

SUPERCAPACITORS – AUXILIARY POWER SOURCES

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Introduction

The electrochemical supercapacitors are the most recent sources of energy [1, 2]. Their specific energy is not very high in comparison to other advanced sources, but they possess a very long lifetime and their charging may be fairly rapid. Two possible principles were developed for their design. The older one uses two identical electrodes of intercalation type such as RuO₂ in aqueous acids and the electrochemical process is based in the insertion of protons into the oxide. Ruthenium oxides are very suitable for this purpose as they undergo several successive steps; therefore, they can cover quite broad voltage range. The other one uses the capacity of electrochemical double layer on the contact of the inert electrode and inert electrolyte. The latter is the subject of present contribution.

The supercapacitors carbon electrodes in general, either chemically etched carbon cloth or carbon in powder form, behave as inert (polarised) electrode in an electrolyte in which no electrochemical reactions may occur.

According to the formula $W = 0.5 C U^2$, the specific energy is higher if higher voltage can be applied to the capacitor. Therefore, we use aprotic solvents for this purpose. Tetraalkylammonium salts dissolved in acetonitrile are preferred by the manufacturers of capacitors. As much as 5-10 F.cm⁻³ and voltage 2.5 V are available now. The properties of supercapacitors must be studied by electrochemical methods such as voltammetry or impedance spectroscopy.

Experimental

Graphite particles with enhanced specific surface area were used for electrode preparation. The Superacryl emulsion was added as a binder. The properties of these electrodes were improved by the addition of a powdered compound (e.g. ammonium hydrogen carbonate), which was dissolved in water and the electrode then carefully dried [3]. The effective surface area was increased in this way and extended holes remained in the electrode composite. Several samples were treated at 110°C. The geometric surface area was close to 1 or 10 cm².

Aluminium foil, carbon cloth E-TEC “A” or stainless grid were used as the current collectors and supports. Anhydrous salts of lithium, sodium, and tetraethylammonium ions

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were dissolved in propylene carbonate to the concentration 0.5M and used as the liquid electrolyte. The same solutions were used for preparation of PMMA based gels as it is described elsewhere [4, 5].

Results and Discussion

An example of the voltammetric curve of a sample prepared from exfoliated carbon with the addition of ammonium hydrogen carbonate by subsequent dissolution of that salt in the TEABF₄ is shown in Fig. 1. The same salt was used as the electrolyte, so that small amount dissolved from the electrode composite did not cause any considerable change of composition. A polypropylene screen served as the separator between the electrodes. The addition of solid salt to the electrode composite increased the capacity obtained by a factor of 2 to 3.

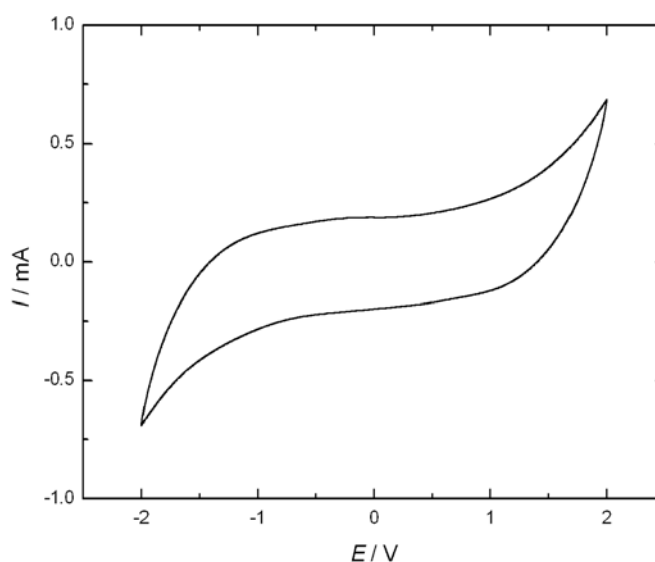


Fig. 1. Voltammogram of a supercapacitor deposited on a stainless steel (scan rate 0.001 V.s^{-1} , electrode area 10 cm^2)

Fig. 2 describes similar voltammetric curve of a set of two electrodes prepared from exfoliated graphite and acrylate binder on an aluminium foil using lithium perchlorate embedded in PMMA gel. The impedance at 0 V of the latter system is shown in Fig. 3. Capacity close to 2-5 mF per 1 cm^2 of apparent surface area of the supporting screen is quite possible. The electrodes can be used in connection to gel polymer electrolytes.

