POLYANILINE IN SUPERCAPACITORS

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ABSTRACT

Supercapacitors (also called as ultracapacitors) are considered as the high power storage devices with very high capacity, typically several hundreds of farads. Supercapacitors can be used as a power source, but the main field of their usage is in application where is it necessary to accept or to release high currents (e.g. fuel cell or hybrid vehicles).

Polyaniline and polyaniline-carbon electrodes were prepared by chemical polymerization. Two methods were used to obtain the composite electrodes. The activated carbon is mixed with aniline in the first method and subsequently this mixture is polymerized. The second method consists of mixing the activated carbon and chemically polymerized polyanilin. The properties of the prepared electrodes were measured by the cyclic voltammetry in the non-aqueous electrolyte.

1. INTRODUCTION

Energy storage devices are divided to the two main groups – batteries and capacitors. Batteries can store high amounts of energy however with lower specific power [W/kg]. On the other hand capacitors are able to accept and release high amounts of energy in the very short time range, but their specific energy [Wh/kg] is lower than most of batteries. Capacitors with very high capacity are generally called as supercapacitors.

Electrochemical double layer capacitor (EDLC) is one of two basic supercapacitors types. This type uses the principles of double layer and high porosity of the electrode material. The second type known as pseudocapacitors works on the base of ions intercalation to the electrode structure. [1, 2]

Electrodes for supercapacitors must be: high porosity, low electrical resistivity, good stability. Activated carbon is highly porous, stable and quite good conductive material. It is important to improve properties of carbon based electrodes to get higher capacity. Carbon can be thermally treated to gain higher purity and porosity. [3]

Better conductivity and porosity of the electrode can be also raised by using conducting polymers. Polyaniline with conductivity close to 2 S/cm belongs to the group of the organic conducting polymers. This work deals with properties of the activated carbon, polyaniline and polyaniline-carbon electrodes, their capacity and conductivity. [2, 4]

2. EXPERIMENTAL

2.1. MATERIAL

The main part of the electrode is activated carbon (AC). It is important for its surface area of the order of 2000 m^2/g. Activated carbon is made from carbon-rich organic precursors (e.g. hydrocarbon gas, petroleum pitch, graphite rod) by the heat treatment (1000 – 2000 ºC) in inherent atmosphere. Polyanilin (PANI) is used as conducting binder and as material to improved porosity of the activated carbon. Polyanilin can be prepared by an electrochemical or a chemical polymerization. The second method was chosen in this work. The chemical polymerization was made in the acid media through the good conductivity. Polyaniline has better electric conductivity, but on the other hand has worst cycle live in comparison with carbon. It is due to ions intercalation during the charging/discharging process. PTFE (polytetrafluoroethylene), an insulating and stable material, was used as the binder in the electrode without polyaniline. [2, 3, 4]

2.2. SAMPLES PREPARATION

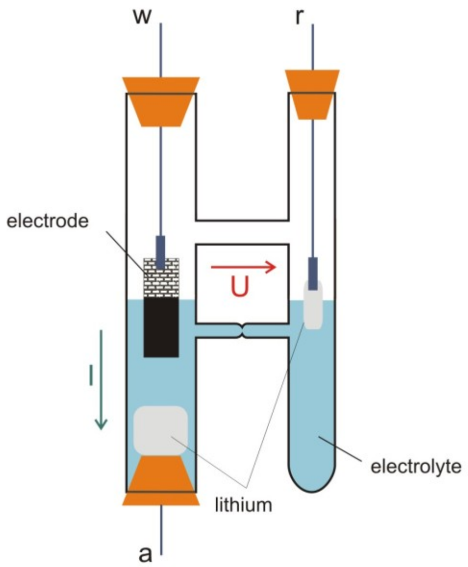
Five types of electrodes were prepared. The first of them was made from activated carbon and PTFE as binder. The second electrode was pure polyaniline (PANI) prepared by chemical polymerization of the aniline by the ammonium persulphate. PAC is the third prepared electrode consisting of polyaniline and activated carbon. It was prepared by mixing activated carbon and aniline. This mixture was then polymerized by ammonium persulphate. The fourth AC+PANI electrode is a mixture of activated carbon and pure polyaniline. The last prepared electrode was made from PAC material and activated carbon in the weight ratio 1:1.

Electrode type	Main electrode material	Binder	Ratio
AC+PTFE	activated carbon	60 % PTFE	1 g : 23 µl
PANI	polyaniline	-	-
PAC	activated carbon	polyaniline	1 g : 1 g
AC+PANI	activated carbon	polyaniline	1 g : 1 g
PAC+AC	PAC and AC	-	1 g : 1 g

Table 1: Types of electrodes

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 propylencarbonate. Lithium electrodes were used as reference and counter electrodes. The three electrode cell was placed in dry box with argon atmosphere on the ground of lithium oxidation on the air. The AUTOLAB PGSTAT 30 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 voltammograms of measured samples (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).

