) suggesting specific interactions between the two constituents should be used in cases of verified interaction effects only (For an introduction and overview see [33]). The approach suggested in [2] to use the adjective hybrid in masses with both organic and inorganic constituents with and without interactions may not be very helpful. Presumably, hybrid is better used for materials where interactions between constituents result in further capabilities of the material beyond simple addition. The same considerations should be applied to use of the term hybrid in hybrid supercapacitor. In the present context, a supercapacitor with two at least initially identical electrodes will be called symmetric whereas one with electrodes operating according to different charge storage principles will be called asymmetric. Different usage observed elsewhere [34,35] does not address the meaning of hybrid. Compared with the Greek origin of the term ὕβρις (hybris) meaning arrogance or presumptuous the common usage suggests something bundled, mixed or interbreeded. Whether this helps in describing a supercapacitor or an electrode material better appears to be at least questionable.

In an even wider and presumably somewhat misleading interpretation of the term composite already the use of a graphene paper as current collector coated with an ICP has been named a composite [36]. This terminology is frequently implicitly or even explicitly applied; but even more frequently the term composite is applied to combinations of two or more active materials participating in charge storage placed on a support and current collector, even with an added conductivity enhancer. Typical examples are the combination of an intrinsically conducting polymer ICP like polyaniline PANI, polypyrrole PPy, or poly-3,4-ethylenedioxythiophene/polystyrene sulfonate PEDOT:PSS (for more see below Fig. 1) with carbon nanotubes CNTs or with a metal chalcogenide like MnO_2. Different from the obviously non-standard classification in [37] where metal oxides are not included in the class of chalcogenides (This overview contains further remarkable misrepresentations regarding metal chalcogenides) the present authors considers metal compounds with all group 16 elements as relevant. To consider conjugated polymers and conducting polymers as synonyms as in [38] or [39] appears to be misleading: Conjugation is a requirement for conduction, but not all conjugated polymers are conducting. For conjugated molecules, oligo- and polymers in electrochemical energy technology see [40], for an example of a composite of such conjugated molecule with graphene and CNTs see [41].

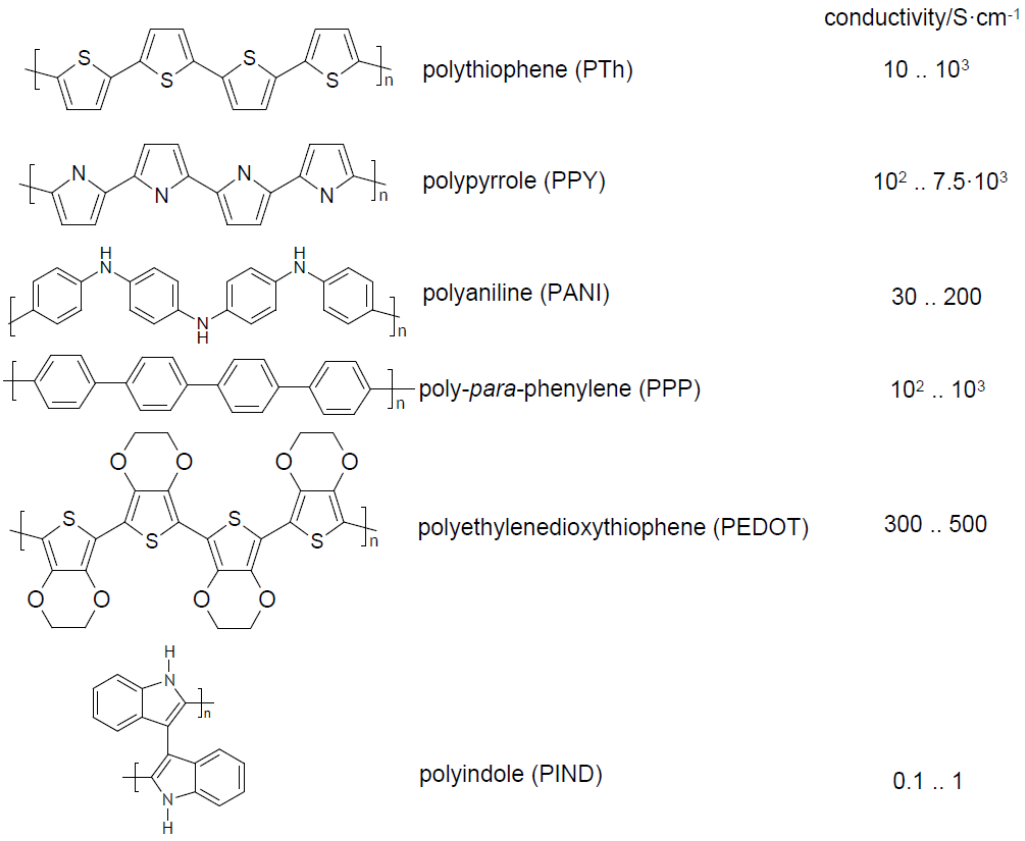


Figure 1. Examples of intrinsically conducting polymers and their monomers (Conductivity data presumably – although practically nowhere

clearly stated – of the oxidized state of the ICP based on literature sources (most of them secondary ones without providing original sources of data) [42-51]. In the neutral (not to be confused with the reduced) state ICPs are insulators or poor conductors/semiconductors with conductivities around 10^{-5} to 10^{-10} $S \cdot cm^{-1}$ [52]).

Both constituents in the first example, the ICP and the carbon nanotubes, contribute to charge storage: The ICP is redox-active and thus provides Faradaic storage, the CNTs provide double layer storage. In addition, the electrochemically active surface of the ICP offers some double layer storage. As already pointed out long ago by Conway when coining the term "pseudocapacitive" the latter truly capacitive contributions are small by comparison, they may amount to a few percent of the redox storage capability [1].

The other "active mass" beyond ICP and metal chalcogenides is high surface area carbon in its numerous forms. With these carbonaceous materials charge storage proceeds only in a capacitive way, the small amount – if any – of surface redox groups is mostly of minor importance only. Although there are (practically) no redox processes going on this material is also called active sometimes and certainly in the present context. Indeed, it is mixed with exactly the same additional ingredients already mentioned above. Thus, it does not come as a surprise that combinations of ICPs with carbonaceous materials are also frequently encountered as composites in the literature. Again, the question for the roles played by the two composite constituents should be asked for a better understanding of the operation of these materials, of their advantages and drawbacks. The twin role played by carbonaceous materials may possibly provide cause for confusion when including a given material in this overview. To minimize this risk, preferably reports explicitly identifying this carbonaceous material as a composite constituent are included. In a review on composite materials of ICPs and metal chalcogenides provided elsewhere [53] already a substantial number of materials has been inspected, this number as well as the number of reports dealing with combinations of carbonaceous materials and ICPs explicitly named composites has grown further in the meantime (for an update see [54]). The present report will not repeat and extend the former review [53] as well as other earlier overviews and reviews covering parts of the field inspected below [55] neither will it attempt to cover every reported composite of an ICP with a carbonaceous material or any other second constituent. It will instead focus on salient aspects and general questions in an attempt to provide an overview and update.

Further combinations of ICPs with other materials and thus more composites have been studied: Combinations of ICPs with metals (see also [53, 54]) and with electrochemically inert but structure-forming materials (scaffold, hard/soft template) have been examined (e.g., cellulose [56-64]). Quantum dots and nanodots synthesized from various materials (including carbon) have been prepared and examined as constituents of composites in devices for electrochemical energy storage including supercapacitors [65 - 73]; those containing carbon are presented below (sect. 4.2). Further carbon allotropes have been reviewed with respect to their suitability as material for electrochemical energy conversion and storage [74, 75].

Beyond binary composites also ternary and even quaternary ones have been proposed and studied [54, 76 - 79]. With respect to the scope of this report limited to binary (nano)composites of ICPs and carbonaceous materials it suffices to notice, that in both ternary and those very few quaternary samples carbon was mostly added as conducting agent. For examples, see [54].

Attractive possible applications of stretchable and/or flexible supercapacitors needing suitable electrodes and electrode/electrolyte materials has stimulated research in respective materials, for examples and overviews see [80-86]. Selected results relevant within the scope of this update are presented below.

Composites designed for combined applications in e.g. a supercapacitor and an electrochromic device have been reviewed [87].

