



# Effect of benzoquinone additives on the performance of symmetric carbon/carbon capacitors – electrochemical impedance study



Mikołaj Meller, Krzysztof Fic\*

Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Berdychowo 4, 60965 Poznan, Poland

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## ABSTRACT

This paper reports on the electrochemical performance of symmetric carbon/carbon electrochemical capacitors operating in aqueous electrolytic solutions with various benzoquinones as a source of pseudocapacitance. The benzoquinones have been introduced for the enhancement of capacitance values and the energy density in the final device. Three isomers, namely hydroquinone, catechol and resorcinol as electrolyte modifiers displayed different electrochemical activity in acidic electrolyte, affecting final electrochemical performance of the capacitors subjected to investigations. Furthermore, the paper demonstrates the electrochemical impedance spectroscopy as a powerful technique for electrochemical capacitor characterization and discusses the potential risk of the overestimation of the data recorded.

## 1. Introduction

Nowadays, electrochemical capacitors became one of the most interesting and promising energy storage devices. Quite often, these devices are called supercapacitors (SCs) or electric double-layer capacitors (EDLCs) due to their properties, performance and the principle way of charge accumulation [1–3]. Because this process is based on electrostatic attractions and takes place at the electrode/electrolyte interface (electrical double-layer), EDLCs can be charged and discharged very quickly, even in a few seconds [4]. Moreover, due to electrostatic nature, i.e., no changes in the structure of the electrode material (dendrites, shrinking) occur. That feature impacts essentially on their cycle life reaching 1 000 000 of cycles. Although the charge accumulation process does not involve (in fact, by definition only) any chemical processes, the performance fade during cycling is observed [5,6] and is assumed to be caused either by specific interactions between the ions and electrode surface or degradation of the electrodes operating at elevated voltages [7–15].

Activated carbons (ACs) appear to be the most suitable electrode materials for electrochemical capacitors [16], mainly for the sake of their very well developed specific surface area ( $> 2000 \text{ m}^2 \text{ g}^{-1}$ ), according to following formula:

$$C = \epsilon S/d,$$

where  $C$  stands for capacitance, proportional to the surface area  $S$  of the electrode material and the relative permittivity of the solution  $\epsilon$  but reciprocally dependent on the thickness  $d$  of the double layer [17].

Therefore, the role of the electrolytic solution should not be neglected, since the thickness of the electric double-layer will be influenced by the ion size. It is also worth noting that activated carbons are excellent and almost irreplaceable materials, especially taking into account their low cost and excellent cycle life [16,18–20]. Furthermore, their versatile properties might be adjusted at the synthesis level, hence, a perfect matching between ion size and pore width might be achieved, ensuring good charge propagation.

All these factors and properties make electrochemical capacitors capable of providing the peak of power in a very short time for many cycles [3]. Therefore, they can be applied in vehicles (start-stop systems, improved acceleration, regenerative braking), pulse power, backup source or even in portable devices, such as digital cameras – e.g. while the flash for snapshot is being used [21]. However, ECs are characterized by moderate energy density (or specific energy), which is considered as their major disadvantage if compared with conventional batteries [2]. Therefore, a lot of efforts is focused on the performance enhancement in order to stimulate their wider commercial use. Notwithstanding, one should be aware, that electrochemical capacitors are the technology which is considered for high-power applications and there is no doubt that for high-energy demands, batteries will always be a primary solution. However, electrochemical capacitors might be considered as reliable and complementary technology, with the protective role for batteries, prolonging their cycle life.

Charging and discharging of the electrical double-layer is not the only way for charge accumulation in electrochemical capacitors. Except for electrostatic forces, there is also the possibility to provide additional

\* Corresponding author.

