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## Review Article

# Redox active electrolytes in carbon/carbon electrochemical capacitors

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The application of redox-active electrolytes to realize carbon/carbon electrochemical capacitors has created a great opportunity to enhance the mediocre energy of these devices. Taking advantage of the faradic current from the redox transformation of electrolyte species, which generates a large capacity at one electrode, the resulting hybrid cells can store twice more energy than typical electrical double-layer capacitors based on the same carbon electrode material. However, among a relatively large number of tested redox active electrolytes, only few are acknowledged to provide ideally performing hybrid capacitors. This review critically discusses the literature data and provides clues for realizing optimized systems.

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## Introduction

The electrochemical capacitors (ECs) technology has been developed at the industrial scale during the last two decades [1,2]. The operational principle of these devices is based on the formation of an electrical double-layer (therefore they are often called electrical double-layer capacitors – EDLCs) of nanometric thickness  $d$  at the surface of two conductive electrodes (generally made of nanoporous activated carbon – AC) immersed in an electrolyte. Since the surface area  $S$  of the carbon electrode/electrolyte interface is very high, the electrode capacitance  $C_H$  expressed by the Helmholtz formula below:

$$C_H = \varepsilon S/d \quad (1)$$

reaches high values, ca.  $100 \text{ F g}^{-1}$  (at electrode material level) [3]. Hence, when considering the formula (2) for an EDLC:

$$E = 1/2 CU^2 \quad (2)$$

where  $C$  (F) and  $U$  (V) are the capacitance and voltage, it comes that the specific energy  $E$  is relatively high. In addition, owing to the electrostatic charge storage mechanism, the time constant is very small, enabling EDLCs to exhibit a high-specific power. Therefore, EDLCs are used as energy storage devices in applications where relatively high amount of energy must be harvested/delivered in very short periods of time [4].

In the EDLC technology, the maximum voltage  $U$  is imposed by the stability window of the electrolyte. Therefore, industrial systems are generally based on organic electrolytes, e.g., tetraethylammonium tetrafluoroborate ( $\text{Et}_4\text{N BF}_4$ ) in acetonitrile or propylene carbonate, enabling to reach voltage up to 2.7–2.85 V per cell [5]. However, since these electrolytes are moisture sensitive, the carbon electrodes must be carefully dried and the cells built under neutral atmosphere, which generates high cost of the devices. In addition, solvents such as acetonitrile are environmentally unfriendly and might as-well be at the origin of fire hazards [6]. Therefore, to widen the spectrum of EDLCs industrial applications, alternative solutions must be considered to solve these issues and also to enhance the energy density.

Based on the aforementioned considerations, other strategies have been investigated in the last decade, while keeping nanoporous carbon as primary electrodes material to satisfy performance and cost criteria. Room temperature ionic liquids (ILs) have been proposed to enhance the voltage window of EDLCs, and consequently the energy. Unfortunately, to-date known ILs display relatively weak transport properties, and their stability window in presence of high surface area carbon electrodes is at maximum ca. 3 V [7–9], that is they do not provide any performance breakthrough in comparison to organic electrolytes. Aqueous electrolytes based on neutral salts, namely lithium sulphate ( $\text{Li}_2\text{SO}_4$ ), have been found very promising for designing environmentally friendly EDLCs, yet the voltage is generally limited to 1.5–1.6 V [10]. In parallel to these new approaches, a lot of efforts have been dedicated to enhance  $S$  in formula (1) by designing so-called “architected” carbons [11,12].

In general, the materials are prepared through tedious processes, which are economically inapplicable at an industrial scale, and the improvements in capacitance are generally incremental.

In this context, the recently proposed concept of hybrid capacitor based on carbon electrodes in redox active electrolyte is a promising solution to develop high energy, environmentally friendly and cost effective electrochemical capacitors. A *hybrid capacitor* is an electrochemical cell, which presents the electrical characteristics of a capacitor (e.g., linear galvanostatic charge/discharge characteristics (GC/GD), rectangular voltammogram, low time constant) while being based on a capacitive electrode (EDL or pseudocapacitive) and a redox (faradaic) battery-type electrode. This type of cell has been proposed for the first time in 2001 by using a faradaic positive electrode ( $\text{PbO}_2/\text{PbSO}_4$  in aqueous  $\text{H}_2\text{SO}_4$  or  $\text{NiOOH}/\text{Ni}(\text{OH})_2$  in  $\text{KOH}$  electrolyte) and a capacitive AC negative electrode [13•]. Then, the hybrid concept has been introduced in a higher energy density system called lithium-ion capacitor, LIC, by combining an AC positive electrode and a graphite intercalation negative electrode [14]. Finally, the most recent research on hybrid capacitors implements two nanoporous carbon electrodes immersed in a redox active electrolyte [15••], such as an aqueous solution of potassium iodide [16••] or hydroquinone [17••]. *Indeed, whereas a porous carbon electrode can be regarded as an EDL electrode in a non-redox electrolyte, it can become a faradaic electrode in a redox electrolyte.* The hybrid AC/AC design in redox electrolyte will be precisely the object of the next sections of this paper.

