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Pseudocapacitance and performance stability of quinone-coated carbon onions

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Abstract
Onion-like carbon, also known as carbon onions, is a highly conductive material enabling supercapacitor electrodes with a very high power density. However, the moderate specific capacitance (circa 30 F/g) is insufficient for many energy storage applications. In our study, we show how decoration of carbon onions with quinones provides a facile method to increase the energy density up to one order of magnitude, namely, from 0.5 Wh/kg to 4.5 Wh/kg, while retaining a high power density and long lifetime. We present data for carbon onions modified with three different kinds of quinones: 1,4-naphthoquinone, 9,10-phenanthrenequinone, and 4,5-pyrenedione. Quinone-decorated carbon onion electrodes are investigated considering the actual quinone loading and the resulting electrochemical performance is probed in 1 M H2SO4 as the electrolyte using cyclic voltammetry and galvanostatic charge/discharge. The maximum capacitance, 264 F/g, is found for carbon onions modified with 4,5-pyrenedione, which also shows the smallest fade in specific capacitance, namely 3%, over 10,000 charge and discharge cycles at a high current density of 1.3 A/g.

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Introduction
Over the last decades, the research on carbon nanomaterials has constantly intensified, fueled by the discovery and application of novel structures, first fullerenes [1], then carbon nanotubes [2], and most recently graphene [3]. A much less known member of the carbon family is onion-like
carbon (OLC), also known as carbon onions, which can be rationalized as concentrically stacked, multi-shelled fullerenes. Initially observed by Sumio Iijima in 1980 [4], they attracted popular attention through the work of Daniel Ugarte in 1992 [5]. Having emerged as a curiosity found during electron beam irradiation in a transmission electron microscope (TEM), carbon onions have been synthesized so far via various techniques [6,7], such as electric arc discharge [8,9], chemical vapor deposition (CVD) [10,11], ion bombardment [12,13], or vacuum annealing of nanodiamond detonation soot [14] or other nanodiamonds [15]. Among these techniques, vacuum annealing of detonation nanodiamonds [11,15] (DND) powder represents a facile method for the large scale production of OLC because of the availability of commercial nanodiamond powders with a narrow size distribution [6]. Following a structural reorganization of the initial sp³-hybridized crystal structure of DND, the size of the resulting sp³-hybridized OLC particles depends on the diameter of the nanodiamond precursor. Many properties, such as the specific surface area (SSA) and the electrical conductivity, not only depend on the type of precursor, but also strongly depend on the annealing temperature. In the case of detonation soot with a diamond content of approximately 25 wt%, the SSA varies from ≈ 400 to ≈ 580 m²/g (OLC synthesized at 1200 °C and 1500 °C, respectively) and the electrical conductivity varies from 2.9 to 4.0 S/cm (OLC synthesized at 1200 °C and 1800 °C, respectively) [14].

Over the years, carbon onions have been used in and developed for various applications, such as field emitters [16], electromagnetic wave attenuators [17], or nanoscale lubricants [18]. OLCs have also been introduced as an attractive electrode material for electrical double-layer capacitors (EDLC) [19], more commonly known as supercapacitors or ultracapacitors. Carbon onions are more expensive, but they are in the same range or even less expensive than carbon nanotubes (i.e., several dollars per gram) [21,22]. Carbon onion films were studied in a two-electrode geometry with 15 wt% PTFE (polytetrafluoroethylene) by Portet et al. [23] and compared to other exohedral carbon nanomaterials (i.e., pores are enclosed between the particles rather than within a particle) like multi-walled carbon nanotubes (MWCNT) or carbon black (CB). It was found that OLC combines a high capacitance retention at increased current density (90% at ≈ 50 A/g) with a, comparatively, high intrinsic capacitance of up to ≈ 40 F/g (MWCNT: 18 F/g, CB: 2 F/g) [23]. This beneficial power handling ability was even more pronounced when Pech et al. [24] tested a binder-free thin film electrode of pure carbon onions, which showed approximately 40% of the initial capacitance measured at low scan rates was maintained at a charge/discharge rate of 200 V/s. Furthermore, carbon onions have been demonstrated to be potent conductive additives to enable fast charge/discharge rates and, thus, improve the power handling ability and equivalent series resistance (ESR) of supercapacitor electrodes composed of activated carbon [25] and mesoporous carbon [26]. In addition to a lower ESR, composites of polyaniline (PANI) and OLC showed a large increase in performance stability over thousands of charge/discharge cycles compared to pure PANI electrodes [22].

