

Electronic Supplementary Information

Self-discharge of electrochemical capacitors based on soluble or grafted quinone

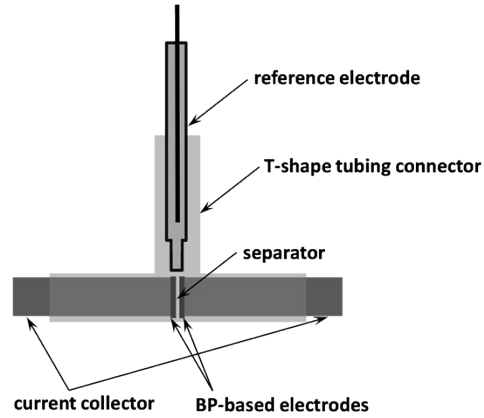
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1. Schematic drawing of the electrochemical cell



Scheme S11. Schematic drawing of the T-shape three-electrode configuration cell.

2. Estimation of the redox potential of the benzoquinone/hydroquinone couple ($E_{BQ/HQ}$)

$$\begin{aligned}
 E_{BQ/HQ} &= E^0 + \frac{0.059}{2} \log \frac{a_{BQ} [H^+]^2}{a_{HQ}} = E^0 + \frac{0.059}{2} \log \frac{a_{BQ}}{a_{HQ}} - 0.059 pH = E^0 + \frac{0.059}{2} \log \frac{c_{BQ} \gamma_{BQ}}{c_{HQ} \gamma_{HQ}} - 0.059 pH \\
 pH &= 0.5 + \frac{0.059}{2} \log \frac{10^{-6}}{0.38 \times 0.855} - 0.059(-0.15) = 0.35 \text{ V vs. Ag/AgCl}
 \end{aligned}
 \tag{1}$$

where,

$$E^0 = 0.5 \text{ V vs. Ag/AgCl};$$

$$c_{BQ} \gamma_{BQ} \text{ is assumed to be } 10^{-6} \text{ M}$$

$$c_{HQ} \text{ is } 0.38 \text{ M}$$

γ_{HQ} is equal to 0.855 (J. Molecular Liquids, 2008, 139, 61-71).

$$K_{a_2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.2 \times 10^{-2} \text{ M}$$

pH is equal to -0.15 (

3. The charge storage as a function of the number of quinone molecules

The charge of the negative electrode during the discharge process of the BP/BP and BP/BP-AQ cells in 1 M H₂SO₄ estimated from the cyclic voltammogram (cell voltage is 1 V, scan rate is 2 mV s⁻¹) is:

$$Q_{BP-AQ(H_2SO_4)} = 96.3 \text{ Cg}^{-1} \text{ (per mass of the negative electrode)}$$

$$Q_{BP(H_2SO_4)} = 50.2 \text{ Cg}^{-1} \text{ (per mass of the negative electrode)}$$

Then, the charge due to only the faradaic process at the negative electrode is:

$$\Delta Q_1 = Q_{BP-AQ(H_2SO_4)} - Q_{BP(H_2SO_4)} = 46.1 \text{ Cg}^{-1}$$

The charge of the positive electrode during the discharge process of the BP/BP cell in 1 M H₂SO₄ and BP/BP cell in 0.38 M HQ/1 M H₂SO₄ estimated from the cyclic voltammogram (cell voltage is 0.8 V, scan rate is 2 mV s⁻¹) is:

$$Q_{BP(HQ/H_2SO_4)} = 57.2 \text{ Cg}^{-1} \text{ (per mass of the positive electrode)}$$

$$Q_{BP(H_2SO_4)} = 34.9 \text{ Cg}^{-1} \text{ (per mass of the positive electrode)}$$

Then, the charge due to the faradaic process at the positive electrode is:

$$\Delta Q_2 = Q_{BP(HQ/H_2SO_4)} - Q_{BP(H_2SO_4)} = 22.3 \text{ Cg}^{-1}$$

Then, the charge per number of moles of quinone for each capacitor is:

$$\frac{\Delta Q_1}{zn_1} = \frac{46.1 \text{ Cg}^{-1}}{1 \times 10^{-7} \text{ mol}} = 4.6 \times 10^8 \text{ Cg}^{-1} \text{ mol}^{-1}$$

$$\frac{\Delta Q_2}{zn_2} = \frac{22.3 \text{ Cg}^{-1}}{8 \times 10^{-5} \text{ mol}} = 2.9 \times 10^5 \text{ Cg}^{-1} \text{ mol}^{-1}$$

Where, n_1 and n_2 are number of moles for the electrochemical capacitors containing AQ and HQ, respectively. z is the number of electrons participating in the faradaic reactions (Eqs. 1 and 2, main article).