### What is the advantage of hybridization in comparison to a traditional EDL cell?

In a typical symmetric EDL cell based on nanoporous carbon electrodes, the potential variation of the two electrodes is almost equal, with some differences depending essentially on the size of cations and anions vs. pore size of carbon. The potential increase and decrease of positive and negative electrodes, respectively, is proportional to the charge stored in the cell (Figure 1a); accordingly, the voltammograms of the two electrodes are rectangular (Figure 1b). The simplest equivalent circuit of an EDLC can be represented by two capacitors in series, of capacitance  $C_+$  and  $C_-$  for the positive and negative electrode, respectively. Accordingly, the capacitance  $C_{\text{sym}}$  of the cell is given by equation below:

$$\frac{1}{C_{\text{sym}}} = \frac{1}{C_+} + \frac{1}{C_-} \quad (3)$$

As the capacitance of both electrodes is generally comparable ( $C_+ \sim C_-$ ), the capacitance of the cell is:

$$C_{\text{sym}} \cong \frac{C_-}{2} \quad (4)$$

However, when implementing a redox active electrolyte [16••], the electrochemical characteristics of an AC/AC cell may be those of a capacitor (rectangular cyclic voltammogram, linear GC/GD characteristics) while the positive electrode operates as a battery one of narrow potential range and the negative electrode remains of EDL type (Figure 2); according to the above mentioned definition, such cell is a *hybrid capacitor of capacitance  $C_{\text{hybrid}}$* .

Figure 3 compares the discharge characteristics of EDL and hybrid AC/AC cells in the same voltage range  $U$ . In the EDL cell described in the foregoing, the discharge capacity is:

$$Q_{\text{sym}} = C_{\text{sym}} U \cong \frac{C_-}{2} U \quad (5)$$

During charging/discharging of the hybrid capacitor, the potential excursion of the negative electrode is almost twice longer than in the symmetric EDL cell (Figure 3), leading to approximately twice higher discharge capacity:

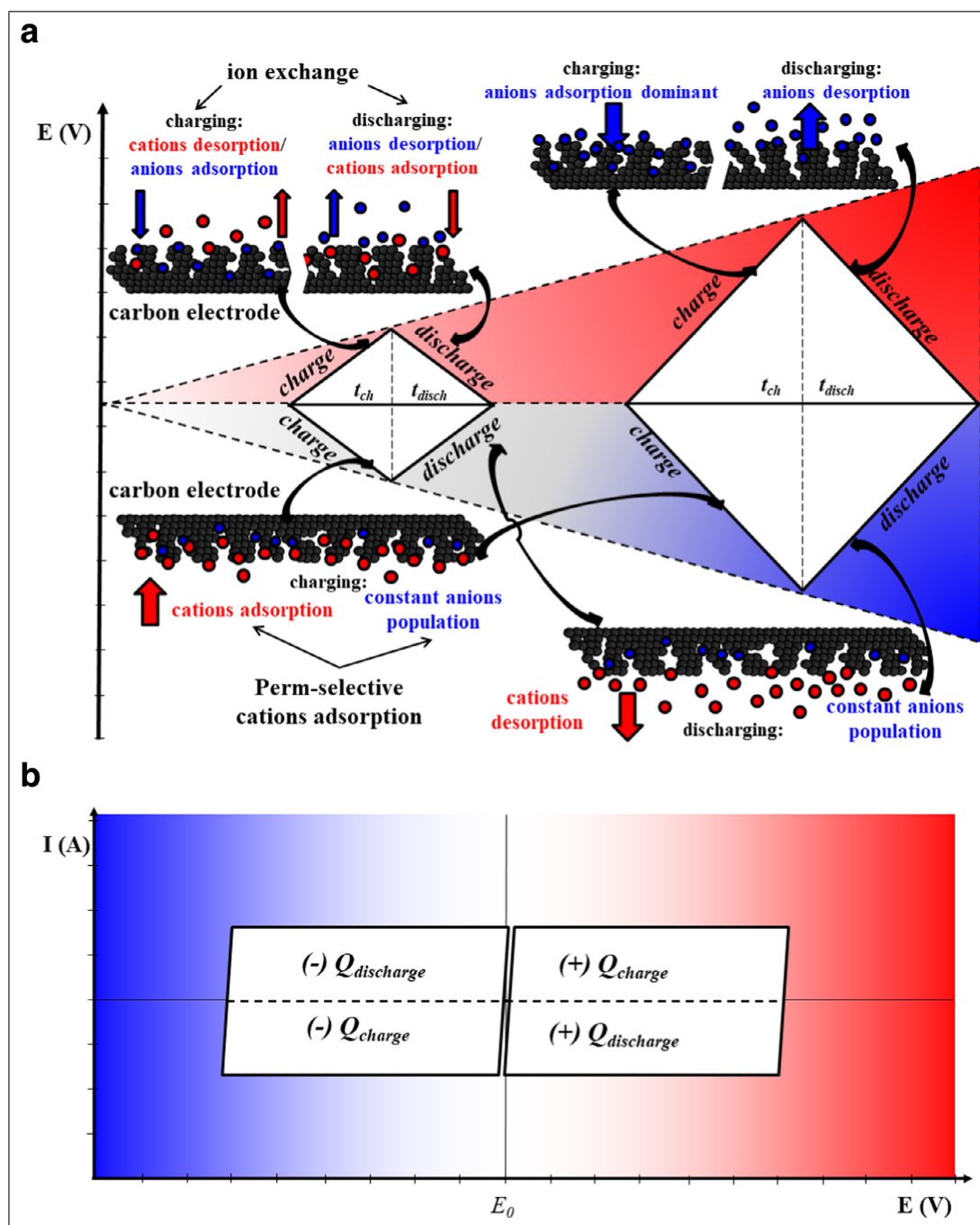
$$Q_{\text{hybrid}} = C_{\text{hybrid}} U \cong 2 Q_{\text{sym}} = C_- U \quad (6)$$