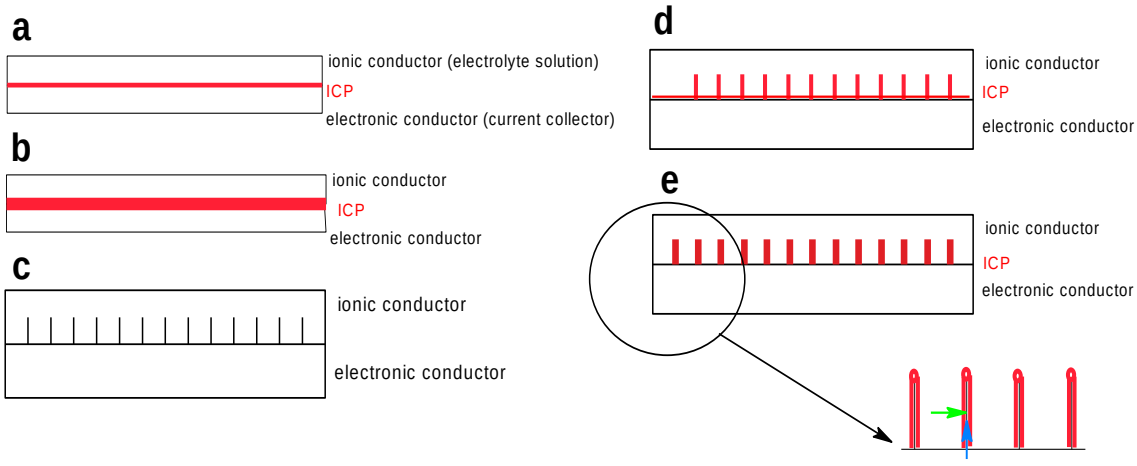
2. Fundamentals

An electrode in a supercapacitor is composed of at least two components: An active material and a current collector frequently also acting as mechanical support. Because many materials, even carbon-based ones as used in EDLC-type supercapacitors, lack sufficient electronic conductance being an essential prerequisite for application in a high-current supercapacitor, highly conductive carbon-based materials like carbon black or acetylene black barely contributing to the storage process and being otherwise inert are added. Frequently a binder is added to provide the necessary adhesion between the various components. The latter two constituents can make up to 30 wt.% and more without contributing to charge storage; accordingly, they will negatively affect the performance data (available charge density). In case of the materials discussed here, the situation is the same, and surprisingly attempts to optimize the actual composition and minimize the "dead weight" have been reported rarely.

In most reviews and reports on composite materials suggested as electrode masses for supercapacitors, neither the intended function of the sometimes rather numerous constituents nor reasons for selection of the employed materials are given. These functions can be conceived for

- ICP
  - material for charge storage
  - mechanical binder
  - mechanical stabilizer compensating volume changes
  - electronic conductance enhancer
  - suppress active mass dissolution
- carbonaceous constituent
  - template for structuring ICP morphology
  - structural/mechanical support for ICP
  - electronic conductance enhancer

Some of these tasks are related to structure, architecture and morphology of an electrode; some like limited solubility of metal chalcogenides are irrelevant in the present context. They can be observed in more or less homogeneous combinations of both constituents as well as in heterogeneous combinations wherein the ICP has been applied e.g. as a "top coat". These tasks can be visualized in simplified and highly idealized sketches of schematically simplified electrode/electrolyte solution architectures (Fig. 2). Most frequently a simple thin coating of active mass – whether a single component (in Fig. 2 an ICP) or a composite one – is studied: Fig. 2a. This design promises high material utilization and large current capability because of the short ways ions and electrons have to travel. It is of limited practical use because the amount of active mass per surface area of a conceivable device will be too small. Such very thin coatings are instead of scientific interest because mass utilization is highest, and calculated charge capacities are also highest [30]. Increased storage capability can be achieved by a thicker coating: Fig. 2b. The longer pathways, both ionic and electronic, in the coating increase Ohmic resistance (electrical series resistance ESR in the complete device) and limit current/rate capability. An artificially enlarged interfacial area is required: Fig. 2c. The active mass is deposited (conformally) onto this three-dimensional support: Fig. 2d. The pathways now traveled by ions and electrons will control the electrode and device current capabilities: Fig. 2e and insert.



(bottom right: black: electronically conducting support, red: active mass with ion (⟶) and electron (⟶) pathways)

Figure 2. Schematic supercapacitor electrode architectures, for details of subfigures see text.

In a slightly different way different architectures have been categorized into anchored, wrapped and sandwich models [88]; examples from the various categories demonstrate the particular task of the constituents when e.g. anchoring a polymer chain on a functionalized CNT surface. Broader considerations of 3D-electrode architectures including synthetic approaches have been reported [89], the same applies to nanostructuring of electrode materials [11, 85, 90 - 92] and mesoporous materials [93]. Advantages of 1D-nanostructures with ICPs and their composites for supercapacitor applications highlighting increased active surface area and higher stability because of the capability to buffer volume changes have been reviewed [94]. Dimensionalities of nanoelectrodes have been discussed in [95]. Materials aspects focused on nanostructured materials with specific attention to asymmetric supercapacitors have been reviewed [96, 97].

Basically, with every electrode material, both a single component one and a composite one, these pathways combined with a sufficiently extended interfacial area and suitable porosity have to be balanced for high charge storage and current/rate capability. As a typical example of structural effect importance for electrode performance the effects of interconnected pores in hierarchically porous carbons from synthetic polymer and biomass sources have been reviewed [98], for further examples and advantageous applications in composites see [99, 100].

The line-of-reasoning presented above in this section may be called "rational design", whether this designation is correct may be more a question of linguistics, sometimes [101] this question is left open with the title and a hard to digest contribution. At least the term is mentioned only in the title. Composites with ICPs appear to be of minor importance in [101] anyway.

3. The Materials

This update provides only a current overview; it does not attempt to list every research report with its details. Instead, examples impressive in terms of stability (a topic frequently and most unfortunately overlooked in many studies or grossly overestimated in some), performance, ease of preparation or other performance criteria are presented with details. Particular attention is paid to review articles addressing some of the combinations addressed below. Organizing the surveyed research according to the identity of the ICP turned out to be less helpful because the particular features of a given form of carbon might be lost in the slightly confused collection following a given ICP. Instead, the type (allotrope) of carbon was selected as the organization criterion. Some typical examples of ICPs are depicted in Fig. 1 above.

Beyond the polymers obtained from the monomers depicted in Fig. 1, substituted monomers, the corresponding polymers, and their composites have been studied rarely. In typical examples [32, 102] their application is claimed, but only very few rather distant examples showing no evidence of improved performance are provided. Modification of an ICP appears to be a fairly diffuse and imprecise terminology. Accordingly, a review of PANI modifications covers aspects as diverse as different counterions inserted for charge-balancing upon oxidation of PANI and polymers of substituted aniline [103]. The solubility of some of the "modified" ICPs may simplify handling and processing, for commercial applications price considerations may turn out to be prohibitive. Because of the large conductance changes associated with their redox transformation a closer look at the electrode potentials wherein these transitions proceed for a comparison with the corresponding potentials of redox processes of the inorganic constituent is recommended. As pointed out elsewhere [104] it might be relevant whether the ICP maintains its highly conducting state during the redox transition of the inorganic material or stays in its neutral, poorly conducting state. The former case preferable from the conductance point-of-view lacks the Faradaic charge storage capability of the ICP just associated with this redox transformation. Even worse is an electrode potential excursion into the region of overoxidation of the ICP (for a discussion see [105]). Consequently conducting additives might be needed or not, and accordingly the ICP can perform some of the functions assigned to it above or not (for an instructive example related to battery technology see [106]). Actually, this question is practically never addressed in research reports. Neither CVs of the single materials are reported for such comparison nor *in situ* conductance data of the employed ICP and the composite measured at electrochemically relevant electrode potentials displayed. Instead, standard amounts of conducting materials (and binder) with 15 wt.% of each being the most common case are added.

ICPs have been proposed as active masses first of primary and secondary batteries and later of supercapacitors soon after the discovery of their reversible redox behavior suggesting employment of the proceeding transitions for charge storage [40, 107 - 113]. Possible charge densities are large enough to advocate further investigations. Table 1 provides some typical data; both calculated values and experimental numbers may vary substantially from report to report in most cases without apparent reasons. Special care should be exercised when theoretical values exceeding even most optimistic assumptions regarding the electrochemical reactions during charge storage are reported [114], for a particularly noteworthy example see [115]. In this example the reported amazing capacitance of 3407 $F \cdot g^{-1}$ is possibly due to a highly vague calculation of the electrode mass. In any case, this confirms concerns regarding measurement and reporting of charge and capacitance data [29]. Possibly a similar case is the remarkable surface area of 41.000 $m^2 \cdot g^{-1}$ of an unspecified nanoporous material for supercapacitor electrodes mentioned in [116].

Table 1. Selected electrochemical data of some electrode materials.[1]

Material	Weight of repeat unit/g	Oxidation level*/-	theor. $Q^{\#}$	measur. Q/F·g^{-1}
PANI	93	0.5	750 F·g^{-1} (ΔE = 0.7 V)	240
PPy	67	0.33	620 F·g^{-1} (ΔE = 0.8 V)	530
PTh	84	0.33	485 F·g^{-1} (ΔE = 0.8 V)	-
PEDOT	142	0.33	210 F·g^{-1} (ΔE = 1.2 V)	92
Quinone/HQ	108	2	1787 As·g^{-1}	-
Ferrocene	185	1	522 As·g^{-1}	-
Li	6.939	1	13904 As·g^{-1}	-
Al	26.98	3	10728 As·g^{-1}	-
PbO_2	239	2	807 As·g^{-1}	-

[1]Data taken from [117], there are many further sources with poorly specified data (mostly secondary ones) of unclear origin, see e.g. [42, 43].

