PREPARATION AND PROPERTIES OF CARBON BASED ELECTRODES FOR SUPERCAPACITORS

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ABSTRACT

The different surfactants were used for modification of commercial available carbon black Vulcan XC 72R as electrode material for supercapacitors in order to improve its specific capacitance and energy storage. Hydrogen peroxide and several types of alcohols were used for this purpose. Properties of electrodes were investigated by the cyclic voltammetry in the non-aqueous 0.5 M solution of $LiClO_4$ and propylene carbonate. The enlargement of specific capacitance is mainly ascribed to improvement in wettability of carbon materials, which results in a higher usable surface.

1. INTRODUCTION

Electrochemical capacitors are unique energy storage devices. ECs can store much more energy than common capacitors and can offer much higher energy density than batteries. Supercapacitors can be used in applications where batteries cannot provide sufficient power or charge-discharge rates. They can also harvest or recover energy from fast repetitive motion that is wasted nowadays. [1, 5]

The group of electrochemical capacitors (ECs) is consisted of two general types, electric double layer capacitors (EDLCs, also known as supercapacitors or ultracapacitors) and pseudocapacitors. The difference between ECs and conventional dielectric and electrolytic capacitors is in the mechanism of the energy storage. The electrochemical double layer capacitors store electrical charge in an electrical double layer at the electrode-electrolyte interface, while the pseudocapacitors use highly reversible surface redox reactions (similarly as batteries).

Carbon based materials are commonly used in electrode substances of supercapacitors because of their low cost, chemical stability and relative high specific surface area (thousands m^2 per gram). However, measured capacitances are usually much lower than was expected. The lower values of the specific capacitance are partially caused by poor electrode wettability, which leads to lower useable surface area. Chemical surface modification in nitric acid or hydrochloric acid solutions has been reported by some authors to improve the wettability. However, there is none observed positive effect in an aprotic electrolyte.[4, 2,6]

To improve the energy storage performance of carbon materials in aprotic electrolyte solutions the hydrogen peroxide and several types of alcohols were used.

2. EXPERIMENTAL

2.1. MATERIAL

The main part of the electrode in supercapacitors is carbon based material. Commercial available carbon black Vulcan XC72R was used for this experiment. The hydrogen peroxide and three types of alcohol, namely isopropyl alcohol (IPA), methanol and ethanol were used as surfactants.

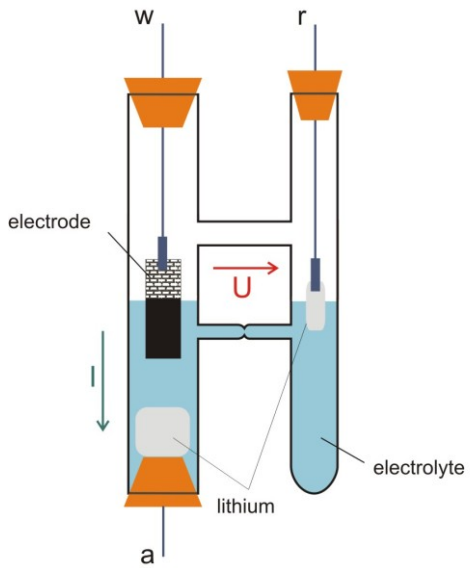
2.2. SAMPLES PREPARATION

Two methods were used to prepare the electrode substances. Vulcan XC72R was heated and stirred in water with surfactant for 1 hour. The rate of carbon, water and surfactant was 0.5 g : 50 ml : 10 ml. At the end 5 wt% PTFE was added as a binder.

In the first method vapors were refluxed. In the second method surfactants were evaporated during boiling. After 24 hours mixtures were washed by distilled water and dried at 100 ^{o}C for 1 hour.

