Adiponitrile-based electrochemical double layer capacitor

A. Brandt, P. Isken, A. Lex-Balducci, A. Balducci*

Westfälische Wilhelms-Universität, Institut für Physikalische Chemie/MEET, Corrensstr. 28/30, 48149 Münster, Germany

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ABSTRACT

In this paper we report on the use of 0.7 M Et_4NBF_4 in ADN as electrolyte in EDLCs. 0.7 M Et_4NBF_4 in ADN displays a wide electrochemical stability window and promising values of conductivity and viscosity. Using this electrolyte it is possible to realize EDLCs with an operative voltage as high as 3.75 V. At RT, these high voltage EDLCs display high coulombic efficiencies, low ESRs and high specific capacitances stable for several thousands of cycles.

The wide electrochemical stability of ADN contributes to preserve the integrity of the electrolyte at potentials in which other conventional organic electrolytes (e.g. ACN) are normally subject to deterioration and/or decomposition processes. Thanks to this intrinsic stability, EDLCs containing 0.7 M Et_4NBF_4 ADN as electrolyte display high capacitance retention over 35,000 cycles carried out with cell voltage as high as 3.5 V.

1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, are today advancing as one of the most promising energy storage technology [1,2]. In EDLCs the charge is electrostatically stored at the electrode–electrolyte interface and, because of this storage mechanism, these devices can be charged and discharged within seconds. Currently, the commercial available EDLCs contain activated carbon as active material and quaternary ammonium salts in propylene carbonate (PC) or acetonitrile (ACN) as electrolyte. These EDLCs have operative voltages in the order of 2.7–2.8 V [3,4], they display high power (up to 10 kW kg^{-1}) and an extremely high cycle life (>500,000) [5]. Because of these characteristics, these systems are nowadays conveniently used in a large number of applications where rapid charge–discharge capability and reliability are required [1,2,5].

In the last years EDLCs have also been proposed for high power/energy applications, such as hybrid and electric vehicles, power quality systems and smart grids [1,6,7]. However, in order to be effectively introduced into these applications, the performance of EDLCs needs to be improved, particularly in terms of specific energy.

The specific energy of EDLCs is defined by the equation $E = 1/2CV^2$, where C and V are the capacitance and operative voltage of the EDLC, respectively. Considering this expression, it is obvious that the enhancement of the operative voltage is the most effective way to increase the energy of EDLCs. Taking into account the charge–discharge storage mechanism of these devices, it appears evident that, in order to realize systems with high operative voltage, the use of electrolytes with wider electrochemical stability windows (ESWs) compared to the state-of-the-art electrolytes is necessary. For this reason, several types of electrolytes have been proposed in the last years as alternative to conventional electrolytes for the realization of high voltage EDLCs.

Generally, the alternative electrolytes proposed so far can be divided in two main categories: ionic liquid (IL) and organic solvent based electrolytes. Regarding IL based electrolytes, several studies showed that by using ILs as electrolytes, EDLCs with an operative voltage as high as 3.5–3.7 V and a high cycling stability can be realized [8–13]. However, because of the relative high viscosity of these electrolytes, the performance of these IL-based EDLCs is often limited at room temperature (RT). Particularly, the equivalent series resistance (ESR) of these devices is considerably higher than that of EDLCs with conventional electrolytes, limiting their power at RT. Regarding organic solvent based electrolytes, some groups proposed the use of mixture of low-viscosity linear carbonates and PC for the realization of EDLCs with an operative voltage as high as 3 V [14,15]. In parallel, new types of solvents have been proposed. For example, Naoi et al. proposed the use of sulfone based electrolytes (e.g. dimethylsulfone) for EDLCs [15] and showed that by employing this electrolyte it is possible to realize EDLCs with an operative voltage of 3.3 V, high performance and high cycling stability.

These reports show that IL based electrolytes allow higher operative voltages with respect to organic solvent based electrolytes whereas latter are superior for the realization of systems with low ESR at RT due to their lower viscosity. Therefore, electrolytes enabling high operative voltages like IL based electrolytes while

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* Corresponding author. Tel.: +49 2518336083; fax: +49 2518336084.
E-mail addresses: a.lex-balducci@uni-muenster.de (A. Lex-Balducci), andrea.balducci@uni-muenster.de (A. Balducci).

displaying viscosities close to that of conventional electrolytes are extremely attractive for the realization of high voltage and high performance EDLCs.

In 1997, Ue et al. investigated the chemical–physical properties of several dipolar aprotic solvents with the aim to identify the best electrolytes for high performance EDLCs [16,17]. Among these solvents, also dinitriles were studied and it was reported that e.g. adiponitrile (ADN) displays an overall ESW of more than 5 V and a decent conductivity at RT. Considering these properties, ADN seems to be an attractive solvent for use in high voltage electrochemical devices. Recently, ADN has been investigated as electrolyte solvent for lithium-ion batteries (LIBs) [18]. However, to the best of our knowledge, the use of ADN as solvent for electrolytes in EDLCs has not been investigated so far.

In this manuscript we report on the use of an ADN-based electrolyte for the realization of high voltage EDLCs. In the first part of the paper the chemical–physical properties of the electrolyte 0.7 M Et_4NBF_4 in ADN are investigated and compared with that of the conventional electrolyte 1.0 M Et_4NBF_4 in ACN. In the second part the performance of EDLCs containing 0.7 M Et_4NBF_4 in ADN are investigated at RT in terms of specific capacitance and cycling stability at various operative voltages and current densities. Finally, in the third part of the paper the influence of the electrolytes 0.7 M Et_4NBF_4 in ADN and 1 M Et_4NBF_4 in ACN on the performance of EDLCs operating at 3.5 V at RT is studied.

