# Effect of pore size distribution in carbon/carbon supercapacitors operating in phosphododecatungstic acid

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Two different commercial carbon materials (micro and mesoporous), namely activated carbon Norit® and multi-walled carbon nanotubes have been selected as materials for symmetric supercapacitors operating in aqueous solution of phosphododecatungstic acid ($H_3PW_{12}O_{40}$) of different concentration (0.1, 0.5 and 0.8 mol $dm^{-3}$). The results have been compared to those obtained in the standard aqueous electrolyte – 1 mol $dm^{-3}$ sulphuric acid.

Phosphododecatungstic acid represents a group of a Keggin type polyoxometallate (POMs). Such features of POMs as their strong acidic properties (superacids), well-defined structures and the ability to undergo fast and reversible redox reactions, made them model inorganic functional materials of potential utility in electrocatalysis, molecular electronics, sensing and in energy storage applications [1]. Here we refer to such attractive properties of $PMo_{12}$ as its high ionic and electronic conductivity even at lower concentrations and excellent chemical and thermal stability. We will also discuss the possibility of pseudocapacitive contribution related with the presence of mix-valence tungsten redox centers.

The utilization of phosphododecatungstic acid will be discussed in terms of effective diffusion coefficient and ionic conductivity determined using electrochemical experiments at microelectrodes in two different time regimes( i.e. under conditions of linear and spherical diffusion) as well as by conventional conductivity methods [2]. Nitrogen adsorption/desorption method is chosen to investigate the effect of pore size and volume of carbon materials on its electrochemical behavior in $H_3PW_{12}O_{40}$ during charging/discharging in two-electrode cells. The detailed characteristics of carbon/carbon supercapacitors will be performed using cyclic voltammetry, constant current methods and impedance spectroscopy. In order to determine the potential range of each capacitor electrode, the experiments with additional reference electrode will be also performed. The stability of the cells will be investigated by applying of over 10 000 cycles of constant charging/discharging.

We are also going to discuss the generation of integrated devices utilizing enzyme-based biobatteries together with high power electrochemical capacitors. The goal is to show that properly selected supercapacitor can help out low power sources by supplying power pulses with fast dynamic response or/and to store the energy generated by these devices for later use. Although the energy delivered by enzymatic power sources (biofuel cells, biobatteries) is high enough to fulfill the needs of small electronic devices, their power is still extremely low. Placing a supercapacitor, with its huge power capabilities, in parallel with a biobattery can easily supply almost any required pulse currents. After delivering the pulse current, the supercapacitor is quickly recharged by the biobattery between the pulse cycles. This reduces the stress on the biobattery, extending the overall life of the device. The results that we are going to show were obtained by coupling a series of supercapacitors and a biobattery based on carbon nanotubes, Nafion™ and enzyme (laccase) as cathodic material. Zn wire served as the anode. In our presentation we would like to show the influence of electrochemical capacitor on power capability of bio-element. Such parameters as specific capacitance, equivalent series resistance and leakage current will be discussed as having great influence on the proper performance of enzymatic power source.

1. M. Skunik, M. Chojak, P. J. Kulesza, *Electrochimica Acta*, 53 (2008) 3862
2. K. Caban, A. Lewera, G. Z. Zukowska, P. J. Kulesza, Z. Stojek, K. R. Jeffrey, *Analytica Chimica Acta* 575 (2006) 144
3. J. Keskinen1, E. Sivonen1, M. Bergelin, J-E Eriksson, P. Sjoberg-Eerola, M. Valkiainen, M. Smolander, A. Vaari, J. Uotila, H. Boer, S. Tuurala, *Advances in Science and Technology Vol. 72 (2010) 331*