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Review Article

Hybrid electrochemical capacitors in aqueous electrolytes: Challenges and prospects

Horst Schrangner¹, Farshad Barzegar² and Qamar Abbas¹

Abstract

In an internal hybrid capacitor, at least one electrode displays battery-like charge/discharge and the other electrode stores charge reversibly at the electric double layer (EDL). Recently, a plethora of hybrid cells in aqueous electrolytes have been proposed by coupling an EDL electrode with a battery electrode, the latter made from a variety of redox-active/redox-mediator species either dissolved in the electrolyte or adsorbed/immobilized in nanoporous electrodes. This review presents current opinions, discusses challenges, and supplies recommendation about the hybrid cells with aqueous electrolytes and carbon electrodes.

Addresses

¹ Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010, Graz, Austria

² Electrical, Electronic and Computer Engineering Department, University of Pretoria, Pretoria, 0002, South Africa

Corresponding author: Abbas, Qamar (qamar.abbas@tugraz.at)

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Hybrid electrochemical capacitor, Battery-like electrode, Electric double layer, Aqueous electrolyte, Carbon material.

Introduction

Electrical energy storage systems are essential support in modern devices to ensure reliability and uninterrupted energy supply [1–3]. Electrochemical capacitors are adapted for systems where bursts of energy are stored and delivered in short periods of time, and the process is repeated for thousands of cycles [4–6]. The capacitance of an electrical double-layer capacitors (EDLCs) is dependent on the electrode/electrolyte interface represented by surface area ‘*S*’ in equation $C = \epsilon S/d$. Therefore, carbon with high surface area (up to $\sim 3500 \text{ m}^2 \text{ g}^{-1}$) is the preferred electrode material to achieve high values. Obviously, the cell capacitance of an

EDLC represents a low value which is half of the individual electrode capacitance ($1/C_{EDLC} = 1/C_- + 1/C_+$ and considering $C_+ \approx C_-$; $C_{EDLC} \approx 1/2 C_{-/+}$). To compensate for low capacitance, commercial capacitors implement organic electrolytes which enable reaching high voltage and improve the energy performance. Nevertheless, use of organic electrolytes raises environmental concerns regarding toxicity of solvents and cost issues due to the extensive drying of carbon electrodes.

