

ASYMMETRIC ELECTROCHEMICAL SUPERCAPACITORS WITH AQUEOUS ELECTROLYTES

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INTRODUCTION

Electrochemical supercapacitors are still one of the most interesting developing types of power sources. High specific power, long service life, easy to adjust into technical units and application simplicity expand spheres of their application and open new ones where use of the traditional power sources is impossible or is economically unjustified.

The development and application of so-called "asymmetric" supercapacitors, possessing higher specific energy in comparison with a well-known carbon-carbon "symmetric" supercapacitors has intensified in the last 3-4 years.

The brief sight in history shows the beginning of these developments in Russia in 1988...1990 (1, 2). There have been executed the basic R&D works on nickel-carbon and lead-carbon systems and a low-volume output of sufficiently large supercapacitor sets of ~600 kJ for electric transport with the fixed traffic route (AGV) was produced (3).

The intensive patenting of these systems took place in 1992-1998 (4, 5, 6, 7). During the same time the serial production of asymmetric electrochemical supercapacitors of $NiOOH|KOH|C$ system for starting internal combustion engines and electric transport (8) has also begun. The use of asymmetric supercapacitors of

$PbO_2/H_2SO_4/$ system for the solution of power quality problems is noted in 2006-2007 (9, 10). It is interesting to observe the application of mixed battery-capacitor electrochemical system $PbO_2/H_2SO_4/Pb\cdot C$ as a basic energy source for acceleration-deceleration of a hybrid car (11).

Though, asymmetric supercapacitors with non-aqueous electrolytes and intercalated active materials are already in development and low-volume output, and their specific energy is higher, than that of asymmetric supercapacitors with aqueous electrolytes, still the latter have specific power, charge-discharge cycle efficiency and safety advantages.

The data of asymmetric systems researches and the analysis of other researches are cited in this article. The special attention was given to the industrial usage of asymmetric electrochemical supercapacitors with aqueous solutions of electrolytes and the opportunity of high-volume output. It is shown that asymmetric systems have functional parameters advantages even in comparison with carbon-carbon systems with electrolytes based on acetonitrile at the production samples level for specific application.

2 ANALYSIS OF ASYMMETRIC SUPERCAPACITOR SYSTEMS

2.1 A general concept of system, a charge storage mechanism, advantages and disadvantages

A terminological uncertainty, concerning a new supercapacitor system came to the end approximately in 2002. And now it is assumed that *the "asymmetric" supercapacitor is the supercapacitor, on polar electrodes of which processes different in their nature are carried out* (12). For example: a redox reaction on one of the electrodes and charge-discharge of double electric layer (DEL) on another. Other widespread name of such systems is "hybrid" supercapacitors.

Thus, two various mechanisms of charge storage are realized in the asymmetric electrochemical supercapacitor (EC): DEL and the electrochemical reaction.

The capacitor which has electrodes differ in mass but made of identical materials (carbon-carbon supercapacitors with various hinge of positive and negative electrodes) cannot be considered asymmetric. The asymmetric EC differ from symmetric in the availability of so-called "non-polarizable" electrode. The electrochemical reaction, characterized by small potential changing, proceeds on it, i.e. the acclivous section of discharging curve of Faraday electrode is used.