The power handling of carbon onions is not only a result of their relatively high electronic conductivity, but also of the almost complete absence of internal pores and the spherical shape [14,27]. However, the major limitation to the use of OLC in supercapacitors is their low specific capacitance of about 30-40 F/g which is a result of their moderate SSA. Activated carbon onions with a surface area of 578 m²/g derived from detonation soot have been demonstrated as an anode material for lithium ion batteries in 1 M lithium hexafluorophosphate (LiPF₆) in propylene carbonate (PC), yielding a specific capacitance of ≈ 70 F/g [28]. The activation process increased the specific capacitance by more than a factor of 2 compared to the material prior to activation exhibiting a SSA of 384 m²/g and yielding less than 30 F/g. Recently, Gao et al. demonstrated that KOH activation is capable of yielding carbon onions with a SSA of up to ≈ 800 m²/g and a corresponding specific capacitance of ≈ 120 F/g in 2 M KNO₃ at a scan rate of 50 mV/s [29]. However, there are physical limitations to the activation of OLC as the necessary post treatment cleaning of tiny carbon onions after chemical activation requires elaborate rinsing, centrifugation, and filtering leading to substantial loss of material.

A simpler alternative way to improve the energy density of OLC electrodes for supercapacitors is to decorate the carbon onions outer surface with redox-active, pseudocapacitive materials. Particularly attractive are quinones for which the redox mechanisms in aqueous electrolytes have been sufficiently studied over the last three decades [30-32]. Yet, there are still a small number of studies on pseudocapacitors employing quinones. For example, Roldan et al. showed that the addition of hydroquinone directly to the acidic electrolyte (i.e., 1 M H₂SO₄) of a symmetrical activated carbon supercapacitor lead to an improvement from 72 to 220 F/g of the capacitance on electrodes [33,34]. The measured capacitance dropped rapidly upon cycling or when run at high current densities possibly due to limited quinone transport to the electrode surface. Alternatively to modifying the electrolyte, it is also possible to increase the energy density by using quinone-containing electrodes, for which a small number of carbon nanomaterials have been used to date. As reported by Balach et al., thin films of hierarchical porous carbon micrometer-sized particles immersed in quinone-containing solutions (9, 10-anthraquinone, 1,4-naphthoquinone, 1,4-benzoquinone) and then rinsed prior to testing reached a specific capacitance of up to 900 F/g (in 1 M HClO₄) corresponding to a five-fold increase compared to bare electrode [35]. In a similar fashion, Wang et al. decorated graphene nanosheets with tert-butylhydroquinone and reported higher electrode capacitance of up to 302 F/g (in 1 M H₂SO₄) without significant deterioration of the power handling ability [36]. Carbon fabrics functionalized with anthraquinones have been studied by Kalimuthu et al. and, at constant current discharge in 1 M H₂SO₄, a total energy density of up to 8 Wh/kg was demonstrated for a complete supercapacitor cell; however, the device suffered from limited capacity retention at higher charge and discharge rates [37]. Indeed, limited cyclability and rate (power) performance are common problems for pseudocapacitive materials [38].

The molecular arrangement of 9,10-phenanthrenequinone on the surface of carbon onions has recently been studied using inelastic neutron scattering, Raman spectroscopy, and density functional theory (DFT) calculations [39].
Spectroscopic differences were observed between adsorbed and bulk quinone molecules related to torsional and out-of-plane ring deformation modes of the adsorbed molecule. In agreement with DFT calculations, these results strongly indicate the arrangement of quinone molecules parallel to the onion surface through π interactions and the absence of covalent bonding. First electrochemical measurements in 1 M H₂SO₄ and a loading of 0.24 molecules/nm² showed very distinct redox peaks with the oxidation peak being located significantly higher than the reduction peak. The high electrochemical reversibility and stability was concluded to be indicative of a good attachment of the quinone molecule to the onion surface that was not lost in the course of consecutive charge and discharge cycles. Unlike pyrrolytic graphite, the latter is almost void of surface oxygen groups that are detrimental to the stability and reversibility of the charge/discharge mechanism.