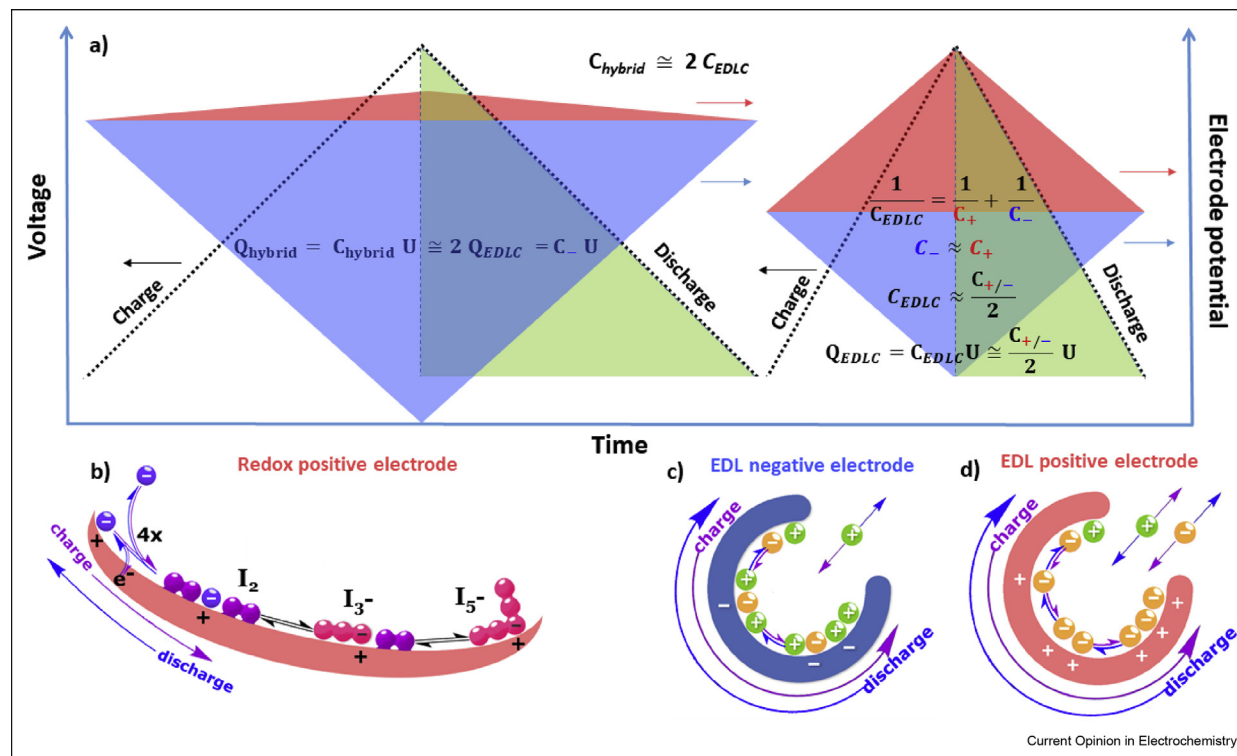
In this regard, aqueous electrolytes-based capacitors offer great opportunity owing to low assembling cost, eco-friendliness and reasonably large potential window [7–11]. Thanks to the universal property of water for dissolving salts, redox-active species can be easily mixed to prepare electrolytes with high ionic conductivity which favors fast redox reactions. Figure 1a shows the difference between the charge/discharge curves of an EDLC and a hybrid capacitor. In accordance with $E = 1/2 CU^2$, energy density of electrochemical capacitors in aqueous electrolytes can be enhanced by increasing capacitance or/and voltage, and an effective way to enhance capacitance is hybridization of battery-like electrodes with an EDL one [12,13]. Owing to almost constant potential of battery-like electrodes, the potential window of the EDL electrode during charge/discharge of the hybrid capacitor is approximately twice longer than in a symmetric EDLC, leading to approximately twice higher discharge capacity (Q_{hybrid}):

$$Q_{hybrid} = C_{hybrid}U \cong 2Q_{EDLC} = C_{-/+}U$$

Historically, hybrid capacitors are comprised of metal oxide-based redox electrodes coupled with nanoporous carbon-based EDL electrodes [14–17]. Razumov et al. [16] and Pell and Conway et al. [14] proposed hybrid capacitors using activated carbon as an EDL electrode with NiOOH/Ni(OH)₂ (alkaline media) or PbO₂/PbSO₄ (acidic media) as the battery-like electrode, and the key aspect in these devices has been the linear charge/discharge curves on a voltage–time scale. In the last decade, a number of hybrid capacitors have been proposed in acidic or basic media by dissolving redox species in the electrolyte or covalently bonding them at the carbon material to transform charging to a battery-

2 Energy Storage

Figure 1



(a) Schematic illustration of charge/discharge curves (dashed black lines) of a hybrid electrochemical capacitor and an electrical double-layer capacitor (EDLC) and charge/discharge curves of individual positive electrodes (red region) and negative electrodes (blue region). Green shaded area is the cell discharge region used for energy/capacitance estimation; simplified charging mechanisms (b) at battery electrode of hybrid electrochemical cell (iodide redox species), (c) negative electrode, and (d) positive electrode of an EDLC in a redox nonactive electrolyte. Q9

like electrode [18–26]. Hybrid capacitors have also been proposed in aqueous solutions of neutral pH as supporting electrolytes for redox-active halides to achieve extended cell voltage [27–31], among which iodide-based hybrid capacitors are of particular interest owing to redox potential being close to the cell equilibrium potential (potential at discharged state) and the charge transfer between iodides and nanoporous carbon electrode (Figure 1b).

