Investigation of a solid formed on the electrode surface of a damaged supercapacitor in order to determine the ageing process

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Abstract: Supercapacitors are important energy storage devices with high power and long life. But they always age much faster than expected by some mechanisms. In addition, despite considerable efforts to understand these mechanisms, there is still a lack of a clear picture of the parasitic reactions that occur in operating devices. Therefore, in this work, based on an experimental study of a damaged supercapacitor, we analyzed a white powder occurring on the surface of the electrodes due to aging. The identification of the elements of this powder is carried out by X-ray diffraction, 13C and 1H NMR spectroscopy and thermogravimetric analysis. The results obtained allow us to determine the causes of ageing and thus to understand their mechanisms.

KEYWORDS: Supercapacitors; Mechanisms; Electrode-Electrolyte; Ageing; Cases.

1. Introduction

In many application areas, among the strongest and most practical technologies for the conversion and storage of electrochemical energy are batteries, fuel cells and electrochemical supercapacitors (ES)[1]. In recent years, ES or supercapacitors have attracted considerable attention, mainly due to their high power density, long life cycle and bridging function for the power/energy difference between dielectric capacitors (which have high output power) and fuel cells (which have high energy storage)[2]. Due to these properties, they are of major importance in sustaining the voltage of a system during increased loads for a large number of applications, from portable equipment to hybrid electric vehicles, passenger cars, buses and locomotives[3]. Starting and accelerating the engine are examples of the exploitation of high specific power. Due to the almost symmetrical charge and discharge behaviour, supercapacitors are suitable for regenerative braking, which means that they can recover energy that would otherwise be lost during deceleration and braking[4].

However, after long periods of operation, supercapacitors based on activated carbon and organic electrolytes can exhibit a decrease in capacity and an increase in resistance, increase in electrode mass, local separation of the metal collector coating layer, as well as macroscopic phenomena such as gas evolution[5], [6]. In addition, several aspects of supercapacitor performance are strongly influenced by operating temperature, including power, energy capacity, reliability, lifetime and cost[7]. Therefore, a much better understanding of the mechanisms of ageing is necessary, in order to define strategies to circumvent these drawbacks. The surface functionality and porosity of activated carbons should certainly be optimized in order to increase long-term electrochemical performance in organic milieu[8].
To date, only a few reviews have focused on studying the aging mechanisms of activated carbon-based SC in an acetonitrile electrolyte\cite{8}–\cite{11}. Among them, Zhu et al. have studied the ageing mechanisms of supercapacitor materials in more detail\cite{8}. Kotz and co-workers detected CO$_2$, propene and H$_2$ in the gas space above a double layer capacitor in carbon electrodes and a solution of tetraethylammonium tetrafluoroborate in propylene carbonate (PC)\cite{12}. Azaïs et al. also observed that activated carbons should have small amounts of surface functionality, appropriate pores and absence of moisture to ensure stable long-term performance\cite{10}. In addition, Azaïs et al. suggested an understanding of the aging mechanism in 2007 \cite{10}. Using two distinct carbon mechanisms, they proposed that ageing of SC is closely related to the decomposition of the organic electrolyte at the surfaces of the activated carbon. In addition, Zhu et al and Bittner et al have specifically noted the chemical and electrochemical ageing of activated carbon in electrodes by various characterization methods\cite{8}, \cite{13}. They identified discoloration of carbon materials, particularly the sealing or depletion of micropores, as the main reason for the deterioration of the performance of AC-based SCs. At the same time, they also identified other components of SC and published many illuminating results and related analytical methods. They found that the separator had turned yellow and that the aluminum foil was corroded. Their work was remarkable and contributed significantly to the aging mechanism of SC. Furthermore, other researchers have reached similar conclusions \cite{14}–\cite{17}.

However, despite all the above-mentioned studies, the aging mechanisms of supercapacitors have so far been very unclear. Therefore, in this work, based on an experimental study of a damaged supercapacitor, we have tried to analyze a white powder occurs on the surface of the electrodes. The identification of the elements of this powder is carried out by X-ray diffraction (XRD), $^{13}$C and $^1$H NMR spectroscopy and thermogravimetric analysis (TGA). The results obtained allow us to determine the causes of ageing and thus to understand their mechanisms.

2. Materials and method

The supercapacitors used in this work were supplied by Maxwell Technologies, Switzerland, and had a nominal capacity of 350F (BCAP0350) (figure 2). The structure of the supercapacitor cell, examined in this paper, is composed of two activated carbon electrodes and a separator impregnated with an organic electrolyte. The electrodes consist of a metal collector, covered on both sides with an active material, which has a large specific surface area necessary for the double layer. The two electrodes are separated by a porous membrane (separator), which prevents electronic conduction between the electrodes but allows ionic conduction between them\cite{1}. The electrolyte was 1M tetraethylammonium tetrafluoroborate (mol/L1) ($\text{ET}_4\text{NBF}_4$) in acetonitrile (CH$_3$CN); and the separator was a porous polypropylene (PP) membrane. Since this technological specification was the standard specification for commercial supercapacitors.

