Influence of electrolyte ion–solvent interactions on the performances of supercapacitors porous carbon electrodes

C. Decaux [a], C. Matei Ghimbeu [b], M. Dahbi [c], M. Anouti [c], D. Lemordant [c], F. Béguin [d], C. Vix-Guterl [b], E. Raymundo-Piñero [a,e,*]

[a] Centre de Recherche sur la Matière Divisée, CNRS — Université, 1b Rue de la Férollerie, 45071 Orléans, France
[b] Institut de Science des Matériaux de Mulhouse (IS2M), UMR-7361 CNRS — UHA, 15, rue Jean Starcky, BP 2488, 68057 Mulhouse, France
[c] Université François-Rabelais, Physicochimie des matériaux et électrolytes pour l'énergie, PCM2E (EA 6299), Fac Sci & Tech, F-37200 Tours, France
[d] Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Piotrowo 3, 60-965 Poznan, Poland
[e] CNRS, CEMHTI UPR3079, Univ. Orléans, F-4071 Orléans, France

HIGHLIGHTS

- A series of porous carbons with tuneable porous texture were prepared.
- Performance of carbon supercapacitors were evaluated in different electrolytes.
- Relationship between porous texture and solvent–salt interaction was studied.
- Highly polarizing ions in polar solvents do not completely loss the solvation shell.
- The optimal carbon pore size depends on the solvent-ion couple used as electrolyte.

ARTICLE INFO

ABSTRACT

The development of advanced and safe electrochemical supercapacitors or hybrid supercapacitors combining a battery electrode material such as graphite and a porous carbon electrode implies the use of new electrolytes containing a tetra-alkylammonium or lithium salt dissolved preferentially in a safe and environmentally friendly solvent such as alkylcarbonates. In those systems, the carbon porosity of the activated carbon electrode controls the electrochemical behavior of the whole device. In this work, it is demonstrated that electrolytes containing highly polarizing ions such as Li^+ dissolved in polar solvents such as alkylcarbonates do not completely loss their solvation shell at the opposite of what is observed for poorly solvated cations like $TEABF_4$. As a consequence, the optimal carbon pore size for obtaining the largest energy density, while keeping a high power density, is wider when strongly solvated cations, like Li^+ are used than for conventional organic electrolytes using acetonitrile as solvent and TEA^+ as salt cations. TEA^+ cations are easily desolvated and hence are able to penetrate in small pores matching the dimensions of bare ions. The dissimilarity of behavior of alkylcarbonates and acetonitrile based electrolytes highlights the importance of ion–solvent interactions when searching the optimal porous texture for the electrode material.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Most industrial electric double layer capacitors (EDLC) are built with porous carbon electrodes, but new devices which combine a battery type electrode and a porous carbon electrode (hybrid supercapacitors or Li-ion capacitors (LIC)) are able to provide higher operating voltages and larger specific energies [1–14]. As the energy stored in an electrochemical capacitor increases, the search of safe and efficient new electrolytes is needed. At this time, the most popular electrolyte is $TEABF_4$ in acetonitrile (ACN), as this its conductivity is very high owing to the low viscosity of ACN and the large dissociation of $TEABF_4$. The main drawback of this electrolyte is a risk of damaging fires which increases with the size of

* Corresponding author. Centre de Recherche sur la Matière Divisée, CNRS — Université, 1b Rue de la Férollerie, 45071 Orléans, France. Tel.: +33 (0) 238257884; fax: +33 (0) 238638103.
E-mail address: raymundo@cnrs-orleans.fr (E. Raymundo-Piñero).

the electrochemical device owing to the high flammability of ACN. Cyclic alkylcarbonates, like PC, which are far less flammable than ACN, have been proposed as an alternative to ACN as solvent and even mixtures of linear and cyclic carbonates are able to provide a better security [15,16]. When a battery type electrode is used as anode or cathode instead of a porous carbon electrode, a salt containing a lithium cation has to be used, like $LiPF_6$ or LiTFSI, the latest being more stable thermodynamically. Hence different type of electrolytes may be used depending on the type of electrode used (porous carbon electrodes for symmetric EDLCs or a battery type + a porous carbon electrode for hybrid capacitors) and the level of security desired.

Many authors pointed out that the pore size distribution of the active carbon material [16–24] and the electrolyte ions size [27–29] play the most important role on the EDLCs capacitance. Indeed, Chmiola et al. [17] and Raymundo-Piñero et al. [18] showed that the capacitance increases when the pore size distribution is close to the bare electrolyte ions size. Such results are in concordance with previous studies proposing that, when using a standard organic electrolyte i.e. $TEABF_4$ in ACN, ions penetrate in a desolvated state in the carbon pores [28]. Further studies showed that for some moderately activated carbons, matching both the sizes of carbon pores and electrolyte ions does not only enhance the capacitance per unit area, but can also lead to the saturation of the active porosity [19]. As a result, increasing specific capacitance can simultaneously reduce maximum voltage. This feature can be of practical significance as the maximum voltage can be lower than the electrolyte decomposition limits. Therefore, the surface area should be sufficiently large to allow ions electroadsorption over the whole electrolyte voltage window. Relationships between porous texture and capacitance are described in the literature for aqueous or organic electrolytes containing $TEABF_4$ and ionic liquids. However, to our knowledge, the correlation between the capacitance and the carbon textural properties in an electrolyte containing other cations than $TEABF_4$ dissolved in an organic solvent has not been yet fully studied.

