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Electrolytes for high voltage electrochemical double layer capacitors: A perspective article

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HIGHLIGHTS

- The electrolytes is a key component in EDLCs.
- A new wave of advanced electrolytes need to be generated.
- A deep chemical-physical investigation of new electrolytes is essential.

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ABSTRACT

The development of innovative electrolyte components is nowadays considered one of the most important aspects for the realization of high energy electrochemical double capacitors (EDLCs). Consequently, in the last years many investigations have been dedicated towards new solvents, new salts and ionic liquids able to replace the current electrolytes.

This perspective article aims to supply a critical analysis about the results obtained so far on the development of new electrolytes for high energy EDLCs and to outline the advantages as well as the limits related to the use of these innovative components. Furthermore, this article aims to give indications about the strategies could be used in the future for a further development of advanced electrolytes.

1. Introduction

Electrochemical double layer capacitors (EDLCs or supercapacitors) are nowadays considered among the most important storage devices [1–4]. In EDLCs the energy is stored through a physical process, the double-layer formation (from which the name), which occurs between the electrodes and the ions of the electrolyte [1–4]. In the commercially available EDLCs activated carbons (AC) are typically used as electrode active material, while the electrolyte consists of solutions containing acetonitrile (ACN) or propylene carbonate (PC) and the salt tetraethylammonium tetrafluroroborate (Et_4NBF_4) (Fig. 1). Since the double layer formation is a very fast process – it can take place in the msec timeframe – EDLCs can be charge and discharge in very short time (seconds or less) and display extremely high power (10 kW kg^{-1}). Moreover, since this physical storage process does not imply (theoretically) any structural change and it can take place with very high efficiency, EDLCs also display extremely high cycle life (>500.000 cycles) [1–4]. These unique sets of properties make possible the use of EDLCs in a variety of applications, e.g. power tool, back-up systems, start/stop systems [1–6]. The market of EDLCs, although is smaller than the one lithium-ion batteries (LIBs), has been constantly increasing in the last years and it is nowadays regarded with high interest by many players of the energy field [5–7]. Many publications indicated that if the energy of EDLCs could be improved, the number of applications for these devices, and thus their market, could increase significantly [5–7]. Therefore, in the last years tremendous efforts have been made to realize high energy EDLCs.

The energy of EDLCs can be described by the equation $E = ½ CV^2$, in which C is the electrode capacitance and V is the operative voltage of EDLCs. Taking this equation into account, it is evident that the most convenient way to increase the energy of EDLCs is to increase their operative voltage, which is currently in the order of 2.7–2.8 V [2,4].

The operative voltage of EDLCs is directly related to the stability of both, electrode and electrolytes. As a matter of fact, in order to

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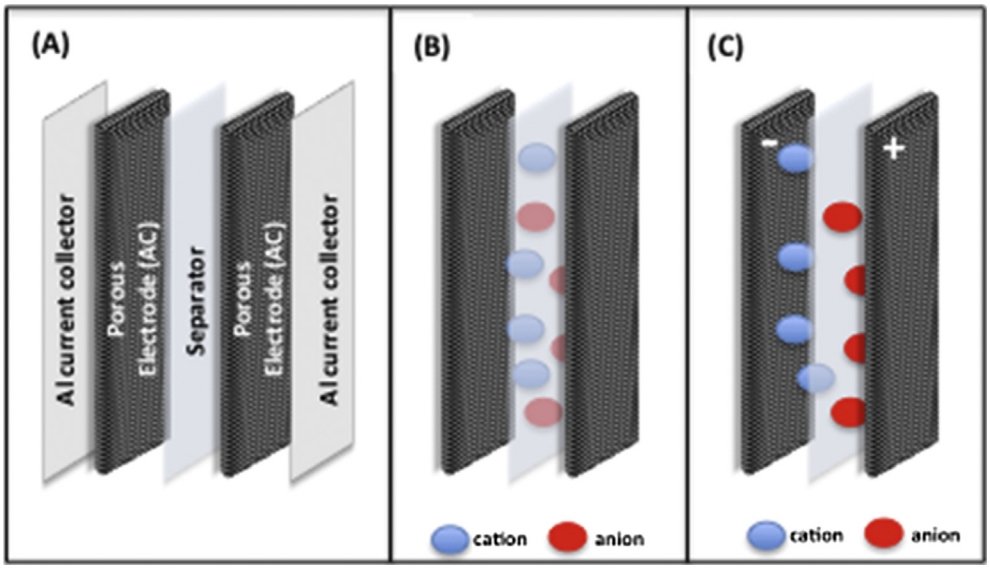