EDL electrode charging mechanisms and enhanced cell voltage

Because the capacitance of a hybrid capacitor is controlled by the EDL electrode, understanding its charging mechanisms is important. Nanoporous carbons adsorb the partially desolvated ions electrostatically [32,33]. In situ electrochemical quartz crystal microbalance and in situ nuclear magnetic resonance applied for neat EMI-TFSI and EMI-TFSI in acetonitrile- and carbide-derived carbons with precise pore sizes [34–37] have shown linear relationship between charge and weight difference at negative polarization of carbon electrode, indicating a permselective (only cations) adsorption/desorption mechanism (Figure 1c). In addition, a larger slope than the theoretical one

proves adsorption of additional molecules at negative polarity, proportional to the charge of the electrode (3.7 solvent molecules per cation). Electrochemical dilatometry has also confirmed that cations carry additional solvent molecules into the carbon pores during negative charging with the relative strain increase from 3.4% to 4.2% after adding acetonitrile to the ionic liquid [38]. Charging mechanism at the positive polarization is mainly ion exchange, confirmed by in situ nuclear magnetic resonance with $\text{PEt}_4\text{-BF}_4$ ionic liquid [37]. Under positive polarization, a loss of mass due to the exchange of the heavier cations (147.2 g/mol) with the lighter anions (86.8 g/mol) confirms that the weight change depends on the molecular weight difference per charge of the cation and the anion. Ion exchange at positive polarity goes on until the depletion of cations, which is then dominated by adsorption of anions (Figure 1d). Prehal et al. have demonstrated with small-angle X-ray scattering the change of ion concentration inside carbon pores due to the local ion rearrangements in aqueous media [39,40], and the charging mechanisms are found to be dependent on the experimental condition, e.g., electrolyte concentration, charging rate, and cell design [41].

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Besides EDL charging, additional redox reactions at the negative electrode in aqueous electrolyte take place, e.g., reversible hydrogen adsorption/desorption. The simplified Nernst equation $E_H = -0.059 \text{ pH}$ suggests that reduction potential of aqueous electrolyte is determined by the pH of the electrolyte [9], and water reduction causes nascent hydrogen generation which chemisorbs within carbon pores [42]. In addition, the OH^- anions accumulate within carbon pores resulting in local pH shift [43]. The pH shift is significant for neutral electrolytes, while for acidic solutions, pH does not change during charging, as confirmed by comparing 1 mol L^{-1} Li_2SO_4 (pH = 6.5) and 1 mol L^{-1} BeSO_4 (pH = 2.1), where the reduction potential (E_H) differs significantly (-0.383 V vs SHE for Li_2SO_4 and -0.124 V vs SHE for BeSO_4) [9]. The dihydrogen evolution in Li_2SO_4 starts at ca. -0.8 V vs SHE , meaning an overpotential of ca. -0.42 V vs SHE is achievable, while for BeSO_4 , it starts at ca. -0.3 V vs SHE very close to the E_H , with less overpotential. The advantageous effects of aqueous electrolyte pH have been harnessed in bifunctional electrolytes either to enhance capacitance or to access large voltage for hybrid capacitors. Clearly, hydroquinone-based, methylene blue-based, and iodide-based hybrid cells have exhibited enhanced capacitance when assembled with acidic media H_2SO_4 [20,21,44], iodides with MnSO_4 (pH = 3.0) [45], or p-phenylenediamine (PPD) in aqueous KOH [26]. On the other hand, hybrid capacitors using bifunctional electrolytes with neutral solution acting as supporting electrolyte (pH = 6.5–7.0) exhibit enhanced voltage up to 1.5–1.6 V [29,46–48], and with concentrated 20 mol kg^{-1} NaTFSI + 0.8 mol kg^{-1} KI up to 1.8 V [49].