It is worth mentioning that the capacity of the BP/BP cell in 0.38 M HQ/1 M H₂SO₄ increases by a factor of 1.5 compare to the BP/BP cell in 1 M H₂SO₄, namely 9.9 mAh g⁻¹ (35.7 F g⁻¹) and 7.0 mAh g⁻¹ (25.1 F g⁻¹), respectively. An enhancement of the capacity of an HQ-containing electrochemical capacitor, with respect to the electrochemical capacitor without HQ, has also been previously observed (J. Phys. Chem C, 2011,

115, 17606-17611). Due to the different carbon supports and the different ways used to report the capacity values, the absolute values obtained in this work are not compared to those reported in the aforementioned work.

4. Cyclic voltammograms of BP and BP-AQ electrodes in 1 M H₂SO₄ and BP in 0.38 M HQ in 1M H₂SO₄ in the three-electrode configuration.

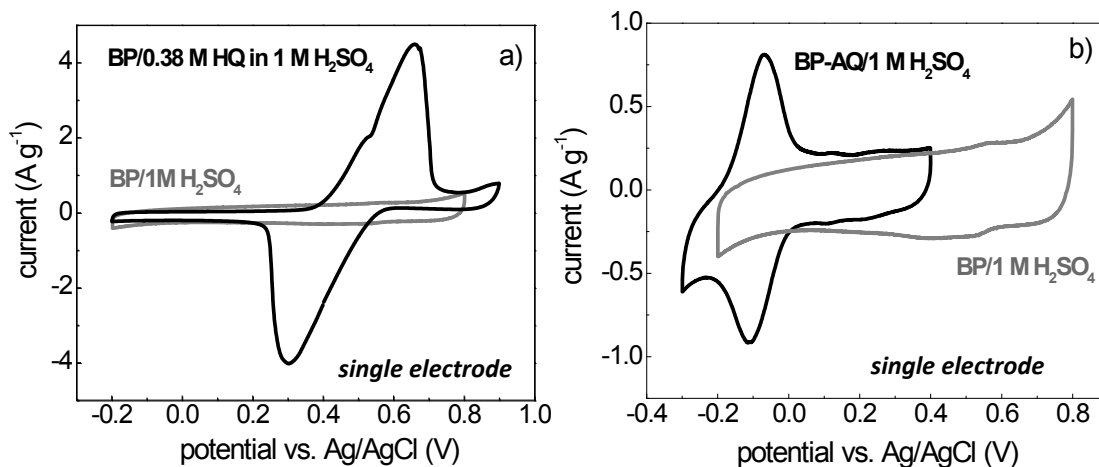


Figure S11. Cyclic voltammograms recorded at scan rate of 2 mV s⁻¹ for a BP electrode in 1 M H₂SO₄ (a and b, grey lines) and 0.38 M HQ in 1 M H₂SO₄ (a, black line); and BP-AQ electrode in 1 M H₂SO₄ (b, black line) in the three-electrode configuration. A Pt mesh and Ag/AgCl/3M NaCl were used as counter and reference electrode, respectively.

5. Galvanostatic charge-discharge profiles for BP/BP-AQ cell with mass ratio of 5:1 and 1:1.

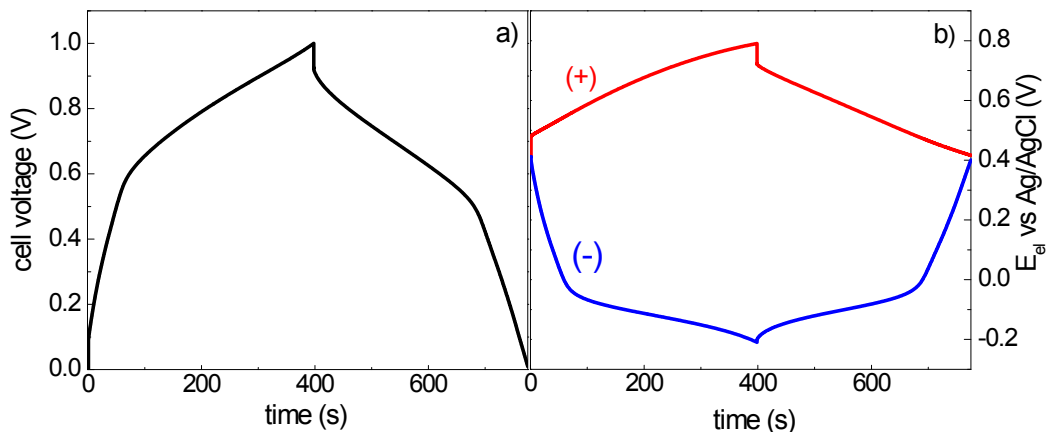


Figure S12. Galvanostatic charge/discharge profiles at a constant current of 40 mA g^{-1} for full cell (b, left axis) and separately for positive (red) and negative (blue) electrodes (c, right axis) of an electrochemical capacitor composed of BP/BP-AQ electrodes (mass ratio is 5:1) in $1\text{M H}_2\text{SO}_4$ electrolyte.

