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1,2-butylene carbonate as solvent for EDLCs

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ABSTRACT

The solvent 1,2-butylene carbonate (1,2-BC) displays a set of properties and a price comparable with that of propylene carbonate (PC). In this work we investigate the use of 1,2-BC in combination with the salt butyl-1-methylpyrrolidinium tetrafluoroborate ($Pyr_{14}BF_4$). We showed that the electrolyte 1.5 M $Pyr_{14}BF_4$ in BC displays good conductivities and viscosities, and that is use allows the realization of EDLCs with operative cell potential as high as 3.15 V. These high potential devices display good cycling stability at room temperature. At higher temperature their stability appears comparable of that of devices containing standard electrolytes.

1. Introduction

Electrochemical double layer capacitors (EDLCs, also known as supercapacitors), are nowadays considered a very interesting class of electrochemical storage devices [1–4]. In these devices the energy is stored via a physical process, the formation of a double layer, occurring at the interface between the electrodes and the ions of the electrolyte. State-of-the-art EDLCs consist of activated carbons (AC) as active materials and mixtures of quaternary ammonium salts, typically tetraethylammonium tetrafluoroborate (Et_4NBF_4), in organic solvents, like propylene carbonate (PC) or acetonitrile (ACN), as electrolytes [5]. These devices have an operative cell potential of 2.7–2.8 V. Since the formation of the double layer is a very fast process, taking place at the millisecond scale, EDLCs can be charged and discharged in very short time (seconds or less), and they can deliver very high power (10 kW kg^{-1}). Furthermore, since the double layer formation does not result, ideally, in any structural change, this process can take place with very high efficiency, allowing to the realization of devices with extremely high cycle life (>500.000 cycles) [1–4]. This unique set of properties makes possible to use EDLCs in a variety of applications such as power tools, back-up and start/stop systems [3,4]. For these applications, the energy of commercial devices, which is in the order of 5 Wh kg^{-1}, is enough. Nevertheless, several studies indicated that in order to introduce EDLCs in new application the energy of these devices should be improved [1–8]. For this reason, over the last few years tremendous efforts have been invested into realizing high energy EDLCs.

Since the energy of EDLCs is related to the squared of the operative cell potential, V ($E = \frac{1}{2} \cdot C \cdot V^2$, where C is the capacitance), it is evident that the most straightforward strategy to realize high energy EDCLs consist on the realization of high cell potential (>3 V) EDLCs. Several studies showed that the state-of-the-art electrolytes cannot be utilized for the realization of stable high cell potential EDLCs [9,10] and, for this reason, many efforts are presently dedicated toward the introduction of novel electrolytes [2,3,5–7,11].

Over the last years, several new solvents for supercapacitors have been proposed. The research focused on the use of nitriles [12–18], sulfones [19] and, more recently, cyano esters [20–22]. Also alternative carbonates have been considered in the past. Lithium-ion battery electrolytes, which are consisting on mixtures of linear and cyclic carbonate used in combination with lithium hexafluorophosphate ($LiPF_6$) have been proposed and utilized [23–25]. It has been shown that the use of these electrolytes enables the realization of EDLCs operating at 3 V. Nevertheless, the flammability of the solvents and the chemical and thermal instability of the salt of these electrolytes are hindering their use in commercial devices.

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Also butylene carbonate (BC) has been proposed by Chiba et al. as alternative for PC [26]. In their work they considered two different isomers of BC: the 2,3-butylene (2,3-BC) and the 1,2-butylene carbonate (1,2-BC). They recommended the use 2,3-BC, showing that thanks to the large electrochemical stability of this solvent, BC-based EDLCs might display operative cell potentials higher than 3 V [21]. Nevertheless, the overall performance of BC-based EDLCs did not appear superior of that of PC-based devices. Furthermore, 2,3-BC is rather difficult to synthesise and, for this reason, is expensive. The far cheaper and easier synthesizable solvent 1,2-BC showed also very good properties, but its use did not allow the realization of high cell potential EDLCs. After the pioneering work of Chiba et al. the interest and the investigations about BC decreased sensibly.

Recently, the realization and use of electrolytes containing alternative salts with respect to the state of the art proved to be a very interesting and successful strategy for the realization of high energy EDLCs [5,27–30]. Our group showed that the use of pyrrolidinium based salts and ionic liquids in PC-based electrolytes allow the realization of EDLCs with operative cell potential of 3.2 - 3–5 V [31,32]. It is important to remark that the nature of the solvent, however, has a dramatic influence on the maximum operative cell potential achievable with these new salt [5,33]. For example, the use of pyrrolidinium based salts in ACN is not allowing a significant increment of the operative cell potential compared to the use of Et_4NBF_4 [34].

As mentioned above, 1,2-BC displays interesting properties but its use was not allowing the realization of high cell potential EDLCs. Nevertheless, to the best of our knowledge, this solvent was never used in combination with pyrrolidinium based salts. Taking into account the favourable properties of 1,2-BC, and the result obtained with these alternative salts in PC, we decide therefore to investigate the behaviour of EDLC containing 1-butyl-1-methylpyrrolidinium tetrafluoroborate ($Pyr_{14}BF_4$) in 1,2-BC. Initially, the solubility of this alternative salt and of Et_4NBF_4 in BC have been investigated and compared with those of PC. Afterwards, the conductivity and viscosity of these electrolytes have been determined. Finally, the electrochemical performance of 1,2-BC-based EDLCs has been evaluated and compared with that of conventional PC-based EDLCs.