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Equilibrium potential and hybrid cell performance

The battery-like electrode in a hybrid cell works in narrow potential range, e.g., in bromine system, around the redox potential of $\text{Br}^-/\text{Br}_3^-$, which is $E^0 = 0.89 \text{ V vs. Ag/AgCl}$ [50]. However, the large potential window of positive electrodes to reach bromide redox potential implies the equilibrium potential or potential of zero charge must be lifted such that the positive electrode works in a small potential range and the negative electrode can go through a large potential window. Yamazaki et al. used 1% bromine water to preimpregnate the positive carbon electrode which worked in narrow potential window and the hybrid capacitor was discharged down to 0.5 V with improved capacitance and coulomb efficiency. Indeed, the adsorption of species on carbon decreases the redox potential by $\sim 0.1 \text{ V}$ [24]. Yoo et al. and Evanko et al. used phase change inside the pores to keep the redox species at the electrodes by implementing tertiary amines—complexing agents such as 1-ethyl-1-methylpyrrolidiniumbromide (MEPBr) producing second liquid phase [51,52]. TBABr (n-Bu₄NBr) [51] and HVBBr₂ (1,1'-diheptyl-[4,4'-bipyridine]-

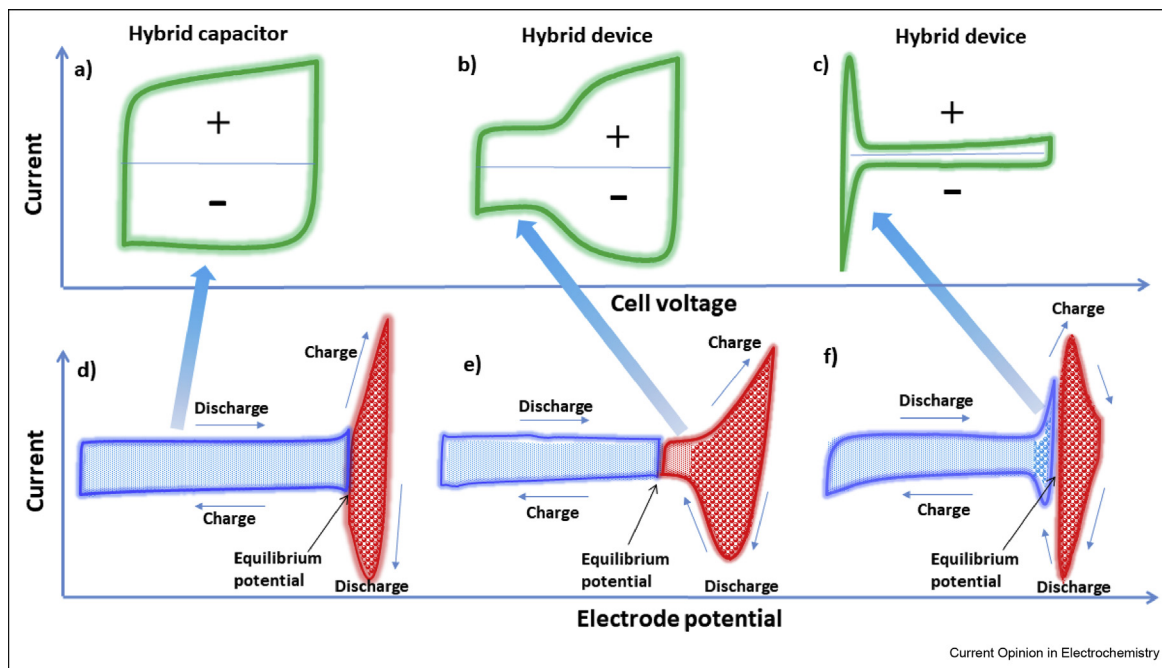
dibromide) were also used [52] to produce solid-phase TBABr₃ which is retained in the pores of carbon upon charging because of strong interaction of Br_3^- , improving cycling stability and slowing self-discharge.