The general view of discharging process is given on the Fig. 1

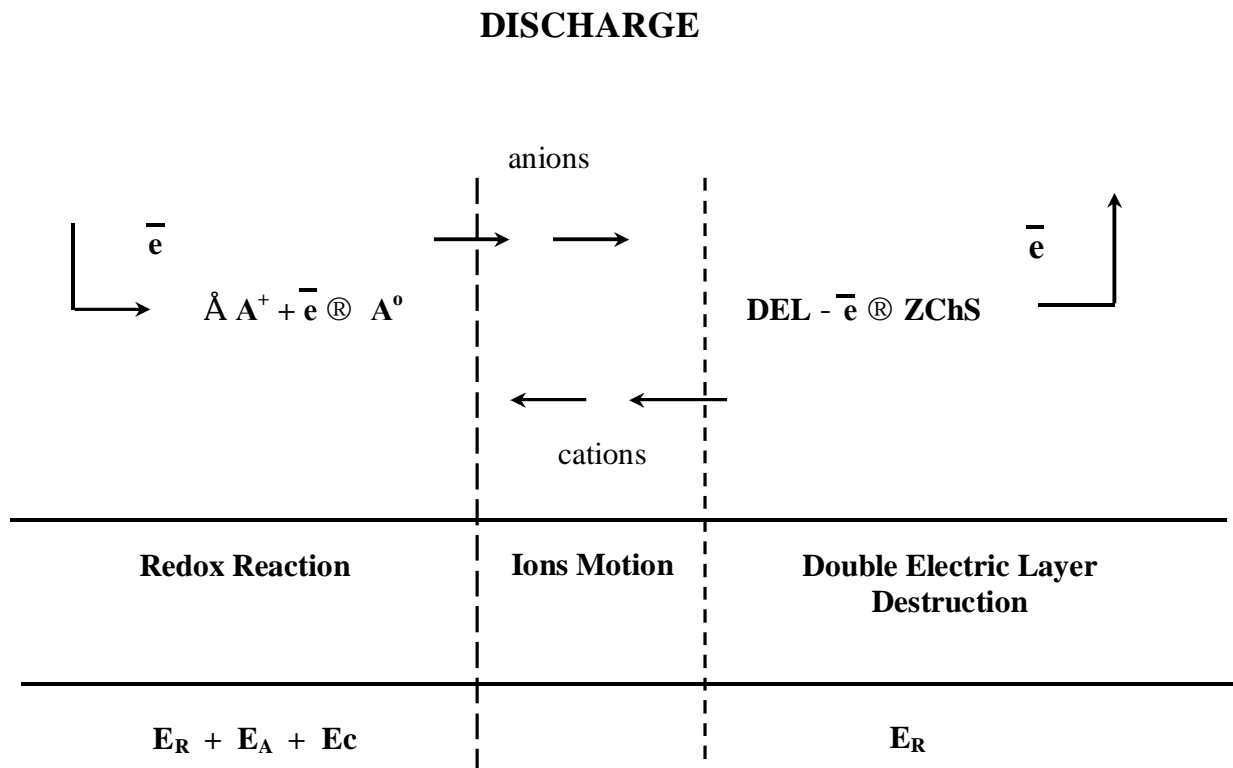


Fig. 1 Discharging process of the asymmetric electrochemical system: A^+ , A^0 reduced or oxide forms of an active material; DEL – double electric layer; ZChS → zero charge state of a polarizable electrode; E_R , E_A , E_c – activation and concentration polarizations.

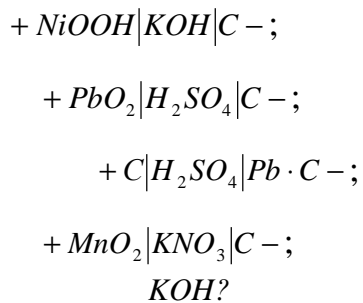
The use of a non-polarizable electrode raises voltage of a single cell and increases a working voltage window of EC. The total electric capacity of the capacitor also increases since the second capacitor connected in series is removed in the equivalent circuit diagram (13). This complex of changes increases specific energy in 2-5 times in comparison with a symmetric design. Low self-discharge level should be also referred to advantages of the asymmetric system since only one carbon electrode instead of two as it is in the symmetric capacitor remains in a cell. Basically just the carbon electrode is responsible for self-discharge of system. Speaking about the service life, there is one weak point in the asymmetric system – the cycling of the Faraday non-polarizable electrode. It is well-known, that «battery» type electrodes have a cycling life from hundreds up to a maximum of several thousands of charge-discharge cycles. It is certainly less than a resource of carbon-carbon capacitor electrodes - millions cycles. However, specific capacity of a non-polarizable electrode is many times higher, than a polarizable electrode has, and a right choice of capacities ratio will allow considerably reduce a depth of discharge of the Faraday electrode. It reach 5-25 % in real products. Hundred of thousands of charge-discharge cycles are realized at such discharge depth easily enough. *But it is necessary to note, that asymmetric capacitors still yields to symmetric carbon-carbon ones in an absolute value of charge-discharge cycles (roughly 1.000.000 against 20.000.000).* Though a correct design choice of energy store in operation allows solving problems of the service life.