Hence, the capacitance  $C_{\text{hybrid}}$  of the hybrid AC/AC capacitor is nearly twice higher than the capacitance  $C_{\text{sym}}$  of the EDL cell, and in the hypothesized case of a positive faradaic electrode (as in reference [16••]), the cell capacitance is controlled by the capacitive negative electrode. *It has to be noted that, by analogy with EDLCs, the capacitance and energy data on hybrid cells in the literature are mostly expressed per electrode (normalized to mass or volume), which is senseless because the electrodes have different charging mechanisms. Therefore, in case of hybrid capacitors, it is more correct to express the capacitance values per cell (normalized to mass or volume of electrodes). In addition, for the ideal cases where redox species are confined in the porosity of carbon, the mass of electrolyte should be also considered. Overall, since the final objective of the research on ECs is to make a device (EDL or hybrid), the capacitance and energy should be always calculated per total mass of electrode materials and electrolyte.*

### Aqueous redox-active electrolytes

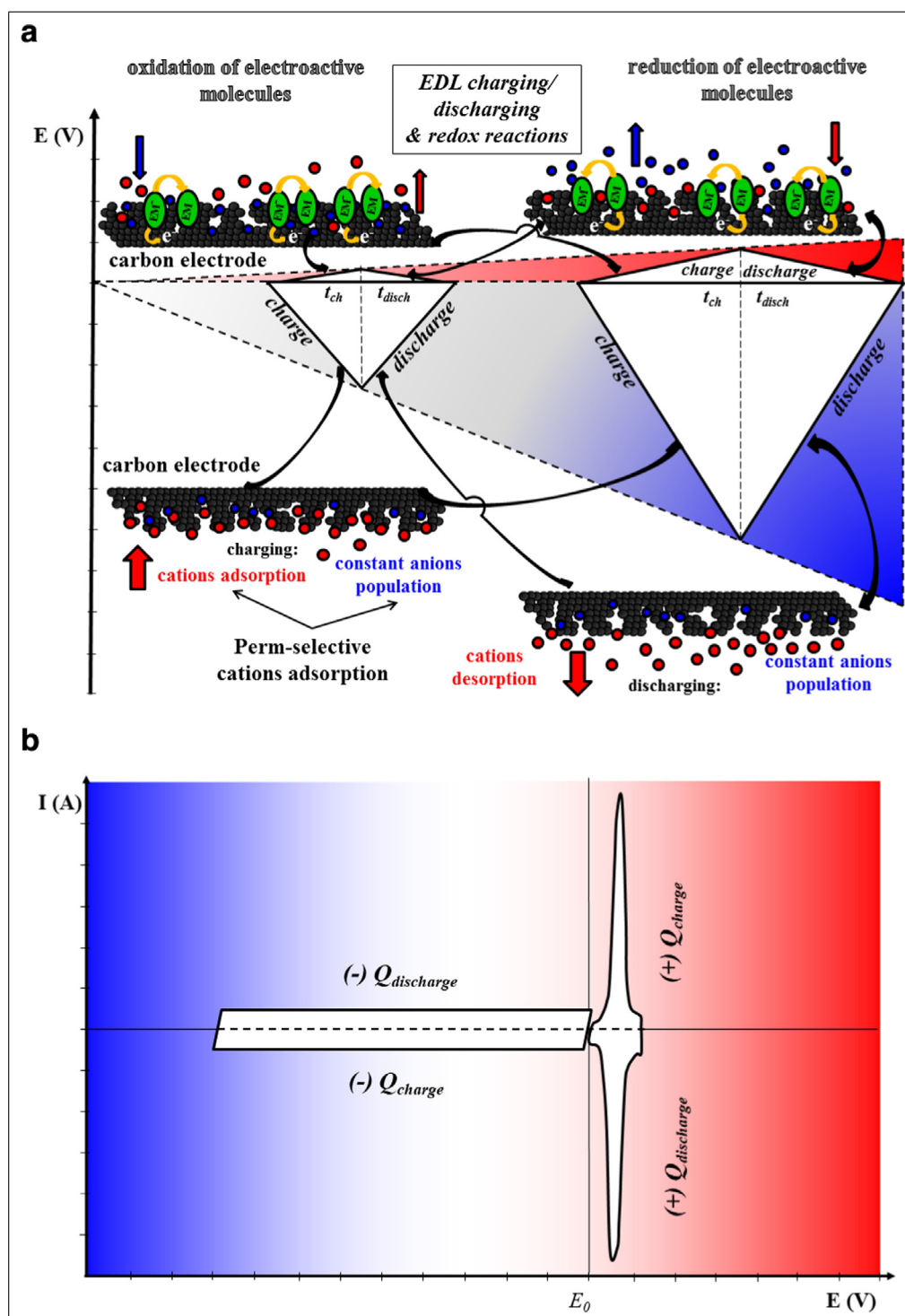
Among AC-based hybrid capacitors realized by the implementation of redox active electrolytes, the ones based on aqueous solutions containing iodides have lately prevailed over others (Table 1) [16••, 20–36]. Already the first report has demonstrated them to be foolproof redox-active species providing good separation of electrodes charging mechanisms for hybrid EC construction [16••]: the negative and positive electrodes demonstrate well-defined *EDL charging* and *battery-like* behavior, respectively. As a result, an AC/AC cell in  $1 \text{ mol L}^{-1}$  potassium iodide exhibits almost doubled capacitance as compared to a cell made with the same carbon in  $1 \text{ mol L}^{-1}$  sulfuric acid [16••]. The capacity of the redox positive electrode depends on the type of iodide counter ion, increasing with