In contrast to bromides, equilibrium potential of hybrid cell in aqueous iodides is close to the redox-active potential region (Figure 2a,d), which makes the cell an almost-perfect hybrid capacitor with linear charge/discharge curves [18,29]. Although hybrid capacitor with 0.08 M KI + H_2SO_4 exhibited twice higher capacitance than a symmetric one with H_2SO_4 [21], the issue of low voltage in these systems was only resolved by using bifunctional aqueous KI + Li_2SO_4 which worked at 1.6 V and exhibited capacitance comparable with the organic electrolyte-based EDLC charged up to 2.5 V [29]. Carbon electrodes in hybrid capacitors with asymmetric configuration improved long-term performance owing to better iodide immobilization in mesoporous positive electrodes and enhanced EDL capacitance of microporous negative electrodes [47]. Lately, a hybrid capacitor showing high capacitance of 50 F g^{-1} at 1.5 V and -40°C was realized with choline cation-based electrolyte (choline nitrate + choline iodide) [53]. Similar to the strategy of Yamazaki et al. with bromide system, shuttling of iodides was prevented by electrochemically immobilizing them in the nanopores of carbon which was then used as a positive battery-like electrode in neat NaNO_3 aqueous electrolyte [54]. Such approach is well justified as iodides adsorb deep in the nanopores [55], which is confirmed also by the gas adsorption analysis on the floated/cycled carbon electrode [45,56]. Redox potential of iodides located close to equilibrium potential also requires careful selection of operation parameters (Figure 2b,e & 2c,f) where a slight capacity imbalance of electrodes may drive negative electrode to work in the iodide-redox region, which could hamper the hybrid cell performance [57]; this can be avoided with a voltage cut at appropriate values [58].

Hydroquinone dissolved in H_2SO_4 makes good redox-active electrolyte for hybrid capacitors to achieve high capacitance [20]; however, the self-discharge and the loss of capacitance during cycling is quite high [19]. To improve cycling characteristics, ion-exchange membranes were used [22] or the carbon electrode grafted with quinones was implemented [23]; the latter strategy results in strong covalent bonding between quinones and carbon which prevents shuttling. Composite of anthraquinone with reduced graphene oxide and carbons with quinone functionalities have demonstrated enhanced capacitance as electrode materials [59–61]. Hybrid device based on LiMn_2O_4 as a positive electrode and anthraquinone-modified carbon as a negative electrode in 1 mol L^{-1} Li_2SO_4 is a good strategy to enhance energy and power parameters [62], and determining correct amount of anthraquinone loading on carbon

4 Energy Storage

Figure 2



Shift of equilibrium potential (potential of electrodes at zero voltage) leading to changed electrochemical charge/discharge. Cyclic voltammograms in two-electrode cell (upper panels) and two-electrode cell with reference electrode (lower panels) for hybrid capacitor (a,d) and two cases of a hybrid device which is as a result of equilibrium potential shift away (b,e) or toward (c, f) the redox potential of active iodide species. An imbalance of relative capacities of electrodes due to net charge difference during hybrid cell operation leads to equilibrium potential shift [58].

appears to be key for achieving optimized performance [63]. Redox activity of PPD in aqueous KOH greatly enhances the delivered capacitance of the hybrid cell [26], and high self-discharge in PPD-based cells could be solved by its covalent bonding to carbon surface [64].

Q7 Polyoxometalate-based redox species as part of electrode or electrolyte gave high capacitance owing to redox reactions which can be useful for improving hybrid capacitance [65–68]. Ferricyanide/ferrocyanide redox couple showed promising results in neutral aqueous electrolyte-based hybrid capacitors up to 1.8 V, and the diffusion of redox species was prevented with ion-exchange membranes [28].

