ELECTROLYTES FOR THE ELECTROCHEMICAL SUPERCAPACITORS

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Introduction

Supercapacitors are electrical components with very high capacity. Classical capacitors reached capacities in microfarads. In the case of supercapacitors capacities are achieved even several thousand farads but for relatively low voltage 4.5 V.
These components have wide applications in the present industrial world because of their properties (high charge /discharge, long-life cycles and high capacity). They could be used as auxiliary systems of electric power, for automobiles or as a base of the equipment for the utilisation of recuperated energy.

Experimental

Preparation of liquid electrolytes

The perchlorates of alcalic salts were used ($LiClOB_4B$, $Mg(ClOB_4B)B_2B$, $Cd(ClOB_4B)B_2B$ and others solved in selected aprotic solutions as propylene carbonate ($C_4H_6O_3$), dimethylformamide (C_3H_7NO), dimethylsulfoxide (C_2H_6OS), γ-butyrolaktone ($(CH_2)_3OCO$) and 1,2-dimethoxyethane ($C_4H_{10}O_2$). In all experiments the solution of 0.5M.lP-1 $LiClOB_4$ was used in all these solvents.

Electrodes

The same properties of electrodes for several measurements of different electrolytes were achieved by several pieces of equal electrodes. The „zero type“ electrode is the label for electrodes made from the following components: expanded graphite (0.25 g) + conditioner - ammonium hydrogen carbonate – NH_4HCO_3 (3.02 g) + binding agent – Sokrat (0.62 g, EASTMAN Inc., Czech Republic).

Measurements in some electrolytes (with dimethylformamid) have shown important findings: the use of Socrat as a bonding detergent causes instability of the electrode mixture. The mix was become to decompose from the screen it was spread on immediately after the sinking into the electrolyte.

For this reason other electrode samples should be prepared. There are signed as the „first type“. The samples were made by the same way as previous ones but instead of Socrat the PTFE emulsion is used. These electrodes have very high stability in all types of solvents. But the lower capacity was problem in this case – no more than about 6 farads per gram of electrode material.

This fact has lead to the formation of another groups of electrodes „second type”, made by a different procedure - teflonation of graphite. This procedure is based on the principle that the electrode material is prepared by boiling of expanded graphite with water and isopropylalcohol with an addition of the PTFE emulsion.
Measurement of capacity in liquid electrolytes.

The measurement apparatus AUTOLAB PGSTAT12 was use for the capacity measurement together with the program GPES. The capacity of selected samples was determined by the method of cyclic voltametry. Voltage of triange waveform was applied on the capacitor and the output current is monitored. Resulted capacity is determined as:

$$C = \frac{1}{2}\frac{\Delta I}{v} \tag{1}$$

where C [F] is capacity, ΔI [A] is the difference of currents, ν [V/s] is scan rate of the triangular waveform.

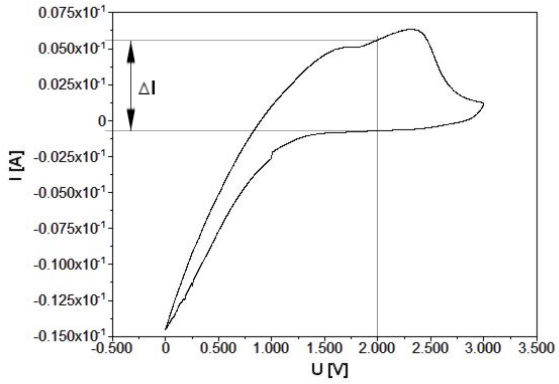

Fig. 1 *Cyclic voltametry of the sample: electrolyte (dimethylformamid+$LiClO_4$) the second type of the electrode*

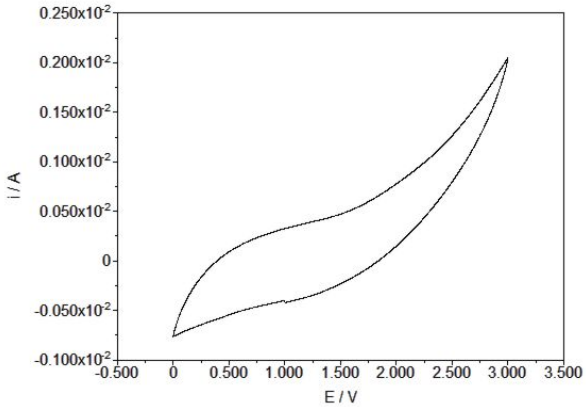

Fig. 2 *Cyclic voltammogram determined for the sample: gel electrolyte γ-butyrolacton. Capacity 0.33 F/g – the most convenient result in experiments with gel electrolytes.*

Gel electrolyte

The substance SUPERACRYL (Czech Republic) had been used for the polymerisation of MMA in our previous papers [3]. This initiator contained 1 % (by mass) of dibenzoylperoxide approximately. Moreover, we found that it was difficult to remove residual water and oxygen from it. Therefore, we have started to use a new method of MMA polzmerisation. The new initiator ABIN is efficient even at 65 °C and the products of its decompositionon are electro-chemically inactive nitrile and nitrogen. The net EDMA was used (0.3 mol.% of monomer) and it contents of initiator is 1 mol. % of monomer.