2. Experimental

ADN (Sigma–Aldrich, purity 99%) was dried over molecular sieve (3 Å). ACN (battery grade Merck, Germany) was used as received. The electrolytes 0.7 M Et_4NBF_4 in ADN and 1 M Et_4NBF_4 in ACN displayed water contents lower than 30 ppm, as measured by Karl Fischer technique.

The conductivity of the electrolytes was measured with a Solartron model 1260 Impedance couple with a potentiostat/galvanostat 273A PAR. A 0.01 M aqueous solution of KCl (VWR) was used to calibrate the sealed glass conductivity cell with platinized Pt electrodes. Electrolyte preparation and assembling of the cell were done in an argon filled glove box. The concentration dependency of the conductivity for the electrolyte Et_4NBF_4 in ADN was determined in the range extending from 0.3 M to 0.7 M at 25 °C.

The viscosity of the electrolytes was evaluated at 25 °C as indicated in Ref. [19].

Table 1
Conductivity and viscosity of 0.7 M Et_4NBF_4 in ADN and 1 M Et_4NBF_4 in ACN electrolytes at 25 °C.

| Electrolyte	Conductivity/mS cm^{-1}	Viscosity/mPa s
0.7 M Et_4NBF_4 in ADN	4.3	6.6
1.0 M Et_4NBF_4 in ACN	55.0	0.6

Carbon electrodes were prepared following a recipe similar to that indicated in Ref. [20] using active carbon (DLC Super 30, Norit) as active material. The composition of the dry electrode was 80 wt.% active material, 15 wt.% conducting agent (Super P, Timcal) and 5 wt.% binder (Sodium carboxymethyl-cellulose, CMC, Dow Wolff Cellulosics). The average active material mass loading was about 2.8 mg cm^{-2} and the electrode area 1.13 cm^2. In all experiments a Whatman GF/D glass microfiber filter (thickness: 675 μm) with a diameter of 12 mm was used as separator and drenched with 80 μL of the considered electrolyte.

All electrochemical tests were carried out at RT with Swagelok®-type 3-electrode cells using a VMP multichannel potentiostatic–galvanostatic system (Biologic Science Instrument, France). In order to evaluate the maximum operative voltage of 0.7 M Et_4NBF_4 in ADN and 1 M Et_4NBF_4 in ACN electrolytes, cyclic voltammetry (CV) was carried out at 20 mV s^{-1} in a 3 electrode configuration. In this test, the counter electrode was a carbon electrode with a mass loading more than 5 times higher than that of the working carbon electrode. An Ag quasi-reference electrode was used as reference electrode. The EDLCs performance was evaluated by galvanostatic charge–discharge tests carried out at RT applying current densities ranging from 5 to 50 mA cm^{-2}. The values of capacitance of active material (C_{am}), ESR, coulombic efficiency (η), average energy density (E) and average power density (P) were calculated as indicated in Ref. [20].

Impedance spectra were recorded at RT using a frequency-response analyzer Solartron model 1260 Impedance couple with a potentiostat/galvanostat 273A PAR with 5 mV ac perturbation in the frequency region from 500 kHz to 10 mHz. The values of capacitance of active material (C_{am}) and ESR were calculated as indicated in Ref. [8,9].
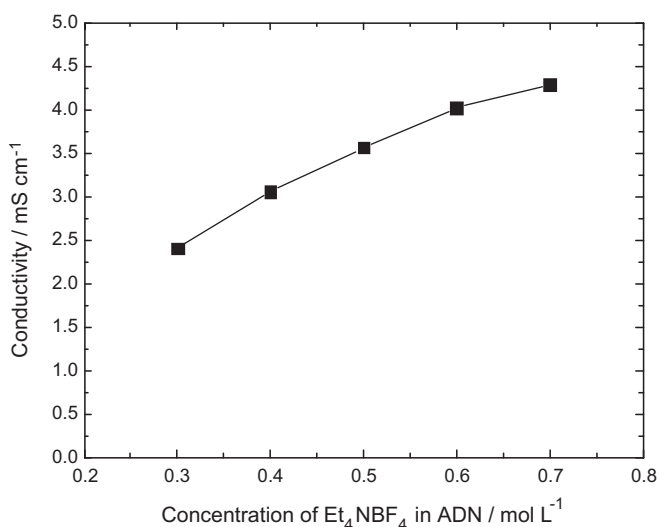
Fig. 1. Ionic conductivity of Et_4NBF_4 in ADN as a function of salt concentration at 25 °C.
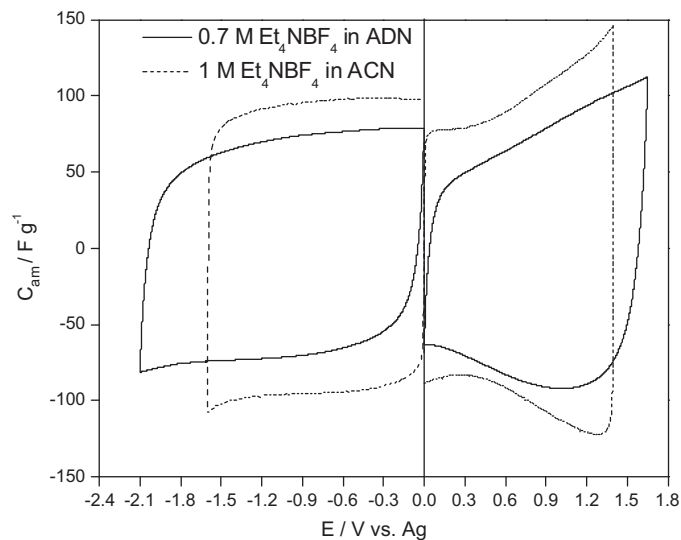
Fig. 2. Specific capacitance values of a carbon electrode in 0.7 M Et_4NBF_4 in ADN and in 1 M Et_4NBF_4 in ACN obtained from CV at 20 mV s^{-1} by dividing the specific current by the scan rate.
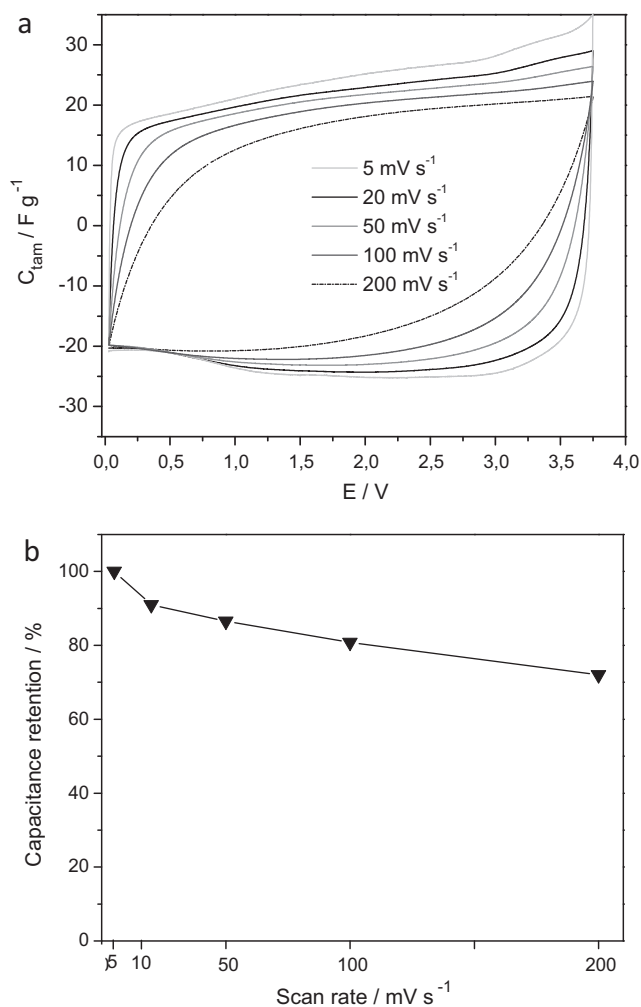
Fig. 3. (a) Specific capacitance values (referred to the total active material) of an EDLC in 0.7 M Et$_4$NBF$_4$ in ADN obtained from CVs carried out at scan rate ranging from 5 to 200 mV s^{-1} by dividing the specific current by the scan rate. (b) Capacitance retention of the same EDLC in 0.7 M Et$_4$NBF$_4$ in ADN obtained from CVs carried out at scan rate ranging from 5 to 200 mV s^{-1}.

