Review

Surfactants as Performance-Enhancing Additives in Supercapacitor Electrolyte Solutions—An Overview

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Abstract: Wetting the surface area of an electrode material as completely as possible is desirable to achieve optimum specific capacity of an electrode material. Keeping this surface area utilized even at high current densities and even when inside pores is required for high capacitance retention. The addition of surfactants at very small concentrations to aqueous supercapacitor electrolyte solutions has been suggested as a way to improve performance in terms of capacitance, capacitance retention at increased current density and stability. Effects are pronounced with carbon materials used in electrochemical double-layer capacitors; they are also observed with redox materials. The causes of the observed improvements and mode of operation of the added surfactants seem to need further investigation; they are inconclusive beyond the obvious statement of increased wetting. Reported examples and the current state of understanding are reviewed.

Keywords: supercapacitor; ultracapacitor; electrochemical capacitor; surfactant; anionic surfactant; cationic surfactant; non-ionic surfactant; pseudocapacitive

1. Introduction

Supercapacitors (for the sometimes confusing usage of their names, trademarks, etc., see [1,2]) are devices in electrical engineering and electronics that accept and deliver extremely high currents, i.e., high power, like a large conventional capacitor. They store electric energy by separating electric charges across electrochemical interfaces at the boundary between an ionically conducting phase, the electrolyte or electrolyte solution; and an electronically conducting phase, the electrode. Two such interfaces or electrodes joined together by the common ionically conducting phase form the complete device. These operating principles characteristic of a supercapacitor of the electrochemical double-layer capacitor type (EDLC-type) and of a redox-type supercapacitor are sketched schematically in Figure 1. Different from the conventional dielectric capacitor, the extremely large surface areas of the participating electrodes, the amount of stored charge and, thus, the amount of stored energy is much larger for a supercapacitor.

The cell voltage of a supercapacitor is limited by the stability of the ionically conducting phase; too-high voltages will result in electrolytic decomposition of the solvent or the electrolyte. A water-based electrolyte solution limits the cell voltage to values in the range of 1.2 V; sometimes, higher values are claimed because said decomposition may be extremely slow at one or both electrodes because of, e.g., kinetic hindrances. With organic-based solvents, larger values are possible. Relationships between the properties of

the employed materials and the considered range of possible electrode potentials and cell voltages have been critically examined [3]. Too-large values may result in overoxidation of the electrode material at the positive electrode (sometimes slightly confusingly called the cathode) [4].
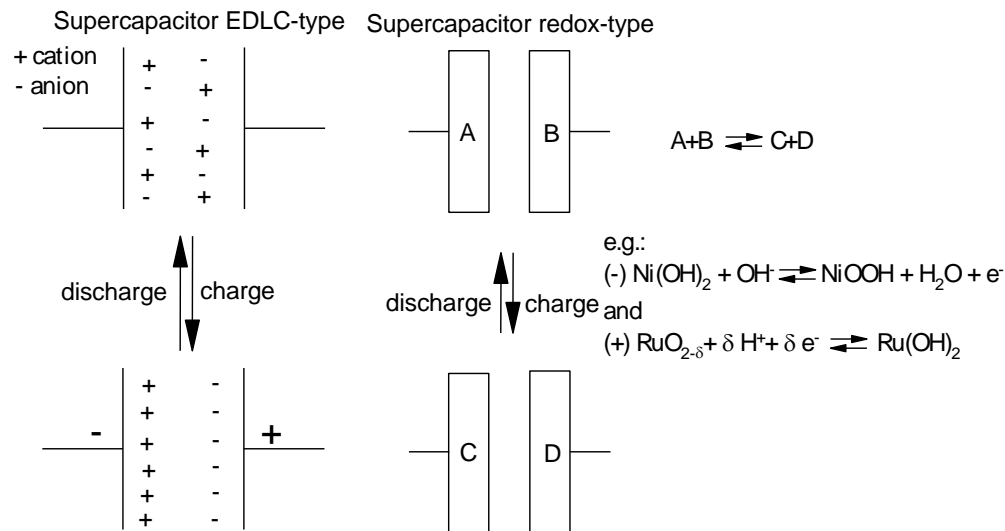

Figure 1. Schematic principles of operation of supercaps.