Figure 1



Electrochemical characteristics of a symmetric EDL capacitor: a) galvanostatic charge/discharge at two different values of maximum voltage showing that the potential variation of positive and negative electrodes is comparable; in-situ EQCM [18] and NMR [19] investigations indicate that cations are adsorbed in the negative electrode porosity while anions are not expelled (perm-selective cations adsorption), whereas under positive polarization cations are replaced by anions; b) in absence of parasitic reactions related with electrolyte decomposition, EDL charging/discharging of both electrodes is characterized by rectangular cyclic voltammograms with almost equal values of  $Q_{discharge}$  and  $Q_{charge}$ .  $E_0$  is the potential of both electrodes at voltage of 0 V.

Figure 2



Electrochemical characteristics of a hybrid AC/AC capacitor implementing a redox active electrolyte: a) galvanostatic charge/discharge at two different values of maximum voltage showing negligible potential variation of the positive faradaic electrode, while the negative electrode behaves as an EDL electrode with linear potential variation; for the negative electrode, a mechanism identical to the one shown in Figure 1 may be assumed, with perm-selective cations adsorption; in the positive electrode, the EDL is charged/discharged and molecules are oxidized/reduced as the potential of this electrode increases/decreases; b) rectangular cyclic voltammogram of the negative electrode characterizing EDL charging/discharging, while the positive electrode displays reversible redox peaks; as long as parasitic faradaic reactions (such as electrolyte reduction/oxidation) do not occur, the  $Q_{discharge}$  and  $Q_{charge}$  values are almost equal for both electrodes.

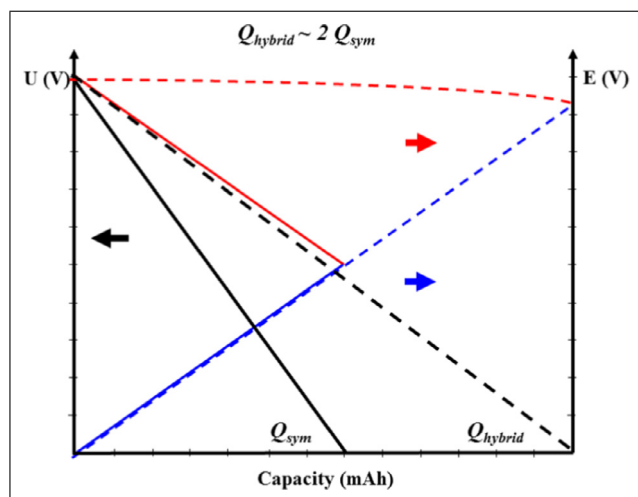
Table 1

Standard redox potential of electroactive molecules and their oxidation/reduction pathways.