2. Experimental

The solvent 1,2-butylene carbonate (1,2-BC, 99%, TCI) was dried over molecular sieves (3 Å) until its water content was below 10 ppm, as measured by Karl-Fischer titration. Propylene carbonate (PC) was purchased from Sigma Aldrich in analytical grade and was used without further purification. The salts Et_4NBF_4, $Pyr_{14}BF_4$ were purchased from Sigma Aldrich and Iolitec, respectively. Both of them have been dried in a vacuum glass oven at $2\ 10^{-2}$ mbar and 65 °C for at least two days.

Activated carbon composite electrodes were prepared following the procedure described in Ref. [27]. The ratio between active materials (Norit DLC Super 30), the conducting agent (Super C65) and the binder (CMC) was equal to 0.9/0.05/0.05. Norit DLC Super 30 exhibits an active surface area of 1618 m^2/g consisting mainly of micropores [35]. Additional information regarding the carbon are described in Ref. [35].

The electrode area was 1.13 cm^2 and the mass loading was between 3 mg and 5 mg. For the determination of the operative cell potential in the investigated electrolytes, oversized AC-based electrodes were used. These self-standing AC electrodes were produced by mixing 2.55 g of Norit DLC Super 30, 300 mg of Super C65 conductive additive and 250 mg of a 60% PTFE emulsion with 60 ml of ethanol according to [27]. The electrode area was 1.13 cm^2 and the mass loading was 25 mg.

The solubility of the salts was measured by preparing stock solutions of the desired electrolyte in successive 0.1 M steps inside the glovebox. Once the maximum concentration of salt in the dried solvents was reached, the mixtures were stirred until no more salt was soluble. The conductivity of the electrolyte has been measured using a ModuLab XM ECS potentiostat. By taking the reciprocal of the alternating current resistance, the conductance of the electrolyte was determined. 450 μl of the electrolyte were inserted into a sealed cell with two even platinized platinum electrodes and a known cell constant. Since the cell constant was determined prior to the test with a KCL solution, the conductivity was calculated out of the conductance. The electrolyte filled cell was then polarized by a cell potential of 5 mV at different frequencies between 100 mHz and 100 MHz. The viscosity has been determined by using an “Anton Paar” MCR 102 rotational viscometer with a shear rate of 2000 s^{-1}. Both, conductivity and viscosity have been measured at 20 °C.

All the electrochemical tests have been carried out using Swagelok type cells. For the determination of the operative cell potential an AC-based electrode was used as working electrode, while the self-standing AC electrodes were used as counter electrodes. A silver wire was used as quasi-reference electrode. For the EDLC testing, two AC-based electrodes were used. Since the cathodic and anodic stability of the electrolytes differ, electrodes with different mass loadings [m] were used. To determine the optimal mass ration between the two electrodes, the expression $C^+ \cdot m^+ \cdot \Delta V^+ = C^- \cdot m^- \cdot \Delta V^-$, where ($C$) is the specific capacitance and (ΔV) is the cell potential excursion was used [36,37]. In all tests, a glass fibre Whatman separators (520 μm) were used. All investigated cells have been filled with 120 μL of the investigated electrolyte.

3. Results and discussion

Fig. 1 compares some properties of the solvents PC, 1,2-BC and of 2,3-BC which are of importance for the use as electrolyte in an EDLC (dielectric constant, viscosity, flash/melting/boiling point and cost). As shown, the properties of PC and 1,2-BC are rather comparable. The dielectric constant of PC is slightly higher, whereas the viscosity is lower compared to those of 1,2-BC. Furthermore, PC is slightly cheaper than 1,2-BC. On the other hand, 1,2-BC has a higher boiling point and a slightly higher flash point compared to PC. Taking these properties into account, the presence of the additional CH_2-group on the 1,2-BC does not appear to have a dramatic influence on the solvent properties. It is interesting to notice that this is not the case for the 2,3-BC, which was suggested and investigated by Chiba et al. As shown in the figure, this isomer displays a significantly lower melting point and, also, is more expensive than 1,2-BC and PC. From this comparison, it is therefore evident that among the two BC isomers,1,2-BC appears to display a better set of properties in view of the use in EDLCs. For this reason, we decided to focus our investigation on this isomer which, for convenience, from now on will be indicated simply as BC.

Initially, we investigated the solubility of the salts Et_4NBF_4 and $Pyr_{14}BF_4$ in BC and PC. We found out that the highest concentration possible for the conventional Et_4NBF_4 in BC is 0.8 mol L^{-1}, against 1.3 mol L^{-1} in PC. In the case of $Pyr_{14}BF_4$, the highest concentration possible in PC is equal 3.0 mol L^{-1}, while in BC it is equal to 2.5 mol L^{-1}. It is important to notice that this latter result confirms that the use of the pyrrolidinium-based salt in carbonate solvents allows the realization of more concentrated electrolytes compared to the state-of-the-art salt Et_4NBF_4.

Fig. 2 compares the conductivities (Fig. 2a) and the viscosities (Fig. 2b) of the electrolytes 1 M Et_4NBF_4 in PC, 0.8 M Et_4NBF_4 in BC, 1 M $Pyr_{14}BF_4$ in PC and 1 M $Pyr_{14}BF_4$ in BC at 20 °C. As shown, the conductivities of all electrolytes are high enough for an use in