



# Strategies for enhancing the performance of carbon/carbon supercapacitors in aqueous electrolytes



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## ABSTRACT

Presented paper describes and critically comments major recent strategies for improving electrochemical capacitor performance. Particularly, carbon based electrodes and aqueous electrolytes have been considered. A novel concept of redox active electrolytes as a source of pseudocapacitance effect as well as profits and cons of such system have been discussed. The electrochemical performance of capacitor operating in such electrolyte solution is reported. Furthermore, some advantageous features of bio-inspired system based on bromine-cerium solution acting as oscillator are also presented.

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## 1. Introduction

Electrochemical capacitors are recently considered as systems for fast and efficient energy storage because of their good cyclability, high power rates and relatively low price [1–3]. Unfortunately, unlike batteries, supercapacitors suffer from moderate specific energy [4], hence, there are a lot of efforts devoted to improve this feature. Taking into account that the energy of electrochemical capacitor is proportional to accumulated charge  $q$  or capacitance value  $C$  and operational voltage  $U$  in square [5] one may easily conclude that the enhancement of energy performance has to be realized by capacitance or preferably voltage increase [6].

Capacitance of electrochemical capacitor is based on electrostatic attraction of ions at the electrode/electrolyte interface dependent mainly on the surface area  $A$  accessible for ion adsorption [7–11] as described by formula:

$$C = \frac{\epsilon_r \cdot \epsilon_0 \cdot A}{d} \quad (1)$$

where  $\epsilon_r$  is relative permittivity of considered medium,  $\epsilon_0$  is the permittivity of the 'free' space between the capacitor plates (basically attributed to the value for vacuum,  $8.9 \cdot 10^{-12} \text{ F m}^{-1}$ ) and  $d$  is the thickness of electrical double layer. Hence, materials with high specific surface area with suitable porosity like

activated carbons in their various forms [12–15] have been accepted as fundamental electrode materials for electrochemical capacitors. Unfortunately, even with specific surface area of  $2000 \text{ m}^2 \text{ g}^{-1}$ , these materials cannot provide real capacitance higher than  $150\text{--}200 \text{ F g}^{-1}$  [12,15] related with ion size and screening effect of the pore walls, which is widely discussed elsewhere [16,17]. Additional charge considered as so called pseudocapacitance might be provided by faradaic reactions occurring in the system upon charging/discharging process. Usually, pseudocapacitive properties are attributed to electrode materials undergoing redox process during polarisation like transition metal oxides [18,19], electrically conducting polymers [20–23], transition metal nitrides [24,25] or carbon materials enriched by heteroatoms such as oxygen or nitrogen [26,27] where the pseudocapacitance originates from faradaic reactions of functional groups present on carbon surface accessible for protic electrolyte [28]. The major disadvantage of the pseudocapacitive system is the redox-dependent solid state kinetics, aggravating power performance and cycle life.

Especially in case of conducting polymers, where the charge is accumulated through the volume of the whole material, specific power is deteriorated. They can be doped and de-doped in the n/p-type polymer configuration, such as p- and n-dopable poly(3-arylthiophene), p-doped poly(pyrrole), poly(3-methylthiophene) or poly(1,5-diaminoanthraquinone). Thus, the reversible faradaic reactions (revealed as single peaks) can be utilized as a source of additional capacitance but such type of current response is typical for battery-like systems where increase of capacitance occurs only in a narrow voltage range. Completely different behaviour is

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observed for some transition metal oxides, such as RuO<sub>2</sub>, MnO<sub>2</sub> where high capacitance values are observed in the whole voltage range.

Electrochemical deposition of polymer on the surface of carbon seems to be the best way to obtain satisfying results in terms of capacitance enhancement. Unfortunately, doping and dedoping process has a strong influence on the shape of electrode because of changes of the volume during cycling. It is the main bottle-neck of this kind of material, furthermore, leading to its degradation by shrinking, swelling and cracking, hence, it aggravates the conductivity and strongly limits the cyclability [2,29–31].

Transition metal nitrides due to their physical and chemical properties, e.g. low electrical resistivity, seem to be another good candidates for capacitance enhancement in supercapacitors. One of the most known and widely investigated material is vanadium nitride (VN) [25]. Well described synthesis of other nitrides, such as titanium nitride (TiN) [32], niobium nitride (NbN) and tantalum nitride (TaN) [33] allows to use them in supercapacitor applications. It is worth to note that the full advantage of using transition metal nitrides can be obtained only by quite complicated preparation methods of the electrode (comparing to activated carbon electrodes). It means that MeN should be mixed with carbon material and very thin film of composite needs to be deposited on glass, silicon substrate or nickel disc to avoid resistive behaviour, particularly when it is covered by layer of metal oxide, which has a poor conductivity ( $\sigma_{\text{bulk}} \approx 1 \sim 10^{-4} \Omega^{-1} \text{m}^{-1}$ ) but can give additional contribution of faradaic reactions due to different oxidation states [2,34,35]. Additionally, there is no need for using corrosion resistive current collectors because they operate in alkaline medium.