3. Results and discussion

3.1. Physical–chemical characterization of ADN-based electrolytes

For the realization of high performance EDLCs, the use of electrolytes with high conductivity represents an important parameter. Considering this point, we initially investigated the dependency of the conductivity of ADN-based electrolytes on the concentration of the conductive salt Et$_4$NBF$_4$. As shown in Fig. 1, the conductivity of the electrolyte increased with increasing conductive salt concentration. The highest conductivity was observed for the electrolyte 0.7 M Et$_4$NBF$_4$ in ADN. This concentration corresponds to the highest concentration of conductive salt soluble in ADN. At room temperature (RT), this electrolyte displayed a conductivity of 4.3 mS cm^{-1}.

Table 1 shows the viscosity and conductivity at 25 °C of 0.7 M Et$_4$NBF$_4$ in ADN in comparison to that of 1 M Et$_4$NBF$_4$ in ACN, one of the electrolytes currently used in commercial EDLCs [3,4]. As shown in the table, the conductivity of 0.7 M Et$_4$NBF$_4$ in ADN is lower than that of 1 M Et$_4$NBF$_4$ in ACN (4.3 mS cm^{-1} vs. 55 mS cm^{-1}, respectively). On the other hand, the viscosity of 0.7 M Et$_4$NBF$_4$ in ADN is higher than that of the 1 M Et$_4$NBF$_4$ in ACN (6.5 mPa s vs. 0.6 mPa s,
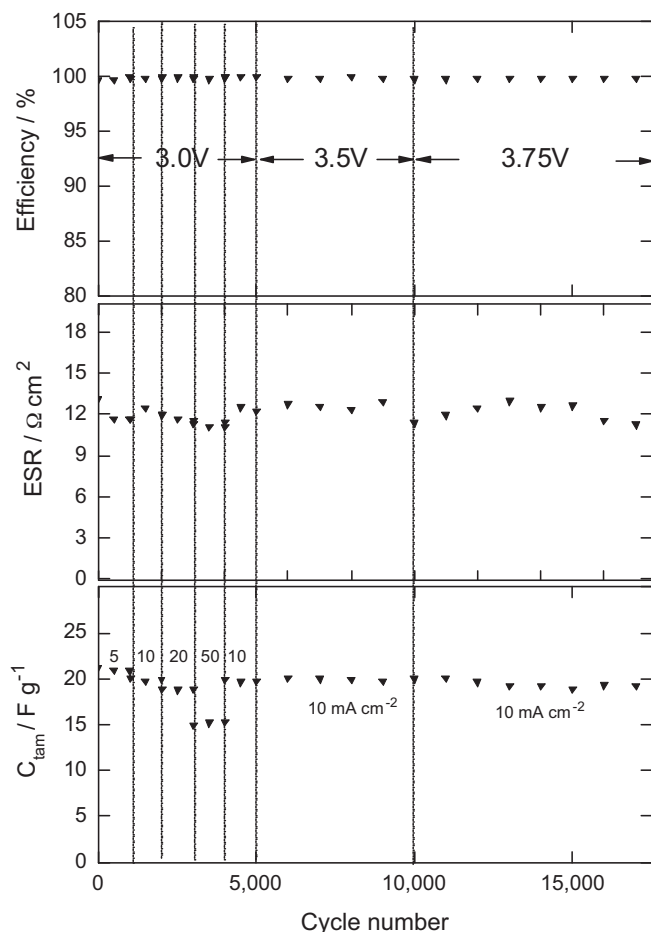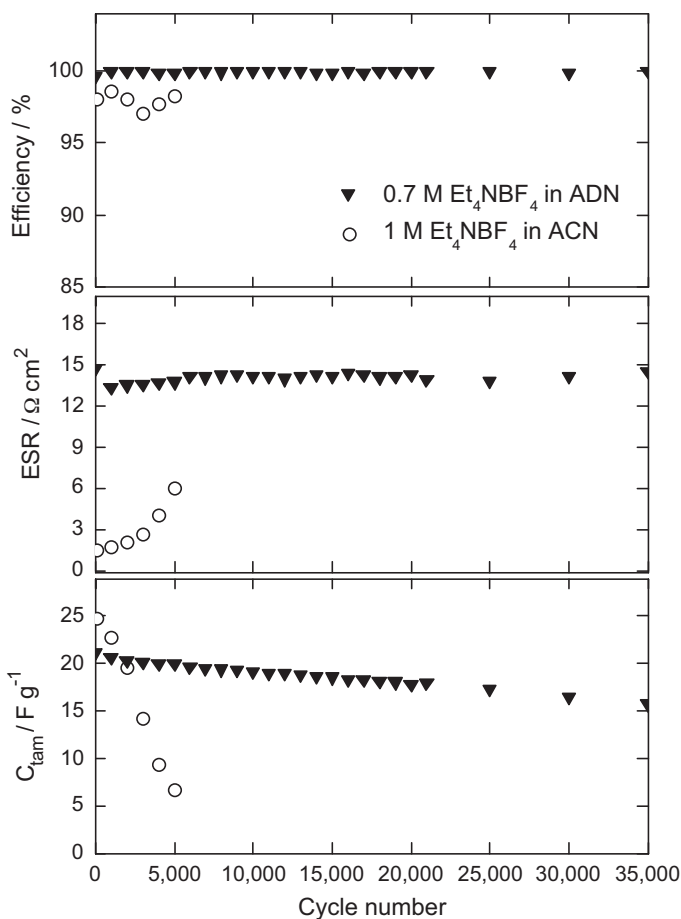