E-mail address: [krzysztof.fic@put.poznan.pl](mailto:krzysztof.fic@put.poznan.pl) (K. Fic).

charge by involving Faradaic reactions to achieve higher capacitance values. Reversible redox reactions of pseudocapacitive materials, such as transition metal oxides ( $\text{MnO}_2$ ,  $\text{RuO}_2$ ,  $\text{InO}_2$ ,  $\text{MoO}_3$ ,  $\text{NiO}$  and  $\text{Co}_2\text{O}_3$ ) [22–28], metal nitrides [29–31] or conducting polymers [32,33] have been widely investigated to date. Composites of conducting polymers with various carbon-based materials [33–44] and metal oxides, hydroxides or organic additives [45–47] have been reported as rational approach for advanced electrode materials with improved capacitance and cycle life. Thin films of metal oxides, like  $\text{Fe}_3\text{O}_4$  have also been reported in literature as promising electrode materials with improved, redox-based capacitance in neutral (1 M KCl) and alkaline (1 M KOH) electrolyte [48]. Nonetheless, one should be aware, that incorporation of redox-based process into charge storage phenomenon always have a detrimental effect on the power response. Furthermore, it has been recently claimed that pseudocapacitance is very often confused with typical redox response and only Mn- and Ru-based compounds should be considered as typical pseudocapacitive materials [49–51]. The main drawbacks of the pseudocapacitive materials are poor diffusion and slow solid-state kinetics. Therefore, the idea of using electrolyte solutions (so-called redox active electrolytes) as a source of additional capacitance might be considered as a promising one [52]. Initially, iodide/iodine redox couple has been introduced as a source of the pseudocapacitance in symmetric carbon/carbon capacitors [53,54]. Afterwards, other redox couples, based on bromine or thiocyanides [55–57] or organic molecules have been reported as interesting approach for capacitance and energy enhancement [18,58–60]. A comprehensive overview of redox-active electrolytes for electrochemical capacitors might be found elsewhere [61–64].

Another way for capacitance enhancement exploits the additives to the electrolytic solution capable of reaction with carbon material and generating new functional groups on the electrode surface during the so-called grafting process. Primary, this process has been introduced to electrochemical capacitors by Belanger et al. [4,65] by using the diazonium chemistry for modification of the carbon powder surface. To date, this subject is studied very intensely and is recognized as an interesting research direction on the electrochemical capacitors field. Several studies have focused on the carbon electrode modification by introducing quinone additives to the major electrolytic solution. Owing to reversible reactions of quinone/hydroquinone (Q/HQ) redox couple, high capacitance values were obtained. Group of Silvia Roldán has investigated that phenomenon and received interesting results. By introducing electrochemically active compound, i.e. hydroquinone (Q/HQ) into the main electrolyte (aqueous solution of  $\text{H}_2\text{SO}_4$ ) they were capable of attaining tremendous specific capacitance value equal to  $5017 \text{ F g}^{-1}$  (by the ‘anode’) and  $477 \text{ F g}^{-1}$  (by the ‘cathode’) [18,59]. It has to be noted here that the term ‘anode’ and ‘cathode’ should not be considered directly as far as electrochemical capacitors are of the major concern. It has to be stated that the electrochemical capacitors community agreed to use ‘positive’ and ‘negative’ electrode since the typical nomenclature taken from redox chemistry might be misleading. Diazonium chemistry has been further developed by others, and promising results have been thus reported. Indigo carmine (IC), applied as additive for sulfuric acid as electrolyte for multiwalled carbon nanotubes (MWCNTs) as electrode materials allowed to obtain higher capacitance comparing to sulfuric acid (increased from  $20 \text{ F g}^{-1}$  to  $50 \text{ F g}^{-1}$ ) but showed moderate cycling performance (30% of capacitance decay after 10 000 cycles) due to redox activity fading of the indigo carmine [58]. Different approach was presented by Peter Pickup’s group. Their idea was to combine two modified electrodes as an asymmetric capacitor, where anthraquinone (C-AQ) was used as a source of redox reactions at the negative electrode, whereas 1,2-dihydroxybenzene (C-DHB) at the positive one. The C-AQ/C-DHB was characterized by the energy density almost two times higher than the device assembled with unmodified carbon [66].