Because the amount of stored energy depends on the amount of stored charge and the electrode potentials/cell voltage associated with this charge separation, it is possible to store larger amounts of energy, preferably by storing larger amounts of charge; the accessible potentials and voltages are limited as described. The charge per unit area of a typical electrochemical interface (the double layer) and voltage difference (i.e., electrode potential) can be expressed in terms of an interfacial capacitance. Taking the Helmholtz model [5] and the common equation for a parallel-plate condenser

$$C = \frac{\varepsilon}{4 \cdot \pi \cdot d} \tag{1}$$

with permittivity $\varepsilon = 6$ F·m^{-1} and distance $d = 300$ pm, a value $C = 18$ µF·cm^{-2} is calculated as the capacitance. The capacitance of the electrochemical double layer C_{DL} can subsequently be considered either in differential form [6,7]:

$$C_{\text{diff}} = \frac{\partial Q}{\partial E} \tag{2}$$

or in integral form:

$$C_{\text{int}} = \frac{\Delta Q}{\Delta E} \text{ or } C_{\text{int}} = \frac{q}{E - E_{pzc}} \tag{3}$$

with the electrode potential E, the electrode potential of zero charge E_{pzc} and $q = \Delta Q$. They are related to each other according to:

$$C_{\text{diff}} = (E - E_{\text{pcz}})\frac{\partial C_{\text{int}}}{\partial E} + C_{\text{int}} \tag{4}$$

Both C_{int} and C_{diff} can be established experimentally [8–13].

The numerical value calculated with Equation (1) is very close to a repeatedly mentioned value of 20 µF·cm^{-2} for a very flat metal surface in contact with an electrolyte solution of moderate concentration. This number may not be applicable for carbon materials. Randin and Yeager studied several high-pressure stress-annealed pyrolytic graphite SAPGs. For the basal plane, they reported $C_{\text{diff}} = 3$ µF·cm^{-2} [14,15]. This low number

was associated with the space charge region inside the SAPG but not with the electrochemical double layer (see also [16]). With boronated SAPG, numbers varied with the identity of the electrolyte solution composition and were slightly higher [17]. Edge-oriented SAPG yielded C_{diff} = 50–70 µF·cm^{-2} [18]. Corresponding numbers for highly oriented pyrolytic graphite HOPG and natural graphite crystals were much lower [19]. Ordinary pyrolytic graphite with a lower degree of orientation yielded for the polished basal plane C_{diff} = 16 µF·cm^{-2} [14]. Numbers stated elsewhere for ordinary pyrolytic graphite OPG showed significant variations [20]. With respect to the major structural differences in carbon [21], a wide variation in the highest values of C_{diff} per m^2 of surface area and correspondingly per gram of material may be anticipated [22]. An approach to bridge the mismatch of surface areas determined with the Brunauer–Emmett–Teller (BET) method without/with further backing by density functional theory (DFT) as well as additional treatments considering further possibilities like structural changes during treatment of carbon materials into a concrete electrode and C_{diff} has been reported [23]. A specific capacitance of 0.1 F per m^2 effective surface area (which may differ considerably from the BET surface area) was tentatively concluded. Exactly the same value was reported earlier by some of these authors [24]. Gagnon stated exactly this value earlier based on a study of carbon blacks with various BET-surface areas in contact with concentrated electrolyte solutions of KOH [25]. A study by Wen et al. added further complications when establishing a correlation [26]. Values of C_{DL} per BET surface area increasing with growing pore size were ascribed to higher utilization of that surface area. Further details are discussed elsewhere [27].