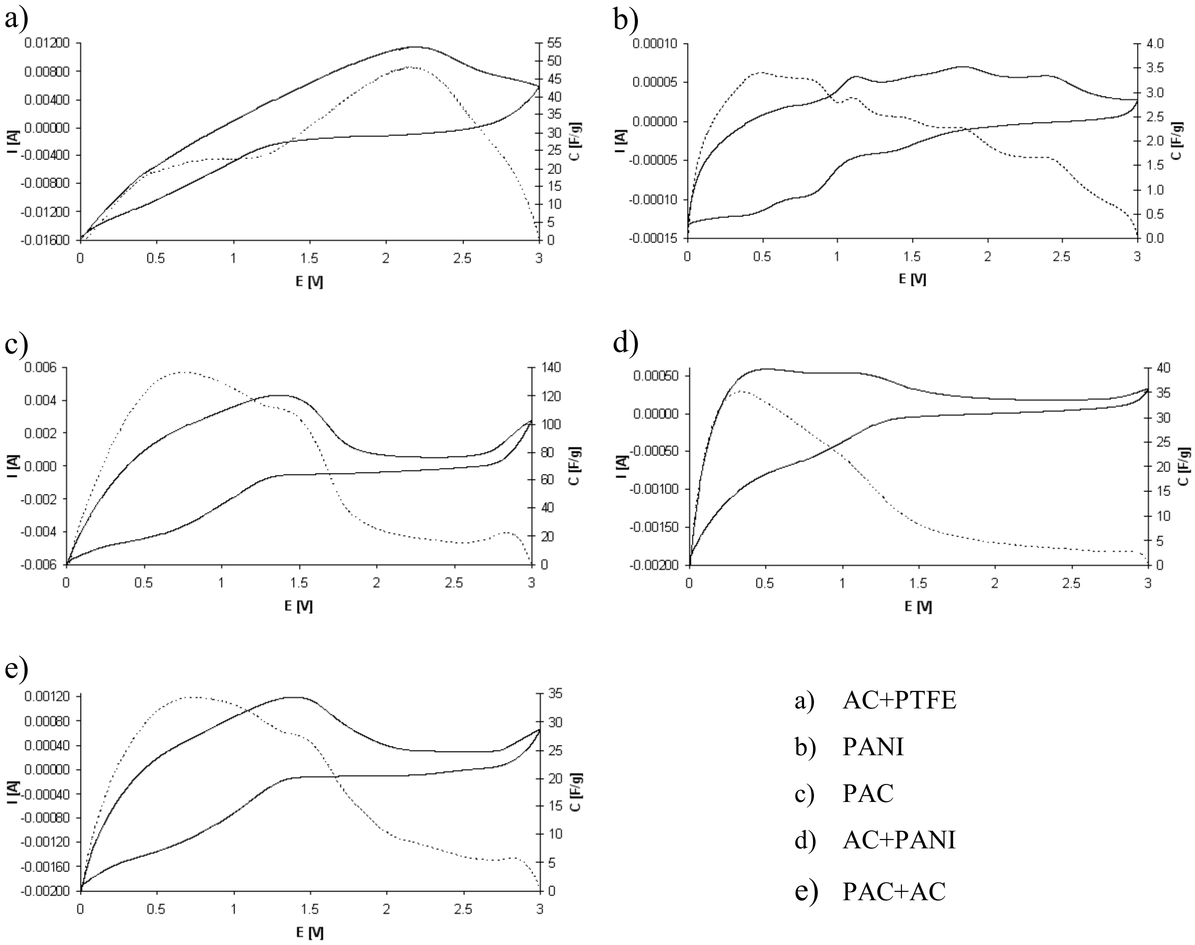
The capacity was calculated by the formula

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

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

AC+PTFE and PANI samples had own specific voltammograms. The AC+PTFE electrode had the highest specific capacity 48 F/g about 2.2 V, the PANI electrode reached the peak 3.4 F/g about 0.5 V. It was the lowest measured specific capacity from all samples, polyaniline has quite good conductivity, but this material hasn't as the high porosity as the activated carbon. The PAC and PAC+AC voltammograns curves had a similar shape, but measured currents and calculated capacity were very different. The PAC sample had the highest specific capacity 136 F/g about 0.7 V and the capacity of the PAC+AC electrode achieved 34 F/g about 0.7 V. These diversities were given by the samples preparation. Intercalated aniline molecules increased their volume during polymerization in the carbon structure so they enlarged the surface area of the PAC sample. The porosity and conductivity of the PAC+AC sample was decreased by adding of the activated carbon. This was the reason why the PAC electrode had the better capacity. The AC+PANI electrode had the specific capacity 35 F/g about 0.35 V. Polyaniline served as binder in this material.

It is interesting to compare polyaniline properties as a binder or as the material to increase the porosity. The material with PTFE used as the binder has the higher specific capacity than the AC+PANI electrode where were used polyaniline. On the other hand polyanile increased porosity in the PAC electrode and the highest capacity was measured (table 2).



a) AC+PTFE

b) PANI

c) PAC

d) AC+PANI

e) PAC+AC

Figure 2: Cyclic voltammograms

Usage polyaniline or other conducting polymers is debatable despite of stability these organic polymer materials. But their potential in supercapacitor's electrode composite material is high. They can conduce to higher capacity by own pseudocapacitive behavior and also extend conductivity and porosity of the electrode material.

Electrode type	Specific capacity
AC+PTFE	48 F/g
PANI	3.4 F/g
PAC	136 F/g
AC+PANI	35 F/g
PAC+AC	34 F/g

Table 2: Specific capacity

4. CONCLUSION

There are many materials suitable as electrode materials with different properties, like high-surface area carbon materials, carbon nanotubes, transition metal oxides and electrical conducting polymers. The aim of this work was to prepare and discuss polyaniline-carbon electrodes.

Polyaniline is cheap and easily accessible material. It has proved as suitable material for supercapacitors electrodes. In this study the polyaniline-carbon electrode achieved 136 F/g. It was shown that polyaniline is better for the increase porosity of the activated carbon then as the binder.

ACKNOWLEDGEMENT

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