PANI = polyaniline, PPy = polypyrrole (also poly(2,5-pyrrolylene)), PTh = Polythiophene (also poly(2,5-thienylene)), PEDOT = poly-3,4-ethylenedioxythiophene, HQ = hydroquinone.

*Oxidation level, also "dopant level", reports the fraction of oxidized repeat units; also number of electrons formally transferred in the electrode reaction.

#gravimetric charge density can be stated with respect to the electrode reaction in units As·g^{-1} or in case of a material where no clear electrode reactions can be stated as amount of charge stored within a change of electrode potential ΔE in units of As·V^{-1}·g^{-1} (i.e. F·g^{-1}).

The challenge already addressed caused by the electronic conductance of the ICP changing as a function of its state of oxidation, i.e. the electrode potential, has been noticed early, various attempts to ameliorate it have been attempted. In addition to the trivial addition of conducting materials structuring at the micro- and nanolevel has been proposed; for overviews on the role of nanomaterials and nanostructured materials for supercapacitor electrodes with Faradaic storage see [118, 119 - 124]. Formation of e.g. arrays of plain and composite ICP nanofibers, nanowires, nanocones, or nanotubes has been studied, for an overview see [125]. Thin wires and tubes (see e.g. for PPy [126]) provide in addition a better material utilization because the active mass is actually present as a thin layer. Unfortunately, thin wires may show significant potential drop along the wire. On the contrary, their arrangement in arrays enables better material utilization because of the better ordering without large bulky particles [127, 128]. PANI nanostructures obtained by electroless (i.e. chemical oxidation) deposition were discussed in [129], stability was not examined. Layered structures of ICP-containing composites are discussed in [130]. An overview including progress with plain ICPs as electrode material is available [131]. Combination of e.g. PANI with silica yielding a material with more exposed PANI surface has been suggested as another approach [132]. The markedly increased surface area enables high currents with low overpotentials.

Electrospinning starting with mixtures of an ICP and a polymer, sometimes with added carbonaceous materials, may provide another approach to fibrous and highly porous materials [133 - 142]. Further variations in methodology have been described, for an example see [143]. A broader overview on nanostructured ICPs and their structure-related advantages has been provided [144], for a typical example (PPy nanotubes) see [145]. In most cases studies of the use of ICPs in supercapacitor electrodes start either with addressing nanostructuring as an option to ameliorate the insufficient stability or focus on the option of using composites as done for example in [146] with PANI as the ICP. Both approaches - a structure-related one and a materials-related one - are hard to separate because they both end up at the same samples and electrodes. In any case, both performance and stability critically depend on the choice of the electrolyte and the electrolyte solution as reviewed in [147].

A further drawback of most ICPs is their limited processeability. They cannot be melted, even more unfortunate is their insolubility in most solvents (despite claims to the contrary in many reports possibly based on misinterpretation or misunderstanding of sources or quoting erroneous reports). Oligomers of some ICPs show limited solubility in some solvents, other ICPs like PEDOT can be handled as dispersion [43]. The latter case, also named solution-processable, actually does not refer to a true solution. Sometimes these advantages come at a price, in particular lower electronic conductivity of the product. Quite obviously difficult handling has implications regarding the formation of their composites. A recent update on soluble but nevertheless highly conducting PANI and its composites shows some options [148]. These options include the use of specific counterions needed for charge-balancing of the ICP in its oxidized, i.e. conducting, form.

In a review of the performance of ICP-based supercapacitors, much beyond a simple recording of storage

capabilities, specific attention has been paid to stability of materials and devices and the reasons for sometimes poor long-term behavior and further general device properties [149].

The use of mathematical models in understanding materials properties and performance as well as in rational design development has been highlighted [150], for reasons presumably beyond the scope of this contribution, not much has been reported on this direction.

4. The Combinations

Following materials are briefly characterized; structural features deemed relevant for material performance are highlighted. Generic claims like "very efficient molecular interaction between the constituents" or "highly suitable porosity" made without providing any evidence are not repeated here. Neither are storage capacity data with respect to the material, an electrode made of this material or a cell quoted here. Without a generally accepted and followed measurement procedure and a standard of reporting results [29, 151 - 153] such data will be most likely confusing. Already the somewhat imprecise term "active mass" leaves room for interpretation and misunderstanding. The term might refer to the actually charge storing material, in the calculation of specific data the mass of binder and conducting carbon (sometimes up to 30 wt.%) is left out. Some materials are tested by applying the active mass as a thin layer on a support (e.g., a glassy carbon electrode). This way uncertainties regarding the term "active mass" are avoided, but the precise determination of the amount of active mass may pose a challenge. A noteworthy example has been addressed above [115].

Because of the raging debate over the question, whether the behavior of a material can be called capacitive, pseudocapacitive or battery-electrode-like (see above, and more on this below, the discussion seems to verge on religious debates sometimes [154]) and the associated suggestion to measure the storage capability of materials acting like (double layer) capacitors in Farad F (= $As \cdot V^{-1}$) and the storage capability of battery-electrode-like materials in some other units like As (which quite obviously does not make sense, because it assumes a well-established electrode reaction equation for a complete conversion of the electrode material, indeed assuming a specified number of transferred electron per reaction which may be expected for a battery electrode but most likely not for a supercapacitor electrode) with a certain electrode potential difference ΔE resulting also in units $As \cdot V^{-1}$ (which is actually and not surprisingly the equivalent of F) the terminology as provided by the quoted authors (mostly capacitance) is used.

As suggested above a major obstacle keeping new materials from being considered for practical application is insufficient stability, whether actually given or only presumed. Consequently, below attention is paid to stability data – even though they may be dismal sometimes at the present state of development. Even these data should be considered with caution. The term cycle means in most cases galvanostatic charge discharge cycles GCD, rarely cyclic voltammograms are meant. The effect of both types of cycle on the material is rather similar, thus no further distinction is made. The potential window is set for every experiment by the authors arbitrarily, i.e. without providing a justification. Its selection will affect both observed capacitance/charge with a wider potential window frequently yielding larger specific values because the possibly higher material utilization is combined with the onset of parasitic reactions (overoxidation [105] and/or oxygen evolution at the positive, hydrogen evolution at the negative electrode in aqueous electrolyte solutions), but resulting also in diminished stability in particular at the positive electrode because of the onset of degradation. Thus, reported stabilities should be taken with precaution. Stability data can be obtained by cycling experiments with the electrode under investigation in a 3-electrode arrangement or in a 2-electrode arrangement more or less resembling an actual supercapacitor. In the latter case both electrodes can be of the same material (symmetric arrangement) or of two different materials (asymmetric arrangement, about the possibly less precise designation as hybrid arrangement see above). In the majority of cases ICPs can be reversibly oxidized (*p*-doped) and reduced again. Reduction yielding the reduced form of ICP (*n*-doping) is less common, if observed at all it is found with polymers of thiophenes and its substituted derivatives [40]. Except for the latter case where the same material provides distinctly different electrode reactions at the positive and the negative electrode (this might even leave the designation symmetric somewhat imprecise) use of the same ICP at both electrodes results in rather poor material utilization because in the discharged state of the device both ICPs must be in the semi-oxidized state. Thus, only half of the possible capacitance is utilized. This limitation has been addressed earlier [155] with authors calling this arrangement a Type I device. In this classification combination of a *p*- and an *n*-doping ICP is called a Type II device (without specifying whether both ICPs are the same as in the described PTh-example or are different). Obviously, in Type II devices materials utilization is much higher. Type III devices finally contain the same ICP in both electrodes

using *p*- and an *n*-doping.

In addition to the various functions possibly performed by the constituents in a composite material the motivations to study and hopefully apply composite materials according to published research are:

- Enhanced stability (includes mitigation of volume changes, inhibition of materials dissolution)
- Enhanced conductivity

Improved conductivity as a general additional benefit has been noticed in an early review on ICPs and their composites in supercapacitors [55]. Enhanced material utilization enabled by suitable structuring balancing stability and mass utilization has been addressed in [146].

In an overview of ICP-based composites, nano- and microstructuring have been identified as key issues for optimized performance [156].

The following organization follows the type/form of carbon. The organization suggested in [6] and not even used in that report is not applied, to organize composites following categories like "reinforcement" or "matrix" appears to be hardly practical and useful. Sometimes no distinction is made between carbon nanotubes CNT, multiwalled carbon nanotubes MWCNT and further tubular forms of carbon. Although many authors appear to consider CNT and MWCNT etc. as synonyms, care was exercised in correct assignment. Following reports where assigned to the actually used type of carbon. Organization following the identity of the ICP as for PEDOT in [43] or for PANI in [157] was not applied.

Different from the plain addition of e.g. carbon black or acetylene black as an electronic conductivity enhancer, which obviouly was not very effective in terms of increased stability of the ICP and also better mass utilization according to the published reports, added carbon in composites addresses these major flaws of ICPs in a more specific and rational way. Most of the employed carbon materials are present in a particular structure (wires, tubes, platelets, nanodots, etc.) or are carbon allotropes (e.g. graphene). Accordingly the composites are sometimes called nanocomposites; for an early overview see [125], for updates see [2, 16, 38, 41, 158 -160]. Nanocomposites with carbon-based components have been placed in a broader context in [161].