Redox couples and standard reduction potential values ( $E^\circ$ )	Possible redox activity of the selected electroactive molecules
<b>Ferricyanide/Ferrocyanide</b> $E^\circ = 0.36 \text{ V}$ [37]	$[\text{Fe}(\text{CN})_6]^{3-} + e^- \leftrightarrow [\text{Fe}(\text{CN})_6]^{4-}$
<b>Ferrocenium/Ferrocene</b> $E^\circ = 0.4 \text{ V (aq)}$ [38] $E^\circ = 0.36 \text{ V (acetonitrile)}$ [38]	$\text{Fc}^+ + e^- \leftrightarrow \text{Fc}$
<b>Iodine/Iodide</b> $\text{I}_2 (\text{aq}) + 2e^- \leftrightarrow 2\text{I}^- (\text{aq})$ $E^\circ = 0.54 \text{ V}$ [39]	$\text{I}_3^- + 2e^- \leftrightarrow 3\text{I}^-$ $\text{I}_2 + 2e^- \leftrightarrow 2\text{I}^-$ $3\text{I}_2 + 2e^- \leftrightarrow 2\text{I}_3^-$ $2\text{IO}_3^- + 12\text{H}^+ + 10e^- \leftrightarrow \text{I}_2 + 6\text{H}_2\text{O}$ [40] $2(\text{SCN})_3^- + 4e^- \leftrightarrow 6\text{SCN}^-$ $3(\text{SCN})_2 + 2e^- \leftrightarrow 2(\text{SCN})_3^-$ $(\text{SCN})_3^- \leftrightarrow (\text{SCN})_2 + \text{SCN}^-$ [42] $\text{Br}_3^- + 2e^- \leftrightarrow 3\text{Br}^-$ $\text{Br}_2 + 2e^- \leftrightarrow 2\text{Br}^-$ $3\text{Br}_2 + 2e^- \leftrightarrow 2\text{Br}_3^-$ $2\text{BrO}_3^- + 12\text{H}^+ + 10e^- \leftrightarrow \text{Br}_2 + 6\text{H}_2\text{O}$ [40]
<b>Thiocyanogen/Thiocyanate</b> $(\text{SCN})_2 (\text{aq}) + 2e^- \leftrightarrow 2\text{SCN}^- (\text{aq})$ $E^\circ = 0.77 \text{ V}$ [41]	
<b>Bromine/Bromide</b> $\text{Br}_2 (\text{aq}) + 2e^- \leftrightarrow 2\text{Br}^- (\text{aq})$ $E^\circ = 1.07 \text{ V}$ [39]	
<b>Benzoquinone (Q)/hydroquinone (HQ)</b> [43] 	In protic electrolyte <sup>(a)</sup> : $\text{Q} + e^- \leftrightarrow \text{Q}^{\bullet-}$ $\text{Q}^{\bullet-} + \text{H}^+ \leftrightarrow \text{QH}^{\bullet}$ $\text{QH}^{\bullet} + e^- \leftrightarrow \text{QH}^-$ $\text{QH}^- + \text{H}^+ \leftrightarrow \text{QH}_2$
<b>Anthraquinone (AQ)/dihydroxyanthracene</b> [43] 	In aprotic medium: $\text{Q} + e^- \leftrightarrow \text{Q}^{\bullet-}$ $\text{Q}^{\bullet-} + e^- \leftrightarrow \text{Q}^{2-}$ (a) The order of Q to HQ transition may change depending on the electrolyte pH [44] (b) Anthraquinone and benzoquinone display analogue redox behavior
<b>2,2,6,6-tetramethyl-1-oxopiperidin-1-ium (TEMPO<sup>+</sup>)</b> <b>/2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)</b> $E^\circ = 0.72 \text{ V}$ [45] 	$\text{TEMPO}^+ + e^- \leftrightarrow \text{TEMPO}$ $\text{TEMPO} + e^- \leftrightarrow \text{TEMPO}^-$



Figure 3



Typical voltage  $U$  and potential  $E$  profiles of AC electrodes during discharging of an EDL capacitor (full lines) and a hybrid capacitor (dashed lines) built with a redox positive electrode. In the hybrid capacitor, the potential excursion of the EDL electrode is almost twice longer than in the EDLC, leading to almost twice higher cell capacity  $Q_{\text{hybrid}}$  as compared to  $Q_{\text{sym}}$ . The capacitance of the hybrid cell is  $C_{\text{hybrid}} = Q_{\text{hybrid}} / U$ .

cation radii  $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ . However, as explained in the foregoing, since the cell capacitance is imposed by the capacitive negative electrode, negligible differences between the various alkali iodides were noticed [20]. The cell capacitance is more efficiently enhanced by tuning the electrolyte concentration, e.g., applying  $2 \text{ mol L}^{-1}$  NaI [25] or  $6 \text{ mol L}^{-1}$  KI [32] compared to the same salt in e.g.,  $1 \text{ mol L}^{-1}$  concentration.