2. Approaches to Increased Material Utilization

A larger storage capability, i.e., a larger capacitance, can accordingly be achieved with a larger interfacial area. The use of highly porous materials as electrodes is thus the central idea in the technical development of the supercapacitor [1]. Larger surface areas can be achieved mainly by utilizing ever-smaller pores, meaning more porous materials must be used. During this step, further aspects of interfacial science come into play: such surfaces inside ever-smaller pores must be accessible for the ionically conducting phase. Surface tension, capillary forces, viscosity and wetting are of growing importance. Initial fears that pores with too-small openings would be inaccessible for electrolyte solutions, in particular for solvated ions needed for charge storage, turned out to be partially incorrect. Starting with early observations [28] in subsequent studies, evidence of at least partial desolvation of ions was reported [29–33]; this extended the range of useful pores to smaller values than initially expected. However, accessibility of the internal pore surface is not all that is needed for materials surface utilization. An electrochemical double layer must be established; in addition, for the surface to become an electrochemically active surface area [5], it must come into contact with the electrode (solution): it must be wetted. Moreover—last but not least—ionic movement into and out of even tiny pores must proceed at a rate compatible with large electric currents typical of a supercapacitor. With ever-smaller pore openings, conceivable interactions between moving ions and the electrochemical double layer on the walls of the pore mouth may become influential.

It is possible that not all surfaces of a material in a supercapacitor electrode, whether it is an activated carbon (AC), a chalcogenide or any other redox-active material showing pseudocapacitive behavior, will be immediately wetted and sufficiently hydrophilic. This depends very much on the material properties of the solid and the liquid phases. Wetting of carbon materials has been discussed before (in the context of fuel cell technology and, later, of supercapacitors) [22]. Some carbons (e.g., carbon black and acetylene black) are highly hydrophobic, and some (many activated carbons and some graphitic materials) are more or less hydrophilic. The hydrophilicity of carbon surfaces can be increased by the creation of surface functional groups containing oxygen. In a typical study, carbon fibers created from polyacrylonitrile were exposed to oxygen at elevated temperatures [34]. An increase in C_{diff} of only a few percent was noticed, but the Faradaic current, presumably due to surface

redox reactions resulting in a pseudocapacitive behavior, increased by several orders of magnitude. Thus, the overall increase in capacitance (about 25%) of a complete device was attributed mostly to redox processes, but only a very small fraction to was attributed to increased utilization because of wetted surface area. Unfortunately, such oxidative treatment may contribute to faster self-discharge of devices [35] and faster aging [36].

Nevertheless, wetting behavior beyond surface properties and pore-size considerations was never ignored. For improved wetting of a material's surface, surfactants may be helpful; their use has been established in various fields and industries for a long time [37,38]. Surfactants of interest in the present context can be classified into non-ionic, cationic and anionic ones. Typical examples and some frequently encountered compounds are depicted in Figure 2. Generally, they contain a hydrophilic section/end containing heteroatoms like oxygen, and a hydrophobic section with aliphatic or aromatic CH-building blocks. The molecular sizes range from about 0.5 to 2 nm.
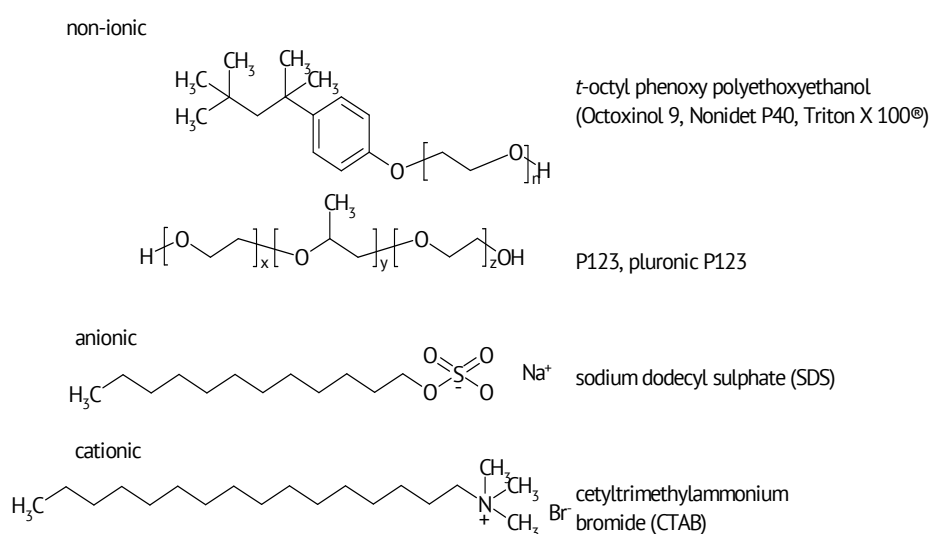

