

DEGRADATION PROCESSES, LEADING TO THE GENERATION OF GAS IN A DEEP POLARIZATION OF SUPERCAPACITORS WITH ORGANIC ELECTROLYTES

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Abstract. Gas chromatography and mass-spectrometry were used to study the process of accelerated aging of supercapacitors (SCs), followed by the gas evolution. These processes were investigated under high voltages and high temperatures for SCs with different electrolyte compositions. It has been shown that the electrolyte composition determines the direction of electrolyte destruction processes. Water plays the particular role in the SC performance deterioration as initiator of the electrolyte destruction reactions.

1. INTRODUCTION

Double-layer supercapacitor (SC) is a pulsed electrochemical energy storage device that accumulates the energy in the electric field generated in the electric double layer at the interface between electrode and electrolyte. The double layer capacitance is proportional to the area of the electrode / electrolyte interface, and the stored energy is proportional to the square of the voltage between electrodes, so it is essential to use high surface area electrode materials and high decomposition voltage electrolytes. Among various energy storage systems, SCs and batteries are systems that have found a broad range of applications. The differences between SCs and batteries lie in their different charge storage mechanisms and their materials. Typically SC are designed to provide high-power density, based on electrochemical double-layer. Therefore, SC are

found on hybrid and electric transport in energy recovery systems, where acceleration or braking of the vehicles requires short-term, emission or absorption of a large electric power. Such consumers exist in many stationary applications - reverse osmosis installation, powered from the wind power [1], systems that require compensation of a powerful starting currents of motors, or high power quality [2].

Supercapacitors exhibit tremendous high cycle life that is measured in hundreds of thousands up to millions cycles. However, in most cases, SCs are affected by degradation, mainly due to electrode and electrolyte reactions. These reactions can be caused by impurities in the composition of electrode and electrolyte, as well as the developed surface of the electrode material possessing some catalytic properties that can reduce the decomposition voltage of the electrolyte. The occurring electrochemical

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reactions can lead to the formation of solid and gaseous products that block the surface of the porous electrode. At the same time, in certain conditions, exactly the study of reaction products can give information about the processes occurring in the capacitor [3].

At the present time organic electrolytes with high decomposition voltage (2.5 – 4.0 V) are used to increase the stored energy of SCs. In addition to ionic salts, the electrolyte generally includes a solvent, the most famous of which are acetonitrile and propylene carbonate (PC). The electrochemical window of the first of them is 2.7 V, the latter has window of 2.5 V [4]. In a real SC electrodes consisting of activated carbon material with a developed surface, the problems of gas formation, that can cause serious damage to the cells of the SC. In all cases, all degradation processes, leading to gassing, significantly reduce the capacity and increase the resistance.

The presence of moisture is one of the main causes of degradation of SCs, since the decomposition of water, associated with hygroscopic electrolyte or electrode material occurs at a voltage substantially less than the operating voltage of the SC with an organic electrolyte. The increase in the moisture concentration leads to a significant decrease of electrochemical stability of the electrolyte. For instance, 0.001% of water dissolved in the electrolyte decreases electrochemical window by about 10 mV. In addition, the water adsorbed in carbon electrodes, may not be fully removed even by drying at temperatures up to 150 °C [3]. Currently a great number of scientific groups and industrial organizations, make efforts to reduce the rate of degradation of characteristics of SCs, which is impossible without understanding the mechanisms of physical and chemical processes leading to degradation. Therefore, in the literature there are quite a large number of works devoted to the analysis of degradation processes of SCs [3,5,6,7-10]. In [8] authors described experiments on accelerated life cycle tests of commercial Boostcap SCs (of Maxwell Technologies) with electrodes based on activated carbon and the electrolyte based on acetonitrile. Accelerated aging under the conditions of charge and discharge of SCs is provided by increasing the temperature up to 70-80 °C and voltage up to 2.8 – 3.5 V. The measurement of the capacitance and equivalent serial resistance of the cells were carried out in each cycle. In extreme conditions (70 °C or 3.5 V) the output of the SC failure was due to the abundant evolution of gas, which leads to the

response of the safety valve, while for lower values of voltages and temperatures that was not observed. However, it was shown that each increase in voltage (manufacturer's recommended 2.5 V) on by 0.1 or temperature to 10 °C increases the degradation rate nearly two times.