Since all the reports on AC/AC cells with alkali iodides indicate a limited voltage ( $0.8\text{--}1.2 \text{ V}$ ) [16<sup>••</sup>, 20, 23–25, 27, 28, 32, 34], it has been proposed to use bi-functional aqueous electrolytes made by mixing a redox electrolyte ( $0.5 \text{ mol L}^{-1}$  KI) and a supporting neutral electrolyte ( $1 \text{ mol L}^{-1}$   $\text{Li}_2\text{SO}_4$  [31<sup>••</sup>, 36],  $2 \text{ mol L}^{-1}$   $\text{MnSO}_4$  [33] or  $8 \text{ mol kg}^{-1}$  bis(trifluoromethylsulfonyl)imide sodium salt, NaTFSI [35]) enabling to enhance the hydrogen evolution over-potential at the negative AC electrode [31<sup>••</sup>, 33, 36]. As a result, the capacitance of the hybrid cells is still almost doubled as compared to the cells manufactured with only neutral salt (without KI), whereas the voltage can reach  $1.5\text{--}1.6 \text{ V}$  with  $\text{Li}_2\text{SO}_4$  [31<sup>••</sup>, 36],  $1.5 \text{ V}$  with  $\text{MnSO}_4$  [33] and  $1.8 \text{ V}$  with NaTFSI [35] supporting electrolytes. However, in case of NaTFSI + KI, the voltage extension is obtained at the expense of the device power output, due to the weak transport properties of the medium.

*Operando* Raman analysis [24] of positively polarized carbon electrodes revealed the presence of  $\text{I}_3^-$  and  $\text{I}_5^-$

polyiodide species on the AC surface, but also newly created  $\text{C-I}_n^-$ ,  $\text{C-I}_3^-$  and  $\text{C-I}_5^-$  bonds. In contrast, *ex-situ* Raman observations [33] proved these species to be confined in the porosity of the positive AC electrode, that is at the origin of low self-discharge as the ions are immobilized [27] compared to e.g., quinones prone to diffuse into the electrolyte bulk, resulting in high self-discharge of these ECs [46<sup>•</sup>, 47].

Since the contribution of iodates ( $\text{IO}_3^-$ ) or periodates ( $\text{IO}_4^-$ ) is attainable at lower potential in high pH electrolyte, a system utilizing oxo-species of iodine was created by mixing  $4 \text{ mol L}^{-1}$  KI with  $1 \text{ mol L}^{-1}$  KOH [26]. Yet, the operation of both, positive and negative, electrodes was dominated by EDL charging mechanism with mediocre impact of redox iodine activity or hydrogen storage appearing only at vertex potentials of electrodes.

Undoubtedly, iodine salts are primary compounds for redox-active electrolytes. However, some cells based on these electrolytes show an undesired impact of the redox reaction when it occurs in a potential range, which overlaps with  $E_0$  (where  $E_0$  is the potential of individual electrodes at cell voltage of  $0 \text{ V}$ ) [32, 36]. In that case, as shown in Figure 4a, the CV of the negative electrode presents a current leap when approaching  $E_0$ , which leads to a redox signature at low voltage on the cyclic voltammogram of the two electrode cell (Figure 4b) and a voltage plateau on the galvanostatic curve (Figure 4c). Therefore, an initial *voltage cut* is required to eliminate these parasitic signals and to obtain the real characteristics of a hybrid capacitor.

In order to circumvent the possible disadvantages of iodides, electroactive redox couples with slightly higher standard potential, such as thiocyanogen/thiocyanate (Table 1) belonging to the pseudohalides family, have been investigated [48]. Despite the considerable impact of such faradaic contribution, the performance of AC/AC cells using aqueous alkali and ammonium thiocyanates is affected by the high potential value of the redox couple as compared to  $E_0$  (alike in Figure 4d, e and f). Notwithstanding, in case of e.g.,  $7 \text{ mol L}^{-1}$  KSCN electrolyte, the high conductivity of  $389 \text{ mS cm}^{-1}$  and cell voltage of  $1.6 \text{ V}$  (80% capacitance retention after 8000 cycles) [48] represent some advantages as compared to single iodide salts.

Aqueous electrolytes containing bromides have been also implemented [28, 49–52]. With a symmetric AC/AC cell containing  $1 \text{ mol L}^{-1}$  potassium bromide, the impact of the redox couple is present only at the upper edge of the potential range attained by the positive electrode (as in Figure 4d–f), due to the very high potential of the bromine redox couple (Table 1) compared to the cell  $E_0$ . Accordingly, the cell shows the characteristics of an EDLC up to  $1.6 \text{ V}$ , whereas an additional hump attributed to the redox activity of bromide species appears when the vertex voltage reaches  $1.7\text{--}1.9 \text{ V}$  [50]. Hence, a hybrid ca-