Figure 2. Molecular formulas, systematical names, tradenames and acronyms of representative surfactants.

The same considerations regarding porosity and wetting apply to redox-active materials showing pseudocapacitive behavior, as first proposed by Conway et al. [39–43], as well as plain battery electrode materials. The particular behavior of some of these materials, showing in CVs a response to a changing electrode potential closely resembling that of a capacitor, has resulted in the designation by Gileadi and Conway [41] of pseudocapacitive behavior; for an update, see [44]. An earlier use of the term "pseudo-capacity" by Grahame [45] refers to redox processes at the mercury electrode/aqueous electrolyte solution interface with reduction and subsequent oxidation of cadmium/cadmium ions, i.e., involving solutions species different from the suggestion by Gileadi and Conway involving redox reactions of surface-attached species.

Complete wetting of the surface area of carbon or any other supercapacitor electrode material may be impeded by insufficient hydrophilicity or pores with openings too small for the electrolyte solution to get inside because of surface tension [46]. To improve this situation, surfactants [38,39] improving wetting by reducing the surface tension of the electrolyte solution and/or reducing surface hydrophobicity [47] have been added to aqueous electrolyte solutions. The first study of surfactant effects has been reported with surfactant-treated carbon materials (no surfactant addition to the electrolyte solution) [48]. The studied materials were soaked in solutions of unspecified surfactants and dried. Enhanced wetting was easily verified visibly. Apparently, and not very surprisingly, some surfactant was trapped in the porous electrode material and was transferred into the device. No experimental results suggesting specific effects of surfactant molecules adsorbed on the electrode material surface were reported. Considering the already mentioned size of surfac-

tant molecules, they may be too large to enter into very small pores, and they may actually block openings of very small pores, resulting in a negative effect on capacitance [49–53].

Most reports on the addition of surfactants into electrolyte solutions (including those inspected within this report) deal with aqueous electrolyte solutions, they will be the focus of interest in the following sections. Nonaqueous solutions have been studied frequently because they permit a wider cell voltage window of operation. Basically, the same considerations apply, but with an inverted perspective: instead of wetting with an aqueous phase, wetting with a nonaqueous phase is required. Instead of hydrophilic surfaces, hydrophobic surfaces are of interest. Accordingly, hydrophobization (instead of hydrophilization) of surfaces is an option to increase better "wetting" of a surface. Surfactants other than those shown in a representative selection in Figure 1 may be effective. Better hydrophobization by vinyltrimethoxysilane than with sodium oleate has been reported with a carbon aerogel (both as-prepared and activated) as electrode material [54,55]. The same benefits (higher specific capacitance and better capacitance retention with increased current density and lower electric series resistance ESR of a complete cell) achieved with surfactant treatment as observed before with aqueous solutions were found. Different from surfactant addition to the electrolyte solution in this example, modification of the carbon surface via grafting (i.e., chemical attachment via covalent bonding) of the surfactant was achieved. Less pronounced effects were achieved by adsorptive treatment of a carbon aerogel with sodium oleate [56]. Another option of surfactant use has been examined in studies of ACs vacuum-impregnated with fluorinated surfactants [57]. Moderate performance improvements (higher capacitance and better stability) were best with a cationic surfactant.

3. The Systems

The effects of surfactant addition to aqueous electrolyte solutions in contact with carbonaceous supercapacitor electrode materials will be examined in the following section. In the section thereafter, effects with other redox-active electrode materials are inspected. Because, in a substantial number of publications, surfactants are used in other ways or play other roles in supercapacitors, in particular in the preparation of the electrode materials, these further applications will be summarized briefly in the final section.