In this paper, we investigate quinones as a facile way to significantly improve the energy density of carbon onion electrodes while retaining a high power handling ability. Unlike pseudocapacitors employing metal oxide particles [40] or coatings [41] or conductive polymers [42], no elaborate chemical synthesis of the hybrid electrode materials is required when using quinones and simple drop casting can be employed. We studied OLC electrodes decorated with 1,4-naphthoquinone (NQ), 9,10-phenanthrenequinone (PQ), and 4,5-pyrenedione (PY) and report the electrochemical performance of such quinone-modified OLC electrodes (Q-OLC pseudocapacitors). In particular, we focus on the performance stability over thousands of charge- and discharge-cycles.

Experimental section

Preparation and gas sorption analysis of carbon onions

UD50 nanodiamond detonation soot was provided by NanoBlox Inc. (USA) and used without further treatment. Carbon onions were prepared via vacuum treatment (10⁻⁵ to 10⁻⁶ mbar) of UD50 powder at 1800 °C for 3 h. There is a small amount of metal impurities in UD50, approximately 1 wt% - mostly Fe in the DND powder; these impurities are removed by the vacuum treatment procedure [14]. Gas sorption analysis was performed with Quantachrome Instruments (USA) Quadrasorb using N₂ at −196 °C. The BET SSA (Ref. [43]) was determined in the linear regime from P/P₀ range between 0.05 and 0.20 and the total pore volume was determined at P/P₀=0.99 as suitable for a material showing a Type II isotherm [44].

Decoration of onion-like carbon with quinones

Quinone decoration of carbon onions was carried out as follows. 50 mg of carbon onions was added to 15 ml of 4.8 × 10⁻³ M of quinone in methanol. The carbon dispersion was sonicated for 20 min and the solution was first filtered without rinsing, using a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.2 μm. Methanol was used to rinse the onions out of the flask. Deionized water was used for second step of filtration and rinsing, and finally, methanol was used for final filtration. The wet carbon onion and quinone mixture was transferred to a round-bottom flask and put to a vacuum line at 67 mPa at 60 °C overnight prior to further handling.

Electrochemical measurements

Using a three-electrode electrochemical setup, the working electrode (WE) was prepared by depositing a thin layer of quinone-modified OLC particles onto a polished glassy carbon surface. The glassy carbon rod (6 mm diameter) was obtained from Tokai Carbon (Japan). Q-OLC was dispersed in water and homogenized via sonication. A drop of the obtained suspension was deposited on the top of the glassy carbon and dried in air at room temperature. From the concentration of OLC in the drop, the volume of the drop, and the measured surface area of the OLC (520 m²/g), the total surface area of OLC on the glassy carbon electrode was calculated. The mass loading of carbon onions per electrode was ≈ 1 mg yielding a layer thickness in the range of several micrometers. The mass loading was not varied to keep this control parameter constant and to directly correlate changes in the electrochemical behavior with the type and content of quinones. A platinum wire and an Ag/AgCl (KCl sat.) electrode were used as counter (CE) and reference (RE) electrode, respectively. Using a Biologic SP-200 system, cyclic voltammetry was carried out on Q-OLC at different scan rates, ranging from 5 mV/s to 10 V/s and compared to pure OLC. Charge/discharge cycles (galvanostatic cycling) between 0 and 0.8 V vs. SHE were carried out applying 1.3 A/g for up to 10,000 cycles to investigate the capacitance and stability of the material.

The specific capacitance C_sp, referred to as capacitance in our paper, was calculated from galvanostatic cycling using the following equation:

$$C_{sp} = \frac{l}{m(dV/dt)}$$  \hspace{1cm} (1)

where l is the discharge current, V is the voltage, t is the discharge time, m is the mass of the carbon electrode, and dV/dt is the slope of the discharge curve.

Cyclic voltammetry was carried out at various scan rates and the capacitance was derived using the following equation:

$$C_{sp} = \frac{\int i dV}{m\Delta U}$$  \hspace{1cm} (2)

where ΔU is the width of the voltage window, and v is the scan rate.