Figure 4

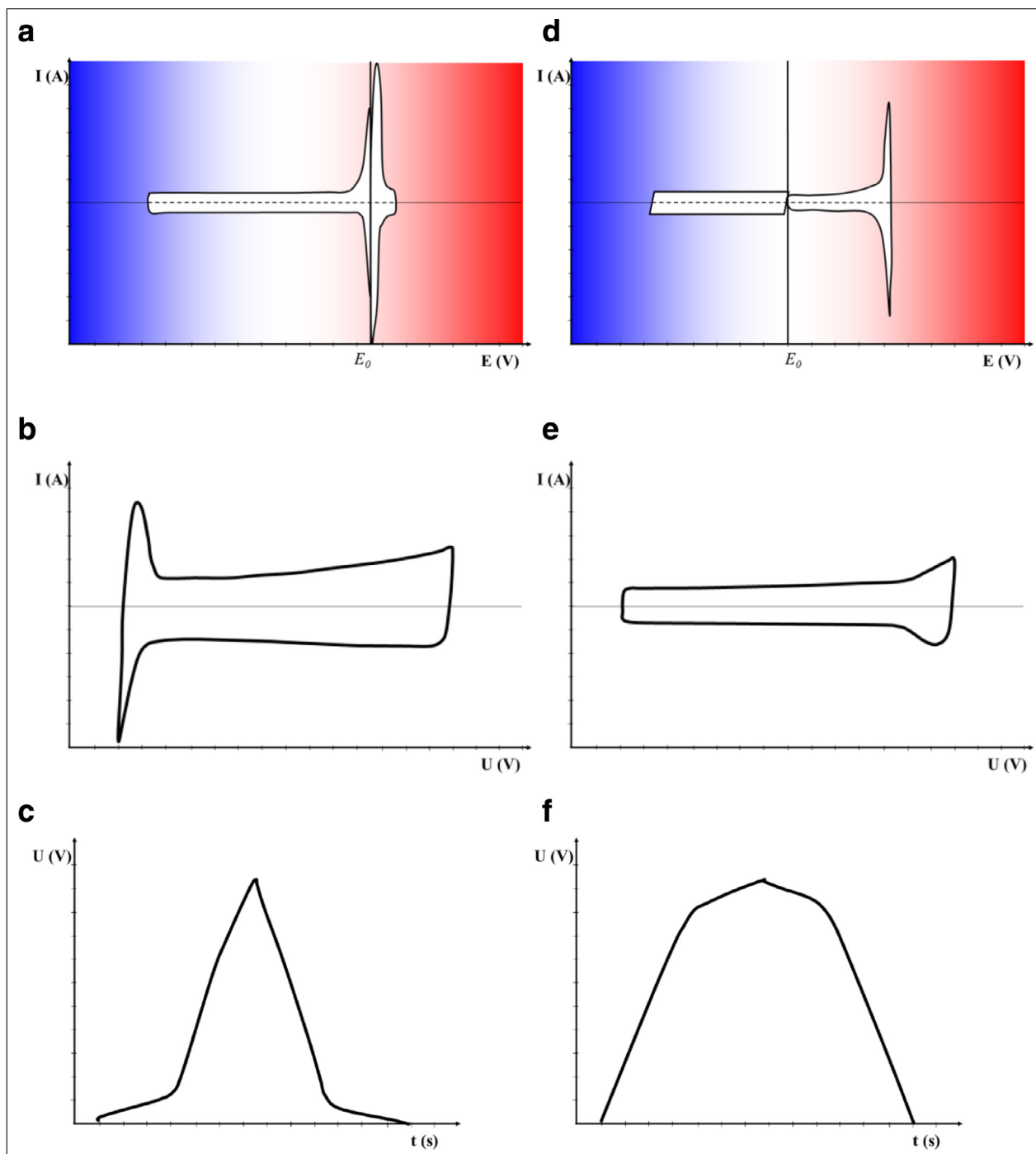


Illustration of cases where the value of cell  $E_0$  is very close to the redox potential of the active couple and consequently does not allow an ideal hybrid cell to be designed: cyclic voltammograms (CV) of electrodes in a two-electrode cell with reference, where the redox couple is (a) essentially active at potential slightly higher than  $E_0$ , but has also some activity below  $E_0$ ; (d) active at potential much higher than  $E_0$ ; (b), (c) and (e), (f) CV and galvanostatic characteristics of the two-electrode cells corresponding to the cases (a) and (d), respectively.

capacitor cannot be realized by the application of potassium bromide with identical AC electrodes.

Since diffusion of soluble redox couples is a recognized problem when using redox active electrolytes, aqueous mixtures of  $0.2 \text{ mol L}^{-1}$  1-ethyl-1-methylpyrrolidinium bromide (MEPyrBr) or tetrabutylammonium bromide (TBABr) with  $1 \text{ mol L}^{-1}$  KBr were implemented in AC/AC cell. Owing to the presence of MEPyrBr or TBABr,  $[\text{MEPyr}^+\cdot\text{Br}_3^-]$  oily or  $[\text{TBA}^+\cdot\text{Br}_3^-]$  solid phases are electrochemically generated, making these electroactive species confined in the electrode porosity [51•]. Consequently, asymmetric cells (i.e. four times higher mass of negative electrode to counterbalance the high capacity of the positive electrode) with such enhanced electrolytes showed limited shuttling of  $\text{Br}_3^-$  compared to cells based on neat  $1.2 \text{ mol L}^{-1}$  KBr, that was evidenced in the lower self-discharge rate. The capacitor with  $1 \text{ mol L}^{-1}$  KBr +  $0.2 \text{ mol L}^{-1}$  TBABr showed the more hybrid-like performance, where the cell GC/GD curves were close to linearity.