3.1. With Carbonaceous Supercapacitor Electrode Materials

Fic et al. [58–60] examined the effect of various surfactants, including *t*-octylphenoxy polyethoxyethanol (Triton X-100), tetrapropylammonium bromide (TPAB), sodium dodecyl sulphate (SDS) and further surfactants added at 5 mM concentration into the 6 M KOH electrolyte solution in a symmetric supercapacitor of the EDLC-type with AC electrodes. Higher surfactant concentrations were inefficient because of micelle formation. Improvements included enhanced capacitance at higher current density, i.e., major improvement of capacitance retention with growing current density; slower self-discharge (of a complete device in terms of, e.g., cell voltage or a single electrode in terms of electrode potential) and increased stability were found with non-ionic Triton X-100. The reported main effect of surfactant addition was a reduction in the surface tension of the aqueous phase, enabling penetrating pores of smaller diameters than is possible without surfactant addition. The polarity of the surfactant affected their influence on observed capacitance values. However, these statements appear to be slightly inconclusive.

Upon closer inspection, further details emerge. At the lowest current density, the addition of any surfactant did not show an increase in specific capacitance (see, e.g., Figure 1 in ref. [59] and Figure 4 in ref. [60]). Accordingly, a simple wetting enhancement is not the full explanation—if it explains anything at all, because it should have resulted in higher values of specific capacitance even at the lowest scan rates. The significantly improved capacitance retention with the studied AC electrode material, as depicted in Figure 3, suggests better utilization of the inner pore surface area than without added surfactant.
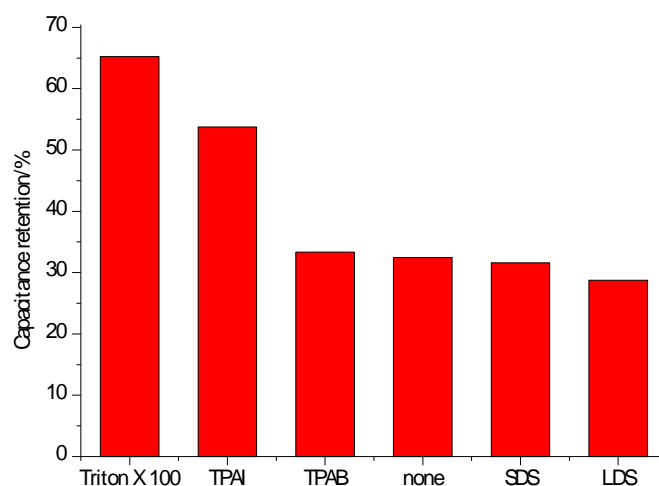
Figure 3. Capacitance retention of a carbon electrode in an aqueous electrolyte solution of 6 M KOH with 5 mM surfactant added at 50 A·g^{-1}; TPAI: tetrapropylammonium iodide, TPAB: tetrapropylammonium bromide, LDS: lithium dodecyl sulphate (based on data in [60]).

Thus, the surfactant—whether adsorbed on the carbon surface or dissolved in the electrolyte solution—seems to accelerate ion transport. This points, in particular, at improved ion passage through pore openings somehow supported by the added surfactant. Whether ion channels formed by surfactant molecules (see [61]) accelerate ion transport is currently only speculation. In a study of layered 2D-nanomaterials, hydrophilic and ionophobic surfaces generated by corresponding surface treatment, in particular by attachment of suitable functional groups, could drastically reduce ion diffusion resistance [62]. Similar considerations with ionic liquids as electrolytes, taking into account the different properties of these materials, have been reported, with conclusions pointing in the same direction [63]. The addition of a surfactant to the electrolyte solutions and subsequent adsorption on the carbon surface may have a similar effect in terms of increased hydrophilicity. The effects of surfactants on ionophobicity are hard to estimate; in addition, the size of the surfactant molecules must be considered with respect to pore sizes. Given the determined morphological data of the AC used in [60], as previously reported in [64], such an effect may be conceivable when the surfactant molecules are adsorbed flat or strongly tilted on the carbon surface.