![Fig 1. Maxwell Technologies, Switzerland, and had a nominal capacity of 350F (BCAP0350)](image)

A damaged supercapacitor is used in this study. After disassembling the supercapacitor according to the protocol illustrated in the figure above (figure 2); we recovered the product on the surface of the electrodes in solid form (white powder). Then, a series of analysis is carried out on the recovered powder (X-ray diffraction, and thermogravimetric analysis).
3. Results and discussion

3.1 Powder XRD

X-ray diffraction (XRD) pattern (10°– 60°) was obtained using PANalytical X’Pert Pro diffractometer with CuKα monochromatized radiation (λ = 1.5418 Å). To study our powder in more detail, we applied X-ray powder diffraction (XRD) (to check for impurities, identify the phases and verify their crystallinity). The results of the X-ray diffraction show many peaks at different angles (2Theta), which represents its high crystallinity. Using phase identification software, we were able to find the majority of the peaks (Peaks 1; 2; 3; 4; 5 (figure 3)). The results obtained show that our powder probably consists of acetamide, unsaturated aromatic organic acids, fluoroacetic acid derivatives, oximes and macromolecular compounds.

3.2 Solid-state NMR spectroscopy

Nuclear Magnetic Resonance Spectroscopy (NMR) is an approach that has shown promise for the study of materials. NMR has the advantage of being selective with respect to the elements, allowing independent observation of different ionic species. In this study the powder is placed in a 4 mm ZrO2 rotor, making sure that the rotor is always correctly filled. The volume is adjusted with the calibrated tools used to fill the MAS-NMR rotors. The spectra were recorded with a 500 MHz Bruker Avance III (Karlsruhe, Germany) apparatus. During signal acquisition, spinal 1H decoupling was applied. The MAS frequency was 12.5 kHz. The results obtained are represented on 13C; 1H spectra (Figures 3 and 4). The figures above show the 13C NMR and 1H NMR spectra. In the first 13C NMR spectrum (fig 4), we can see three indexed signals, one signal at d= -0.4 ppm, the literature allows to attribute this chemical shift to the acetonitrile trace[18]. Another signal is observed at d= 46 ppm.
corresponding to the acetylene carbon CH₂=CH₂, and the last signal at δ=123.7 ppm (light peak) corresponds to the carbon of an amide carbonyl group, then the spectrum obtained in ¹H NMR (Fig 5) is composed of two signals, which are attributed to protons of the acetonitrile molecular group as detailed in the article by Borchart et al[18]. These results confirm the hypotheses suggested by the XRD analysis, in particular the presence of amide and acetylene.

On the basis of these conclusions, it is clear that the aging process of supercapacitors certainly takes place through chemical reactions. These reactions are considered to take place within the framework of well-defined thermodynamic and kinetic factors. However, the environment and the operating conditions of these components may favour certain reactions. We can therefore propose that our powder, which consists mainly of amide, acetylene and other compounds, is obtained by hydrolysis and thermal decomposition of acetonitrile (electrolyte). It is well noted that the water molecule that reacts with acetonitrile during hydrolysis is obtained from the trace amounts of water that are resistant during carbon activation[15].

Fig 4. MAS ¹³C NMR of the powder formed on the surface of electrodes

Fig 5. MAS ¹H NMR of the powder formed on the surface of electrodes

3.3 Thermogravimetric analysis (TGA)

In order to confirm the previously proposed hypotheses, we conducted a thermogravimetric analysis study. Mass loss measurements are performed on our sample (formed powder) in a temperature range of 20 to 800°C using a
SETSYS (SETARAM, Caluire, France) analyzer (heating rate of 5 °C·min⁻¹ under 40 mL·min⁻¹ flow of air)[19]. The thermogravimetric curve shows that the mass loss of the sample was progressive and occurred at three temperature levels. There is a significant peak at 90 °C, which is due to the loss of moisture and the evaporation of acetylene. Then, until the temperature reached 350 °C, a mass loss was observed, which was due to the decomposition of the acetamide[15]. The third step at 540 °C corresponds to the decomposition of traces of the electrolyte, mainly the alkylammonium ion, followed by the more stable tetrafluoroborate[14]. These results definitely confirm our previous explanations.

Fig 6. TGA curve of the powder formed on the electrodes

4. Conclusion

Aging of supercapacitors based on carbonaceous materials in the acetonitrile electrolyte is very slow, and even under conditions of forced aging (increase in temperature and electrochemical potential). After the life cycles of supercapacitors expire, they are damaged, therefore a crystalline mass is produced on the electrode surface. The study of this crystalline mass in the present work is carried out by X-ray diffraction (XRD), ¹³C and ¹H NMR spectroscopy and Thermogravimetric Analysis (TGA). Thanks to the results obtained, we have been able to collect the first information on the mechanisms of thermal decomposition of acetonitrile, as well as on their hydrolysis reaction. Our experiments also gave clear indications on the formation of amides, acetylene and other compounds. This finding should lead to new considerations in the design of supercapacitors, such as the addition of additives that are capable of blocking or inhibiting chemical reactions, and in the case of temperature gradients, placing the electrodes in a colder environment.

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