4.1 Particular carbon

Already during early investigations insufficient stability of ICPs as electrode materials first in secondary batteries, later also in supercapacitors, has been noted (despite frequently stated different but unsupported claims). Unfortunately, stability of ICPs during cycling was not examined sufficiently in many reported studies. As aready addressed above insufficient stability was attributed to the significant volume change during cycling with associated ingress/egress of counter-anions needed for charge balancing causing mechanical degradation [36, 55].

Effects of carbon particle shape and morphology (actually carbon blacks, CNTs, graphene nanosheets GNS) on the electrochemical behavior of their composites with PANI have been reviewed [162]. The slightly better performance of the composite with GNS was attributed to the 2D planar morphology enabling nucleation of large amounts of PANI and formation of a layered material. A composite of porous carbon microspheres and PANI nanofibers chemically formed on them was examined as electrode material, at optimum carbon content (20 wt.%) it provided 72 % capacitance retention after 1000 cycles [163].

Biomass-derived carbon microspheres combined with PANI yielded an electrode material, which kept 95 % of its initial capacitance after 5000 cycles [164]. Carbon materials of widely different dimensionalities have been reviewed with particular attention to their application in supercapacitors [165].

4.2 Quantum, nanodots and nanocarbons

Composites of PANI with quantum dots of various carbonaceous materials have been reviewed, very few examples of tests as supercapacitor electrodes were mentioned [72, 166], for further examples see [167 - 169]. In the latter case the gravimetric storage capability of the composite increased by a factor of five at the optimum composition (10 wt.% quantum dots), 80 % of the initial capacitance were left after 3000 cycles. Surface amino-functionalized nitrogen-doped quantum dots combined with PANI yielded a composite with significantly increased storage capability as compared to plain PANI depending on the quantum dot fraction [170], unfortunately the capacity retention was poor with a major drop after a few thousand cycles. Sulfur- and nitrogen-doped graphene quantum dots combined with PANI yielded a composite tested for supercapacitor electrode suitability. Addition of the quantum dots yield increased capacitance, stability was not examined [168]. Further examples of composites of ICPs with various carbonaceous quantum dots can be found in [171]. Obviously, no distinction

between carbon and graphene quantum dots was made (for the distinction see [167]), apparently even assignments in original reports were possibly overlooked. Quoted stabilities range from not-defined to 96 % after 6000 cycles for a PANI/carbon quantum dots composite coated with graphene [172]. In a review on polymer dots nothing is reported on application of such polymer dots in supercapacitors [173].

Overviews on the use of "nanocarbons" and their composites with further materials including ICPs [174 - 176] and an update on carbonaceous materials [177] for supercapacitors are available. Noticed stabilities vary wildly, the need for optimization of ICP vs. carbon material ratio was stressed.

Nanocomposites of PANI and graphene nanoplatelets (defined as a graphene derivative consisting of a few, actually up to 30 .. 40 graphene nanosheets) have been reviewed [178]. Beyond mentioning impressive applications in supercapacitor electrodes, no relevant facts were revealed. In very few actual research reports graphene nanoplatelets are not defined either [179, 180]. The latter report deals with a cobalt-ion-doped PANI/graphene nanoplatelets composite yielding in the best case a capacitance retention of 85 % after 500 cycles based on an experimental methodology barely explained. The former example refers to a ternary composite of PANI, MoO_3 and graphene nanoplatelets with 92 % capacitance retention after 1000 cycles. A nanocomposite of graphene nanoplatelets, SWCNT and PPy retained 84 % of its initial capacitance after 5000 cycles in an all-solid-state flexible supercapacitor with a gel electrolyte [181].

4.3 Graphene

Graphene GN in its various types and forms as a typical 2D-material [182] is already an attractive material for supercapacitor electrodes of the EDLC type [116, 183, 184], particular attention has been paid to thermally expanded graphene for this application in [185]. Applications of electrophoretic deposition in supercapacitor electrode application have been inspected in [186]. In addition graphene oxide GO and reduced graphene oxide rGO (for unknown reasons rGO is also called chemically converted graphene CCG [187]) have been studied for supercapacitor electrode application. An early review of composites of CCG and ICP is available [187], overviews on graphene/ICP composites have been provided [125, 188]. An rGO/PANI hydrogel with a top layer of graphite as current collector tested as supercapacitor electrode kept 86 % of its initial capacitance after 5000 cycles [189]. Graphene as the carbonaceous component with ICPs and further constituents has been inspected [190, 191]. Graphene prepared by electrochemical exfoliation combined with electropolymerized PANI yielded a composite electrode material of stability unspecified in the barely comprehensible report [192]. PANI nanorods grown on graphene sheets and subsequently wrapped with PANI fibers enabled an asymmetric supercapacitor with a negative GN electrode keeping 93 % of its initial capacitance after 10000 cycles [193].

Effects of preparation details on synergistic effects between PANI and graphene (including variants of graphene) in their composites have been discussed, stabilities of devices up to 100 % capacity retention after 10000 cycles were listed [194]. The higher stability of the composite in comparison to that of plain PANI attributed to the presence of graphene did not yet show practically relevant results in the collected data. As a conclusion careful optimization of all process parameters was stressed, introduction of a third constituent (see below section 4.6) was proposed. Amine-functionalized (i.e. surface modified) graphene was combined with chemically polymerized PANI [195]. The composite had a smaller specific capacitance than the composite obtained with unmodified graphene, but capacitance retention after 500 cycles grew from 86 % to 89 %.

PANI has been covalently attached to GO [196]. A uniform rod-like morphology of PANI was observed and attributed to the covalent attachment, without this attachment, a nonuniform morphology was obtained. At optimum PANI vs. GO composition a capacitance retention of 83 % after 2000 cycles was observed, the material without covalent attachment and simple PANI showed much worse performance. Holey *N*-doped GO was combined with chemically polymerized PANI and subsequently reduced with hydrazine [197]. As an electrode, the material kept 97 % of its initial capacitance after 2000 cycles; with plain rGO, only 96 % were kept.

A layered composite of graphene oxide and PANI (up to five layers) has been examined; different from the claim of the authors for a stable capacitance within 1000 cycles the displayed figure showed a retention of about 88 % only [198]. Such layered structures have also been prepared with PPy [199]. Capacity retention of 70 % after 1000 cycles is certainly an improvement when compared with 30 % for plain PPy, but still far away from practical relevance. Further reports on PPy/graphene composites have been surveyed [43], observed capacity retention vs. cycle number data could not match those found with PPy/CNT (see above). Possibly the more likely electronic percolation with CNTs may be the crucial advantage; this requires further investigation and once more recommends optimization of the carbonaceous constituent fraction.

Further increase of storage capabilities, possibly also improved handling of graphene, by forming composites with ICPs have been suggested, some examples have been presented in [38, 200 - 206].

Nanocomposites of graphene with PANI [207 - 211] and with PTh [212] have been reviewed. Oxidative chemical and electrochemical preparation were compared. Electropolymerization yielded deposits faster, unfortunately mostly as thin films with irregular structure as compared to the more or less developed structures obtained by chemical polymerization. Numerous different materials and morphologies have been reported, determined storage capabilities range widely unfortunately not supported by stability data. Composites of graphene with various ICPs and with redox-active organic materials have been reviewed [213], more on the latter aspect can be found in [214]. The high electronic conductivity of graphene helps in charge delocalization in the material [213] and subsequently in enhancing material stability presumably by avoiding uneven electrode potential distribution inside the electrode causing e.g. overoxidation. Sometimes the interaction (presumably the strength of attachment up to covalent functionalization or grafting (the terms are obviouly used as synonyms), for an overview see [202]) has been found to be insufficient and thus negatively affecting both performance and stability. Results for various composites of ICPs with graphene for use in microsupercapacitors have been collected in [215], the combination of reduced graphene oxide with PEDOT:PSS showed promising stability. A very elastic and thus compression-tolerant electrode could be prepared with a graphene aerogel and PEDOT with MnO_2 as a third constituent [216]. The material kept about 80 % of the initial capacitance after 3500 cycles.

Using the essentially 2D-surface of graphene (platelets or particles) as platform to attach ICPs has been highlighted as a possibility [201]. It appears, that graphene/ICP composites need further research and optimization in terms of better attachment of the polymer to graphene with a suitable porosity supporting fast ion movement and thus high current capability [217].

Flakes of PANI-coated GO subsequently reduced were studied as electrode materials [218]. Beyond the statement that with optimal composition the capacitance decreased to 83 – 92 % of its initial value after five (!) cycles; no further stability data were reported. Aniline adsorbed inside GO particles and subsequently chemically polymerized into PANI nanofibers was made into an electrode with addition of 20 wt.% of carbon black and 5 wt.% of a binder keeping 91 % of its initial capacitance after 1000 cycles [219]. A GO/PANI composite formed by chemical polymerization showed nanoarrays of something not defined, the prepared electrode lost 4 % of its initial capacitance during 5000 cycles [220].