The authors [9] investigated commercial SCs based on acetonitrile provided by Maxwell Technologies (350 and 2600 F). SC were studied at temperatures 65 and 70 °C and a constant voltage 2.7 V. The aging at constant voltage and temperature was built up on the basis of the Arrhenius law dependence of chemical reaction rate on temperature. The activation energy for a set of reactions that cause the aging of the SC was estimated on the basis of the experiments. The authors studied the effect of temperature cycling on the lifetime of SC (-20 to + 80 °C, and hold at each temperature for 2 hours). The internal resistance of the SC using the method of impedance spectroscopy was evaluated after 20 cycles of charge/discharge at a voltage of 2.7 V. Thermal cycling led to an increase in internal resistance at 12-15%. The capacity decrease was about 3%.

The influence of temperature on the rate of degradation of the SC was investigated in [6]. Also there was considered influence of activated carbon and polymeric binder on the degradation rate characteristics due to the side redox reactions. Accelerated aging of SCs were provided at 60 °C and at the voltage 2.6 V. During the tests recorded impedance curves SC cells and analyzed the self-discharge currents. Decrease of self-discharge currents is evidence of neutralizing surface functional groups on account irreversible chemical reactions that can lead to emission and formation of solid precipitate at the electrodes. Test data was used for verification of the developed mathematical model of supercapacitor. Based on the development of these studies [5] SC cells with a capacity of 3000 F were tested to determine the degradation in the storage (for the purposes of accelerated degradation tests were carried out at a voltage of 2.8 V, the temperature 30, 45, and 60 °C), were also recorded capacity and the equivalent serial resistance of SC in the mode of cycling (40-50 °C, 40-60 °C, 50-60 °C). In parallel, based on the equivalent circuits was carried out mathematical modeling of the SC. Analysis of experimental and calculated data showed that thermal cycling in the range 40-60 °C leads to a significant increase in the rate of growth of resistance, than at a constant temperature of 50 °C, which may be attributed to the decomposition

of the binder and the rearrangement of the pore structure of the active layer.

Effect of the electrode's mass ratio on the degradation rate of on activated carbon YP17 (Kuraray Chemical) based SCs with traditional 1 M tetraethylammonium tetrafluoroborate in acetonitrile or propylene carbonate electrolyte was studied in work [6]. Authors conclude that in the case when the mass of the positive electrode is larger than mass of negative one the electrochemical window of the electrolyte utilized more effectively. Difference in potential grows rates at the electrodes can be decreased by the electrodes capacitance optimization. It was shown that 0.65 is an optimal of the positive electrode mass ratio to the total carbon electrodes weight in acetonitrile based electrolyte and 0.5 for propylene carbonate based electrolyte.

Gas evolution in SCs based on acetonitrile and other solvents at voltages above 2.5 V were studied in [10]. It was shown that for propylene carbonate based electrolytes gas evolution is 10 times more intensive than for acetonitrile with the same salts of the same electrodes. However a leakage current for propylene carbonate only two times higher than for the acetonitrile, suggesting different mechanisms of the electrolyte decomposition in this electrolytes.

Attempts to clarify the mechanism of organic electrolyte SCs aging were undertaken by the authors of [11] by mass spectroscopy analysis of gases evolved from the 1 M $(C_2H_5)_4NBF_4$ in propylene carbonate electrolyte solution during the tests. Hydrogen and propylene have been detected during cyclic voltammetry tests with a low sweep rate. Supposedly, they were the products of the negative electrode decomposition. Carbon dioxide (CO_2) was detected on the positive electrode side. In spite the fact that water amount in the electrolyte was quite small (less than 20 ppm), the hydrogen evolution began at 1.6 V, which indicates that the reasons of hydrogen evolution is presumably decomposition of organic components of the electrolyte and the hydrogen-containing groups on the surface of the electrodes.

The detailed study of SC aging processes was carried in [3], where 1 M $[(C_2H_5)_4N]BF_4$ in acetonitrile electrolyte based SCs were investigated. At high voltages and temperatures (above 4 V and 70 °C), crystalline solid mass of residual electrolyte decomposition products, organic acids, acetamide, aromatic compounds and polymers were formed in the experimental cell. The solid and gaseous products of the electrolyte decomposition were analyzed using infrared spectroscopy, UV-

spectroscopy, liquid and gas chromatography-mass-spectrometry, thermogravimetric analysis, X-ray diffraction.

Thus, one of the most informative approaches in studying the SCs degradation mechanisms appears to be the accelerated aging of SC at high voltages and temperatures with subsequent analysis of the reaction products.