When an EDLC or a hybrid supercapacitor is operating, both cations and anions are adsorbed/desorbed at the carbon surface while charging/discharging the supercapacitor and it would be necessary to evaluate the relationship between the carbon pore size and ion size for both of them. Moreover, Morita et al. [25–27] showed that not only the nature of the ionic species, size and chemical properties, but also the solvent or solvent mixture is able to modify the EDLC capacitance owing to ion solvation. The main objective of this work is to investigate the effect of ions size and ions solvation on the electrochemical behavior of symmetrical supercapacitors using as active material a series of porous carbon activated carbons with controlled pore size distribution. The following electrolytes are selected : (I) a 1 mol L^{-1} LiTFSI solution in EC/PC/3DMC (1:1:3 by volume), which has been already identified as an efficient electrolyte for LIC [14], (II) a 1 mol L^{-1} $TEABF_4$ in ACN and (III) a 1 mol L^{-1} LiTFSI in ACN. These electrolytes were prepared for understanding the role of the salt (Li^+ vs TEA^+) and its solvation (alkylcarbonates vs ACN) on the electrochemical performances of porous carbon based electrodes. In this work, the electrochemical behavior of such electrodes will be characterized by cyclic voltammetry, galvanostatic charge/discharge cycles and impedance spectroscopy.

2. Experimental

2.1. Materials

Activated carbons with different textural properties were synthesized by CO_2 activation on precarbonised coconut shells (supplied by PICA) as raw materials. Prior to the activation process the coconut shells were washed with concentrated HF (48%) for 12 h at room temperature, followed by washing with concentrated HCl (32%) for 3 h at 60 °C in order to eliminate the metal impurities. The as-purified precursor was washed with distilled water and then dried at 80 °C in air. Subsequently, the coconut shells (5 g or 10 g) was heated-up to the desired temperature (800 °C or 900 °C) under argon with a heating rate of 5 K min^{-1}. Once the temperature was reached, the Ar flux was switched to CO_2 (3, 4 or 6 L per hour) for several time periods (8–28 h) (see Table 1). After the CO_2 activation phase, the sample was still kept at the same temperature for an hour under Ar before cooling down in the same atmosphere. The as-obtained activated carbons were manually grinded and then sieved with a 40 μm mesh sieve.

All reactants for electrolyte preparation: tetraethylammonium tetrafluoroborate ($TEABF_4$), lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) ethylene carbonate (EC), propylene carbonate (PC), dimethylcarbonate (DMC) and acetonitrile were supplied by Sigma Aldrich and used without further purification. Electrolytes were prepared in an Ar filled glove box and the water content of electrolyte solutions were below 20 ppm as indicated by Karl Fisher titration.

2.2. Chemical and textural characterization

Influence of the activation temperature, activation time and CO_2 flow rate on the characteristics of the activated carbons was studied by several techniques. Material morphology and composition were examined by scanning electron microscopy (Philips model FEI model Quanta 400) equipped with an energy dispersive spectrometer. The textural properties of the carbons were determined from the study of the adsorption isotherms of N_2 at 77 K and CO_2 at 273 K using a Micromeritics ASAP 2020 instrument.

Prior to the analysis, the carbons were out-gassed overnight under vacuum at 300 °C on the degassing port followed by a supplementary out-gassing (4 h) on the analysis port in order to eliminate the backfill gas which could possibly be adsorbed in the micropores during the backfilling step of the analyze tube. This preliminary step appears as of great importance to obtain good quality isotherms in the low pressure range ($P/P_0 < 10^{-6}$) and correct pore size distribution particularly at the microporosity range. The BET surface area (S_{BET}) was calculated from the N_2 adsorption isotherm in the relative pressure range of 0.02–0.3. The microporous (pore diameter < 2 nm) and ultramicroporous (pore diameter < 0.8 nm) volumes were calculated by applying the Dubinin–Raduskevich method respectively to the N_2 ($V_{DR\,N_2}$) and the CO_2 adsorption isotherms ($V_{DR\,CO_2}$) in the range $10^{-4} < P/P_0 < 10^{-2}$. Thus, the volume of mesopores ($2 < d < 50$ nm) can be obtained from the difference of the total pore volume (obtained from the amount of N_2 adsorbed at a relative pressure of 0.95) and $V_{DR\,N_2}$ and the volume of the so-called super-micropores is estimated by the difference $V_{DR\,N_2}$ and $V_{DR\,CO_2}$. The average pore size (L_0) was calculated from the application of the Stoeckli equation to

Table 1
Experimental conditions used for the activation of coconut shell char and burn-off.

Carbon name	Temperature (°C)	Time (h)	Flow rate (l h^{-1})	Burn-off (%)
CA-L	800 °C	28	3	42
CA-I	800 °C	28	4	46
CA-F	800 °C	28	6	53
CA-1	900 °C	8	6	56
CA-2	900 °C	10	6	60
CA-3	900 °C	12	6	66
CA-4	900 °C	14	6	72
CA-5	900 °C	16	6	76