Somewhat surprisingly, the effect of surfactant molecules possibly displacing water molecules in the electrochemical double on the specific double-layer capacity has not been considered. Elsewhere, in studies of the adsorption of aliphatic alcohols (being somewhat related to surfactant molecules) with different chain lengths on a polycrystalline gold electrode, a significant decrease in the specific double-layer capacitance was observed; it was particularly pronounced at maximum coverage [65,66]. With increasing chain length of the studied alcohols, the capacitance continuously decreased. Perpendicular adsorption of the alcohol molecules was concluded. With the surfactant molecules employed in the studies reviewed here, such orientation is highly likely. Adsorption studies of these surfactants on carbon or the electrode material inspected below are not reported. Thus, the degree of coverage and any decrease in specific capacitance remains unknown; more research needs to be carried out to investigate the underlying mechanism in the future.

Beyond said kinetic effects, improved stability has been noticed. As shown in Figure 4, after 5000 galvanostatic charge/discharge (GCD) cycles at 1 A·g^{-1}, addition of the non-ionic surfactant Triton X 100 resulted in significantly higher capacitance retention.
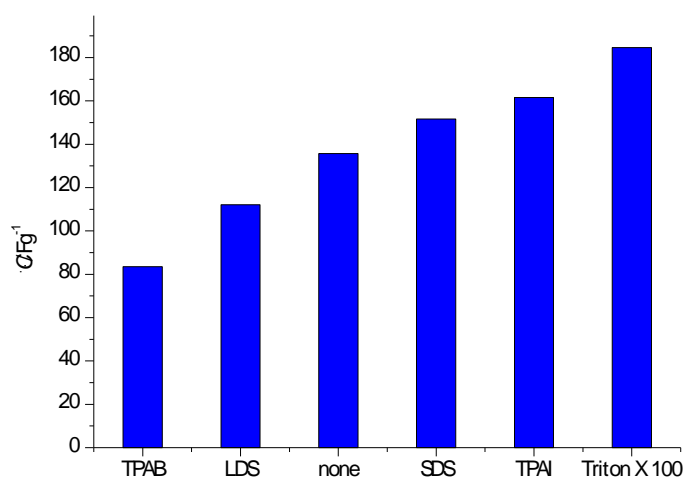
Figure 4. Capacitance retention after 5000 cycles at 1 $A \cdot g^{-1}$ of a carbon electrode in an aqueous electrolyte solution of 6 M KOH with 5 mM surfactant added; TPAI: tetrapropylammonium iodide, TPAB: tetrapropylammonium bromide, LDS: lithium dodecyl sulphate (based on data in [60]).

3.2. With Redox-Active Supercapacitor Electrode Materials

Tremendous power densities have been achieved with EDLC so far, whereas energy densities are still disappointingly low [1,67–86]. Metal oxides employed as active materials in supercapacitor electrodes to overcome this limitation have been examined only very infrequently with surfactants added into the electrolyte solution. To the fundamentally different surface compositions of carbon-based materials used in ECDL supercapacitors and metal oxides used in redox capacitors, the different charge storage mechanisms—ion accumulation vs. superficial redox reactions—add a further dimension of properties and behaviors. Composites of metal oxides with carbon materials or intrinsically conducting polymers as a further class of redox-active materials may cause further differences in properties and behavior [87,88]. These differences may result in different effects of added surfactants. Presumably, the concentration of added surfactant should again be kept below the critical micelle concentration (CMC), in particular to avoid blocking of pores by micelles [50–54]. The results obtained with these three classes of materials will be inspected.