2.3. INSTRUMENTATION

The cyclic voltammetry (CV) was carried out in a three electrode cell (fig. 1) in 0.5 M electrolyte of $LiClO_4$ and propylen carbonate. Lithium electrodes were used as reference and counter electrodes. The three electrode cell was placed in the dry box with argon atmosphere on the ground of lithium oxidation on the air. The AUTOLAB PGSTAT 12 was used for measurement.



w...working electrode

r...reference electrode

a...auxiliary electrode (counter electrode)

Figure 1: The three electrode cell

3. RESULTS AND DISCUSSION

Fig. 2 shows the cyclic voltammogram of measured sample (solid line) between 0 V and 3 V taken at a scan rate of 0.01 V/s. There are also curves of the calculated capacity per gram of the electrode material (dotted line). All results are in the table 1.

The capacity was calculated by the formula

$$C = \frac{1}{2} \cdot \frac{\Delta I}{\alpha} \qquad [\mathrm{F}] \tag{1}$$

where ΔI is a subtraction of the currents for one voltage and α is the scan rate.

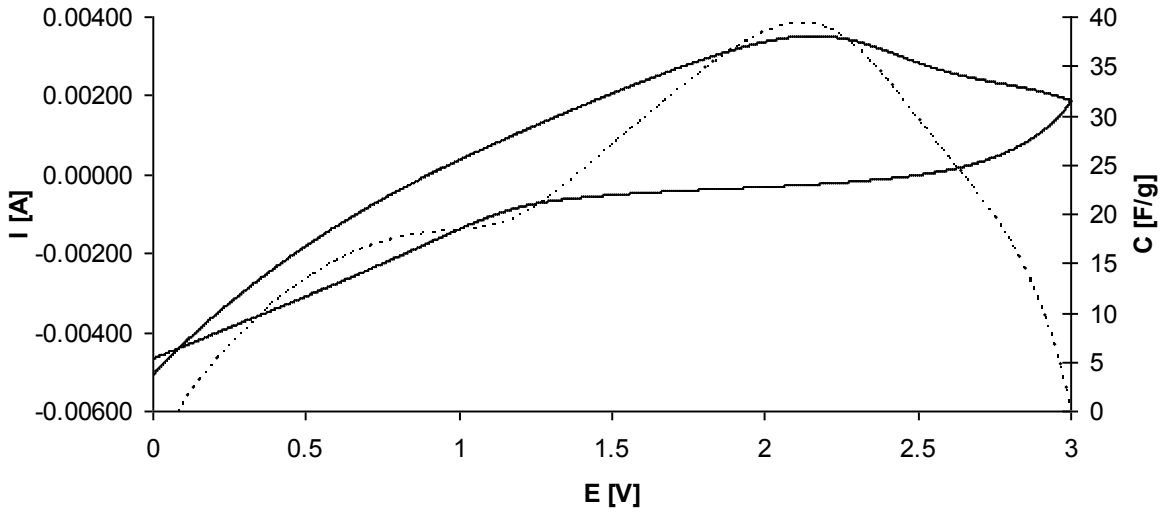


Figure 2: Example of the cyclic voltammogram

There is a clear difference between used methods. The capacity reached by the second method is just about three times higher. It can be caused by refluxed vapors of surfactants, which influence porosity and internal resistance. Interesting are differences between methanol and ethanol. They are the simplest and quite similar kinds of alcohols, but with diverse effect at the capacity.

Surfactant	I. Method	II. Method
IPA	3 F/g	16 F/g
Methanol	11 F/g	33 F/g
Ethanol	15 F/g	46 F/g
Hydrogen peroxide	21 F/g	38 F/g

Table 1: The influence of different surfactants to specific capacity

Because of purity, properties and chemical formula similarity to distilled water the hydrogen peroxide was used. It wasn't achieved the highest capacity with hydrogen peroxide, however 38 F/g was the 2nd highest measured capacity in this experiment.

4. CONCLUSION

Wettability of carbon based materials in aprotic electrolyte can be improved by surface modification with hydrogen peroxide and some kind of alcohol. The best result was obtained by methanol. The effect of refluxed vapors was shown. The capacity in the first method was just about three times lower then in the second method. Therefore, the modified carbonaceous materials are more suitable for use in EDLCs for high current applications for their better properties as the electrode materials.

ACKNOWLEDGEMENT

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