



The decisive role of electrolyte concentration in the performance of aqueous chloride-based carbon/carbon supercapacitors with extended voltage window



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ABSTRACT

In the present study aqueous alkali metal chloride electrolytes are investigated as potential candidates for carbon/carbon supercapacitors. High-current capacitance retention is greatly enhanced by using the electrolyte concentrations at the maximum electrical conductivity, *i.e.* 6 M LiCl, 5 M NaCl and 2 M KCl, in supercapacitor cells working at 1.6 V. The resistance of the symmetric cells is also significantly diminished by using the optimum electrolyte concentrations, with remarkable improvements not only in the equivalent series resistance, but also in the distributed resistance. Both high-rate capacitance and lower resistance are beneficial to increase the energy of supercapacitors working at high discharge rates. The small size of electroadsorbed dehydrated chloride ions allows the use of less expensive carbons with narrower micropores instead of strongly activated carbons with larger micropores required for bulkier anions.

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1. Introduction

Electrochemical capacitors or supercapacitors have found their niche as a promising solution for fast charging and regenerative energy acquisition. In most of the applications they are used to complement batteries but, owing to their excellent low temperature performance, calendar and cycle life, fast charge-discharge and reliability [1], they can even replace them in those applications where size and weight are not of primary concern. One of the key parameters hindering the more extensive use of supercapacitors is indeed their low energy density; in the best cases about an order of magnitude lower than batteries [2]. Two main approaches can be followed to increase the energy density of supercapacitors; one involves the usage of active materials of higher capacitance and the other one the enlargement of the cell voltage by using novel electrolytes and asymmetric/hybrid cells [3]. Although several transition metal oxides and polymers have exhibited capacitance values that exceed by far those obtained with carbonaceous materials (up to 1000 F g⁻¹ vs. 250 F g⁻¹), the latter ones continue to be the materials of choice as they provide the best trade-off between performance and cost. Linked to environmental consciousness, the exploitation of sustainable and renewable systems

for the preparation of electrode materials is nowadays a priority, and thus, activated carbons (ACs) derived from biomass feed-stock or natural wastes are acquiring increased importance in the field of supercapacitors [4].

The use of aqueous over organic electrolytes has the advantage of providing lower equivalent series resistance (ESR), higher ionic conductivity, and higher capacitance. Safety is another important parameter that is strengthened when working with water instead of organic solvents such as acetonitrile or propylene carbonate [5]. For instance, acetonitrile can cause cyanide poisoning and has a flash point of only 6 °C [6] (Flammability of Chemical Substances, 2003–2004). Nevertheless, the energy stored in a supercapacitor is proportional to the square of the cell voltage as expressed in Eq. (1),

$$E = \frac{1}{2}CV^2 \quad (1)$$

where C is the capacitance and V the cell voltage. Thus, most of the commercially available supercapacitors work in organic-based electrolytes due to the limited voltage window of alkali- and acid-based aqueous systems, typically below 1 V (thermodynamic stability window of water is 1.23 V) while organic systems can easily reach 2.5–2.7 V [7,8].

Very recently several studies have shown that electrodes made of AC can work in aqueous sulphate salts in a voltage window of about 1.9 V without significant capacitance fading [9–11]. A local

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increase in the concentration of OH⁻ ions in the porosity of the negative carbon electrode due to water reduction and concomitant weak chemisorption of atomic hydrogen seems to be the reason for the extended voltage window [11], shifting the potential of molecular hydrogen evolution at the negative electrode to lower values (according to the Nernst equation) [12]. All these results have opened up the possibility of using inexpensive and less hazardous electrolytes without drastically sacrificing the energy density of the device. On the electrode side, the compatibility between the size of ions and pores should be sought at least to maximize volumetric capacitance. Additionally, some studies claim that areal capacitance can be enhanced if the pore size and ion size are matched [13–15]. However, for an efficient power response, the ion size should be slightly smaller than the carbon pore size [16]. Monovalent anions such as Cl⁻ are electroadsorbed in the nonhydrated state whereas sulphate ions are adsorbed in the hydrated state with a size exceeding 0.733 nm [9]. In this sense, if smaller ions such as Cl⁻ (a diameter slightly larger than 0.362 nm [13]) could also be successfully used in an extended-voltage cell instead of a much bulkier sulphate anion, a larger variety of ultramicroporous carbon electrodes with moderate specific surface area (SSA) could be employed. Importantly, such carbons can be expected to be somewhat denser (because of their moderate pore volume) and less expensive (milder activation conditions). However, the main problem caused by the presence of chlorides is pitting corrosion occurring on several metals, which reduces the choice of well-suited current collectors. To conclude, the affordability and variety of compatible carbons make chlorides an alternative to other neutral salts, provided inexpensive chloride-resistant current collectors are used.

This work concentrates on the enhancement of chloride-based aqueous symmetric supercapacitors through the optimization of electrolyte concentration using two microporous carbons with significantly different pore size distributions.