Fig. 4. Evolution of coulombic efficiency, ESR and specific capacitance of the total active material (C_{tam}) vs. cycle number for a 0.7 M Et$_4$NBF$_4$ in ADN based EDLC obtained from galvanostatic charge–discharge measurements at 5, 10, 20 and 50 mA cm^{-2} carried out using cell voltages ranging from 3.0 V to 3.75 V.

respectively). However, even if the values of conductivity and viscosity of 0.7 M Et$_4$NBF$_4$ in ADN appear less favorable than those of 1 M Et$_4$NBF$_4$ in ACN, it is important to note that also other organic solvent based electrolytes proposed in literature for the realization of high voltage EDLCs show comparable values [15]. Moreover, the viscosity of 0.7 M Et$_4$NBF$_4$ in ADN is considerably lower than that of several ILs proposed as electrolyte solvents for EDLCs [8–13,21].

3.2. 0.7 M Et$_4$NBF$_4$ in ADN as electrolyte for EDLCs

One of the main advantages related with the use of 0.7 M Et$_4$NBF$_4$ in ADN is its wide ESW which should allow the realization of EDLCs with high operative voltages [16]. Considering this point, we initially determined the maximum operative voltage possible with this electrolyte. The positive and the negative potential limits were defined as the highest and the lowest values of potential, respectively, in which the efficiency of the charge–discharge process was higher than 99%. As shown in Fig. 2, a positive potential limit of 1.65 V vs. Ag and a negative potential limit of −2.1 V vs. Ag were determined when using 0.7 M Et$_4$NBF$_4$ in ADN as electrolyte in combination with AC based electrodes. This corresponds to a maximum voltage of 3.75 V. This operative voltage is comparable with that possible with IL-based electrolytes [9–22] and it is significantly higher than that of conventional electrolytes. For example, the maximum operative voltage which can be reached using 1 M Et$_4$NBF$_4$ in ACN in combination with the same electrode was 3.0 V. This voltage could be improved using other kind of carbonaceous

Fig. 5. Evolution of coulombic efficiency, ESR and specific capacitance of the total active material (C_{tam}) vs. cycle number for 0.7 M Et$_4$NBF$_4$ in ADN and 1 M Et$_4$NBF$_4$ in ACN based EDLCs obtained from galvanostatic charge–discharge measurements at 10 mA cm^{-2} carried out using a cell voltage of 3.5 V.

Fig. 6. Evolution of power density and energy density vs. cycle number for 0.7 M Et$_4$NBF$_4$ in ADN and 1 M Et$_4$NBF$_4$ in ACN based EDLCs obtained from galvanostatic charge–discharge measurements at 10 mA cm^{-2} carried out using a cell voltage of 3.5 V.

materials [14]. However, as reported in the introduction, when 1 M Et$_4$NBF$_4$ in ACN is used in commercial EDLCs, which mainly contain activated carbons as the active materials, only operative voltage as high as 2.7–2.8 V are applicable [5]. It is interesting to note that even if the conductive salt was the same, the potential limits determined during the test were significantly different for the two electrolytes. Particularly, the negative limit of the ADN-based electrolyte (−2.1 V vs. Ag) was much higher than that observed for the ACN-based electrolyte (−1.5 V vs. Ag). This difference is most likely related to the higher electrochemical stability of ADN with respect to ACN [16].