The ferricyanide/ferrocyanide redox couple based on the change of iron oxidation state was also investigated in AC/AC configuration (Table 1) [53•, 54]. Although the cells themselves do not fall within the hybrid capacitor classification (e.g., non-linear GC/GD characteristics) highlighted in this article, the reference [53•] addresses a very important issue of undesired redox species shuttling at the origin of cell self-discharge, and proposes to apply an ion exchange membrane as a solution. Such system displays a high cell voltage of 1.8 V with a high capacity enhancing the device energy.

Hybrid AC/AC cells have been also realized with organic electroactive molecules such as the benzoquinone/hydroquinone (Q/HQ) redox couple (Table 1) undergoing a proton-coupled electron transfer in acidic aqueous medium, making the positive electrode a battery-like one, whereas the negative electrode displays EDL charging (with some impact of hydrogen storage) [17•, 23, 46, 55]. However, due to the use of sulfuric acid, the cell voltage is at maximum 1.0 V, and expensive noble metal current collectors are required. In addition, as in the former case, an important self-discharge due to migration of the active species between the two electrodes is observed, and the self-discharge may be reduced by introducing an ion exchange membrane [46•]. The Q/HQ redox activity has been also demonstrated with more complex redox couples like dibromquinone/dibromohydroquinone [23, 56], as well as a benzoquinone isomer – catechol, itself [23] or within pyrocatechol violet [57].

### Ionic liquids and organic electrolytes

The organic counterparts of iodine and bromine salts were tested in ILs as electrolytes with enhanced elec-

trochemical stability. In comparison with aqueous media, a reversed situation is observed in the respective performance of iodide and bromide-based cells. The cells based on 1-ethyl-3-methylimidazolium iodide (EMIm I) with EMIm  $\text{BF}_4$  supporting electrolyte show the benefits of ILs (high voltage) and redox electrolyte (faradaic contribution), yet the electrochemical characteristics are not those of a hybrid capacitor. Indeed, due to the high voltage, the positive electrode operates beyond the iodine redox activity, hence through an EDL mechanism [58, 59]. In turn, owing to higher bromine redox potential, the AC/AC cell with EMIm Br in EMIm  $\text{BF}_4$  demonstrates the performance of a hybrid capacitor after initial voltage cutting [60••].

Similarly, benzoquinone in IL electrolyte (N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, BMPyr TFSI) exhibits redox properties, and it is assumed that the quinone dianion,  $\text{Q}^{2-}$ , is formed by reduction (Table 1). Despite a high initial energy, the cell galvanostatic characteristics are not linear and additionally the system shows a poor cycle life [61].

Apart from adding redox active species to ILs, an interesting and original approach is based on the design of a biredox IL consisting of perfluorosulfonate anion and methylimidazolium cation, which are functionalized with anthraquinone (AQ) and 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) moieties, respectively (Table 1). A combination of the biredox IL ( $0.5 \text{ mol L}^{-1}$ ) and a typical IL - 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm TFSI) – as supporting electrolyte allows the AC/AC cell to operate up to 2.8 V with enhanced energy [62]. However, such construction is beyond the EC or (in the foregoing introduced) HC design.

Another example is with ILs consisting of ferrocene (Table 1) tethered either to the ethylimidazolium cation or to the bis(trifluoromethanesulfonyl)imide anion (FcEMIm TFSI or EMIm FcTFSI, respectively). Due to the high melting point of these ILs, 80% solutions in acetonitrile were applied. Unlike using FcEMIm TFSI + EMIm TFSI, the AC/AC cell with EMIm FcTFSI + EMIm TFSI displays the galvanostatic characteristics of a hybrid capacitor, with almost doubled capacitance and enhanced energy as compared to a cell with non-functionalized analogue (EMIm TFSI), yet a disadvantage is a huge ohmic drop and higher cell self-discharge [63••].

### Essence and looking ahead

Redox-active electrolytes have stormed academic research on boosting ECs energy. The application of iodides into water medium has been proved to be a cost-effective and environmentally friendly approach to develop a new generation of high performance capacitors. Besides, the



development of electroactive ILs represents a synergetic strategy to enhance energy by both voltage and capacitance enhancement. Still, it is worth focusing on a large panel of redox-electrolytes in order to find conditions for turning the electrochemical cells into harmonized hybrid capacitors offering the most advantageous performance. Accordingly, the following criteria should be taken into account for further research in this domain: 1/ the electrodes should demonstrate well-differentiated charging mechanisms; 2/ the activity potential range of the redox couple should be as close as possible to the cell  $E_0$ ; 3/ the cell self-discharge should be prevented by confining the electroactive species in the pores of carbon or by finding a solution for preventing the ions shuttling without increase of cell resistance; 4/ and finally the capacitance (normalized to mass or volume) should be always calculated for cell to give realistic values and permit a correct comparison of various systems performance.

## Acknowledgments

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## Conflict of Interest

The authors declare no conflict of interest.

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Papers of particular interest, published within the period of review, have been highlighted as:

- Paper of special interest
- Paper of outstanding interest.

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