A slow response in the range of discharges by duration of up to 0,5 sec should be referred to the disadvantages of asymmetric systems, for example: the carbon-carbon capacitor peaks the maximum power in 20-40 microseconds (14), while the asymmetric systems start to act later in the millisecond range. The high inertness of asymmetric systems is defined by a relatively slow electrochemical reaction on a non-polarizable electrode (15). One of the fastest electrochemical reactions – a proton

exchange in a solid phase, is still slower, than a process of DEL formation on the phase boundary solid/electrolyte.

Therefore the discharge time constant of series-produced asymmetric EC (RC) is more than 1 sec, while the RC of carbon-carbon capacitors in the range – 50-300 ms.

The following asymmetric supercapacitors of electrochemical systems will be analyzed further on:



Electrodes based on mixed oxides of ruthenium (RuOx) were not accepted for the analysis because of their high cost and practical inapplicability in a large scale production.

2.2 + NiOOH|KOH|C – system

This is one of the oldest and well-studied electrochemical systems with serial industrial production and mass application.

In most cases a sintered nickel-oxide electrode, 0,3-0,7 mm thick is used as a non-polarizable electrode. It is usually a well-known electrode of the nickel-cadmium aviation battery, characterized with high power of discharge and long service life. More capacious metal-fibrous electrodes are used in some particular applications, for example – motive power.

Negative electrodes are mostly made of woven activated carbon fibers, and sometimes – of activated carbon powder composites with binder. The design is also similar to storage batteries: the single cells of high capacity, connected into the series on the required voltage range, are used. Modules on most commonly used voltages:

12-24-36-48 Volt are produced in lots. EC for powerful discharges have specific energy of 1,2-2 Wh/kg at specific power 1000...2000 W/kg (16). The voltage of a single cell of 1,4-1,5 Volt is on the border of the gas emission in a system (hydrogen), therefore cells are equipped by pressure relief valve.

It is interesting to observe the usage of the so-called "hydrogen" capacity of a carbon electrode. Since there is an adsorption stage for hydrogen on the carbon surface at the water decomposition potential on a negative electrode, the capacity at this potential is anomalously high (several hundreds Farads per gram of an active material). A cell voltage in this system is 1,5-1,7 Volt. The use of "hydrogen" capacity of a carbon electrode raises specific energy of the asymmetric EC systems $NiOOH|KOH|C$ up to 10 Wh/kg, but specific power seldom exceeds the value of 200 W/kg. The cyclic resource of such systems is high enough - tens of thousands of charge-discharge cycles.

Constant gas emission is the disadvantage of the abovementioned system. Since it is practically impossible to reach a potential of the adsorption hydrogen stage on several (or several tens) cells connected in series simultaneously during charging, cells with lesser capacity constantly «hydrotreat».

For normal operation of such system a good ventilation and an equipment for adding water is required, i.e. the algorithm is very similar to the "open" (vented) traction battery.

A basic application of "open" supercapacitor systems is an electric transport with the fixed traffic route. Closed systems with a lower level of specific energy, but conditionally encapsulated, are operated in the ICE starting systems and can be applied in the booster systems of so-called "heavy" hybrids (a trolley bus, trams,..).

The attempts of bipolar electrodes creation where the nickel foil served as a bipolar collector have been undertaken in the development of this electrochemical system (17). Thus sufficiently high data was obtained: ~5 W·h/kg and more than

800 W/kg. However, the works have not reached the production, probably because of constantly increasing prices for nickel and its compounds.

The application researches of the conductive polymers for a bipolar collector were also carried out, they have given ambiguous results because of nonreproductivity of the plastic's corrosive characteristics in conditions of the charged nickel-oxide electrode potential.

As it has been said, the system $NiOOH|KOH|C$ is spread enough and applied to the ICE starting and the electric transport, *however the wider spread will probably be limited by the growing prices for nickel and its compounds and the restrictions of potential growth of the specific parameters. In a number of cases the application is limited by the "nonabsolute" hermiticity of the system.*

It is quite possible, that this system will get «the second long life» with the development of Nanosystem industry.

2.3 + $PbO_2|H_2SO_4|C$ – system

Potentially, this is, probably, one of the best electrochemical systems for asymmetrical supercapacitors, regarding the price/quality ratio.