Energy/capacitance metrics for hybrid capacitors

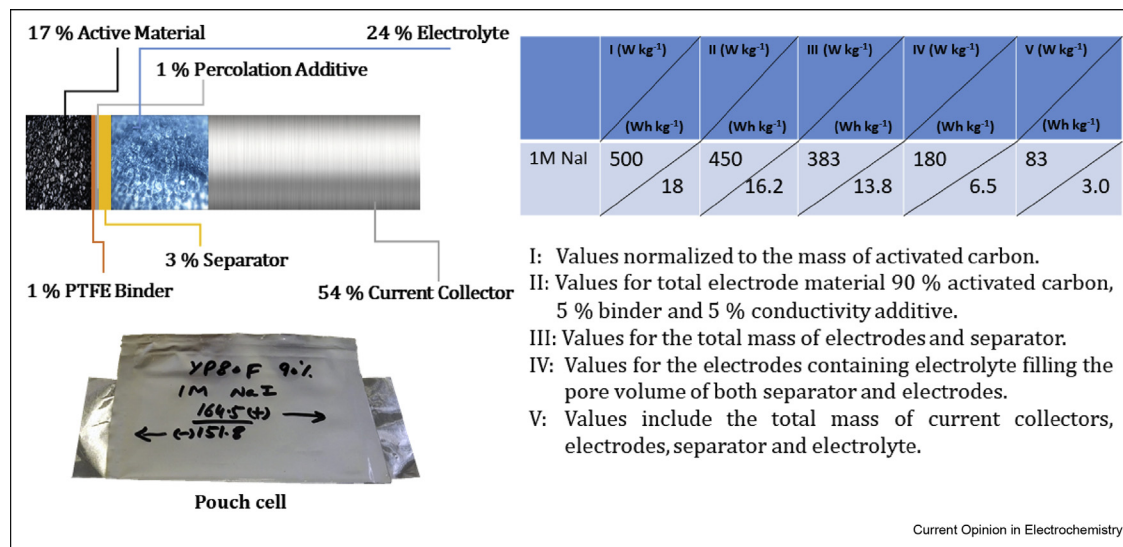
Capacitance in hybrid electrochemical capacitors must be calculated from total stored energy (area under discharge curve) [69–71]. Energy efficiency can be calculated from the ratio of charge and discharge surface. Moreover, the mass of electrolyte should be taken into account while performing calculations [31,72], and for highly concentrated electrolytes (e.g., 20 mol kg⁻¹ LiTFSI), the mass contribution of electrolyte could be even higher. Figure 3 shows the percentage contribution

of each component to the total mass of an electrochemical capacitor. Energy values obtained by constant power test in Figure 3 are given for hybrid capacitor in 1 mol L⁻¹ sodium iodide, normalized with mass of various cell components. High mass contribution from a current collector could be reduced by finding alternatives with lower density than stainless steel, e.g., surface-treated aluminum or aluminum alloys [73].

Temperature window for hybrid capacitors with aqueous electrolytes

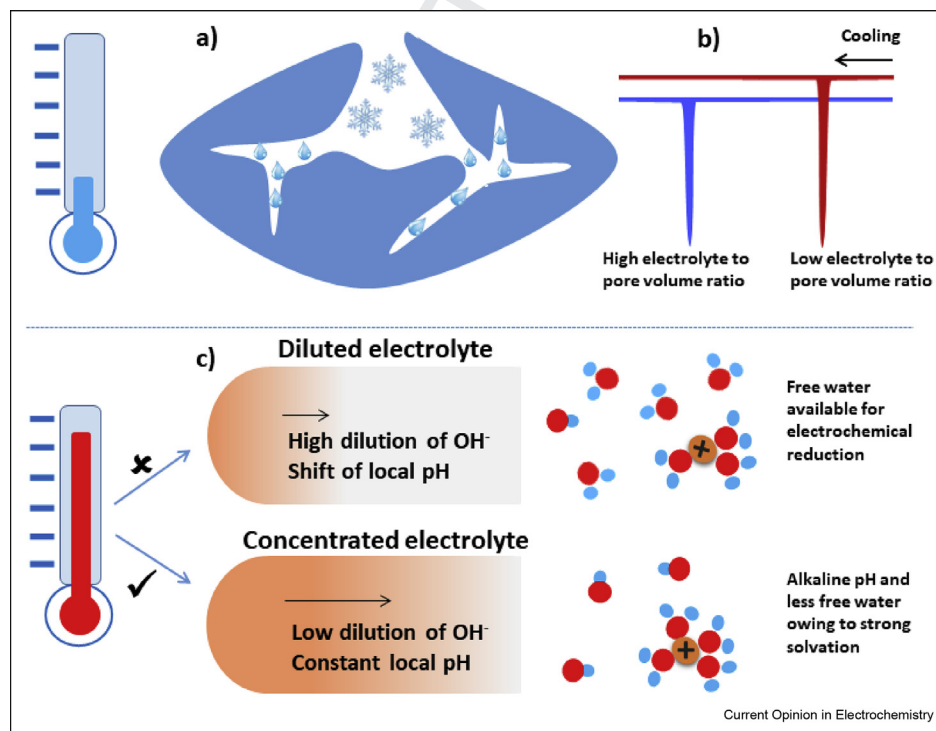
For neutral aqueous electrolytes-based capacitors, freezing at ca. -10 °C and enhanced electrochemical reactions due to water oxidation and reduction at high temperature restrict their application spectrum. Additives such as methanol [74] and ethylene glycol [75] improve the capacitor performance down to low temperatures. However, the preferential adsorption of alcohols in carbon porosity [74] modifies the local electrolyte composition in carbon nanopores resulting in performance fade down to low temperature (Figure 4a and b). Recently, capacitors using aqueous choline chloride at 5 mol kg⁻¹ demonstrated excellent performance down to -40 °C [76] because of eutectic-like character of the electrolyte (choline chloride