In the present study we investigate the aging processes for SCs based on Yunasko Ltd activated carbon electrodes. Gas evolution was accompanied by enlargement of internal pressure following the swelling of SC cell. The gases were analyzed using gas chromatography and the mass-spectrometry which is quite informative methods for electrochemical power sources aging processes investigation [9,11]. The origin and the mechanism of changes in SCs were studied by accelerated aging at high voltage and cycling at high temperatures. As electrolytes were Tetraethylammonium tetrafluoroborate (Et_4NBF_4) and azonidspiro[4,4]nonane tetrafluoroborate ($SBPBF_4$) in acetonitrile and propylene carbonate were performed as solvents.

2.2. MATERIALS AND METHODS

2.1. Electrolytes

The aging has been studied for the SC cells with tetraethylammonium tetrafluoroborate (Et_4NBF_4) and azonidspiro[4,4]nonane tetrafluoroborate ($SBPBF_4$) in acetonitrile and propylene carbonate organic electrolytes (BASF).

2.2. Electrochemical characterization

SC cells were polarized and cycled. The polarization was performed using a DC power source Kaito HY3005D (Japan) at temperature of 60 °C and a voltage of 2.9 V for 72 hours. Cells were heated in a dry oven (Utenos Elektrotechnika, Lithuania).

Lifetime electrochemical characterization was carried out by the constant current charge / discharge tests by Chemical Power Sources Analyzer ASK150.24.1500.1 (Russia) at currents up to 100 A, and voltage up to 2.7 V.

The high voltage polarization was used to identify the possible routes of the electrolyte destruction and electrodes impact in this process. The process of polarization was accompanied by the gases evolution. Identification of the gas phase components was realized by the chromatogram retention times with the mass spectra involvement.

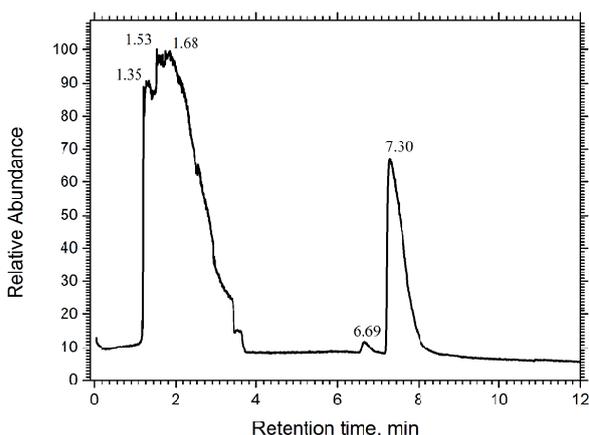


Fig. 1. Gas chromatogram of the products formed during polarization of SC with $\text{SBP}\cdot\text{BF}_4$.

2.3. Gas chromatography and mass spectrometry

Analysis of the gases evolved during the cycling and polarization of SC cells was performed with gas chromatograph Focus GC and mass-spectrometer DSQ (Thermoelectron corporation). Chromatographic separation of gas mixture was carried out using a 30 m length and 0.32 mm inner diameter nonpolar TC-Bo1VD/Q capillary column. The helium, which was filtered before injection into the column, was used as carrier. The gas flow rate in the column was 1.2 ml/min, the column oven temperature was 60 °C, injector temperature was 80 °C, the temperature of the chromatograph / mass spectrometer transition bridge was maintained at 60 °C and the ion source temperature was 180 °C.

Sampling of gases and liquids test portions from swelled cell cavities were performed using a microsyringe by means of puncturing its shell puncture and posterior sealing the punctured shell by adhesive tape. Gas test-portions were collected using gas-tight 100 μl syringe, liquid test-portions were collected using 10 μl microsyringe. The chromatograph column injection volume was ranged from 60 to 100 μl for gas injection and 1-2 μl for liquid injection.

Mass-spectrometer settings were controlled automatically. Filament current was 250 μA , emitted electron energy 70 eV. The ionization of the compounds was carried out in the positive ions producing mode. Investigated atomic weights were in range of 1-120 a.m.u. The identification of compounds and their structural formulas was determined using The NIST Mass Spectral Search Program for the NIST/EPA/NIH Mass Spectral Library Version 2.0 d (National Institutes of Standards (NIST)).

3. RESULTS AND DISCUSSIONS

3.1. Supercapacitor cell based on propylene carbonate with $\text{SBP}\cdot\text{BF}_4$

Fig. 1 depicts the chromatography of the gaseous products formed during polarization of SCs. Data decoding of these chromatograms, conducted by mass spectrometry is presented in Table 1.