The additional charge storage related to the presence of quinones, Λ (C/mol), was calculated from subtracting the charge determined for a pure carbon onion electrode (i.e., DL charge storage) from the measured Q-OLC electrode charge and normalizing this value by the quinone loading (see Table 1).

The maximum energy (E_max) of a supercapacitor can be calculated from the following equation [45]:

$$E_{max} = \frac{1}{4m} \Delta U^2$$  \hspace{1cm} (3)

with the device capacitance C defined as C/m=1/2 C_sp. Thus, it follows for the specific energy (i.e., maximum
energy density; Eq. (4)):

\[ E_{\text{wp}} = \frac{5}{144} C_0 \beta \Delta V^2 \]

We note that values obtained from this equation do not represent the data of a full cell that would include the mass of the current collector, separator material, and casing [46,47].

Structural characterization and thermal analysis

X-ray diffraction on the powder sample was carried out using a D8 system (Bruker, Germany) using a Lynxeye detector. Within the 2\( \theta \) range between 5 and 150 2\( \theta \), the step width was 0.02\(^\circ\) and the measurement time per each step was 1 s.

Transmission electron microscopy, TEM, was carried out on a JEOL 2010F microscope using an acceleration voltage of 200 kV. For TEM investigation, samples were prepared by dispersing the powder in ethanol and placing the solution over a copper grid with a lacey carbon film.

Raman spectra were collected at ambient temperature using an argon ion laser operating at 514.5 nm to irradiate the sample. The laser was focused to a spot size of 100 \( \mu \text{m} \) using a D8 system (Bruker, Germany) using a Lynxeye spectrometer having a Peltier-cooled charge-coupled device (CCD) array detector. The peak energies and line widths were obtained from multiple-peak Lorentzian fitting and the experimental resolution of the peak positions is approximately 1/cm.

Thermogravimetric analysis, TGA, was carried out using a SDT Q600 system (TA Instruments) with a heating rate of 10 K/min in nitrogen. For the calculation of the desorption activation energy, we applied the Redhead method (Ref. [48]) assuming that the exponential prefactor and the activation energy are independent of the surface coverage. Thus, the following equation can be used:

\[ E_{\text{des}} = R T_{\text{max}} \left[ \ln \left( \frac{\omega T_{\text{max}}}{\beta} \right) - \ln \left( \frac{E_{\text{des}}}{RT_{\text{max}}} \right) \right] \]

with \( E_{\text{des}} \) as the activation energy of the desorption, \( R \) is the gas constant, \( T_{\text{max}} \) is the temperature at which the desorption rate is maximum, \( \beta \) is the heating rate, and \( \omega \) is the desorption rate constant which, as common practice, was assumed to be \( 10^{13} \text{s}^{-1} \) in our experiment. For simplification, we also assume the second term, \( \ln(E_{\text{des}}/RT_{\text{max}}) \), to be 3.64, as suggested by Redhead and which will yield an error of less than 1.5% for the used \( \omega/\beta \) ratio [48]. Redhead analysis is based upon single desorption, but in this TGA multiple adsorption-readsorption is expected and the calculated \( E_{\text{des}} \) values represent the upper limits on the desorption energies.

Results and discussion

Structure and properties of OLC and quinone-modified OLC

Vacuum annealing of DND yielded fully transformed carbon onions (Figure 1). No remaining sp\(^3\)-hybridized carbon core was found in the OLC particles as confirmed with X-ray diffraction (XRD, see Supplementary material Figure S1). The most prominent signal in the X-ray diffractogram is the (002)-reflection of graphitic carbon at 2\( \theta \) = 26.61 which is indicative of a high level of crystallinity [49,50].

As typical for higher annealing temperatures (e.g., 1800 \(^\circ\)C), the carbon onions shape ranges from spherical to polygonized contours (Figure 1A). Carbon onions can be considered as multi-shell fullerenes, and, as seen with TEM, the particle size of most of the carbon onions ranged between 4 and 8 nm (Figure 1B) [51]. Nitrogen gas sorption analysis of the dry powder measured at –196 \(^\circ\)C showed a BET SSA of OLC of 520 m\(^2\)/g which, considering the size of
the carbon onions, is consistent with the presence of dense carbon nanoparticles (see Supplementary material, Figure S1C). Only a few larger particles could be found which consisted of coalesced carbon onions. On a larger scale, agglomerates of 100–500 nm size can be found which are also common for the DND material used for the OLC synthesis [52].