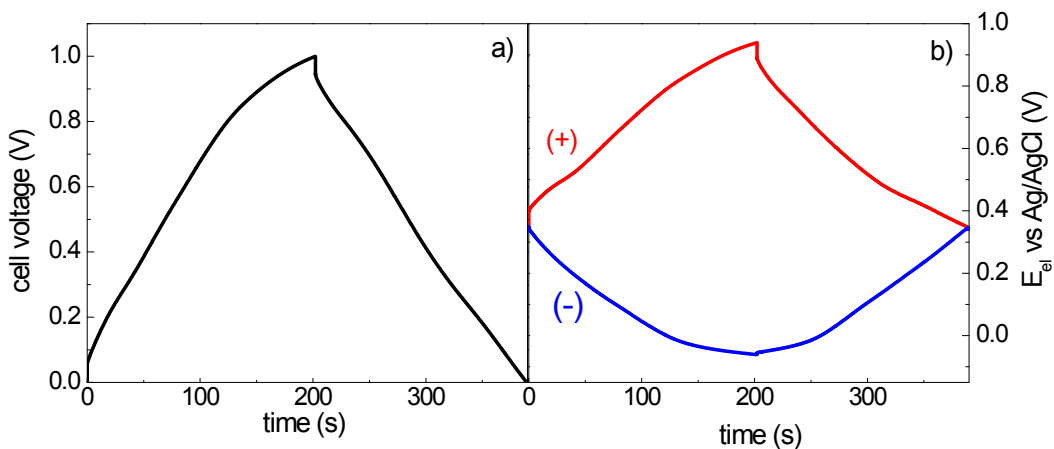


Figure S13. Galvanostatic charge/discharge profiles at a constant current of 140 mA g^{-1} for full cell (b, left axis) and separately for positive (red) and negative (blue) electrodes (c, right axis) of an electrochemical capacitor composed of BP/BP-AQ electrodes (mass ratio is 1:1) in $1\text{M H}_2\text{SO}_4$ electrolyte.

6. Diffusion-controlled mechanism of Conway kinetic model.

The decrease of the potential of the negative electrode for the diffusion-controlled mechanism of Conway's model is expressed by the following equation (J. Power Sources, 1997, 65, 53–59):

$$V_t - V_i = -\frac{2zFAD^{1/2}\pi^{1/2}c_0}{C}t^{1/2} \quad (2)$$

where V_i and V_t are the initial voltage and the voltage at a specific time (t), respectively. Taking into account that, during the charge and discharge processes, the potential of the positive electrode remains almost unchanged, Eq. 2 can be rewritten as follows:

$$E_t - E_i = \frac{2zFAD^{1/2}\pi^{1/2}c_0}{C}t^{1/2} = mt^{1/2} \quad (3)$$

z is the charge of the ion (in our system benzoquinone is neutral but have 2 electrons per molecule that could be involved in self-discharge), F the Faraday constant, A the electrode area ($7 \times 10^{-6} \text{ m}^2$), D the diffusion coefficient and m is a diffusion parameter that corresponds to the slope of 0.006 of the linear region of the E_{el} vs. $\text{time}^{1/2}$ plot (Fig. 5 c). Nonetheless, even if the Conway's model was derived using Fick's law diffusion to a planar electrode, it can be also applied to highly porous electrodes, due to depletion of the reactive species in the pores. According to previous studies (J. Phys. Chem. C, 2011, 115, 4283–4288), we assume that the self-discharge is limited by diffusion of benzoquinone to the external surface of the negative carbon electrode. Thus, the diffusion coefficient can be found from Eq.3:

$$D = \left(\frac{mC}{2zFA\pi^{1/2}c_0} \right)^2 \quad (4)$$

C is the capacitance of the electrode (100 F g^{-1}), c_0 is the initial concentration of benzoquinone in the electrolyte after cell charging and is calculated from:

$$c_0 = \frac{n}{V} = \frac{\Delta Q / Fz}{V} = \frac{Q_{BP(HQ/H_2SO_4)} - Q_{BP(H_2SO_4)}}{VFz} \quad (5)$$

where n is the initial number of moles of benzoquinone calculated using Faraday's law, $Q_{BP(HQ/H_2SO_4)}$ and $Q_{BP(H_2SO_4)}$ are the charge of the positive electrodes during the charging process which also include the charges that accumulate during 10 min. of the hold time, for BP/BP cell in 0.38 M hydroquinone/1 M H_2SO_4 and BP/BP cell in 1 M H_2SO_4 , respectively. Thus, ΔQ is the charge of the positive electrode that is associated only with the faradaic reaction of benzoquinone formation and is equal to 23 C g^{-1} . V is the volume of the electrochemical cell.

