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# Ageing of electrochemical double layer capacitors

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ABSTRACT

The activated carbon in electrochemical double layer electrodes undergoes slow ageing. The effect becomes only apparent when capacitors are polarized to voltages at or above specified limits, or at high temperatures, for at least several months. A combination of "post mortem" analysis methods shows that the pores in the carbon are modified structurally, mainly by clogging up with organic species, but also electrochemically by decomposition of electrolyte, and by reduction and oxidation of the carbon in the electrodes. Key chemicals are trace water, the solvent acetonitrile, and the salt tetraethyl ammonium tetrafluoroborate. The changes differ hugely between negative and positive pole; the positively polarized electrode is much more affected. Also other compounds of the device, e.g. aluminum electrode support and paper separator, exhibit chemical ageing.

## 1. Introduction

### 1.1. Electrochemical double layer capacitors (EDLCs)

EDLCs are based on the purely electrostatic principle of accumulation of ions close to surfaces (electrodes) in a liquid solvent. Cations of an electrolyte salt accumulate at the negatively charged surface (hereinafter "cathode", which is electrochemically correct only during charging), and anions at the positively charged "anode". Both electrodes are highly porous to achieve a high surface to mass (or volume) ratio, but the details of pore size and pore volume can be as important as the surface area. The process of charging is nearly reversible; consequently, EDLCs are expected to have a much longer cycle life than batteries. While charge–discharge cycles in batteries are usually slow (due to the electrochemical processes), charging the EDL is very fast, even in porous electrodes. Such rapid cycles (technical range: seconds) allow for devices with high specific power, which can be an ideal add-on to devices of high specific energy (batteries or fuel cells) [1]. EDLCs and EDLC modules can be used in portable electric devices, hybrid electric vehicles, passenger cars, buses and even locomotives. In low-power portable devices, EDLCs can sustain low drain-rate memories, microprocessors, and real time clocks [2]. Higher powers are used for engine start and acceleration, and for regenerative braking [3]. Other important application areas are devices that cannot be connected to conventional power supplies, e.g. windmills or short stretches of tram lines [3].

Especially for widespread use in huge numbers, low-cost manufacturing is required, and simple designs based on cheap materials are necessary. At the same time, volume and mass should be kept small. A standard setup has emerged over the last decade: aluminum contact foils, coated on both sides with activated carbon (AC) [4], an organic electrolyte, and a separator (e.g. paper). We here focus on tetraethyl ammonium tetrafluoroborate ($TEA^+$ $TFB^-$) in acetonitrile (AN), which has the advantage of high conductivity even at low temperatures. The electrodes are composed not only of AC, but contain a polymeric binder in order to allow facile coating of the aluminum foils, and a conductive additive, usually carbon black, to enhance electrical interconnections between AC particles. EDLCs can show a short "burn-in" phase where their electrical characteristics change considerably; however, this is very fast (hours to days). In contrast, slow ageing processes are of utmost importance since the devices are supposed to run for many years with nearly constant properties. High temperature or high voltage, or even reversal of polarity, can induce irreversible processes, such

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as capacitance loss and performance deterioration, which are very slow (typical range: months) [1,4–14]. We carried out a detailed characterization of EDLCs, connected to a DC voltage over up to 15 months, supplemented by "post mortem" analysis by nitrogen porosimetry, Raman spectroscopy, elemental analysis, X-ray photoelectron spectroscopy (XPS), and infrared (IR) spectroscopy. In this way we determined ageing mechanisms for further improvement and development of EDLCs.

Many ageing processes are of physical nature, e.g. gas evolution and accumulation in closed systems increase the internal pressure, which in extreme cases causes structural destruction of EDLCs. These processes are tackled by improvements of the container, the venting system, etc. Here we focus on chemical mechanisms, which are of special relevance for long times. The prime targets are the electrolyte, whose ageing has been investigated in detail [9,13,14], and the electrodes, whose carbon is supposed to be electrochemically and structurally very stable. This is in fact true, but it is often overlooked that carbon is thermodynamically unstable with respect to oxidation and reduction. Especially in electrochemical systems, the redox chemistry of carbon can overcome kinetic barriers at very long time scales. We already characterized two electrode components, AC and conductive additives, in detail [15], carefully avoiding any complication of real systems, such as presence of aluminum [14], inhomogeneities, binder material. Here we include all materials by exclusively targeting complete capacitors of the type "ultracapacitor" (Epcos AG), sealed in aluminum casings. Ageing effects are expected to change the structural (physical) and chemical characteristics of the electrodes, the chemistry of the electrolyte [13,14], and – in extreme cases – even other components, and in this way the capacitance decreases, and the equivalent series resistance (ESR) increases. These two values can be employed to detect ageing quantitatively, even during use. We decided not to simulate actual temperature–current–voltage–time profiles close to applications, but to keep all values constant (a constant voltage translates into a constant near-zero current). We systematically varied temperature and voltage because a longterm use requires defined limits on their values.