3D-Graphene and its composites have been highlighted in [221]; self-assembled 3D-graphene macrostructures have been examined for supercapacitor application in [222]. For a 3D PANI/reduced graphene oxide composite 94 % capacity retention after 10000 cycles was reported [223]. 3D-graphene oxide has been combined with CNTs and PANI into a freestanding paper-like electrode [224]. The good performance was ascribed to the highly conducting support of the carbonaceous constituents, stability was not examined.

Composites based on 3D-graphene monoliths and their superior properties have been presented; beyond general claims no stability data were included [225]. Particular advantages of 3D-architectures obtained with graphene/ICP-composites were highlighted in [226]. Synthetic methods, observed morphologies and performance data were presented without identifying a particular one as most promising. Further improvements of stability were demanded without providing a critical look at least at the state of the art. Graphene/ICP hydrogel composites have been studied [227]. Although some materials showed noteworthy capacity retention during cycling the authors stated the water content (freezing and evaporation) as a potential source of stability limitation. The real meaning of this concern was left open.

For possible use in printed electronics and related applications, graphene inks including inks made of ICP-containing composites have been reviewed [228].

Nitrogen-doping of CNTs and graphene as a way to modulate electronic and surface properties of the materials has been discussed [229]. Regarding supercapacitor electrode materials enhanced wetting resulting in better material utilization and creation of surface functionalities by *N*-doping enabling redox charge storage or enhanced interactions with other redox-storage materials like PANI were observed.

Different from the examples and overviews addressed above, wherein (with the exception of graphene monoliths and layered composites) graphene is homogeneously combined with the ICP (the term mixed is avoided because physical mixtures of ICPs with carbon materials showing poor performance have been reported elsewhere) the use of graphene as an option to create a highly conducting substrate which can be coated subsequently with an ICP is a significantly different approach. Actually – as mentioned above – it might even not be considered as a composite. Anyway, in a typical example a combination of PANI with graphene was exactly this construction was applied [230]. By vacuum filtration graphene paper was created and subsequently electrochemically coated

with PANI. This coating approximately doubled the storage capability of the graphene paper.

Nylon lycra® fabric dyed with GO, which was subsequently reduced, and coated with PPy kept about 90 % of the initial capacitance after 2000 cycles when 50 % strain was applied; without strain about 75 % were left [231]. An electrode made of polyethylene terephthalat PET fabric made conductive with rGO and subsequently coated with PPy kept 76 % of its initial capacitance after 6000 cycles [232].

4.4 Carbon nanotubes

Addition of carbonaceous material with suitable 2D-shape (fibers, nanotubes, nanowires) was suggested as an option to mitigate the undesired effects of the volume change, for early examples see [233, 234] with the first example in [235]. Among the various combinations of PEDOT and CNTs, explored in [233] ranging from mechanical mixing to electrodeposition the almost complete capacity retention of the mechanically prepared mixture after 3000 cycles is noteworthy. The further quite obvious benefits of enhanced and electrode potential-independent conductivity supporting higher electrode currents and a better electrode potential homogeneity inside the electrode were not explicitly addressed; they can be assumed nevertheless. This suggestion is tentatively supported by experimental evidence reported in [233]: Addition of acetylene black with a particulate morphology resulted in lower charge densities than with carbon nanotubes CNTs. Preparation of a composite material by plain mechanical mixing yielded an inferior material, obviously intimate mixing of both components – the already formed nanotubes or AB particles and the polymer formed by chemical or electrochemical oxidation – is a prerequisite for preparation of a promising material. The better performance with CNTs instead of AB was attributed to "CNTs providing a better support", possibly "better dispersion" is a more adequate description [233]. CNTs coated with PANI showed a fourfold charge storage capability as compared to plain CNTs [236]. Calling the carbonaceous component in a composite "filler" may be misleading [38, 237, 238]. Incorporation of CNTs as reinforcing nanowires has been reported with a reference to use of these materials in supercapacitors [239]. A hydrogel of electrochemically deposited PANI and CNT-film has been prepared and characterized [240]. An all-solid-state symmetric supercapacitor kept its capacity for 500 cycles. The initial decrease (initial 300 cycles) was attributed to decreasing mass utilization, the following recovery to about 100 % to slow penetration of the gelled electrolyte into the porous electrode. The mechanical properties of a CNT/PANI composite were improved by combining poly(ethylene-co-vinylacetate) PVA with CNT into a film first coated with PANI subsequently yielding an all-solid-state supercapacitor showing 66 % capacitance retention after 3000 cycles [241].

Combining solution-processable PANI:CSA (camphorsulfonic acid) with CNTs yielded a flexible electrode and 98 % capacity retention after 13000 cycles [148]. A flocculent CNT/PANI composite was prepared by chemical oxidation of aniline adsorbed on CNTs [242]. For electrode preparation further carbon black was added beyond the binder, the apparent question whether this addition was necessary at 30 wt.% of CNTs in the composite was not discussed. The statement provided earlier regarding the rather uncritical approach in electrode preparation lacking rational considerations is possibly confirmed. Reported specific capacitances were derived from CVs with a rather high upper potential limit well into the second oxidation peak of PANI possibly risking overoxidation [105]. The "middle potential peak" [243, 244] indicating PANI degradation supports this concern. GCD-measurements also performed were obviously not evaluated in terms of capacity. Capacitance retention was 68 % after 3000 cycles. Aligned CNTs have been explored as constituents in various composites including those with PANI [245]. Beyond stated flexibility and bendability no technically relevant properties have been reported. PANI covalently attached to CNTs has been prepared and characterized [246]. When applied as a supercapacitor electrode a capacitance retention of 64 % after 5000 cycles (as compared to a simple composite with only 48 %) was reported.

Another way to enhanced interactions between CNTs and an ICP is surface functionalization by, e.g., attachment of carboxyl groups. A major increase of specific capacitance as compared to the composite with the unmodified CNTs and 92 % capacitance retention after 1000 cycles were noticed in a typical application [247]. Aligned PANI nanowires have been electrodeposited on a CNT network yielding a supercapacitor electrode material with about 15 % capacity losses during the initial 1000 cycles [248]. A thin film of PANI on an array of aligned CNTs (actually on the CNTs themselves and not on the CNT-film according to the experimental description) on aluminium foil yielded a binder-free electrode with a loss of 2 % of the initial capacitance after 2000 cycles [249]. The influence of the thickness of the PEDOT-coating on aligned CNTs on electrode performance has been studied [250]. Presented results are hard to follow, stability is not addressed. A composite of aligned CNTs and electropolymerized PPy did not show the performance improvements noticed elsewhere and with other ICPs as

addressed above; stability was not examined [251].

PANI grown on CNT assisted by β-cyclodextrin kept 97 % of its initial capacitance as electrode after 5000 cycles [252].

An ultrasound-assisted method for the preparation of a PTh/CNT composite has been reported [253]. An advantage of the ultrasound application has not been noticed, stability of the prepared electrodes was not examined. Horizontally aligned CNTs coated chemically with poly-3-methylthiophene have been tested as electrode material, in an asymmetric cell 92 % of the initial capacitance were left after 5000 cycles [254].

Silver-doped (1 wt.%) PEDOT:PSS combined with CNTs yielded an extremely stretchable electrode [255]. The capacitance barely changed after many cycles, but capacity retention as a function of GCD cycles was not reported. Oxygen-containing functional groups on CNTs were used as oxidants in a hydrothermal process to transform EDOT in its polymer [256]. Combined with a xanthan gum/H_2SO_4 gel electrolyte a flexible symmetric supercapacitor with about 60 % capacitance retention after 10000 cycles was obtained.