The analysis of various references shows a wide dispersion of specific energy and power parameters.

The value of ~24 Wh/kg should be considered the biggest one of specific energy (practically reached) (18), however the level of specific power does not exceed 100 W/kg. Besides, RC of this system is hours. So, it is difficult to call such devices as the capacitors though the kind of discharging curve is typical for EC. There is data (10) that specific power of such EC is several times higher, than the one of a starter battery, and reach more than 150 W/kg.

The specific power increasing lays in reduction of a collector thickness of a positive electrode. In the above-stated publications, a standart positive electrodes with

the thickness of 0,9-1,2 mm, as for starter SLi batteries, are used in the cell design. The composition of a grid's alloy vary or special anticorrosive coverings are used.

Thickness reduction of grid which means increase in quantity of pairs \oplus and \ominus in the set volume could lower internal resistance and increase power. However, lead and its alloys are thermodynamically unstable at the potential of charged lead-dioxide electrode. Therefore, the grid always corrodes, i.e. the EC service life is determined by the grid thickness of a positive electrode. The service life of a lead-dioxide electrode at thickness less than 0,8 mm falls drastically because of mechanical strength loss of a grid due to its corrosion.

ELIT JSC experiments with the use of "all-over" (non-grid) collectors have shown achievability of the specific power value ~ 570 W/kg at the delivered specific energy $\sim 6,9$ Wh/kg (weight of the battery case is not included). Collectors of nonantimonial alloy, $\sim 0,2$ mm thick and service life was about 2 months were used in this case. Cells with a current grid collector and a positive electrode 0,6-0,7 mm thick, turned out to be more practical, and the following parameters were reached:

15 Wh/kg at 191 W/kg;

10 Wh/kg at 450 W/kg;

3,2 Wh/kg at 660 W/kg;

(Weight of the battery case is not included).

But it should be noted that service life of this design does not exceed 3-4 months.

The charge storage mechanism on negative carbon electrode is combined: a double electric layer and "hydrogen" pseudocapacity (19). At the operation of EC system $PbO_2|H_2SO_4|C$ at the same voltage, as the lead-acid storage battery: 2,1-2,33 V, a carbon electrode is always «hydrotreat» in the end of charge, spending the electrolyte, that means that the system is not isolated with gas.

The increase of contact resistance at the border of an active material/collector is another unpleasant feature of the negative electrode overcharge. It is determined by

the hydrogen permeation from charging active mass to the surface of a metal collector and its hydrogenated (saturation metal with H₂).

A simple technical solution – lowering operating voltage of a cell down to 2,0 V in the full state of charge (19), simultaneously reduces potentials of positive and negative (carbon) electrodes at the proper ratio of capacities. Thus the system service life increases and losses of electrolyte decrease. However, this time specific energy of a cell also decreases.

It should probably be spoken about the values of 8-12 Wh/kg at 100-200 Wkg for an industrial product.

Analyzing the aforesaid, it is possible to note, that there is no high power EC of PbO₂|H₂SO₄|C system with an acceptable service life.

The absence of industrial samples of powerful EC of this system in the power sources market proves this fact.

On the other hand, EC system PbO₂|H₂SO₄|C with standart battery type positive electrodes possess a high cycling service life resource from 5000 up to 150000 cycles, depending on the depth of discharge. 5000 deep cycles (1 time per day) provide service life of ~13 years. Therefore such supercapacitor systems successfully enter the field of power quality application. For example, energy storing at night and delivery at day time. The noncriticality to sulfation of the electrodes' surface, low maintenance and low specific cost will allow the EC system PbO₂|H₂SO₄|C to compete successfully with other power sources in the market of large energetic systems.

Some words about a bipolar design of this kind of EC. Wishing to reduce passive weight of a cell, it is desirable to reduce thickness of a bipolar collector, but effective thickness of ~0,1 mm (from a lead alloy) does not block the corrosion and the system practically does not work. Another problem is the formation of a passive layer PbO·PbSO₄ on the collector/PbO₂ interface and sharp increase of internal resistance. A reliable bipolar design of this EC system has not been developed yet.