Figure 3



Mass percentage of electrochemical capacitor components and specific energy values calculated for a carbon/carbon hybrid capacitor with NaI (1 mol L^{-1}) by constant power test ($1.4 \text{ V} - 0.7 \text{ V}$, 0.1 A g^{-1}). Thickness of separator, $30 \mu\text{m}$; thickness and density of current collector, $10 \mu\text{m}$ and 7.9 g cm^{-3} , respectively; carbon specific pore volume, $1.01 \text{ cm}^3 \text{ g}^{-1}$.

Figure 4



Low temperature (upper panel) and high temperature (lower panel) for carbon electrode- and aqueous electrolyte-based systems. **(a)** Freezing behavior of the water-based electrolyte under confinement in nanoporous carbon, the presence of micropores favors the lowering of melting/freezing temperature [77,78], while the water crystallizes at relatively high temperatures in mesopores. **(b)** Increasing the ratio of water-/methanol-based electrolyte volume to carbon electrode pore volume decreases freezing temperature [74]. **(c)** Low concentration of the electrolyte provokes the electrochemical reduction of water due to high fraction of free water molecules, while electrochemical water reduction in concentrated electrolytes is suppressed and the local pH is almost constant, favoring both high cell voltage [79] and high temperature reach.

6 Energy Storage

$t_m = 302\text{ }^\circ\text{C}$, $\text{H}_2\text{O } t_m = 0\text{ }^\circ\text{C}$, the resulting binary mixture at $5\text{ mol kg}^{-1} t_m = -60\text{ }^\circ\text{C}$).

The hybrid capacitor containing 5 mol kg^{-1} choline nitrate + 0.5 mol kg^{-1} choline iodide in water was able to operate down to $-40\text{ }^\circ\text{C}$ with excellent performance of $\sim 50\text{ F g}^{-1}$ at $-40\text{ }^\circ\text{C}$ and reach the power performance of organic electrolyte-based EDLC at low temperatures [53]. For aqueous capacitors working at high temperature, concentrated electrolytes could be useful owing to low amount of free water (Figure 4c). In concentrated electrolytes, most of the water is used in solvation of ionic species; less free water molecules mean less electrochemical reduction of water and related hydrogen gas production. In addition, increased local pH inside the nanopores of carbon electrode favors high overpotential [79].

Conclusion and recommendations

- 1) Nanoporous carbon-based electrodes accommodate well the solid phase that prevents diffusion of redox-active species. As solid phase tends to dissolve in acidic/alkaline media, neutral aqueous solutions are recommended in the form of *bifunctional* electrolytes for hybrid capacitors.
- 2) Equilibrium potential can be adjusted close to the redox potential by appropriate balancing of electrodes capacities, e.g., mass balancing; hence, better cell engineering is key to design hybrid capacitors.
- 3) For better power handling, carbon materials with high surface area and developed microstructure should be used for efficient EDL electrodes.
- 4) True performance metrics can be presented by taking into account the mass/volume of each cell component and particularly the electrolyte.
- 5) Choline cation and nitrates/chloride anions greatly differ in hydration strength; these electrolytes with eutectic-like properties could be tuned further to achieve wide temperature window for hybrid capacitors.

Conflict of interest statement

Nothing declared.

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8 Energy Storage

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