Composites of CNTs with PPy have been reviewed [104, 126, 257, 258], further examples without any details on stability have been published [259]. Stability or capacity retention (if that is meant by "cyclability" in [257]) varies widely, a best value of 95 % retention after 10000 cycles in a device with a gel electrolyte has been reported [260]. 99 % capacity retention after 5000 cycles has been found with carbon (i.e. MWCNT, CB)/PPy composites with different specific capacitance values depending on the type of carbon and their fraction in the composite [261]. PPy-nanotubes prepared with curcumin as a template has been combined with functionalized CNTs by a simple mixing procedure [126]. With the optimized (in terms of pyrrole vs. curcumin ratio and polymerization conditions) PPy-nanotubes addition of f-CNTs caused a major growth of specific capacitance, the rate capability (capacitance vs. current density) deteriorated slightly. A symmetric supercapacitor with these electrodes showed 118 % capacitance retention after 1200 cycles. Electrodeposited PPy on oxidized CNTs formed on carbon fibers have been prepared and studied [262]. An all-solid-state flexible symmetric supercapacitor kept its initial capacitance for 5000 cycles. Air-plasma-treated CNTs used in a composite with PPy yielded an electrode with performance significantly better than without such pretreatment [263]. After 1000 cycles 89 % of the initial capacitance were left, without pretreatment only 76 %. In addition to stronger interaction between PPy and CNT due to functional groups (oxygen- and nitrogen-containing) the possibility of covalent attachment was identified as possible cause of improved stability. These surface modifications also improve dispersion of the CNTs in the polymerization solution supporting formation of a more homogeneous composite. Various procedures to obtain composites of CNT and PPy with the ICP in and around the carbon tubes by chemical and electrochemical oxidation of the monomer have been compared [264]. The obtained materials were combined into a symmetric supercapacitor with both electrodes made of the same materials despite earlier vented concerns about significant limitations of this approach [155]. The tenaciously used assignment of this arrangement as being a Type I supercapacitor without providing a reference for this presumably refers to [155]. Specific capacitances for the electrochemically prepared composites were consistently higher and rather stable within 1000 cycles than those prepared by chemical oxidation. A composite of CNTs deposited on a melamine covered with PPy and finally with CNTs again has been prepared [265]. The material keeps 96 % of its initial capacitance after 450 cycles (unfortunately the displayed figure indicates a much poorer performance). Electrochemically formed PPy on CNTs has been examined as electrode material, among the several advantages of the material stability was not even mentioned [266]. Chemically modified CNTs have been decorated with hollow PPy-spheres [267]. Carboxylated CNTs present in the chemical polymerization solution with pyrrole yielded hollow composite microspheres which were made into an electrode that kept 60 % of the initial capacitance after 500 cycles; without CNTs only 40 % [268].

A CNT-sponge has been coated with a thin layer of PANI, this coating improved the initially poor mechanical stability of the sponge yielding a supercapacitor electrode with about 82 % capacitance retention after 2000 cycles [238]. Further details on CNT sponges and other CNT-based materials can be found in [269].

A sponge of CNTs and graphene subsequently coated electrochemically with PPy yielded a compressible electrode thus addressing the challenge of using rather soft 3D-materials under mechanical compression in a real cell [270]. After compression 90 % of the initial capacitance were retained after 1000 cycles.

Whereas the slow hydrolytic degradation of PIND compared with that of other ICPs has been noticed as an advantage in [271] the various drawbacks and limitations of PIND have been described [272], even composites with various carbonaceous materials showed hardly promising performance. At best 91 % capacitance retention after 5000 cycles were observed [273]. A composite of CNTs and PIND prepared in the presence of nanoclay kept up to 96 % of the initial capacitance after 2000 cycles [274]. These authors repeated this approach with PANI as

an ICP, the electrode kept 92 % of its initial capacitance after 2000 cycles [275]. Further materials with PIND have been reviewed [201]. Freestanding electrodes prepared from nanofibers of PIND and of a PIND/CNT composite provided 95 % capacitance retention after 2000 cycles [276]. Nanorods of α-MnO_2 grown hydrothermally on functionalized CNTs finally wrapped with PIND kept 92 % of the initial capacitance after 5000 cycles as a supercapacitor electrode [277].

Numerous applications of CNT/ICP composites including those in supercapacitors have been reviewed [278 - 280]. The influence of the length of CNTs has been studied, with longer CNTs a better overall performance and enhanced stability were observed [281]. A further beneficial effect of defects on super-long CNTs arranged in an array and coated with PPy was noticed, the defects cause an increase of the specific capacitance to a six-fold value when compared with the defect-free material [282]. This increase was attributed to the (also experimentally verified) much improved wetting behavior of the CNTs. Capacitance was stable during 1000 cycles.

A few further examples of composites of graphene and CNT with some ICPs can be found in [283]. Flexible supercapacitor sheets with embedded nanomaterials (e.g. CNT, but TiO_2 particles and graphene flakes were also mentioned) have been prepared and tested, nothing was stated regarding stability [284].

The use of CNTs as a support is possible when CNTs are assembled into a paper-like shape (for an overview see [125]), which is subsequently coated with an ICP. Coating CNTs with PANI yielding a flexible paper-like film has been reported [285]. Flexibility of the thin film (as compared to brittle masses of composites described elsewhere) is an advantage; thinness may be an advantage in terms of material utilization but may limit achievable storage density. A suspension of graphene oxide and CNTs was first filtered, chemical reduction of the GO was afforded with HI [286]. This all-carbon paper-like film was decorated with PANI-nanoparticles. When compared with graphene-paper the addition of CNTs increased the storage capability significantly. The conceivable better mass utilization did not show up in better capacitance retention with increasing current despite the much-increased electronic conductance. Capacity was stable for about 600 cycles. A simple one-step procedure to obtain a GO/CNT composite combined with PPy or PEDOT has been developed, with both ICPs capacitance stayed rather constant within 5000 cycles [287]. PANI deposited electrochemically onto a 3D CNT sponge yielded a bendable electrode with 94 % capacitance retention after 1000 cycles [288]. A CNT/graphene/PANI paper-like composite electrode showed 80 % capacitance retention after 1000 cycles, without graphene only 50 % [289]. A preparation method for free-standing binderless composite electrodes from CNTs and various ICPs by a dispersion filtration method has been developed [290]. With PANI highest specific capacities were achieved; given the claimed advantages of the preparation procedure the absence of any stability data surprises. A CNT-film has been combined with PANI into a flexible self-supporting material [291]. At optimum composition 95 % of the initial capacitance were still available after 2000 cycles. CNT-paper covered with CNTs deposited by plasma-enhanced chemical vapor deposition was used as a scaffold for electrodeposition of PANI [292]. The obtained *N*-doped 3D-electrode with optimum PANI-loading kept 92 % of the initial capacitance after 10000 cycles. A flexible and porous substrate of polylactic acid and CNTs has been coated with PANI by chemical polymerization [293]. The free-standing electrode showed 111 % of its initial capacitance after 2000 cycles.

Flexible electrodes from CNT-paper coated with PPy showed 107 % capacitance retention after 12000 cycles [294]. A paper-like composite of cellulose and functionalized CNTs was coated with PPy by chemical polymerization yielding an electrode with 104 % capacitance retention after 5000 cycles [61]. An electrophoretically deposited scaffold of CNTs has been coated with PPy by electropolymerization, the freestanding electrode kept 68 % of the initial capacitance after 1000 cycles [295]. A hydrogel of mediator-oxidized cellulose nanofibrils, sulfonated CNTs and PPy provided 163 % of its initial capacitance as electrode after 2500 cycles [296].

CNTs in their various forms have been discussed as part of polymer composites [297], their possibilities in supercapacitor electrodes has been addressed [298]. Vibrational spectroscopies as tools for investigations of CNT/ICP composites have been reviewed [39].

Nitrogen-doped CNTs deposited on biomass-derived porous carbon subsequently coated with PANI by chemical oxidation has been prepared, the material kept 97 % of its initial capacitance after 1000 cycles [299].

Wool felt made conductive by a coating with CNTs was covered with PPy kept 84 % of its initial capacitance after 1000 cycles as a supercapacitor electrode [300]. Cotton fibers to be used in textiles coated with CNTs to confer electronic conductivity and also with PPy kept around 80 % of the initial capacitance after 2000 cycles [301]. For a yarn-shaped supercapacitor, PPy was chemically formed on CNT-covered cotton yarn yielding an electrode with 88 % capacitance retention after 5000 cycles [302]. A pineapple-polyester blended fabric coated with a composite of CNTs and PANI lost 34 % of its initial capacitance during 1600 cycles [303]. A polyester fabric first made conductive by deposition of CNTs and GN was coated with PANI by chemical polymerization

[304]. The prepared electrode kept 76 % of its initial capacitance after 3000 cycles. CNTs grown on ceramic paper and subsequently coated chemically with PPy kept 85 % (66 % without CNTs) of the initial capacitance after 5000 cycles [305].

4.4.1 Single-walled carbon nanotubes

Single-walled carbon nanotubes SWCNTs have been coated electrochemically with PANI [306]. During subsequent electrodegradation (i.e. electrode potential cycling in a specified range of electrode potentials) a significant increase of capacitance was observed, it was attributed to removal of only loosely attached fragments and increase of polycrystalline PANI regions.

In the architecture described in [307] SWCNTs serve in several functions. Initially deposited on cloth they serve as support and constituent for composite formation with PANI subsequently deposited by chemical oxidation. After 3000 cycles, 90 % of the initial capacitance were retained, without SWCNTs, only 39 % were retained. This significant improvement was attributed to the close interactions between PANI and the SWCNTs as well as between the latter and the cloth. The much improved and highly isotropic electric conductance along the electrode presumably also helped to improve stability for reasons discussed above; with SWCNTs the electrode basically operates like a highly dispersed PANI-electrode with the associated flaws and limitations. The use of carbon cloth might have resulted in even bigger improvements. A fundamental problem caused by the use of relatively thick support, which may hinder fabrication of the mostly rather thin electrodes in currently produced supercapacitors, may require new concepts. Coating a skeleton with an electrochemically active skin has been proposed towards obtaining a free-standing SWCNT/PANI film yielding improved energy density without compromising power density [308]. 85 % of the initial capacitance were retained after 1000 cycles. Better performance of a CNT/PANI-composite included significantly increased stability [309].