2.4 +C|H₂SO₄|Pb·C – system

This system is relatively poorly studied. Low appeal is apparently explained by impossibility to reach high charging potential on a positive carbon electrode - an irreversible oxidation of carbon in sulphuric acid begins above +0,5 V (NHE). Besides, Faraday reactions on a carbon electrode in this potential window, which could provide significant pseudocapacity, are absent. That's why a charge storage method on +C is purely double electric layer.

OCV of this system, depending on state of charge of negative lead electrode is 1,3-1,4 V.

In spite of low operating voltage of a cell, this EC system possesses a number of practical, constructional advantages:

- *low potential of a positive carbon electrode expands a spectrum of constructional materials for Å collector, and for the bipolar system, including glassy carbon and the plastics filled with carbon;*

- *negative metallic Pb electrode is morphologically more stable at cycling, than oxide PbO₂;*

- *there is always an excessive store of H₂SO₄ for reaction on Pb, both due to carbon in Pb mass, and to permanent surplus of H₂SO₄ in Å carbon electrode;*

- *absence of contact resistances on positive electrode and high conductivity of negative Pb electrode assume low internal resistance and high power.*

All advantages mentioned give an opportunity to create a high power, inexpensive EC with long service life.

Standart flat-pack cells (fig. 2) and bipolar blocks assembled from these cells were analyzed in the present article.

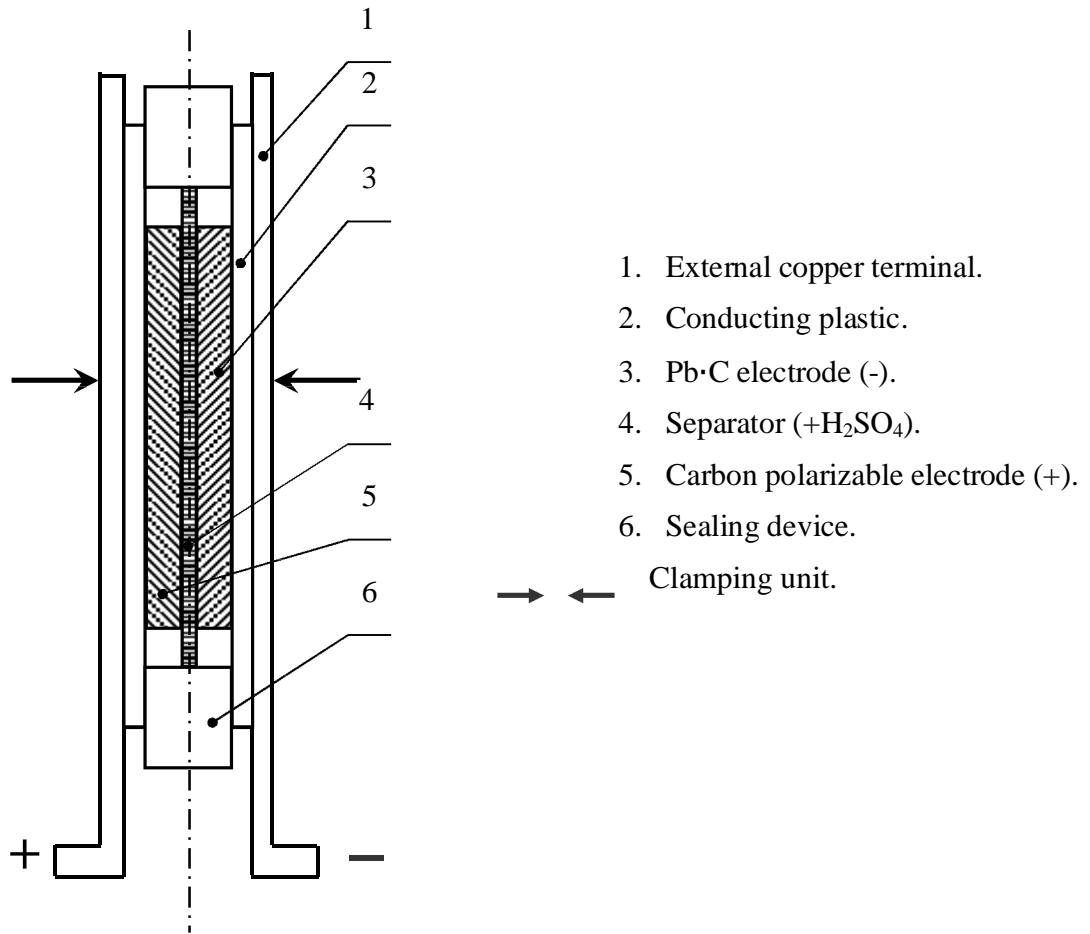


Fig. 2 General form of testing cell

Thickness of a cell analyzed, is 1,2 mm, weight – 36 g. (without external collectors). The family of discharging curves of this cell is given on the fig. 3.