Fig. 1. (a) Schematic illustration of the configuration of EDLCs; (b) components involved on the double layer formation (electrode and ions of the electrolyte); (c) visual representation of the rearrangement of charges (ions) taking place during the charge process (double layer formation).

form the double layer, both components need to be intact. Typically the electrodes used in EDLCs, which consist mainly of carbonaceous materials, are electrochemically and chemically more stable than the electrolyte components. Consequently, the operative voltage of EDLCs is mainly limited by the stability (electrochemical and chemical) of the electrolyte. For this reason, the introduction of alternative electrolytes represents nowadays one of the keys for the realization of high energy EDLCs [1–4].

In the last years many studies have been dedicated to the development of innovative electrolyte components suitable the realization of high voltage, high energy EDLCs. This perspective article aims to supply a critical analysis of the results obtained till now and, at the same time, it also intends to give indications about the strategies could be used in the future for a further development of advanced electrolytes.

1.1. Electrolyte in EDLCs: theoretical considerations

As mentioned above, in EDLCs the charge is stored at the interface between the electrodes and the ions of the electrolytic solution (see Fig. 1). Consequently, in these devices the electrolyte is an active material, just like the electrodes [8–10].

Ideally, the electrolyte of EDLCs should display a number of different chemical and electrochemical properties [3,4]. A list of these properties is reported below. For each property, a short comment about its influence on the EDLCs behavior is included.

- *Large electrochemical stability (ESW).*

As the energy ($E = ½ CV^2$) and the power ($P = V^2/4R$, where R is the resistance) are both depending on the squared of the operative voltage, it is desirable to use an electrolyte with wide electrochemical stability [2]. Furthermore, the use of electrolyte components electrochemically stable is also necessary to guarantee high cycle life [4].

- *High conductivity and low viscosity.*

The double layer formation is strongly affecting the power of EDLCs and the faster is double layer formation, the higher is the resulting power [3]. Therefore, electrolytes with low viscosity and high conductivity are desirable for the realization of a high power EDLCs.

- *Solvent-free*

Since the ions of the electrolyte are involved on the double layer formation, it is desirable to realize highly concentrated electrolytic solution [3,7]. Ideally, the electrolyte should not contain solvent (the so-called solvent-free systems) as this electrolytic component is not directly participating to the storage process and it reduces the energy and the power densities of the devices [8]. Furthermore, as the solvent might be easily flammable, e.g. ACN, the use of solvent-free systems would also improve the safety of EDLCs.

- *Low melting and high boiling points*

In order to be used in large temperature range, as it is required for many applications, the electrolyte should be stable over a broad range of temperatures [3]. Ideally, it should be usable in a range comprise between 100 °C and −60 °C.

- *High chemical stability*

As the ions of the electrolyte are directly involved in the double layer formation, their integrity is essential for the realization of this process and, also, to guarantee a long cycle life [3]. Clearly, this is also true for the solvent of the electrolyte (when it is present). Therefore, ideally, both the ions and the solvent should not react (and decompose) when in contact with the other EDLCs components (carbonaceous electrodes and binders).

- *High flash point*

Since the formation of the double layer does not imply any chemical change on the electrode and electrolyte, this storage process can be considered intrinsically safer than the chemical process used in other electrochemical devices, e.g. LIBs. Nevertheless, in the case a solvent is present in the electrolytic solution, it is desirable to use one with high flash point is order to reduce the risk