The quinones were adsorbed onto the OLC from methanol solution (see Supplementary material) and their loadings were determined by TGA (Table S1). Two different loadings of PQ were used in the present work. Recently, we have studied the alignment of PQ molecules parallel to the carbon onion surface through π–π stacking via inelastic neutron scattering [39]. The results showed that although a single PQ molecule is somewhat confined to the surface of a carbon onion, it is nevertheless capable to move within clusters of the molecule and we expect the same behavior on the adsorption of quinone with 2 and 4 rings [53]. The parallel alignment of a quinone molecule on a flat carbon surface is schematically depicted in Figure S2 in Supplementary material. For the largest quinone molecule, PY, we can assume a size of approximately 1.0 nm$^2$ compared to a diameter of circa 5 nm for a single carbon onion, corresponding to a surface area of $\approx 80$ nm$^2$ (see Table S1, Supplementary material). Hence, on a geometric basis, one single carbon onion may yield a maximum coverage of 75 PY molecules and this number is higher for the smallest of the studied quinones, namely $\approx 115$ for NQ. Considering the size difference between the quinones and the OLC particles, we can assume a slight curvature and a limited deviation from a flat plane; however, we also have to consider surface defects and a small amount of other oxygen-containing surface groups which are present on the curved surface of carbon onions.

Thermogravimetric analysis (TGA) of pure carbon onions in nitrogen shows a very low amount of surface groups (Figure S3, Supplementary material). TGA was also used for temperature programmed desorption to determine the activation energy related to the single desorption peak associated with the quinone desorption process. The assumption of a single desorption peak is justified, as shown by the thermal analysis plots presented in Figure S3 in Supplementary material. From the results shown in Figure 2, we see that there is a linear dependency between the desorption activation energy and the number of carbon and oxygen atoms of the three quinone molecules. There is only a slight deviation between the two samples of PQ-OLC with high and low quinone loading, which is consistent with the assumption of the desorption activation energy, $E_{\text{des}}$, being independent of the surface coverage. As we see, PY is bound the strongest to OLC compared to the other quinones with an activation desorption energy of around $-1.9$ eV (see also Table S1, Supplementary material). In case of PQ, the experimentally derived value of approximately $-1.8$ eV is larger than what has been reported from DFT ($-1.1$ eV) [39]. This difference may be related to a stronger interaction between the quinone molecules and surface defects which are present on the non-ideal and slightly curved OLC surface, whereas the DFT calculations in Ref. [39] had assumed an ideal flat surface void of any functional termination.

**Electrochemical performance**

Electrodes composed of carbon onions without the addition of quinones exhibit a charge storage behavior indicative of double-layer (DL) capacitance expressed by the rectangular shape of the cyclic voltammogram (CV) shown in the inset in Figure 1. The interaction of the quinones with the OLC changes the capacitance behavior, as shown in Figure 2.
Figure 3A. The absence of faradaic reactions during the anodic and cathodic sweeps in the CVs is in clear contrast to the large redox peaks found for OLC decorated with PQ (Figure 3A), or the other two quinones (Figure 3B). The additional faradaic charge stored by fully reversible quinone oxidation and reduction is, when comparing OLC and Q-OLC electrodes, significantly larger than pure DL capacitance. During positive polarization of the electrode, the oxidation peak, at a slow scan rate of 5 mV/s, lies around 0.44–0.49 V vs. SHE, while the reduction peak ranges around 0.46–0.42 V vs. SHE (see Figure S4 in Supplementary material). At a slow scan rate like 5 mV/s (Figure 3), the separation between the forward and reverse peak potential ($\Delta E$) ranges up to 30 mV for PY-OLC and NQ-OLC to smaller values for PQ-OLC under both loadings. For a reversible electron transfer reaction in which both the oxidized and reduced forms of the molecules are adsorbed to a substrate, as in the case of Q-OLC, the potential dependence of the ratio of the oxidized and reduced forms is dictated by the Nernst equation. The peak potential is the redox potential of the couple, and the peak separation of anodic and cathodic waves is predicted to be zero. A slight deviation from ideality of CV profiles may be related to capacitive losses, ionic resistance between the working electrode (WE) and the counter electrode (CE), electrode sizes, mass transport, and internal resistance within the OLC film. The separation between oxidation and reduction peaks increases with increasing scan rate, and this separation rate is often used to determine the reaction kinetics [54,55]. Considering a two-step, two-electron transfer typical for quinone redox reactions (proton-coupled electron transfer) [31], the interpretation of peak separation with scan rate becomes more complex due to the role of proton transfer on the reaction kinetics as well as the possibility of one-electron transfer intermediates. These processes have consequences for the shape of the CV peak. The peak separation observed at higher scan rates for Q-OLC can be a result of the kinetics of the reaction. It could also be a result of mass transport limitations of protons from or to the surface in the OLC electrode. PY-OLC shows, to a stronger extent than the other Q-OLC CVs, the presence of two additional peaks in both forward and reverse scanning direction, located at around 0.54 V vs. SHE with a peak separation of less than 50 mV. For a $2e^-/2H^+$ reaction of surface-bound species such as for quinones, this may be related to kinetic limitations of the redox-reaction during cathodic and anodic sweeps [56].