A freestanding PANI/SWCNT-film composite electrode in a flexible supercapacitor kept 60 % of its initial capacitance after 5000 cycles [310]. *N*-(6-hydroxyhexyl)pyrrole covalently bonded to carboxyl group-functionalized SWCNT was electropolymerized with dissolved pyrrole, the obtained product was analyzed [311]. A similar approach was tried with aniline and SWCNTs functionalized with diphenylamine, results were as inconclusive as in the preceding report [312].

4.4.2 Multiwalled carbon nanotubes

After an early comparison of MWCNTs coated with various ICPs [313] and of promising results obtained with aligned MWCNTs coated with PPy [314] as supercapacitor electrodes these composites with ICPs (as also with other second constituents) have been reviewed [15, 16]; the higher stability of the composites as compared to the plain ICP was highlighted. The particularly suitable pore size distribution (many mesopores) as compared to simple activated carbons enabling easy electrolyte solution and ion access was stated as an advantage. This was also concluded from a study of a composite PANI/MWCNT [315]. PANI formed by interfacial polymerization in the presence of functionalized MWCNTs yielded an electrode for an asymmetric supercapacitor with 97 % capacitance retention after 5000 cycles [316]. A PANI/MWCNT composite with 8 wt.% of the carbonaceous material yielded an electrode with 84 % capacitance retention after 10000 cycles for a solid state supercapacitor [317]. Sulfonated MWCNTs composited with self-suspended PANI had 93 % capacitance retention after 5000 cycles as an electrode [318].

Accelerated ion and electron transport evidenced from e.g. electrochemical impedance measurements was identified as a major improvement for PPy coated on MWCNTs in comparison to the plain ICP [319]. Although no equivalent circuit was provided for evaluation of the impedance measurements it appears that the large low-frequency capacitance corresponds to the circuit element assigned elsewhere to the redox process in the ICP [29, 320]. Further support for the line of argument provided above suggesting that CNTs of any kind increase conductivity of the material can be found in [321]: Electrodeposition of PANI in the presence of MWCNTs in the deposition solution yielded a composite film of MWCNTs coated with PANI showing a lower internal resistance and a significantly greater specific capacitance. A comparison of composites of MWCNTs with PANI, PPy and PTh is available [322]. Cycling stability significantly depends on the upper potential limit, although no reasons where offered overoxidation is the likely cause [105]. Acetylene black was tested as an alternative; it turned out to be less effective confirming earlier observations and conclusions by the authors [233]. As pointed out elsewhere [155] symmetric electrode material configurations in a supercapacitor, even of different ICPs, yield lower possible

cell voltages. Stability data were limited to a few hundred to thousand cycles; because of the symmetric design poor performance of the negative electrode, being mostly in the neutral, poorly conducting state, was the limiting factor. A composite of MWCNTs and chemically formed PPy kept 88 % of its initial capacitance after 1000 cycles [323]. A buckypaper of MWCNT coated with chemically or electrochemically formed PPy kept about 80 % of the initial capacitance after 10000 cycles for the more stable electrochemically formed material [324].

A composite of MWCNTs with poly-3-hexylthiophene with the monomer covalently attached to the MWCNT has been prepared [325]. The material with the ICP covalently attached showed a superior performance at various parameters (capacitance, conductivity, charge transfer resistance) and a capacity retention of 65 % after 3000 cycles. The advantages of covalent attachment of the ICP-monomer observed also in further cases elsewhere in this report have been confirmed; for practical application, they need to be balanced with the extra preparation steps.

Further performance improvements could be achieved by using aligned MWCNTs combined with PANI [326]. Compared with plain MWCNTs the specific gravimetric capacitance was increased 36-fold, compared with PANI 23-fold and even compared with a composite containing only randomly oriented MWCNTs a 3-fold increase was found. At optimum PANI-content (70 wt.%) after 1000 cycles an actual capacitance increase was found. A specific reason for the last observation was not provided; the reported considerable improvement of rate performance suggests increased electronic conductivity of the composite also supporting better mass utilization. In a highly similar study by the previous authors, a capacitance retention with basically the same material of 99 % after 1000 cycles was observed [327]. PANI coated on MWCNTs doped with protons and Ni^{2+}-ions showed a minor increase in specific capacitance with added nickel ions [328]. 92 % capacitance retention was found after 700 cycles. Specific reasons for the minor improvement after exchanging nickel ions for protons were not provided. Somewhat at variance with findings regarding the influence of the CNT-length discussed above [281] are results obtained with super short MWCNTs combined with PANI doped with ferric chloride [329]. As the advantage of these modified MWCNTs as compared to pristine ones better dispersibility in water, larger specific surface area and more homogeneous distribution in the composite were suggested. The composite with the modified MWCNTs showed a larger BET-surface area. With added Fe^{3+}-ions the composite showed a capacitance retention after 1000 cycles increased from 75 % to 92 %. Despite the higher electronic conductance of the composite with the modified MWCNTs, the rate capability was barely improved. PANI was deposited on a composite of MWCNTs with PVC; the prepared electrode kept 90 % of its initial capacitance after 2000 cycles [330].

MWCNTs deposited onto carbon fibers and coated with PANI yielding a supercapacitor electrode retained about 2/3 of its initial capacitance in a symmetric supercapacitor (Type I) [331].

A film of cross-linked MWCNTs was obtained by vacuum-filtration, subsequent coating with PANI yielded electrodes with different types of cross-linking and PANI loadings [332]. The optimized electrode kept 95 % of the initial capacitance after 1000 cycles.

PANI coated on MWCNTs and subsequently covered with graphene oxide, which was subsequently reduced, yielded a composite with 76 % capacitance retention after 2500 cycles [333]. The trace of *p*-phenylene diamine (0.03 of the aniline content in the polymerization solution) was claimed to enhance aniline polymerization because of its lower oxidation potential, because this comonomer will be consumed, it appears unclear how this effect will continue during the polymerization. Any further advantage of its presence in the claimed copolymer is not addressed, whether a copolymer was really formed was not discussed. For critical considerations of such copolymers see [334]. A ternary composite of MWCNTs, GO and PANI kept 89 % after 3000 cycles [335]. Formation of a copolymer of aniline and *o*-methoxyaniline was claimed without providing evidence [336], this product was "doped" with graphite and MWCNTs and showed as electrode about 2/3 of its initial capacitance within the initial 500 cycles.

A copolymer of aniline and pyrrole was deposited on MWCNTs [337]. Formation of a copolymer was concluded from specific infrared bands. Addition of copper ions resulted in a significant capacitance increase according to displayed GCD-results, reasons for this were named tentatively. Stability data were not reported. In an earlier study also only a general performance improvement by the added copper ions was stated; after 1000 cycles 86 % of the initial capacitance were retained [338, 339]. In a similar later study, simultaneous addition of copper and nickel ions at various concentrations was explored [340]. With growing metal ion concentration, the recorded specific capacitance increased. Stability was not examined, the participation of the metals in the charge/discharge reactions was not specified. A core-shell structure of MWCNTs coated with PANI formed chemically using dioxygen as oxidant and an enzyme as catalyst has been prepared [341]. After 1000 cycles, 93 % of the initial capacitance were retained.

Counteranion (dopant ion) effects on electrode performance were examined for a composite of PPy and MWCNT [342]. Different from the title the description of the PPy-preparation procedure suggests that anion effects during the chemical polymerization in the presence of MWCNTs were actually studied. With diamine green black as anion better stability of the MWCNT-dispersion was found improving coating of the ICP on the MWCNTs. At optimum composition (20 wt.% MWCNTs), a capacity retention of 92.4 % after 1000 cycles was observed. Anion effects (in particular on the electrodeposition electrode potential) during electropolymerization of pyrrole were studied [343]. A beneficial effect of one anion (4,5-dihydroxy-1,3-benzene-disulphonic acid disodium salt) on dispersion of MWCNTs was noticed. Utilizing this effect a composite of MWCNTs and PPy an electrode was prepared and tested, it showed 85 % capacitance retention during 1000 cycles.

The influence of various anions on PEDOT-structures obtained by chemical polymerization in the presence of GN has been examined, electrochemical stability was not inspected [344].

A composite of MWCNTs with various fractions of PEDOT:PSS has been examined as supercapacitor electrode [345]. Somewhat unexpectedly highest specific capacitance was found at a rather low fraction of ICP (5 wt.%) with only moderate capacitance losses during the initial 300 cycles. A flexible composite of MWCNTs and PEDOT kept 94 % of its initial capacitance after 5500 cycles [346]. Composites of MWCNTs modified in various ways and PEDOT [347]. Carboxylated MWCNTs provided the highest specific capacitance, after 750 cycles 18 % of the initial capacitance were lost. The electrochemical performance of a composite of GO, PEDOT and oxidized MWCNTs has been compared with different aqueous sulfate-containing electrolyte solutions [348]. With $MgSO_4$ the highest capacitance retention of 88 % after 10000 cycles was found.