### 1.2. Carbon materials in EDLCs

ACs can be obtained from a wide variety of carbonaceous materials. The cheapest and most frequently used on a commercial scale are peat, coal, brown coal, wood and coconut shell. However, it is not easy to control the extent and size distribution of resultant porosities when natural feedstocks are used, since they have large structural and chemical variability; even non-carbon atoms are present in sizeable amounts. Synthetic carbon-rich precursors (polymer resins) are purer, and result in reproducible pore size distributions. The basic structural element of AC is graphite with its $sp^2$ carbon, and indeed small graphitic units are present in AC. However, Byrne and Marsh [16] suggest $sp^2$ units arranged mainly in five-, six-, and seven-membered rings, and detailed models for AC have to incorporate also $sp^3$-bonded carbon atoms. Carbon black is electrically conductive and is widely applied for conductivity improvement in polymer engineering and electrochemical industry. When carbon black particles of diameters in the 100 nm range are homogeneously dispersed and mixed with AC, agglomerates of the aggregates are formed, in which a compact one-, two- or three-dimensional network of the conducting phase is obtained, thereby increasing the conductivity. In the electrodes used in ultracaps, AC was blended with carbon black and with a fluoropolymer binder.

### 1.3. Other materials in EDLCs

A simple and cost-effective setup implies the use of various compounds that make the system much more complex than a porous carbon electrode in electrolyte. As mentioned above, the microparticle nature of the carbon(s) requires a binder, here a fluoropolymer, in order to spread it as paste on the aluminum foil current collectors. The adhesion to the aluminum is promoted by a glue, usually carboxymethylcellulose, which is only present at the aluminum/AC interface. Aluminum is also used for the casing, and all aluminum surfaces have a thin layer of oxide, which does not impede electrical conduction significantly. The separator in our case was made from paper, with its intrinsically high porosity.

## 2. Experimental

### 2.1. Electrical testing

100 $\mu$m thick AC electrodes were produced from activated carbon (particle size around 3 $\mu$m, but many particles well below 1 $\mu$m) mixed with carbon black and binder, coated on aluminum foils. These were assembled in dry atmosphere with paper separators into 200 F ultracapacitors, housed in aluminum casings, and filled with electrolyte under reduced pressure. The electrolyte was tetraethyl ammonium tetrafluoroborate ($TEA^+$ $TFB^-$) in acetonitrile at a concentration of $\approx$1 M (mol $l^{-1}$) (battery grade). The technical specifications were as follows: mass 65 g, volume 56 ml, rated voltage 2.5 V, capacity 140 mAh (504 C), energy 625 J at 2.5 V, specific power 3.3 kW $kg^{-1}$ and 3.9 kW $l^{-1}$, ESR max. 3.5 m$\Omega$ (DC), operating temperature $-30\,^\circ$C to $70\,^\circ$C, cycle life time 500,000. The ultracapacitors were then polarized at various constant voltages, under various temperature conditions (Table 1), which define our ageing conditions I to VI. About every 600 h, capacitance and equivalent series resistance (ESR) were measured by electrochemical impedance spectroscopy with a PGSTAT30-FRA2 electrochemical analyzer (Autolab) in the frequency range from $f$ = 1 kHz to 10 mHz. The capacitance $C$ was calculated from the imaginary part of the complex impedance $Z$, according to $C = 1/(2\pi f|Z''|)$. The value at 2.5 V, 25 °C, and 50 mHz was used. This part of work was completed at Epcos AG in Heidenheim.

### 2.2. Sample preparation

After ageing, the ultracapacitors were transferred to MPI-FKF in Stuttgart, and cut open in an argon-filled box. Our analysis conditions allowed, different from the fabrication, for a certain level of

**Table 1**
Ageing conditions of ultracapacitors. The ageing factor is calculated from Ref. [10].

| Ultracap code | Potential/V | Temp./°C | Time/h | Potential excursion/V | Temperature excursion/K | Ageing factor | Condition |
|---|---|---|---|---|---|---|---|
| I | 2.5 | 80 | 3048 | 0.2 | 55 | $2^{7.5}$ | Failure |
| II | 2.3 | 80 | 3115 | 0 | 55 | $2^{5.5}$ | Failure |
| III | 2.5 | 70 | 3700 | 0.2 | 45 | $2^{6.5}$ | Damaged |
| IV | 2.8 | 50 | 2919 | 0.5 | 25 | $2^{7.5}$ | Working |
| V | 2.3 | 70 | 2904 | 0 | 45 | $2^{4.5}$ | Working |
| VI | 2.5 | 50 | 2924 | 0.2 | 25 | $2^{4.5}$ | Working |
| Reference | 2.3 | 25 | 24 | 0 | 0 | $2^0$ | Working |