As shown in Figure 4A and Table 1, the specific capacitance, as derived from CV, of OLC electrodes is significantly increased after quinone decoration, namely by a factor of 3.8 (NQ-OLC), 6.8 (PY-OLC), and 12.6 (PQ-OLC, high loading) at a scan rate of 5 mV/s in 1 M H$_2$SO$_4$. The normalization is related to the mass of carbon, that is, the mass of carbon onions. It is important to note that at 5 mV/s, the specific capacitance of PQ-OLC with a high PQ molecule loading (267 F/g) is the highest reported value for carbon onion electrodes so far. The only report of a higher capacitance (640 F/g) in Ref. [22] refers to a PANI-OLC composite which only contains 3 wt% carbon onions and which reflects the high capacitance of PANI rather than the capacitance of OLC. At a scan rate of 50 mV/s, PQ-OLC (high loading) still shows a capacitance of 235 F/g which is approximately twice what Gao et al. have reported for chemically activated carbon onions in 2 M KNO$_3$ ($\approx 120$ F/g) [29]. It is
necessary to take into account that thin samples with a low mass loading per electrode were used; therefore, they can be compared to thin film onion electrodes [17], but not conventional supercapacitor electrodes of ~100 μm thickness [46]. Still, an order of magnitude increase in capacitance compared to pure OLC is observed for carbon onions with a quinone coating.

From the specific capacitance and knowing the SSA of OLC, one can calculate the specific capacitance normalized by surface area (F/m²). For pure carbon onions, the capacitance normalized by SSA of 0.057 F/m² (=5.7 μF/cm²) is close to the value of 0.055 F/m² (=5.5 μF/cm²) reported by Huang et al. [27] (based on data from Ref. [23]) in 1.5 M tetraethylammonium tetrafluoroborate (TEA-BF₄) in acetonitrile. Even when considering the increase of specific areal capacitance with decrease in the diameter of an OLC particle [27], to achieve a specific capacitance in excess of 200 F/g, one would need to synthesize carbon onions with a SSA larger than 2000 m²/g. This could be achieved with onions smaller than 1.5 nm in diameter or with a significant internal pore volume within the onions. Such small carbon onions would pose significant limitations to the accessibility of pores at onion/onion contact points [57] and probably suffer from poor electrical conductivity because of the very low number (1-2) of carbon shells and high curvature of these fullerene-like structures. When subtracting the DL contribution of the total measured charge, the remaining charge can be normalized by the amount of adsorbed quinones. The resulting parameter \( \Delta_{\text{quinone}} \) (C/mol), see Table 1, does not vary significantly for the studied quinones which illustrates that the charge storage contribution of all the studied quinones is, when normalized to their amount, rather constant within the statistical error of the calculation. The calculated values (0.12-0.16 C/μmol) are also close to the ideal value for a 2 electron/2 proton charge transfer (0.19 C/μmol).