2. Experimental

2.1. Preparation of microporous carbons by alkali activation

The activation of carbons was conducted after carbonization of raw olive pits as described elsewhere [17]. Briefly, the raw material was heated under an Ar flow of 100 ml min⁻¹ at a ramp rate of 5 °C min⁻¹ in a tubular furnace to a predefined temperature and further holding the temperature for 2 h at 700 °C (the carbonization yield for olive pits is 25 ± 1%). After carbonization, the resulting char was physically mixed with potassium hydroxide, KOH, in a mass ratio of 1 to 6 and 1 to 2. The materials mixed with KOH were placed in an Inconel® boat and activated by heating up to 700 °C under Ar flow (100 ml min⁻¹) inside a horizontal stainless steel tube within a tubular furnace. The heating ramp rate was 5 °C min⁻¹ and the holding time at 700 °C was 2 h. After activation, the resulting microporous carbons, hereafter referred to as AC16 and AC12 (see Table S1), were washed off with a diluted solution of hydrochloric acid and water until neutral pH was reached and then dried at 120 °C under vacuum. The activation yield was 65 % and 75 %, correspondingly.

2.2. Textural and X-ray photoelectron spectroscopy characterization

Nitrogen adsorption isotherms were measured at -195.8 °C using a Micromeritics ASAP 2020 instrument for relative pressure (P/P₀) between 10⁻⁸ and 0.995 for samples preliminarily outgassed for 24 h at 200 °C. The SSA values and pore size distribution were calculated by applying the recently-developed 2D Non Local Density Functional Theory (2D NLDFT) treatment to N₂ adsorption isotherms using the data reduction software SAEIUS [18]. The

average pore size (L_0) was calculated as a weighted average from the DFT data according to the formula:

$$L_0 = \frac{\int_{V_{\min}}^{V_{\max}} L dV}{V_{\max} - V_{\min}} \quad (2)$$

where V_{\max} and V_{\min} are the total pore volume and the pore volume at the minimum pore size, correspondingly, and L the pore size corresponding to the total pore volume V accumulated by the pores with size $\leq L$.

XPS C1s and O1s spectra were recorded using PHOIBOS 150 analyser (SPECs, Germany) and monochromated Mg K_α X ray source.

2.3. Electrode preparation and electrochemical measurements

Electrodes were prepared by mixing AC (95 wt. %) and polytetrafluorethylene (PTFE) binder (5 wt. %, from a 60 wt. % aqueous dispersion, Sigma-Aldrich) with a few millilitres of ethanol until plasticity was achieved. The plastic composite was then rolled to a thickness of ~200 μm and dried under vacuum at 120 °C overnight. Electrodes of 11 mm in diameter were then cut, weighed, and their thickness was measured again. Finally, two-electrode symmetric supercapacitor cells were assembled in a Nylon Swagelok® airtight system, using two titanium current collectors, a porous glass fibre (Whatman GFB) membrane separator and Li, Na and K chloride solutions of various concentrations as supporting electrolytes. A saturated calomel electrode (SCE) was used to monitor the potential evolution of each electrode in some of the symmetric two-electrode cells.

Cyclic voltammetry (CV), galvanostatic (GA) charge-discharge cycling and electrochemical impedance spectroscopy (EIS) measurements were conducted using a multichannel VMP3 generator (Biologic, France). EIS measurements were carried out by applying a low sinusoidal amplitude alternating voltage of 10 mV at frequencies from 1 MHz to 10 mHz using the same instrument.

The average gravimetric capacitance per electrode of a two-electrode symmetric cell was calculated from the data of the GA experiments according to the formula:

$$C = 2 \frac{\int Idt}{\Delta V m_{am}} \quad (3)$$

where C is the gravimetric capacitance per electrode (F g⁻¹), Idt the differential charge (A s), ΔV the cell voltage (V), m_{am} the mass of active material per electrode (g). The capacitance values are reported for the voltage range between 0V and the maximum cell voltage, excluding the voltage drop from equivalent series and distributed resistance.

The differential gravimetric capacitance per electrode of a two-electrode cell in the CV experiments was calculated according to the formula:

$$C = \frac{2i}{\left(\frac{dV}{dt}\right) m_{am}} \quad (4)$$

where C is the gravimetric capacitance per electrode (F g⁻¹), i the instant current (A), dV/dt the scan rate (V s⁻¹), m_{am} the mass of active material per electrode (g).

Three-electrode CV measurements were conducted in Swagelok cells by scanning an activated carbon (AC12 or AC16) pellet as the working electrode vs. a saturated calomel electrode in 6 M LiCl, 5 M NaCl, and 2 M KCl electrolytes using an oversized Norit DLC Super 30 activated carbon as the counter electrode.

The floating test procedure applied to the cells was described previously by Kötz et al. [19]. Briefly, a maximum voltage was applied to the cells and during this voltage holding period, 5 GA charge/discharge cycles at a constant current of 1 A g⁻¹ were

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