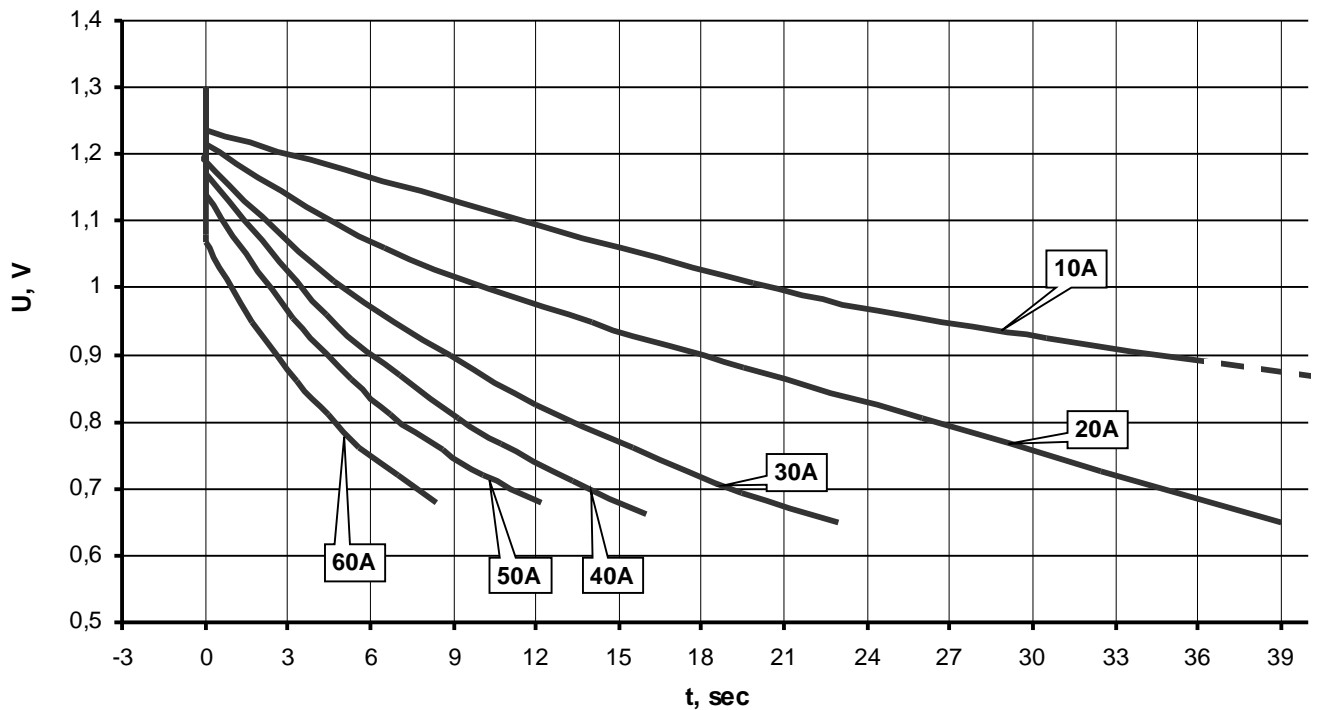
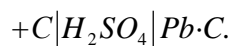


Fig. 3 Discharging curves family of a cell of the asymmetric EC system



The analysis of the type of curves shows "capacitor" linearity on low currents with insignificant "sagging" of line on high currents.

Bipolar blocks consisted of the above described cells, connected in series by laying one on another and fixed with some force, are assembled and analyzed.

Blocks were analyzed in discharging modes by direct currents after that specific energy and power recalculation was made. The Ragonie plot for one of sorts of blocks (14 V, 144 F) is given on the fig. 4 (weight of packaging is not included). RC time constant is 1,62 sec. (1 kHz).