The power handling, meaning, the decrease in the apparent capacitance with increase in charge-discharge rate, is an important parameter of electrical energy storage. While it is not expected to maintain the very high power handling of pure OLC electrodes when adding quinones, Figure 4A shows that for PQ-OLC at high loading up to 100 mV/s, a specific capacitance in excess of 200 F/g can be maintained but it decreases to around 75 F/g at 1 V/s, which represents a better power handling capacity compared to porous carbons [16]. From all studied samples, PQ-OLC and NQ-OLC showed the deepest capacitance decay. At 1 V/s, PQ-OLC and NQ-OLC retain 28% and 24%, respectively, of the capacitance measured at low scan rates, while pure carbon onions maintain more than 70% of the capacitance. PY-OLC also fades in apparent capacitance and drops to approximately half of the initial value (i.e., 73 F/g at 1 V/s). NQ as the quinone with the lowest sorption energy showed the highest loss in apparent capacitance at higher scan rates (see Table S1 in Supplementary material). This may be related to a less efficient charge transfer between the quinone and the OLC substrate with smaller sorption energy on the surface of carbon onions.

Calculation of the apparent capacitance from CV is complicated at very high scan rates by the distortion of the CV shape as a result of the non-equilibrium condition and the high internal resistance of the device under such conditions (see Figure S5, Supplementary material). To evaluate the performance stability, we carried out galvanostatic charge/discharge testing at 1.3 A/g over thousands of cycles (Figure 4B). At a level of around 25 F/g, pure OLC electrodes show almost no decrease (<2%) in capacitance over the course of 10,000 charge and discharge cycles. PY-OLC and PQ-OLC (low loading) maintain 97% and 94%, respectively, while NQ-OLC loses approximately 20% of the initial capacitance. Employing the definition of device failure of Kötz et al. [58] that is, 20% loss of the initial capacitance and/or 100% increase in ESR, we see that in all cases no failure has occurred prior after 10,000 charge and discharge cycles at a current density of 1.3 A/g.

The observed behavior may also correlate with the increasingly stronger sorption energy (NQ < PQ < PY; see Table S1 in Supplementary material) and demonstrates the importance of the optimization of the quinone / carbon onion interface on a molecular level. We also note that the overall charge efficiency (i.e., coulombic efficiency as the
ratio of charge and discharge capacity) remains, at all times, higher than 99% for all Q-OLC and OLC samples. We also see that the sample with the higher PQ loading shows a more pronounced fade of capacitance of approximately 5% after 1,000 charge and discharge cycles. This capacitive loss was still comparable for NQ-OLC which showed a much lower molecular loading.

The performance fade is also reflected by changes in the CV and in the galvanostatic charge/discharge patterns when comparing them before and after cycling. As exemplified for PQ-OLC with a low quinone loading, both, the shape in the CV as well as the position of the oxidation and reduction peaks in the forward and reverse polarization sweep change significantly after 10,000 cycles (Figure S6, Supplementary material). We notice in the CVs that the peak separation of the cathodic and anodic wave is larger than before lifetime experiment, and the anodic and cathodic peak current decreases. Correspondingly, we see in the galvanostatic charge/discharge, that shorter periods of time are required for charge and discharge with a preset current density which is indicative of a decrease in specific capacitance. This deterioration may be related to chemical or pH-related changes of the electrolyte and either the migration, structural degradation, or loss of quinone molecules.

A facile method to investigate the charge storage mechanism and its kinetic limitations are log(I)-log(v) plots (Figure 5), where the measured current at a certain potential is plotted against the scan rate. For this sort of analysis, the slope (s) of the obtained plots is considered and we can differentiate two boundary conditions:

1. **DL behavior** with s = 1 considering Eq. (7) (Ref. [19, 59, 60]):
   \[ I = CV \quad \text(s) \]
   
   with I as the current, C the capacitance, and v the scan rate.

2. **Diffusional limitation** of the charge transfer mechanism with s = 0.5. This value is derived from the Randles-Sevcik equation (Eq. (8), Ref. [61]):
   \[ I = 0.4463(nF)^{3/2}Ac(D/RT)^{1/2}v^{1/2} \quad \text(s) \]
   
   with I as the current, n is number of electrons involved in the charge transfer process, F is the Faraday constant, A is the surface area, c is the concentration of the diffusing species, D is the diffusion coefficient of the diffusing species, R is the universal gas constant, and T is the temperature.