As seen from the chromatogram, peaks of argon and carbon dioxide are not resolved. As to carbon dioxide, its presence is detected as a shoulder on the right side of the peak with a retention time of 1.68 min. Detection of argon in the gas mixture is due to the fact that it is dissolved in the electrolyte while assembling and desorbs during cell polarization. Analysis of the data shows the decomposition of the electrochemical solvent – propylene carbonate. The reason of the decomposition of the propylene carbonate is water that was not completely removed from the electrodes, which serves as depot for residual water. At higher voltages at the negative electrode the electrolysis of the water is begin



Atomic hydrogen is very active reagent and reacted with a propylene carbonate

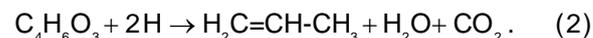


Table 1. Composition of the gas mixture formed after the polarization of the cell based on propylene carbonate with $\text{SBP}\cdot\text{BF}_4$.

Retention time, min	Molecular entity	Qualitative characteristic
1.35; 1.53	Argon	Very high intensity
1.68	Carbon dioxide	Very high intensity
6.69	Propylene	Low intensity
7.30	Propane	High intensity peak

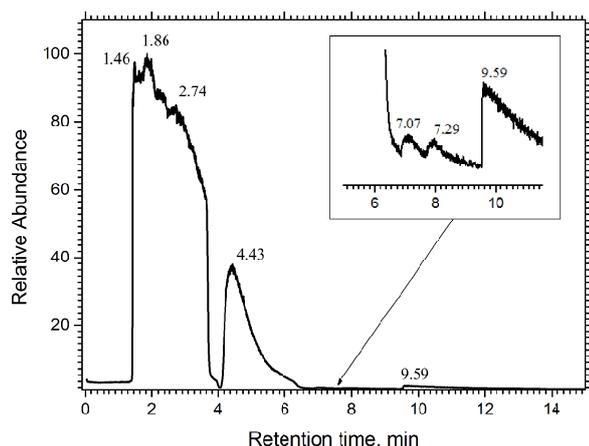
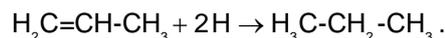


Fig. 2. Gas chromatogram of the products formed during polarization of SC with SBP·BF₄.

Thus, as a result of chain reactions water is reproduced, and the cycle repeats the above mentioned reactions. Propylene was formed in the reaction (1) is subjected to hydrogenation to form propane:

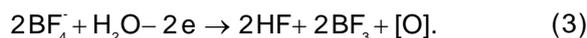


It is necessary to point out the absence of gaseous decomposition products of compounds that would indicate destruction of azonidspiro[4,4]nonane tetrafluoroborate in this electrolyte.

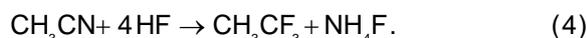
3.2. Supercapacitor cell based on acetonitrile with SBP·BF₄

Results of the analysis of gaseous products of SC on acetonitrile with SC SBP·BF₄ are shown in Fig. 2 and Table 2.

It is evident that the gaseous products produced during acetonitrile with SBPBF₄ based cell polarization could be formed as a result of reactions in which both the solvent (acetonitrile) and BF₄ anion takes place. Reaction sequence may be the following: the anion BF₄ reacts with water:



The resulting hydrogen fluoride reacts with acetonitrile:



The formation of trifluoroethane is explained by this reaction (4). Propyl alcohol is probably formed by the reaction of propylene, the product of polypropylene depolymerization with water.

Comparison of degradation products formed during cell polarization with different solvents suggests the important role of the solvent in these processes. Propylene carbonate has the ability to direct interaction with water, emitting carbon dioxide, in the case of acetonitrile the main product is trifluoroethane. It should be emphasized that in a PC environment the ionic salt is not involved in the reactions of the decomposition. It seems to be protected by the solvent. Therefore, this system is not formed fluorinated products.

In a system with acetonitrile solvent the ionic salt is attacked by water because of acetonitrile has less ability to hydrolytic degradation under the assumed conditions. Thus, in both systems considered here, the water leads to undesirable reactions. In light of these results it can be concluded that one of the measures of protection against water but its complete removal, which in practice, is a very time-consuming procedure, may be search for an additive to the electrolyte, which would react with water, protecting the system from its injurious exposure.

3.3. Supercapacitor cell based on acetonitrile with Et₄NBF₄

Fig. 3 depicts the chromatography of cell Et₄NBF₄/AN. Table 3 shows the peaks of the chromatogram transcript.

