

FROM: M.Sc. Irina Yu. Sapurina, Dr.Sc.

SUBJECT: Report on Doctoral Thesis

“Fabrication of flexible supercapacitors with high electrochemical performance”

or in Czech:

“Výroba flexibilního superkondenzátoru s vysokým elektrochemickým výkonem”

submitted by

Haoji Fei

to the

Tomas Bata University in Zlín

DATE: 5th February 2018

OPINION: Recommended

The doctoral thesis is focused on the development of miniaturized energy storage device, supercapacitor (SC), for rapidly developing micro-electronics. The relevance of the research task is related to the fact that, generally, it is the mass and dimensions of the power supply that limit the further miniaturization of the electronic device. Among the systems that are used to store energy, SCs demonstrate higher power density and cyclic stability than batteries, as well as higher energy density than conventional capacitors. Supercapacitors are especially necessary for the devices that occasionally consume high power in short period of time while the rest of time operating in normal mode. Besides, flexible SCs have drawn interest for electronic skins, curved smart phones and some implantable medical devices.

Within the PhD study, two types of miniaturized flexible SCs are developed, i.e SCs based on reduced graphene oxide/polyaniline, and, reduced graphene oxide/manganese dioxide (MnO_2). Both SCs demonstrate high power and energy density even under mechanical deformation, and, high cyclic stability during charge-discharge.

It should be noted that all raw materials (graphene, RGO, MnO_2) for SCs were synthesized and characterized by the applicant himself. An important stage of the work was the preparation of stable aqueous dispersions of raw materials. Moreover, Haoji Fei also developed original techniques to obtain multicomponent electrode materials by coprecipitation of components on the porous membrane with subsequent peeling of the deposited layer. As a result, thin homogeneous and binder-free electrodes have been obtained. Furthermore, he elaborated original method for creating a graphene-based current collector by deposition of graphene flakes over the electrodes. The electrode-current collector pair thus obtained has low resistivity of the order of a few ohms, which allows one to provide high power characteristics of the device.

As an example of successful technological solution is the method of fabrication of a highly flexible asymmetric SC using MnO_2 and RGO nanosheets piled hydrogel films and a novel bacterial cellulose (BC) filled polyacrylic acid sodium salt- Na_2SO_4 (BC/PAAS- Na_2SO_4) neutral gel electrolyte. Apart from being environmentally friendly, this BC/PAAS- Na_2SO_4 gel electrolyte has high viscosity and is adhesive, which enables combining two electrodes together. Meanwhile, the intertangling of the filled BC in the gel electrolyte hinders the decrease of the viscosity with temperature and forms a separator to prevent two electrodes from short circuit. Thanks to the high mechanical properties of this gel, SC obtained demonstrates high flexibility, where bending and even rolling have no obvious effect on the electrochemical performance.

In sum, the PhD thesis of Haoji Fei represents an important original contribution to the study of an important class of materials. Haoji Fei is very well oriented in the field of the above-stated topics, which enabled him to do successful research work from synthesis of raw materials to design and testing the functional sample of SC. Based on the results obtained, two articles in journals with impact factor and three papers in the conference proceedings were published.

I recommend to award Haoji Fei the degree of "*Philosophiae doctor*".

I have some questions and comments that can initiate discussion during and after the defense.

1. What is the DC conductivity and specific surface area of graphene synthesized by applicant?
2. What is the pressure difference used for preparation of the electrodes by filtration method?
3. In the preparation of a hydrogel based on polyacrylate, the cross-linker includes salts of CaSO_4 and CaCl_2 . Will these ions then participate in electrochemical processes?
4. The description of the results of cyclic voltammogram of PANI/RGO/G (Fig 6-6 (b)) is wrong. Peaks C_1/A_1 at 0.3-0.4V do not belong to the redox transition between leucoemeraldine/emeraldine forms of PANI since this transition occurs at 0-0.1V (Ag/AgCl). More probably, the transition observed is caused by transition of redox forms of phenazine groups in polymer.
5. The applicant confirmed that "PVA- H_2SO_4 gel electrolyte can freely move during the bending of PANI/RGO/G devise" (P. 54). Can it result in short circuiting of the element?
6. How necessary is the use of two types of crosslinking agents in the formation of polyacrylate hydrogel? Is it possible to use one curing agent instead of two?

Formal remarks

1. Page.8, the second paragraph. "pseudo-active materials" should be replaced with "pseudo-capacitive materials".
2. Page 19 "bybirnessite" should be replaced with "birnessite";
3. Page 65. " MnO_6 " should be replaced with " MnO_6 ";
4. Page 68 "7 V" should be replaced with "above 0.7 V";
5. Page 74 "poly-acryle and poly-acryl amide" have to be written in one word;
6. Page 75 "hdyrgel" should be replaced with "hydrogel"
7. The chapter and section cannot start with a figure (Page 25 fig. 2-12, 2-13; page.36, Fig. 3-8; p. 38 Fig. 3-11). Text must precede a figure.

Zlin, 5 February, 2018



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