Used chemicals:
methylmethacrylate MMA (Aldrich, distilled, stored at 4 °C)
ethylenglycol dimethacrylate EDMA (Aldrich, stored at 4 °C)
ABIN (Fluka, re-crystallised, stored at 4 °C)
Liquid electrolyte – see above

Table 1 *Ratio of individual components of the gel*

Component	Amount
MMA	1.75 ml
EDMA	10.51 μl
ABIN	0.027 g
electrolyte	1 ml

Electrodes for gel electrolytes

Electrodes were prepared from electrode materials using by the method of teflonation of graphite. The procedure is the same as the one used for the liquid electrolytes. The difference is only in the shape of the net which serve for the spreading of the material. The net has the circular shape. This shape was fitted to bottom part of Petri plate. The upper electrode cap is cut opposite to outlet to eliminate electric connection with the bottom electrode.

Results and Discussion

Table 2 *Measured values of capacities*

Used solvent	Capacity The first type of the electrode [F/g]	Capacity The second type of the electrode [F/g]
dimethylformamid (DMF)	1,0	28,7
dimethylsulfoxid (DMS)	5,2	20,0
propylenkarbonát (PPC)	1,6	15,2
Dimethoxyetan	1,3	9,9
Gamabutyrolakton	0,4	2,0

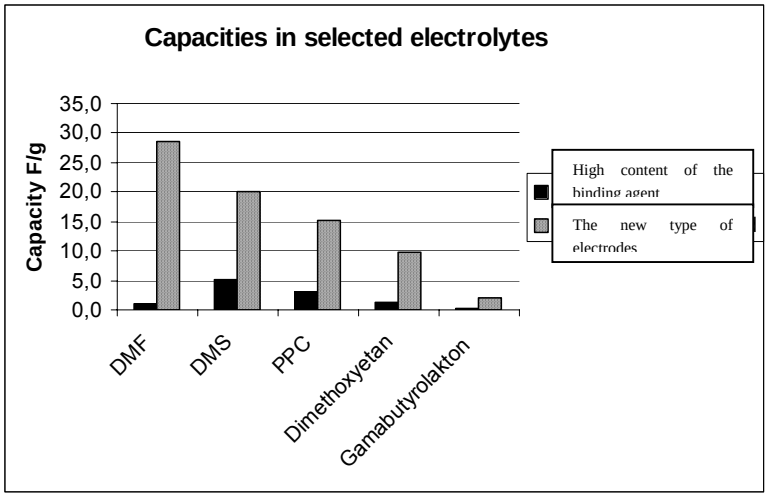

Fig. 3 *Capacities of selected types of electrolytes for two types of electrode materials*

Table 3 *Measured values of relative capacities for gel supercapacitors*

Used solvent	Capacity [F/g]
γ-butyrolacton	0.33
dimethylformamid (DMF)	0.32
propylenkarbonát (PPC)	0.13
dimethylsulfoxid (DMS)	0.11
Dimethoxyetan	0.03

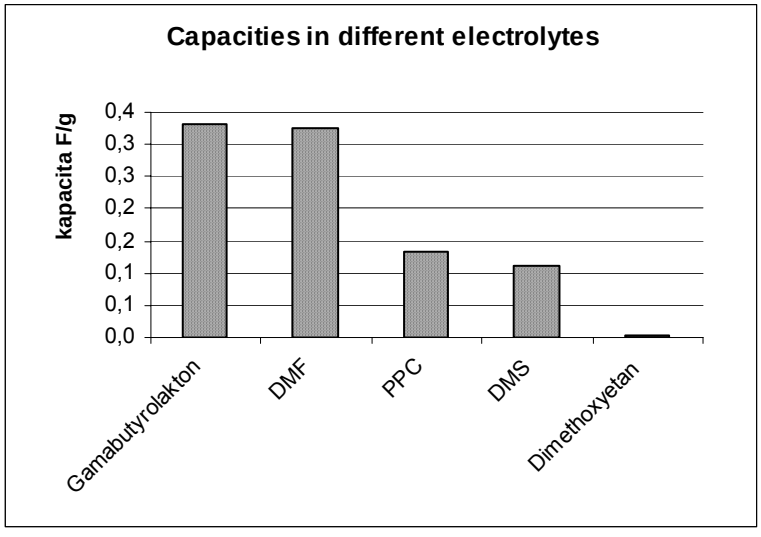

Fig. 4 *Capacities of gel electrolytes*

Conclusions

The highest capacity has been achieved in electrolyte from dimethylformamid – the use of the electrode of the „second type“ as it is obvious from figure 1. The experiment with the electrode of the „first type“ has showed the better result for the use of dimethylsulfoxid. It should be resulted in a conclusion that this solvents convenient for electrode materials which have not much bonding agent. It is possible to expect practical applications of this variation for example in the case of high reliability and stability of electrode materials with lower capacity tolerance.

Gel supercapacitors have higher capacity in the case of the use of the electrolyte prepared from solvent of gamabutyrolacton and dimethylformamid (nearly the same values 0.33 F/g). The less convenient is the use of solvent of dimethoxyetan, where the capacity were significantly lower about several digital places.

References

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2. Výběr rozpouštědel pro superkondenzátory, Jaroslav Kněžínek, VUT Brno 2004.