Combining Eqs. 4 and 5, it can be shown that:

$$D = \left(\frac{mC}{2zFA\pi^{1/2}\Delta Q / FzV} \right)^2 = \left(\frac{mCV}{2A\pi^{1/2}\Delta Q} \right)^2 = \left(\frac{mCh}{2\pi^{1/2}\Delta Q} \right)^2$$

(6)

where h is the thickness of the electrodes and electrolyte (5×10^{-4} m). From Eq. 6, the diffusion coefficient of benzoquinone is calculated to be 1.35×10^{-7} $\text{cm}^2 \text{s}^{-1}$, that is two order of magnitude smaller than the diffusion coefficient of benzoquinone in H_2SO_4 (1.08×10^{-5} $\text{cm}^2 \text{s}^{-1}$) (Energy Environ. Sci., 2014, 7, 1750–1759). To understand this discrepancy, the evaluation of the models for diffusion-controlled self-discharge with regards to our system is presented below.

Self-discharge of an electrochemical capacitor initially containing electroactive hydroquinone (HQ) in the electrolyte and benzoquinone (BQ) after charging is a dynamic multicomponent process having several unknown parameters. Firstly, the initial concentration of benzoquinone is not uniform, because during the charging step, a fraction of benzoquinone molecules could have already reached the negative electrode and being reduced. Secondly, the diffusion of benzoquinone in the electrochemical cell occurs within the porous positive carbon electrode as well as from the positive to the negative electrode.

In the literature, three models are available to describe the diffusion-controlled self-discharge. The mechanisms of Conway and coworkers for an individual electrode (J. Power Sources, 1997, 65, 53–59) and that of Ricketts and Ton-That for an electrochemical cell (J. Power Sources, 2000, 89, 64–69) are based on a concept that a Faradic reaction produces a surface excess of ionic species near the electrode in addition to the maximum allowable charge given by the capacitance of the electrode. In our system benzoquinone as well as hydroquinone molecules are neutral but have 2 electrons per molecule that could be involved in self-discharge. The third available model derived by Chen et al. for an electrochemical cell (Energy Environ. Sci., 2014, 7, 1750–1759) involves the reduction of benzoquinone on the negative electrode by coulostatic electrolysis. For simplicity, the authors assumed that the initial benzoquinone concentration is uniform throughout the cell and in their analysis of the data, a two order of magnitude underestimation of benzoquinone diffusion coefficient was found. Thus, a model for diffusion-controlled self-discharge taking into account all dynamic issues must be developed.

7. The effect of presence of oxygen.

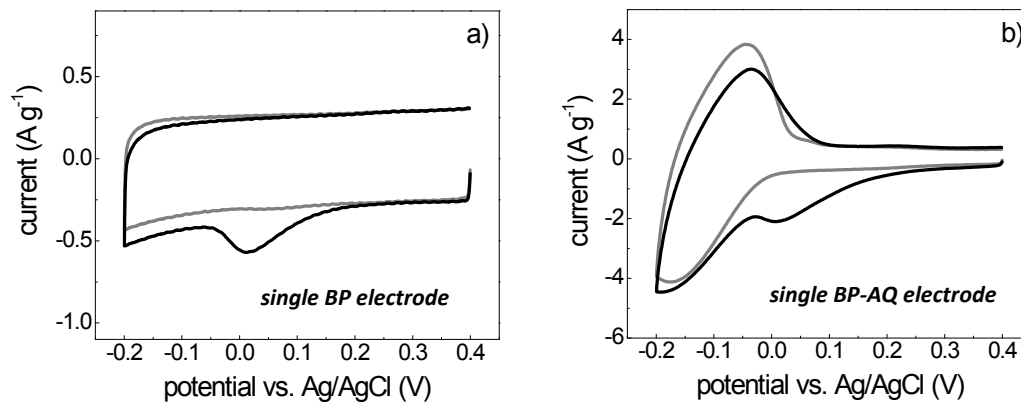


Figure S14. Cyclic voltammograms of unmodified BP (a) and BP-AQ (b) electrode recorded in 1 M H₂SO₄ saturated with O₂ (black lines) or N₂ (grey lines) at scan rate 5 mV s⁻¹ in the three-electrode configuration. A Pt mesh and Ag/AgCl/3M NaCl were used as counter and reference electrode, respectively.