As the scan rate or current density is increased, charge and discharge will not achieve a dynamic equilibrium. For that reason, all non-ideal supercapacitors will transition from a near-to-ideal slope s of approximately 1 to 0.5 at fast charge/discharge. We find for an electrode composed of pure carbon onions a value of s very close to 1 up to a high scan rate of 1 V/s (Figure 5A), while all Q-OLC electrodes exhibit, even at low scan rate, a slope s of between 0.6 and 0.8. Ultimately, all materials transition towards a value of s ≈ 0.5 as the scan rate is constantly increased beyond the threshold of 1 V/s. Another explanation for this effect in the

![Figure 5 Scan rate dependency of the measured current using log-log plot (A). Data is shown for carbon onions (OLC) and OLC decorated with 1,4-naphthoquinone (NQ-OLC), 4,5-pyrenedione (PY-OLC), and 9,10-phenanthrenequinone (PQ-OLC; low loading). Slope of the log-log-curves in panel A plotted as a function of the scan rate (B) for OLC and NQ-OLC. The values for OLC transition from the ideal behavior of an electrical double-layer capacitor (EDLC: s = 1) to fully diffusion controlled (s = 0.5). The current is taken, for pure OLC, at 0.5 V, whereas the analysis of NQ-OLC was carried out at two potentials: one at the redox peak at around 0.49 V, the other one at 0.74 V. The peak at 0.49 V corresponds to the pseudocapacitor regime, while the other peak at 0.74 V is within a double-layer like regime.](image)

Q-OLC systems is the depletion of the protons (or the ability to accept protons) in the limited volume of the solution filled pores due to the proton-coupled electron transfer reaction.

For an ideal supercapacitor, and on first approximation, the result of this analysis does not vary with the voltage used for the calculation of the slope as long as the CV shape remains rectangular and there are no faradic side-reactions to be considered. For pseudocapacitive systems, it is important to consider the current at, for example, the cathodic peak and the resulting log(I)-log(v) plots are shown in Figure 5B. Now, deconstructing a typical CV, such as the one for NQ-OLC, one can examine the power handling at the anodic peak and compare this value to the current response on variation of the scan rate for the DL range in the CV (e.g., at +0.74 V vs. SHE). The result illustrates that the charge transfer associated with the redox reaction is much slower than DL formation. At scan rates up to 100 mV/s, the slope s, as determined via derivation of the data presented in Figure 5A, the charge associated with pure DL formation in a quinone-modified OLC electrode behaves almost identical to
the fast response of pure carbon onions (i.e., the slope s is close to 1). In contrast, even at 5 mV/s, the value for s at the redox peak never exceeds \( \approx 0.7 \). Again, here we see that all three, the response at the redox peak and DL region of NQ-OLC and pure OLC electrodes transition towards ideal diffusion limitation of the capacitance with a value \( s = 0.5 \).

**Conclusions**

Carbon onions can be used to obtain electrodes for supercapacitors with extremely high power handling. To overcome the intrinsically low specific capacitance and energy density of OLC supercapacitors, both charge storage and recovery associated with the electrical double layer and proton-coupled electron transfer can be utilized in quinone-modified OLC electrodes (Q-OLC; see Figure 6). Quinone decoration of the exohedral surface of carbon onions increases the energy density by maximum 900%, that is, from 0.5 Wh/kg to 4.5 Wh/kg. The reported capacitance of 264 F/g is very high compared to the capacitance of unmodified OLC electrodes (\( \approx 30 \) F/g) and is even higher than found for activated carbon onions. Furthermore, the performance remains for most quinones highly stable when tested in 1 M H\(_2\)SO\(_4\) for thousands of charge and discharge cycles at a high current density of 1.3 A. The smallest decrease of capacitance with increased scan rate was identified for the quinones with the highest binding energy to the OLC surface (i.e., 4,5-pyrenedione), the highest capacitance was found for the sample with the highest loading with quinone molecules. We believe that quinone modification of exohedral carbon particles presents a facile way to significantly improve the energy density without sacrificing the cycling stability for electrical energy storage devices.

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**Appendix A. Supplementary material**

Supplementary data associated with this article can be found in the online version at [http://dx.doi.org/10.1016/j.nanoen.2013.08.003](http://dx.doi.org/10.1016/j.nanoen.2013.08.003).

**References**


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