Wang et al. have examined the influence of SDS, Triton X-100 and P123 (poly(ethylene glycol)-block-poly (propylene glycol)-block-poly(ethylene glycol)) added at 5 mM concentration to an aqueous electrolyte solution of 2 M $LiNO_3$ on the properties of manganese ferrite $MnFe_2O_4$ suggested as supercapacitor electrode material [89]. The highest capacitance increase of 36.8% was found with SDS. This was attributed to "enhanced lithium ion penetration" as already suggested elsewhere [90]. At a moderate current density of 0.5 $A \cdot g^{-1}$, 82% of the initial capacitance was retained after 1000 cycles. Capacitance retention with increasing current was markedly improved, particularly with SDS. Surfactant concentrations above 5 mM (e.g., 10 mM with SDS) resulted in a decrease in capacitance because of micelle formation impeding ion movement and because of diminished efficiency of the surfactant, which is now presumably in part assembled in micelles instead of being active at the solution/carbon interface. Improved capacitance retention at higher current densities was also noted, again with SDS showing the most pronounced effect. Different from a previous report by Wu and Kuo [91], the CV response showed a pronounced pseudocapacitive shape, and no current peak due to a redox process of the ferrite was found. The absence of plateaus in the galvanostatic charge/discharge curves confirms this conclusion. Quite notably, self-discharge—an inherent problem possibly limiting the use of supercapacitors for long-term energy storage—is significantly slowed down with added SDS. During 1000 cycles, capacitance losses again depended on the added surfactant, with Triton X-100 and P123 performing slightly better. $Co(OH)_2$ on nickel foil was prepared via electroreduction of $Co(NO_3)_2$ in an aqueous solution [92]. Reduction of nitrate anions yielded nitrite and hydroxyl ions, the latter formed the expected precipitate of

sheet-like $Co(OH)_2$. The addition of 0.05% Triton X-100 yielded significant increases in storage capability and stability. The effect of representative surfactants from the three classes presented above with electrodes made from a specific type of α-NiOH)$_2$ and $MgCo_2O_4$ has been reported [93]. With the former oxide, beneficial effects in terms of greater capacitance, better capacitance retention with increased current density and higher stability were noticed, whereas the latter mixed oxide did not show any improvement. From these results, the surfactants appear to work in different ways; the working mode may also be completely different.

Ghasemi and Ahmadi have compared the effects of added Triton X-100, SDS and cetyltrimethylammonium bromide (CTAB) on the performance of a composite of reduced graphene oxide (rGO) and Fe_3O_4 [94]. The capacitance of 154 $F \cdot g^{-1}$ at a current density of 1 $A \cdot g^{-1}$ was increased upon the addition of Triton X-100 to the electrolyte solution to 236 $F \cdot g^{-1}$; after 500 cycles, a capacity retention of 97% was observed. Effects of the addition of other surfactants are depicted in Figure 5; for comparison, the value for plain rGO is indicated.
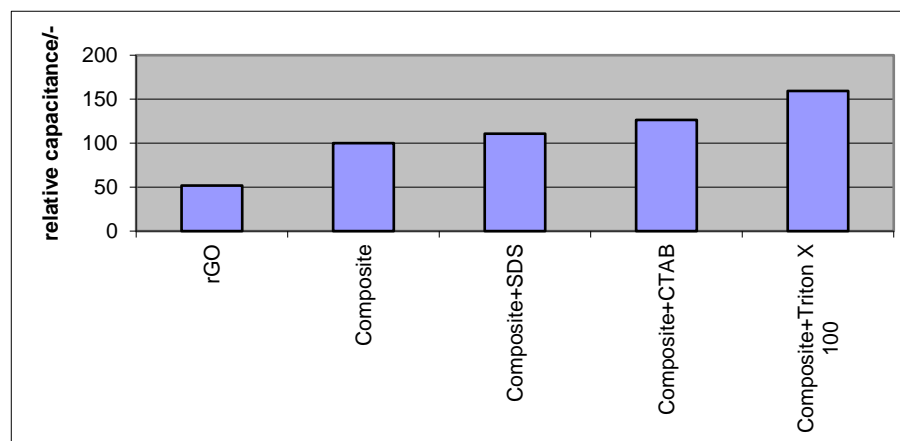

Figure 5. Comparison of GCD-cycle duration (equivalent to capacitance) for plain composite, rGO and a composite of rGo and Fe_3O_4 in an aqueous electrolyte solution of 0.5 M Na_2SO_4 and 5 mM surfactant at 1 $A \cdot g^{-1}$; (based on data in [95]).