The major purpose of this paper is to study the behavior of the electrochemical capacitor operating with different electrolytes by using

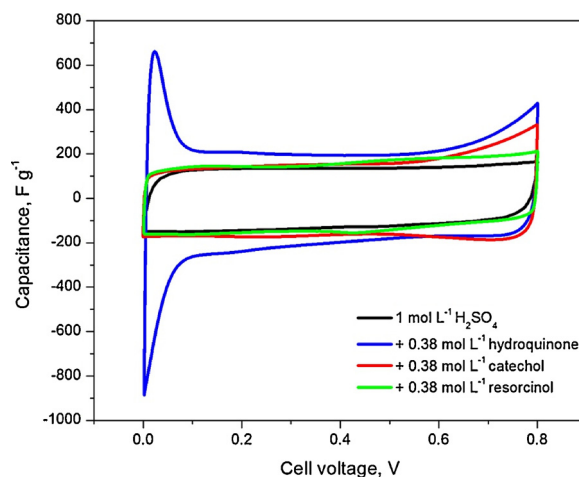


Fig. 1. Cyclic voltammograms for capacitors operating in  $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  solution with different dihydroxybenzenes. Current response has been re-calculated prior to the scan rate ( $5 \text{ mV s}^{-1}$ ).

electrochemical impedance spectroscopy. This technique might help in determination of the contribution of faradaic reaction in total capacitance. The primary electrolyte was sulfuric acid, further modified by various dihydroxybenzenes with the different substitution of  $-\text{OH}$  group, such as 1,2-dihydroxybenzene, 1,3-dihydroxybenzene and 1,4-dihydroxybenzene, used as redox-active additives (source of pseudocapacitance). The aim was to observe the influence of  $-\text{OH}$  group location on the capacitor performance. Another purpose of this paper is to demonstrate that electrochemical impedance spectroscopy is an extremely powerful technique for determination of the electrochemical performance of the electrochemical capacitors but requires very careful analysis and understanding of the data recorded, since the measurement is quite easy with modern equipment, but the conclusions might be very misleading.

## 2. Experimental

Each electrode consisted of 85 wt.% of activated carbon, 10 wt.% of polyvinylidene fluoride (PVDF Kynar Flex) and 5 wt.% of acetylene black. More detailed information about investigated activated carbon can be found elsewhere [67]. Briefly, commercial carbon Norit<sup>®</sup> XS32 was activated by KOH (1:4) giving microporous material with surface area of  $1400 \text{ m}^2 \text{ g}^{-1}$ , micropore volume of  $0.96 \text{ cm}^3 \text{ g}^{-1}$  and average micropore width 1.36 nm. The carbon and oxygen content were estimated by Thermo Programmed Desorption at the level 94%<sub>wt</sub> and 5%<sub>wt</sub>, respectively. Electrodes were prepared in the form of pressed pellets (7–10 mg) with a geometric surface area of  $0.785 \text{ cm}^2$  per electrode and thickness about 0.3 mm. 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol) and 1,4-dihydroxybenzene (hydroquinone) were purchased from Sigma Aldrich. Investigated electrolytes were prepared by mixing  $1 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  with catechol, resorcinol, and hydroquinone at the concentration of  $0.38 \text{ mol L}^{-1}$ . This concentration has been estimated to be an optimal one for all the compounds; this allowed us to ensure the same concentration of the redox specimen in all electrolytic solutions.

Electrochemical experiments were carried out in two- and three-electrode cells (Swagelok<sup>®</sup> system) and investigated by using several electrochemical techniques: cyclic voltammetry ( $1\text{--}50 \text{ mV s}^{-1}$ ), constant current charging/discharging ( $0.5$  and  $1 \text{ A g}^{-1}$ ), electrochemical impedance spectroscopy and staircase potentiostatic electrochemical impedance spectroscopy in frequency range  $100 \text{ kHz}\text{--}1 \text{ MHz}$  and voltage/potential amplitude  $\pm 5 \text{ mV}$ . The maximum operating voltage for all capacitors was limited to 0.8 V. The capacitance values have been expressed per single electrode.

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