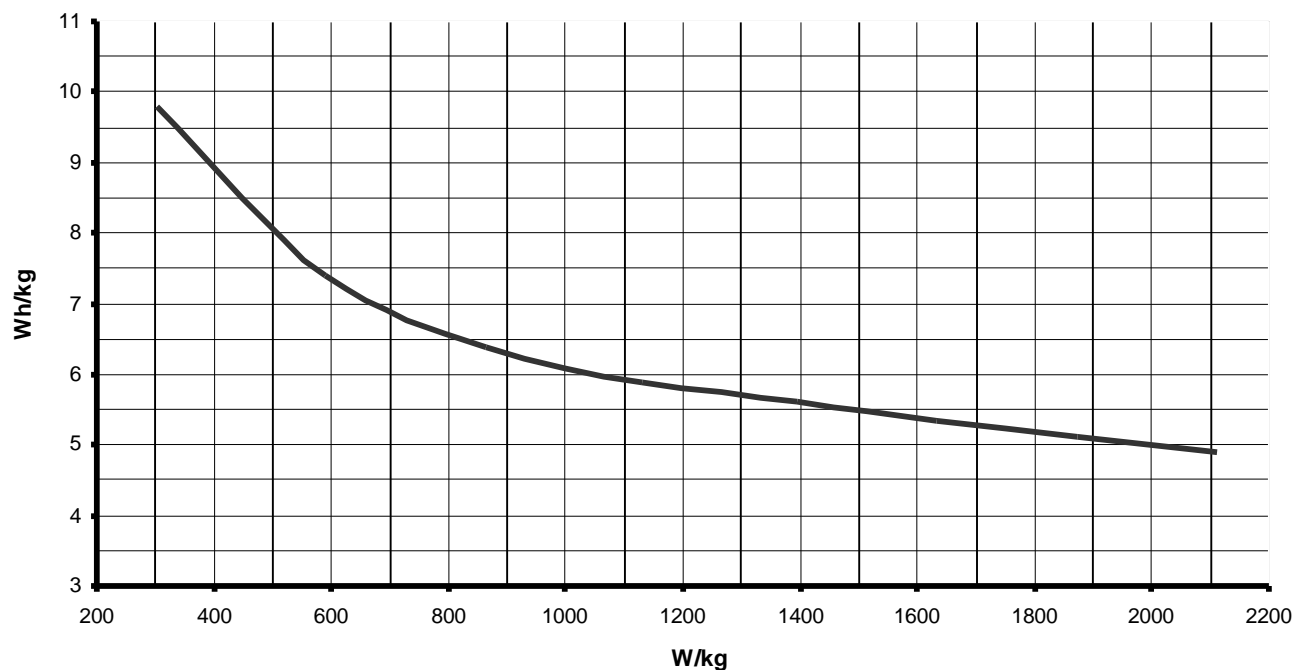


Fig. 4 The Ragone plot for block 14 V, 144 F of $+C|H_2SO_4|Pb \cdot C$.

The Ragone curve is very typical for asymmetric systems with the Faradaic electrode: high specific energies are much higher than the ones at symmetric capacitors in the field of low powers. The strong influence of electrochemical reaction and its basic contribution to current forming process is demonstrated here. Then - an obvious bend (500-700 W/kg) and sloping characteristic curve where a non-polarizable electrode operates with overload by current and delivered energy reduction.

The analysis of this plot shows that a block yields up 8 Wh/kg of delivered energy at 500 W/kg and 6 Wh/kg - at 1000 W/kg.

Preliminary experiments have proved, that the obtained results on specific energy and power for EC system $C|H_2SO_4|Pb \cdot C$ are very close to parameters of supercapacitor systems with non-aqueous electrolytes on acetonitrile basis.

The calculations and a working designing of EC set for application in heavy hybrid electric transport - trams (trolley-buses) have been carried out for more objective comparison.

The comparative data of an available product (HTM, 125 V) and the design data of the set system $+C|H_2SO_4|Pb \cdot C$ are given in the Table 1.