As expected, the EDLC comprising 0.7 M Et$_4$NBF$_4$ in ADN displayed a lower specific capacitance compared to that with 1 M Et$_4$NBF$_4$ in ACN due to the differences in conductivity and viscosity (see Table 1). However, the specific capacitance obtained with the ADN based electrolyte was not dramatically lower than that obtained in the ACN based one, even if the tests were carried out at RT. Considering the significantly higher electrochemical stability these results show that 0.7 M Et$_4$NBF$_4$ in ADN is certainly a promising electrolyte for the realization of high voltage EDLCs.

In order to take full advantage of the wide ESW of 0.7 M Et$_4$NBF$_4$ in ADN it is important to use electrodes with different mass loadings as the values of the negative and positive potential limit are quite different with the negative being much larger than the positive one (−2.10 V vs. +1.65 V). This strategy was reported by Lazzari et al. for EDLCs employing IL based electrolytes, which display similar operative voltages like ADN [9]. It was shown that the use of electrodes with different masses enables a better utilization of the
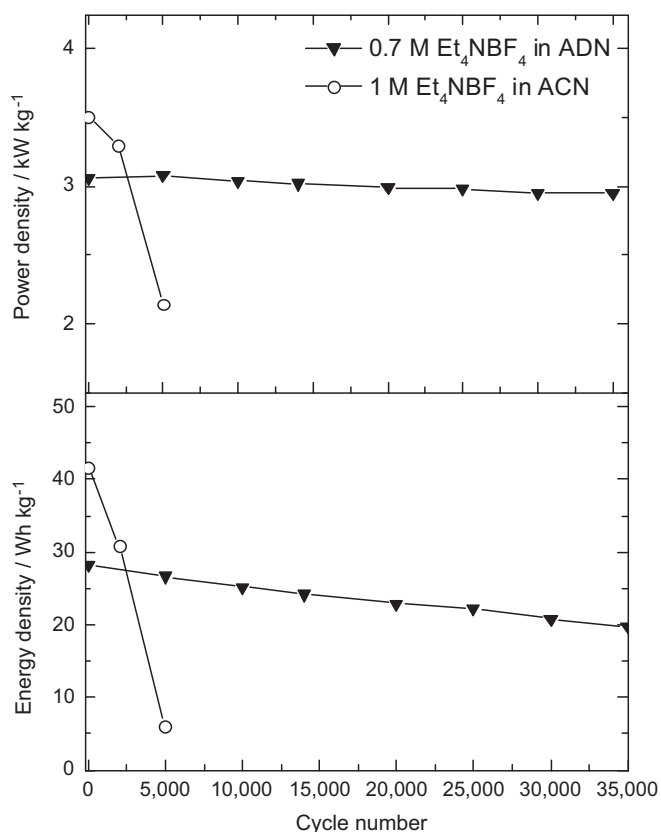
electrochemical stability of the electrolyte compared to the use of two identical electrodes. Recently Cericola et al. showed that this approach can be successfully employed also for reducing the aging of EDLCs containing ACN-based electrolytes cycled at 3.5 V [23].

The optimal mass ratio between the positive and the negative electrode can be calculated using the equation $C_+ m_+ \Delta V_+ = C_- m_- \Delta V_-$, where C is the specific capacitance of the electrode, m the electrode mass and ΔV the voltage excursion at which the positive and the negative electrodes are subjected [9]. Considering a specific capacitance of 75 F g^{-1} in the whole operative range of potential defined in the previous experiment (from −2.1 V to 1.65 V vs. Ag), a mass ratio m_+/m_- equal to 1.3 results to be the optimal for the realization of EDLCs with an operative voltage of 3.75 V.