In the chromatogram there are traced seven peaks. The main components of the gas mixture

Table 2. Composition of the gas mixture formed after the polarization of the cell based on acetonitrile with SBP·BF₄.

Retention time, min	Molecular entity	Qualitative characteristic
1.48	Argon	Very high intensity
1.86	Carbon dioxide	Very high intensity
4.43	1,1,1-Trifluoroethane	High intensity
7.07	1,1-Difluoroethane	Very low intensity
7.29	Propane	Very low intensity
9.59	Water	Low intensity

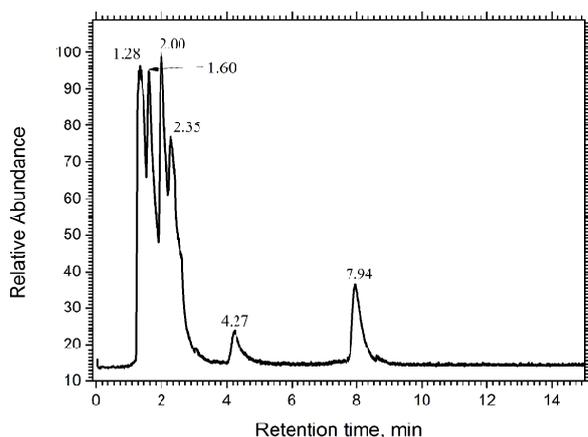


Fig. 3. Gas chromatogram of the products formed during polarization of SC with Et_4NBF_4 .

are carbon dioxide, ethylene, ethane, 1,1,1-trifluoroethane and propane. Such a composition of the gas mixture indicates that significant amounts of them are formed by the decomposition of the electrolyte and salt Et_4NBF_4 . For example, trifluoroethane is formed due to the interaction of the anion BF_4 with water and HF with acetonitrile, Eqs. (3) and (4). The formation of ethylene and ethane can be attributed to electrochemical decomposition of tetraethyl ammonium cation.

The precipitated NH_4F (Eq. (4)) can settle on the surface of the electrodes and block their pores. Atomic oxygen oxidizes the carbon electrodes and acetonitrile:



Oxidation of the electrodes leads to the formation of carbon monoxide and carbon dioxide gases.

During the redox reaction new portions of water are generated, so even a small amount of them, whether in the electrodes or in the solvent can lead to the formation of considerable amounts of decomposition products. As seen from the above

reactions, along with the gaseous products, solid polymeric products are also formed. They can block the pores of the active carbon and reduce the capacity.

To determine whether the gas formation is a result of only temperature without electrical polarization, an experiment was carried out by holding at 60°C for 48 hours was conducted. In these conditions the gas evolution was not observed, indicating that gas formation in the cells of the SC is the result of electrochemical processes.

4. CONCLUSIONS

The features of the aging of three types of SCs have been studied. Two of them had the same solvent for the electrolyte – acetonitrile and the third has the propylene carbonate solvent. Two of them had the same ionic salt - azonidspiro[4,4]nonane tetrafluoroborate. This combination of electrolyte composition revealed the features of electrolytes destruction and mutual influence of the conductive salt and a solvent under the influence of SC temperature and applied potential. In the system with PC solvent SBPBF_4 salt is not exposed to destruction. In the case of SBPBF_4 and Et_4NBF_4 in acetonitrile, both components of the electrolyte are participated in the reactions of electrolyte destruction.

The destruction of the electrolyte starts from the water electrolysis. Evolved hydrogen and oxygen are reacted with components of the electrolyte, contributing deterioration of the electrical properties of SC. The solvent has an impact on the progress and the way of electrolyte destruction. In the SC, with an electrolyte consisting of a PC and SBPBF_4 conductive salt is not exposed to destruction, since the hydrogen reacts primarily with the PC. In the case of SBPBF_4 and Et_4NBF_4 in acetonitrile, both components of the electrolyte salt and the solvent react with water and the product of electrolysis. It is

Table 3. Qualitative composition of the components of the gas mixture extracted from the space inside the shell SC based on acetonitrile with Et_4NBF_4 .

Retention time, min	Molecular entity	Qualitative characteristic
1.28	Argon	Very high intensity
1.60	Carbon dioxide	Very high intensity
2.00	Ethylene	Very high intensity
2.35	Ethane	Very high intensity
2.64 (sh)	Carbon monoxide	High intensity
4.27	1,1,1 - Trifluoroethane	Low intensity
7.94	Propane	High intensity

suggested to remove the remaining water with the water binding additives.

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