Electrically conducting polydiacetylene deposited on aligned MWCNTs by photopolymerization has been tested as supercapacitor electrode material [349]. After 7000 cycles, 97 % of the initial capacitance were retained.

A flexible electrode made of cotton textile made electronically conducting by deposition of MWCNTs, and PPy has been prepared [350]. With electrodes of optimum composition a symmetric all-solid supercapacitor provided 72 % capacitance retention after 400 cycles, a single electrode kept 97 % after 1000 cycles. Cotton first made conductive with MWCNTs subsequently coated with PANI kept 89 % of its initial capacitance after 3000 cycles [351].

General aspects of MWCNTs are discussed in [352].

4.5 Miscellaneous carbon materials

Carbon cloth or carbon paper and the corresponding graphitized materials appear to be suitable substrates, they may also be considered as constituents in composites. Different from the title of [353] carbon cloth is barely mentioned in the report, only two examples of composites with ICPs are mentioned. PANI nanowires formed on carbon cloth yielded a flexible electrode with 86 % capacitance retention after 2100 cycles [354]. CNTs were grown on carbon cloth and subsequently coated with electropolymerized PPy [355]. At optimum composition, 82 % of the initial capacitance were retained after 10000 cycles. Arrays of α-Fe_2O_3 on carbon cloth coated with PPy were studied as electrode in an asymmetric solid-state supercapacitor with 97 % capacity retention after 5000 cycles [356]. Earlier a similar approach with Ti-doped Fe_2O_3-nanorods on carbon cloth coated with PEDOT yielded an electrode with 96 % capacity retention after 30000 cycles [357].

PANI deposited on a porous carbon rod has been examined [358]. Experimental determination of deposited mass of PANI was not addressed; because in the calculation of specific capacitance the carbon mass was not included this material may actually not be considered as being a composite at all. 2/3 of the initial capacitance were left after 1000 cycles.

Carbon foam coated with rGO served as scaffold for growth of PANI nanofibers [359]. In a symmetrical supercapacitor, 94 % of the initial capacitance were left after 2000 cycles.

Carbon nanofiber yarn obtained by carbonization of polyacrylonitrile nanofiber bundles was coated first with PPy, then with rGO [360]. The product was assembled (apparently in a symmetric configuration) with a gel electrolyte into a flexible and binder-free device with 86 % capacitance retention after 10000 cycles.

Further overviews and reviews dealing with composites of PANI with various carbonaceous materials are available [146, 361 - 363]. A capacity retention of 96 % after 10000 cycles has been reported [364]. Other ICPs combined with carbon materials have been briefly reviewed [365].

Combinations of ICPs with biopolymers (e.g. lignin) opening the way to utilization of materials from renewable sources have been examined [366 - 368]. CNTs modified with lignosulfonate were combined with PANI and MoS_2 into a composite showing 86 % capacitance retention after 10000 cycles [369].

Pyrolysis of biomass or other treatments may also yield carbonaceous materials with large nitrogen content favorable in supercapacitor applications including composite formation [370 - 373] (Why such material is called in [373] an electrocatalyst in this application remains mystifying, the article is confusing also elsewhere). A biomass-derived porous carbon material high in nitrogen because of its natural origin (chitosan) [370] was uniformly coated with PANI; the supercapacitor electrode had 80 % of its initial capacitance left after 5000 cycles.

Preparation of carbon black-filled nanocomposites by melt compounding has been discussed in [374]. Given the poor processability of most ICPs as addressed above new methods should be taken into consideration, in particular when extending the range of supercapacitor towards structural and functional applications. More on multifunctional carbon-based or -containing nanocomposites can be found in [237].

A review on applications of carbonene fibers in electrochemical energy technology including supercapacitors and ICP-containing composites is available [375].

4.6 Miscellaneous combinations

For the formation of specific advantageous morphologies of ICPs and of their composites addressed in the preceding sections, processes from biotechnology may be adapted, for examples and a review see [376]. Most ICPs of interest in electrochemistry and in electrochemical energy technology contain heteroatoms like N, S, or O. When they are carbonized or pyrolised, these heteroatoms may stay in the obtained carbonaceous materials providing them with enhanced electronic conductance and higher electrochemical activity. In addition, a particularly suitable morphology or architecture may be maintained [146, 361, 377, 378]. A nitrogen-doped carbon layer on CNTs was obtained by pyrolysis of PPy-coated CNTs [379]. Although the BET-surface area was only doubled by this procedure the capacitance increased eight-fold. After 2000 cycles, 94 % of the initial capacitance were left. Given that the material works basically like an EDLC-material this stability is disappointing, it suggests that the nitrogen-doped layer may contain still considerable amounts of redox-active PPy-fragments.

The addition of redox-active compounds to the electrolyte solution of an EDLC-supercapacitor resulting in significantly increased specific capacitance possibly at the expense of significantly accelerated self-discharge has been discussed elsewhere [17, 19]. The carbon electrodes in such devices can be replaced by composite electrodes like a MWCNT/PANI composite electrode in [380]. In a symmetric device with hydroquinone added into the electrolyte solution provided 96 % capacity retention after 1000 cycles, frustratingly self-discharge was nowhere mentioned in the report. The liquid electrolyte solution of this device has been replaced with redox-active polymer gel (containing again hydroquinone) in an all-solid-state supercapacitor [381]. The poorer stability noticed in terms of a poorer capacitance retention of 69 % after 2000 cycles for plain PANI as compared to 78 % for the composite was attributed to the well-known weaknesses of PANI. Self-discharge with a gel electrolyte is most likely significant lower than with an electrolyte solution [382] but is not even mentioned in this report.

Thermal effects due to Joule heating and overpotentials and -voltages also converted into heat are a common problem in electrochemical energy storage and conversion devices. Their effects grow with current and power delivered by a device or put into a device during charging. It is somewhat surprising that in particular in studies of high power cell and supercapacitors this problem has barely been addressed. Certainly, in many experimental cell sometimes barely larger than a coin cell this problem is hardly noticeable. Thermal effects during charging and discharging of PANI/CNT composite electrodes have been studied [383]. Changes of thermal diffusivity as a function state of charge of the electrode were recorded.

For some applications, devices for electrochemical energy conversion and storage should be transparent. Transparent supercapacitors have been reviewed [384]. Stabilities of devices containing composites discussed here (for examples see above [326] and [385]) were within the range of numbers already mentioned. Further functions of a supercapacitor (functional application) are conceivable in, e.g., the body of a car. An overview can be found in [386].

Ternary, quaternary or other composites (for typical examples of a composite GN/Ti@CNT/Fe_3O_4/PANI see [387], for TiO_2/SWCNT/PPy see [388]) have been reviewed elsewhere [53, 54].

ICPs can be formed by chemical or electrochemical oxidation of the respective monomers, either directly on the substrate or in the presence of the other, in the present context carbonaceous, constituents, or in a solution with the formed ICP obtained as a powder. Details are provided in the quoted research reports, an overview of electrochemical preparation methods is available as a further source of information [389]. Nanocomposites of PTh and polymers of substituted thiophenes, their preparation and properties are briefly reviewed [390], the term supercapacitors is mentioned only in abstract and introduction.

5. Conclusions

Composite materials combining an ICP with carbon in one or more of its many forms have been established as an option to remedy some of the flaws and limitations of the single compounds when applied in or as supercapacitor electrodes. The limited charge storage capabilities of practically all carbonaceous materials is increased up to orders of magnitude by the added ICP whereas some of the stability-limiting drawbacks of ICPs, in particular their rapid mechanical degradation by swelling/shrinking during charge/discharge and their change of electronic conductance as a function of the state of charge, i.e. electrode potential, are ameliorated. The latter tends to limit mass utilization by creating unwanted Ohmic resistance in the bulk and uneven electrode potential distribution during the flow of current when the active mass is reduced/discharged. These considerations were addressed in electrode architectures aiming at a compromise between the various fundamental requirements. In a nutshell a promising electrode will not need a binder and no added conducting carbon because it is based on a highly conducting support (e.g. CNT paper) covered with further 2D-material (some type of nanotubes) with the ICP deposited again in 2D-shape (fiber, cone etc.). Possibly addition of some nanosized carbon material to the polymerization solution can further improve performance in particular of the ICP-component.

Further development should aim at optimized mass ratios of the various constituents and selection of the most suitable ICP and carbonaceous component in terms of the variables addressed above: Performance, stability, price, environmental compatibility. After selecting a promising material(s) combination establishment of a suitable and optimized electrode architecture taking into account high mass utilization and high current capability should be rationally pursued. External as well as internal wetting of the active material is not always a natural result, in particular with gelled or solid electrolytes. Accordingly, for such materials beyond noticing practical effects of slow electrolyte infusion and wetting suitable means to accelerate this process should be studied. Surface treatment of carbon materials ranging from simple oxidation to more complicated chemical functionalization appears to be a promising way compatible with the previous considerations to enhance wetting and dispersion of the material in the polymerization solution, and to improve interactions with the ICP.

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Conflict of Interest

There is no conflict of interest for this study.

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