Using this electrode mass ratio, an EDLC containing 0.7 M Et$_4$NBF$_4$ in ADN as electrolyte was assembled and CVs using a cell voltage of 3.75 V and different scan rates ranging from 5 mV s^{-1} to 200 mV s^{-1} were carried out. Fig. 3a shows the CV profiles recorded at the investigated scan rates. It can be seen that the EDLC displayed the typical capacitive behavior in this operative voltage. At 20 mV s^{-1} the specific capacitance of the EDLC (referred to the total active materials) is in the order of 25 F g^{-1}. With increasing scan rates, the shape of the CVs become less rectangular, but the coulombic efficiency of the charge–discharge process was always 100%. As shown in Fig. 3b, a decrease of capacitance occurred during cycles carried out at high scan rate. However, such decrease was not dramatic and at 200 mV s^{-1} the EDLC displayed almost 80% of its initial capacitance. These results clearly indicate that using 0.7 M Et$_4$NBF$_4$ in ADN as electrolyte EDLCs with a very high cell voltage and a good electrode specific capacitance at RT can be realized.
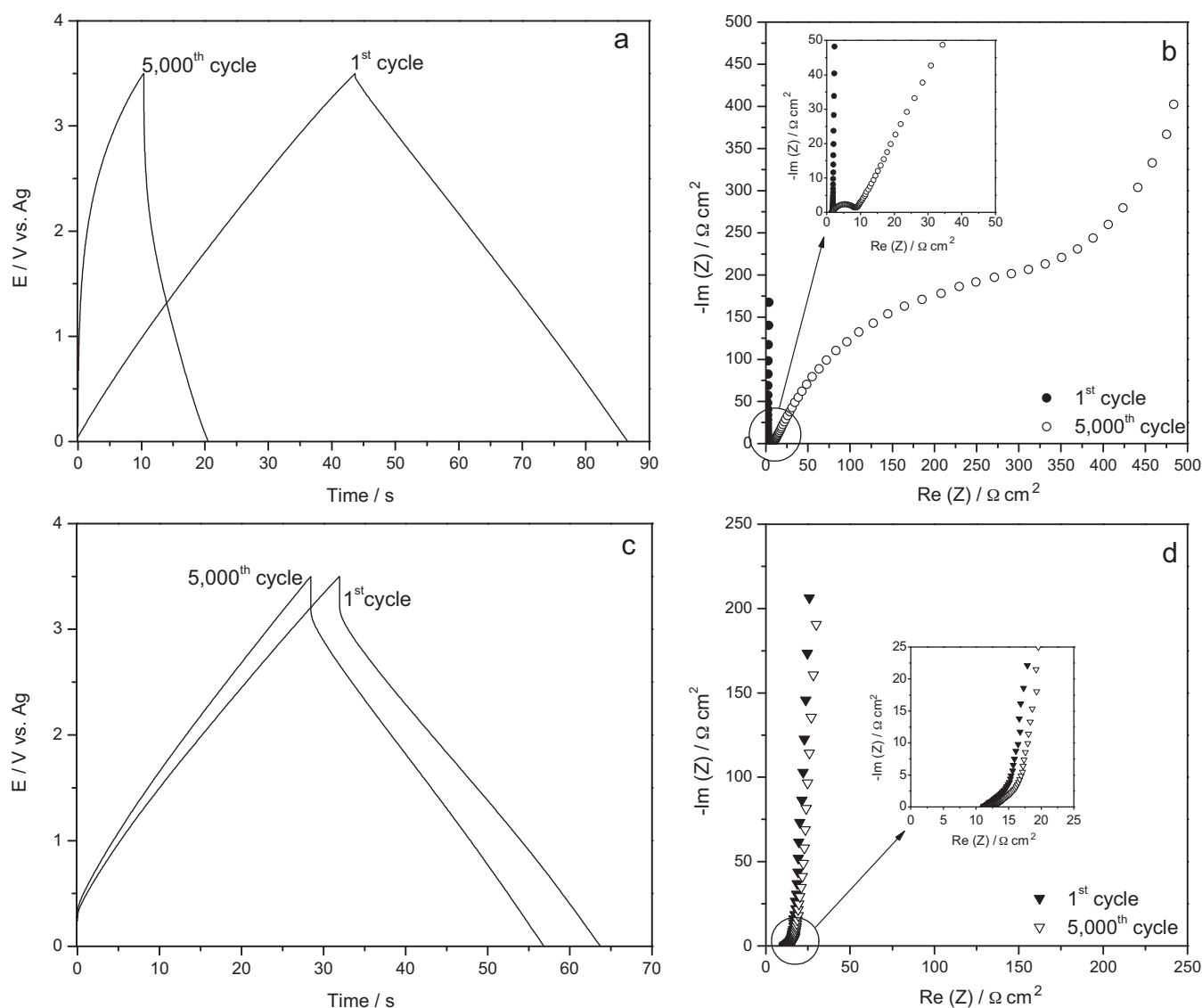
Fig. 7. Evolution of voltage profiles during galvanostatic charge–discharge cycles carried out at 10 mA cm^{-2} using a cell voltage of 3.5 V of 0.7 M Et$_4$NBF$_4$ in ADN (a) and 1 M Et$_4$NBF$_4$ in ACN based EDLCs (c). Evolution of impedance spectra of 0.7 M Et$_4$NBF$_4$ in ADN (b) and 1 M Et$_4$NBF$_4$ in ACN (d) based EDLCs during galvanostatic charge–discharge cycles carried out at 10 mA cm^{-2} using a cell voltage of 3.5 V.

To confirm these promising results, the performance of an EDLC containing 0.7 M Et$_4$NBF$_4$ in ADN as electrolyte during charge–discharge tests was investigated attaching particular importance to the influence of the operative voltage. The EDLC was initially charged and discharged at an operative cell voltage of 3.0 V for 5000 cycles with different current densities ranging from 5 to 50 mA cm^{-2}. After these cycles, the cell voltage was increased to 3.5 V and 5000 cycles at 10 mA cm^{-2} were carried out. Finally, the cell voltage was further increased to 3.75 V and additional 6000 cycles at 10 mA cm^{-2} were conducted. As shown in Fig. 4, the efficiency of the charge–discharge process was close to 100% during all cycles, independently of the applied current density and of the used operative voltage. For all the duration of the test, the ESR was in the range of 12 Ω cm^2. This value is higher than that observed for conventional electrolytes, however, it is much lower than that observed for IL-based EDLCs, even at 60 °C [9–22]. The specific capacitance displayed by the cell (total active material) at 3.0 V was around 21 F g^{-1} at a current density of 5 mA cm^{-2}. With increasing current density the cell capacitance decreased, however, up to 20 mA cm^{-2} it just slightly decreased to 19 F g^{-1}. Only at a

high current density of 50 mA cm^{-2}, the cell specific capacitance decreased to a value of about 15 F g^{-1}. When the applied cell voltage was increased to 3.5 V and 3.75 V, the specific capacitance reached with a current density of 10 mA cm^{-2} was the same like at 3.0 V. Thus, also these results confirm that the use of the electrolyte 0.7 M Et$_4$NBF$_4$ in ADN allows the cycling of EDLCs at operative voltages up to 3.75 V with a high performance and good cycling stability at RT. It is than reasonable to suppose that the use of carbonaceous electrodes with higher affinity for this electrolyte with respect to the actual electrode might even improve the performance of this EDLC.