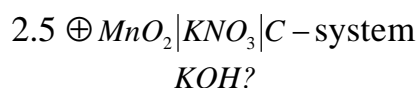
Table 1

Parameters	HTM Power 125 V Module (USA, Maxwell)	EC System Set $C H_2SO_4 Pb \cdot C$ 15 modules, 125 V
1	2	3
1 Nominal Operation Voltage	125 V	125 V
2 Maximum Operation Voltage	130 V	130 V
3 Surge Voltage	134 V	140 V
4 Delivered Energy, (150 A)	101,7 Wh	458 Wh
5 ESR DC	18 mOhm	22 mOhm
6 ESR AC(1 kHz)	14 mOhm	11 mOhm
7 Maximum Discharge Current	750 A	1200 A
8 Weight	58 kg	85 kg
9 Volume	85 liters	97 liters
Specific Parameters		
10 Specific Energy (Delivered)		
-by weight:	1,76 Wh/kg	5,39 Wh/kg
- by volume:	1,18 Wh/lit	4,72 Wh/lit

Table 1 (cont. d.)

1	2	3
11 Specific Operation Power ($J_{\max} \times U_{op/m(v)}$) -by mass: - by volume:	1616 W/kg 1092 W/lit	1764 W/kg 1546 W/lit
Specific Requirements, Potential Hazardous		
12 Content of explosive and toxic components	Contains acetonitrile	not contained
13 Additional requirements for monitoring and safety systems	Control and emergency fire-fighting system required	not required

The above-stated data of Table 1 demonstrates the superiority of EC system $C|H_2SO_4|Pb \cdot C$ towards the EC with non-aqueous electrolytes on acetonitrile basis on specific energy (at closer specific power level), operation and utilization safety.



The appearance of alkaline rechargeable $MnO_2 | KOH | C$ cells on the background of $NiOOH | KOH | C$ supercapacitor system caused a great interest to this system. There was pursued a purpose of creating a cheaper electrochemical system for EC, nickel free.

A limited reversibility of a non-polarizable electrode of this system $-MnO_2(MnOOH)$ at cycling was found by long researches. It was explained by a morphology change of an active material and contact loss with the conductive "skeleton" in the electrode volume.

On the other hand, the kinetics of the electrode reaction of MnO_2 cathodic reduction is strongly limited by an activation stage and the ions transport. The electrodes containing 60-80% of electrochemically passive additive (carbon black, graphite) operate well enough. But even in this case its specific capacity does not surpass 150 F/g, that is below the one of cheap powder activated carbon available.

Attempts of using oxy-hydroxide electrodes obtained by combined precipitation of salts: $\text{NiOOH}\cdot\text{MnOOH}$ were made.

The service life of such systems was not confirmed, though the initial data was promising enough.

The further development of this electrochemical system has proceeded with the appearance of nanomaterials. The electrodes, modified by nanotubes, reach specific capacity values of 140 F/g (197 F/g for MnO_2) (20). The recent data of nanomodified active masses of MnO_2 shows values of 250 F/g at the beginning of cycling, and ~120 F/g to 1000 cycles (21).

Nowadays, it is possible to summarize, that the EC, based on MnO_2 non-polarizable electrode, are inert devices with limited service life and specific energy which is not exceeding the one for systems with NiOOH electrode.

The industrial output of EC of this system is not developed, though original materials are characterized by availability and low cost.

It should be noted that many researchers study morphology and efficiency of MnO_2 in sulphate (Na_2SO_4), nitrate (KNO_3) electrolytes which will never be applied in the industry because of its insignificant conductivity. And the data, obtained in KOH electrolytes, unfortunately, demonstrates low specific capacity.

3 CONCLUSION

Four basic electrochemical systems for asymmetric supercapacitors with aqueous electrolytes, having potentially wide practical applicability and an opportunity of a large-scale production were analyzed.

Now EC systems $NiOOH|KOH|C$ are mostly spread, but its development is limited by the cost increase of incoming materials.

The most perspective systems are $PbO_2|H_2SO_4|C$ and $C|H_2SO_4|Pb \cdot C$. The first of them has low power, but has a long service life; the second – high power with a long service life.

It is shown, that the asymmetric capacitors of $C|H_2SO_4|Pb \cdot C$ system as modules and complete devices in the objects of customers, have parameters close or superior to the ones for supercapacitors with non-aqueous electrolytes (including those, on acetonitrile basis).

Besides, there are advantages on ecological compatibility and operation safety.

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