Without added surfactant, the losses amounted to 13%. For practical applications, such retention would be demanded after 10^5 to 10^6 cycles. The beneficial effects of the other ionic surfactants were less pronounced. How the presence of surfactant shall accelerate charge carrier transport along the electrolyte/electrode interface is not explained; attribution of this claim to an earlier report [60] wherein such a claim is not made does not help. An explanation along the lines of reasoning presented above may be applicable.

Surfactants have been incorporated into polypyrrole during oxidative chemical polymerization of pyrrole monomers [95]. The ionic surfactant reportedly acts as a counterion in the oxidized polymer. Neither the function of the surfactant nor the improvement achieved when comparing the performance of this polymer with polypyrrole formed with other counter anions was explained.

3.3. Other Uses of Surfactants Related to Supercapacitors

The vast majority of publications related to surfactants and supercapacitor electrode materials deal with either the use of surfactants during synthesis and electrode preparation [96–146] (for an overview see [147]) or explicitly claim a surfactant-free process [148–164]. During synthesis, surfactants served as soft templates by increasing the wettability of reactants [165] or by controlling particle morphology, pore size distribution and surface area [146,166,167]. In electrode preparation, they helped again by increasing the wettability of electrode constituents. Further uses of surfactants have been mentioned. Tan et al. have coated a polyelectrolyte-ferrocenyl surfactant complex on carbon paper for use as a supercapac-

itor electrode [168]. Anionic surfactant ionic liquids mixed with ordinary ionic liquids have been suggested for use in supercapacitors to increase surface utilization, which is sometimes impeded by the viscosity of ionic [169]. Capacitance value increases with the addition of 10 wt.% of a surfactant–ionic liquid are attributed to improved pore accessibility. With the larger size of the surfactant–ionic liquid, pore blocking was observed during extended operation. At elevated temperatures, the decreased viscosity resulted in increased ionic conductivity, supporting a high current performance. Surfactants have been used as "pillars" in layered compounds to facilitate the movement of ions into and out of interlayer spaces during intercalation and deintercalation processes [170]. Intercalation has been named here as a third charge storage process beyond the two well-established ones commonly discussed with supercapacitors (ion accumulation possibly including adsorption in double-layer charge in EDLC devices and redox processes in redox capacitors). These suggestions appear rather unneeded because intercalation itself is not an electrochemical process; it just indicates the mode of storage of species and their location. Consequently, this "third mechanism" has not received further attention. The use of surfactants in flow capacitors has been proposed [171].

4. Conclusions and Perspectives

The addition of surfactants to electrolyte solutions results in faster and better wetting of electrode surfaces and may thus increase the electrochemically active surface area and, thus, the interfacial capacitance. Surprisingly, this is not noticed in the reported studies of EDLC-type electrodes—the observed specific capacitance at very low currents (unfortunately, no extrapolation to zero current has been tried) does not change significantly upon surfactant addition. This is generally observed with carbonaceous materials for EDLC-type supercapacitors; in the case of redox materials, the increase in capacitance is not always observed. Instead, better capacitance retention with increasing current density and better stability of performance data are observed. This cannot be explained by invoking wetting effects and expected larger capacitances; it must instead be based on faster charge transport and lower effective electrolyte resistance. Explanations are inconclusive based on the reported examples—when this question is addressed at all. An ideal surfactant showing improvements in all relevant performance parameters for all materials and electrolyte solutions is not evident, but frequently, Triton X 100 performed best. Accordingly, fundamental studies of surfactant effects on C_{diff} with smooth electrodes are required to put the already reported evidence on a more solid support.

Given the pronounced interest in devices with aqueous electrolyte solutions (because of higher safety, cheaper materials and production, lower internal resistance and lower cell voltage) more systematic investigations of the most efficient surfactant and the optimum concentration are needed.

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