3.3. The use of 0.7 M Et$_4$NBF$_4$ in ADN and 1 M Et$_4$NBF$_4$ in ACN in EDLCs operating at 3.5 V

In Fig. 5 the cycling stability of EDLCs containing 1 M Et$_4$NBF$_4$ in ACN and 0.7 M Et$_4$NBF$_4$ in ADN, respectively cycled at a cell voltage of 3.5 V is compared. Considering the work of Cericola et al. [23] and taking into account the results shown in the previous section,
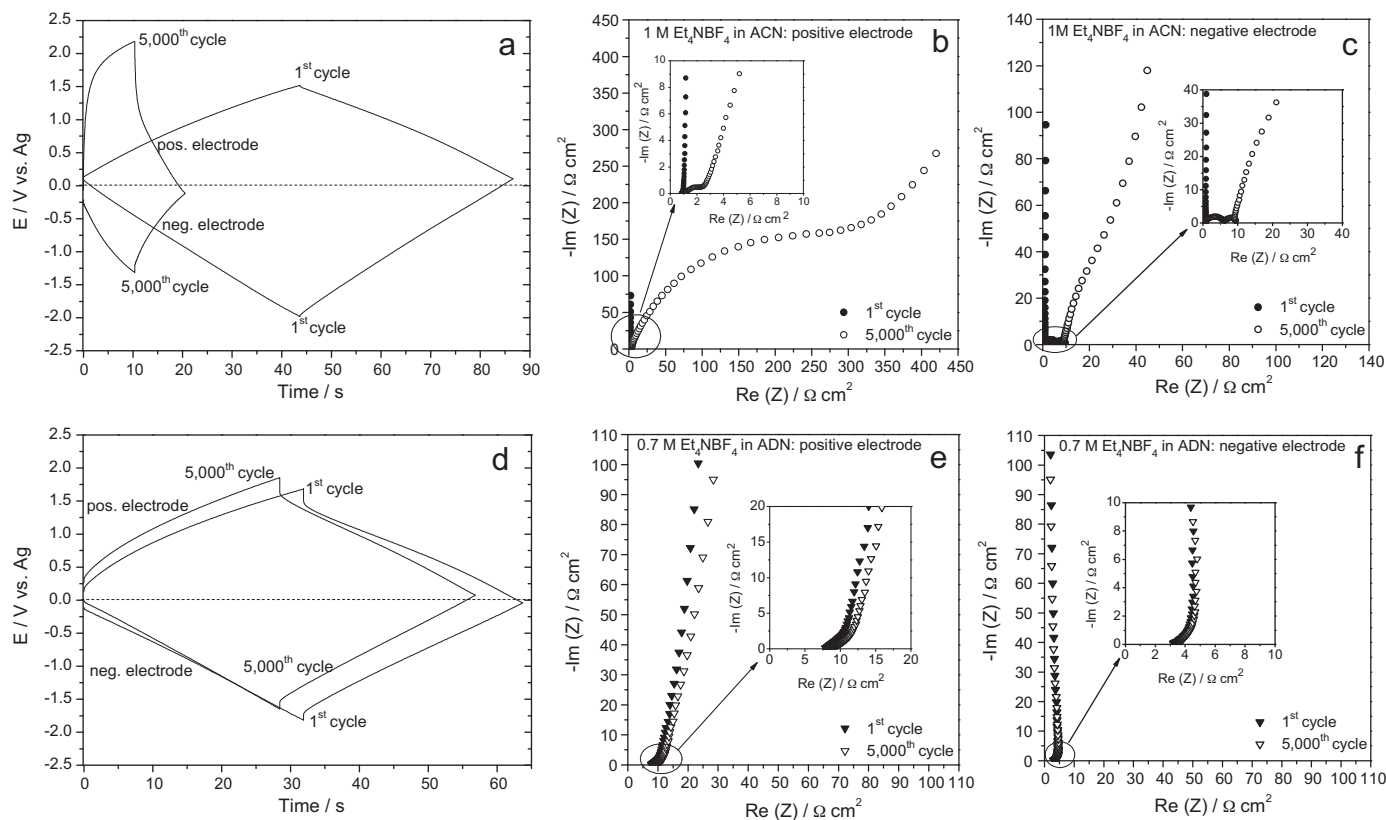
Fig. 8. Evolution of voltage profiles of the positive and negative electrode during galvanostatic charge–discharge cycles carried out at 10 mA cm^{-2} using a cell voltage of 3.5 V of 0.7 M Et$_4$NBF$_4$ in ADN (a) and 1 M Et$_4$NBF$_4$ in ACN based EDLCs (d). Evolution of impedance spectra of the positive and negative electrodes of 0.7 M Et$_4$NBF$_4$ in ADN (b and c) and 1 M Et$_4$NBF$_4$ in ACN (e and f) based EDLCs during galvanostatic charge–discharge cycles carried out at 10 mA cm^{-2} using a cell voltage of 3.5 V.

both EDLCs were assembled using a mass ratio m_+/m_- equal to 1.3 and tested with a current density of 10 mA cm^{-2} at RT.

As can be seen, the EDLC containing 1 M Et$_4$NBF$_4$ in ACN displayed a strong performance fading upon cycling. The efficiency of the charge–discharge process was always lower than 100% and the ESR constantly increased reaching a three times higher value with respect to the initial one already after 5000 cycles. Additionally, the specific capacitance of the active material dropped from 25 F g^{-1} down to almost 5 F g^{-1}. The 0.7 M Et$_4$NBF$_4$ in ADN based EDLC, on the contrary, displayed a very stable behavior for over 35,000 cycles with a charge–discharge efficiency close to 100% and a constant ESR in the range of 13 Ω cm^2. The initial specific capacitance of the active material was about 20 F g^{-1}. The capacitance retention was 85% after 20,000 cycles and still 74% after 35,000 cycles.

Fig. 6 shows the variation of the energy and power densities over cycling for the two EDLCs. As can be seen from the figure, the EDLC containing 1 M Et$_4$NBF$_4$ in ACN displayed initially the highest energy and power. This performance was related to the fact that at the beginning the specific capacitance of the active material was higher and the ESR lower with this electrolyte compared to the one obtained initially with 0.7 M Et$_4$NBF$_4$ in ADN (see Fig. 5). However, already after 2000 cycles both, energy and power, of the ACN-based EDLC strongly decreased and became similar to that of the ADN-based EDLC. Upon cycling the energy and the power of the ACN-based EDLC decreased further (6.0 Wh kg^{-1} and 2.2 kW kg^{-1}, respectively) and were significantly lower than that of the ADN-based EDLC (26.7 Wh kg^{-1} and 3.1 kW kg^{-1}, respectively) after 5000 cycles.