Another example shows a supercapacitor with electrodes deposited on an Al foil and with a thin sheet of the gel electrolyte as a separator. Impedance spectrum is shown in Fig. 2.

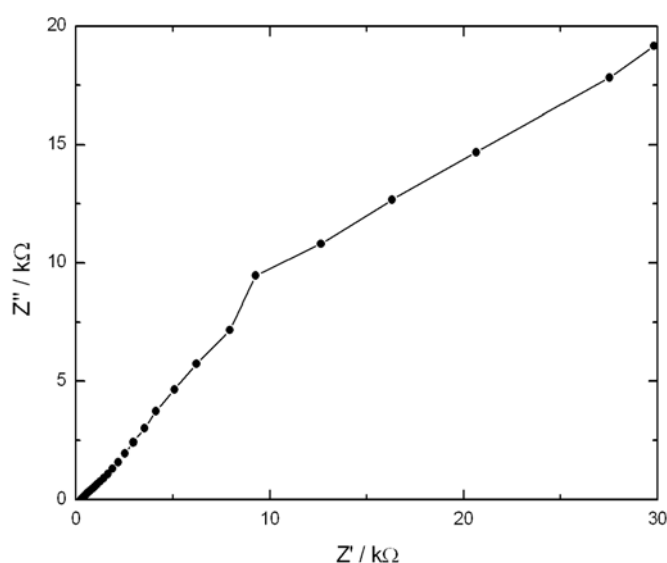


Fig. 2 Impedance spectrum of a capacitor deposited on aluminium

An equivalence circuit was estimated using the software of AUTOLAB potentiostats from the impedance spectrum at the voltage 0.4 V (see Fig. 3). It consisted of a series resistance 289 Ω , pseudocapacity 1.38 μF (with phase angle corresponding to 65°) and the Warburg type admittance 4.14 μS , apparently corresponding to porous structure of a polarized internal surface. The resistance of self-discharge was equal to 762 Ω .

A voltammetric scan at scan rate 1 $\text{mV}\cdot\text{s}^{-1}$ is shown in Fig. 3. In the central part, the curve contains two almost horizontal lines; the distance of them corresponds to the effective capacity 434 μF . The Warburg component of the equivalence circuit (4.14 μS) at the angular frequency 0.001 Hz^{-1} corresponds to apparent capacity 328 μF , which is similar to that found from voltammetry.

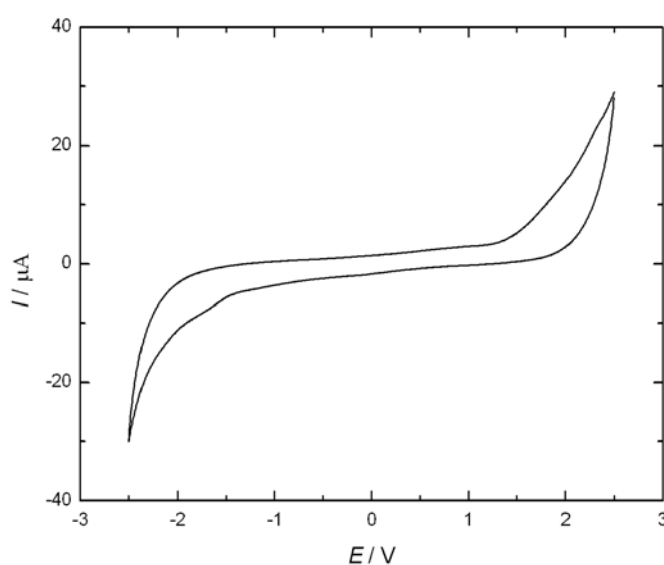


Fig. 3 Voltammetry of a supercapacitor deposited on aluminium (scan rate 0.01 $\text{V}\cdot\text{s}^{-1}$)

In voltage range from -1.2 to $+1.2$, the behaviour of the capacitor is almost theoretical. The waves out of that interval are caused probably by film formation or insertion of cation into graphite.

Conclusions

According, the exfoliated graphite is a suitable material for the production of the design of electrochemical supercapacitors, especially with a PMMA based gel electrolyte. Optimisation of electrode assembly with respect to specific capacity per unit volume would be necessary. Attention must be paid to the broadening of the voltage span to ± 2 V at least.

Acknowledgements

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