On the other hand, a novel approach for pseudocapacitance phenomena was invented by exploiting electroactive species like iodide/iodine/iodate moieties [36,37] coming directly from electrolyte and giving tremendous capacitance for positive electrode. Iodide-based system was further improved by combining electroactivity of iodides with vanadium species [38]; both redox couples were conjugated in one cell, separated by Nafion® 117 membrane, giving high capacitance values and moderate specific power. Recently, redox activity of other species such as hydroquinone have been investigated and reported [39,40]. The work concerning redox activity of substituted benzenes performed by our research group demonstrated strong influence of hydroxyl group substitution as well as electrolyte pH on their electrochemical activity and final capacitance values [41]. It is not yet fully confirmed but additional capacitance in case of hydroquinone might be explained not only by faradaic reactions taking place directly in electrolyte solution but also as a consequence of grafting process. During electrochemical polarization, hydroquinone dissolved in acidic medium (with presence of protons) behaves as a redox active electrolyte and can generate functional groups on the surface of carbon electrode, able to undergo reversible redox reactions. It is a great advantage over pseudocapacitance received directly from the electrode material because the influence of poor diffusion and electrolyte penetration into electrode structure are significantly reduced. This method is also more convenient than chemical generation of electroactive groups on the electrode surface, e.g., during synthesis of electrode material. Furthermore, redox response (reversible peaks) can be also observed in alkaline medium because of strong intramolecular hydrogen-bonding interactions between the quinone and the hydroxyl groups. In neutral electrolyte (pH=7) there is no redox activity because of balance between protons and hydroxyl groups.

Apart from typical electroactivity of the species present in the electrolytic solution, hydrogen electrosorption on negative carbon electrode [42,43] might result in capacitance enhancement. However, the contribution of this process appears to be significant rather at mild current regimes [44,45]. It is worth noting that hydrogen

electrosorption might play also an important role in terms of operational voltage widening in aqueous solutions; this issue will be discussed later in the manuscript.

Aforementioned issues were related with capacitance enhancement. As it was mentioned, the energy density of capacitor depends also on the operational voltage of the device. This feature is related with applied electrolyte. Aqueous systems (solutions of 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, 6 mol L<sup>-1</sup> KOH, 1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, etc.) have the thermodynamic limit of 1.23 V, given by water decomposition process, but their great advantage over other electrolytes (organic, ionic liquids) is their high conductivity resulting in high power density (principal property of supercapacitors), usually higher capacitance values and relatively low cost because of less-demanding assembling process. However, recent works in this field demonstrated that the barrier of water decomposition could be overcome in neutral electrolyte, especially in 1 mol L<sup>-1</sup> Li<sub>2</sub>SO<sub>4</sub> either by strong solvation effect of SO<sub>4</sub><sup>2-</sup> anions or Li<sup>+</sup> cations [46], hydrogen electrosorption on negative electrode [47] or mass balancing of the electrodes with unequal capacitances [48] resulting in capacitor voltage up to 2.2 V. To date, there is no full agreement concerning the origin of observed phenomenon as the experimental conditions and examination protocols were slightly different in referred papers. The strong influence of electrode material on the electrolyte decomposition voltage cannot be neglected as well. Hence, to achieve such extraordinary results for that kind of aqueous electrolyte, it is necessary to use microporous activated carbon with significant contribution of mesopores; they play a role of channels for big, slow and strongly solvated ions during their transport to micropores where charge accumulation process takes place. As expected, other carbon materials do not demonstrate such specific properties when operating in lithium sulphate aqueous solution, probably because of not suitable porosity (micropores/mesopores ratio).

Application of organic electrolytes might result in maximum voltage as high as 3.0 V. Obviously, taking into account energy dependence on the capacitor voltage, this is a great advantage of organic electrolytes. The most commonly used solvents are acetonitrile and propylene carbonate [49–51]. Acetonitrile is more often used because it can dissolve larger amounts of salts than other solvents; unfortunately, it suffers from environmental and toxic problems. Propylene carbonate-based electrolytes are more environmental friendly and demonstrate a wider electrochemical window, an extended range of operating temperature and good conductivity. As a source of ions, organic salts such as tetraethylammonium tetrafluoroborate, tetraethylphosphonium tetrafluoroborate, and triethylmethylammonium tetrafluoroborate (TEMABF<sub>4</sub>) have been reported as commonly used for organic electrolytes. Regarding their properties, it is well known that compounds with less symmetric structure are characterized by lower crystal-lattice energy and increased solubility. Unfortunately, the water content in organic electrolytes have to be maintained below 5 ppm, otherwise, the voltage will be remarkably reduced.

Apart from organic salts dissolved in acetonitrile or propylene carbonate, ionic liquids, composed only of ions play a significant role as electrolytes for high-voltage capacitors. Low vapour pressure, high thermal and chemical stability, low flammability, wide electrochemical window ranging from 2 to 5 V, typically about 4.5 V, as well as conductivity at the level of 10 mS cm<sup>-1</sup> [52,53] make them promising alternative for conventional electrolytes [54]. The main ionic liquids considered for capacitor applications are based on imidazolium, pyrrolidinium cations and asymmetric, aliphatic quaternary ammonium salts with anions such as tetrafluoroborate, trifluoromethanesulfonate, bis(trifluoromethanesulfonyl)imide, bis(fluorosulfonyl)imide or hexafluorophosphate [55]. Quaternary ammonium salts such as tetralkylammonium [R<sub>4</sub>N]<sup>+</sup> and cyclic amines such as aromatic pyridinium, imidazolium and saturated piperidinium,

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