The results of this tests indicated that it is not possible to apply a cell voltage of 3.5 V when using 1 M Et$_4$NBF$_4$ in ACN since this electrolyte does not display a sufficient cycling stability. This is in

agreement with the results reported by another group for tests carried out with similar conditions [5]. On the other hand, it was shown that the use of 0.7 M Et$_4$NBF$_4$ in ADN as electrolyte allows the realization of high performance EDLCs with high operative voltages. As a matter of fact, EDLCs operating at a cell voltage of 3.5 V are able to display good values of energy and power and a stable performance at RT over 35,000 cycles.

In order to understand the different behavior of the two EDLCs, the evolution of the voltage profiles as well as of the electrochemical impedance spectra during cycling were compared. Fig. 7 displays the voltage profiles and the impedance spectra of the two EDLCs at the beginning of cycling and after 5000 cycles. It can be seen that the voltage profile of the EDLC containing 1 M Et$_4$NBF$_4$ in ACN changed considerably and after 5000 cycles the presence of faradic processes was clearly visible (Fig. 7a). As shown in the impedance spectra (Fig. 7b), an increase of distributed resistance as well as of the imaginary part of the impedance at low frequency, which corresponds to an overall reduction of capacitance, occurred during the cycling (see Fig. 7b) [5]. As a consequence, the ESR of the system increased more than 5 times and the specific capacitance of the devices decreased of more than two times (from 19 F g^{-1} to about 8 F g^{-1}) with respect to their initial values. To the contrary, both, voltage profiles and impedance spectra of the EDLC containing 0.7 M Et$_4$NBF$_4$ in ADN changed only slightly during cycling at 3.5 V, confirming the stability of this system (see Fig. 7c and d, respectively).

Fig. 8 shows a comparison of the voltage profiles and the impedance spectra of the positive and negative electrode of the two EDLCs during the considered 5000 cycles. As can be seen from the figure, the behavior of the positive electrode seems to be the main reason for the fading of the EDLC containing the electrolyte 1 M Et$_4$NBF$_4$ in ACN. During cycling, the operative voltage of the

positive electrode of this EDLC increased from 1.5 V to 2.25 V. After 5000 cycles the electrode worked in the range between 0 and +2.25 V vs. Ag (Fig. 8a). At this voltage, the electrolyte was not longer electrochemically stable and faradic processes occurred most likely during the charge–discharge process, as evidenced by the shape of the voltage profile. As a consequence, the specific capacitance of the positive electrode decreased from initially $77\,F\,g^{-1}$ to $21\,F\,g^{-1}$. At the same time, the ESR associated with this electrode increased more than 3 times, from $0.8\,\Omega\,cm^2$ to $2.6\,\Omega\,cm^2$ (see Fig. 8b). In contrast, the negative electrode showed a different behavior. During cycling the operative voltage of this electrode decreased and after 5000 cycles the negative electrode was working in the range between 0 and -1.25 V vs. Ag (Fig. 8a). Also in this case the presence of faradic processes was visible after 5000 cycles but the specific capacitance did not decrease as dramatically as that of the positive electrode. However, the ESR associated with the charge–discharge process of this electrode increased quite considerably. As shown in Fig. 8c, a depressed semi-circle appeared after 5000 cycles. As suggested by Ruch et al., the presence of this semi-circle may reflect an increased contact and distributed resistance [5,24]. This increase of resistance could be associated with the shift of the EDLC operative voltage towards more positive potential during cycling.

The behavior of the positive and negative electrodes in the EDLC containing 0.7 M Et_4NBF_4 in ADN as electrolyte was completely different. As shown in Fig. 8d, also in this EDLC a shift of the operative electrode voltage occurred and, like in the case of the EDLC containing 1 M Et_4NBF_4 in ACN, both the positive and the negative electrode moved towards higher potential. However, the shift experienced by both electrodes after 5000 cycles was only 0.25 V, which was much smaller than that observed for 1 M Et_4NBF_4 in ACN. As a consequence, the voltage profile of both electrodes did not change significantly during 5000 cycles. In Fig. 8e and f it can be seen that also the impedance spectra of both electrodes was almost the same after 5000 cycles resulting in a nearly unchanged ESR and specific capacitance.

The results displayed in Fig. 8 show that the wide electrochemical stability window of ADN seems to contribute to preserve the integrity of the electrolyte at potentials at which other conventional organic electrolytes (e.g. ACN) are normally subject to deterioration and/or decomposition processes. As a consequence, the electrode/electrolyte interface is preserved in a wider range of potential with respect to other organic electrolytes and the charge–discharge process can be carried out for thousands of cycles at 3.5 V without significant failing.

4. Conclusions

The use of of 0.7 M Et_4NBF_4 in ADN as electrolyte in EDLCs appears certainly promising. The electrolyte 0.7 M Et_4NBF_4 in ADN displays a wide electrochemical stability window and promising values of conductivity and viscosity. Using this electrolyte allows the realization of EDLCs with operative voltages as high as 3.75 V. At RT, these high voltage ADN-based EDLCs display high coulombic efficiencies, low ESRs and specific capacitances stable for several thousand cycles. The performance of this EDLC could be further improved, particularly in term of energy and power, using carbon electrodes with higher affinity for this electrolyte.

The wide electrochemical stability of ADN contributes to the preservation of the integrity of the electrolyte at potentials at which other conventional organic electrolytes (e.g. ACN) are normally subject to deterioration and/or decomposition processes. As a consequence, EDLCs containing 0.7 M Et_4NBF_4 in ADN as electrolyte display high capacitance retention over 35,000 cycles carried out at a cell voltage of 3.5 V.

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