



Electrochemical capacitors as attractive power sources



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ABSTRACT

The electrochemical performance of various carbon materials as supercapacitor electrodes with redox active electrolytes has been presented. In situ Raman investigation was carried out to show possible iodine species, polyiodides and carbon/iodine interactions during electrode polarization. Apart from the electrolyte also the kind of current collector plays an important role. Gold current collector is not adapted because of its reactivity with iodides whereas stainless steel is convenient. The conjugated iodide and vanadium species as the electrolyte were also investigated with Nafion separation. The best performance was obtained for AAC 1 and AAC 2 carbon material especially after adding 10% of carbon nanotubes.

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1. Introduction

There is an extremely fast growth in market of all digital and electronic devices that are destined for portable applications. Simultaneously with their resilient development one can observe unrelenting increase of demands for high energy sources. Instead of commonly used lithium-ion (Li-ion) and nickel metal hydride (Ni-MH) batteries, there is possibility to consider electrochemical supercapacitors for this purpose. Unfortunately, there are still some difficulties to fulfill the market demand.

It is well known that electrochemical double layer capacitor (EDLC) can serve as an excellent energy storage device for all applications with high power requirements. That fact is caused by the nature of the electrical charge accumulation mechanism, which is based on the electrostatic forces. Hence, it can be charged and discharged in a very short time and release enormously high peak of power [1,2]. The problem is that the energy of this system is incomparably lower than for mentioned batteries and that is the reason why they cannot be replaced so easily by the electrochemical capacitors. Because capacitance value strictly depends on the surface of the electrode/electrolyte interface, the best materials for electrodes should be made from activated carbons due to their well developed specific surface area (up to $2500 \text{ m}^2 \text{ g}^{-1}$). They might be used in different forms, such as powders, woven cloths, felts or fibers [3–6]. Moreover, the surface functionalities of applied carbon material cannot be neglected [7].

In order to achieve higher capacitance values and increase the energy of the electrochemical capacitor, the electrode materials capable to reversible redox reactions might be considered. This phenomenon of capacitance enhancement consists of pseudocapacitance effects which are related to the surface functionalities of carbon and/or to the presence of electroactive oxides from such transition metals as Ru, Ir, W, Mo, Mn, Ni and Co [8–12]. However, these materials have some limitations that do not allow them to be applied efficiently, mainly because of their slow solid state kinetics and, what is also very important, significantly higher price than for the activated carbons, especially in the case of ruthenium and iridium.

Another way to increase the energy is using electrolytes that can stand as a source of redox reactions. There are some papers focused on that matter concerning various possibilities, like for example, using additives to electrolytes with oxygen functionalities, e.g. quinone/hydroquinone groups [13–20]. These groups might be able to graft on the electrode surface with generation of new oxygen functional species that can react reversibly during charging/discharging process and provide additional charge [16]. It is also possible to introduce pseudocapacitance from redox active electrolytes in the form of alkali metal iodide aqueous solutions. It has been shown by our group [21–23] that iodides supply enormous capacitance but only at the positive electrode. Our preliminary investigations indicated that a binary electrolyte based on iodides and vanadyl sulfate could be a good option to enhance capacitance of full system [24].

Taking into account all advantages of such binary redox electrolytes we decided in a present paper to investigate in more detail their activity on several activated carbon materials with different porous structure, especially, mesoporosity. A

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comparison will be shown between the various activated carbons operating in the redox active electrolytes based on sodium and potassium iodide as well as vanadyl sulfate in the form of a single electrolyte component or as a redox active pair operating as catholyte and anolyte. The effect of separating such two redox couples as well as the role of nanotubes as an additive to active mass of electrodes will be elucidated. The consequence of using two different current collectors will also be discussed. The detailed study of carbon/iodine species interface by Raman spectroscopy will be presented.

2. Experimental

Physicochemical properties, such as specific surface area and pore size distribution as well as oxygen content with type of surface functionalities of all carbon used, were determined by nitrogen adsorption (ASAP 2020 instrument from Micromeritics, USA) and thermogravimetry coupled with mass spectrometry in order to recognize evacuating species (TGA F1 Iris and Aeolos MS instruments by Netzsch, Germany). In some cases electrodes have been also investigated. All electrochemical experiments were made in two- and three electrode capacitor configurations using Swagelok® cell. Electrode materials were prepared from different commercially available activated carbons, i.e. SX2 (AAC 0) and DLC Super 30 Norit (AAC 1), composed of 85 wt.% of carbon, 10 wt.% of polyvinylidene fluoride (PVDF) and 5 wt.% of carbon black. In order to receive carbon material with better developed micro/mesoporosity, carbon SX2 was activated by KOH (1:4) giving carbon AAC 2. Additionally, activated carbon tissue ACC 507-20 (AAC 3) from Kynol was also applied, because of its microporous character and high specific surface area. The physicochemical properties of all utilized materials are described in more detail in the next paragraph. In the case of AAC 1 and AAC 2 carbons, their electrochemical properties were also modified by adding different amounts of carbon nanotubes as a good source of mesopores and conducting percolator. Carbon nanotubes (purity >97% C) were purchased from Sigma Aldrich (773840) and used as received. They were simply mixed with activated carbon, binder and carbon black. The composition of one pellet was 10 wt.% of CNTs, 75 wt.% of activated carbon, 10 wt.% of PVdF and 5 wt.% of carbon black. All compounds were mixed together with acetone in order to get homogenous mixture. Acetone was removed by evaporation. Each electrode was prepared in the form of pressed pellets with a geometric surface area of 0.785 cm² per electrode. All electrode materials were assembled in Swagelok® cell in a symmetric configuration and investigated with different electrolytes, such as 1 mol L⁻¹ KI (or 1 mol L⁻¹ NaI) and 1 mol L⁻¹ VOSO₄, using gold current collectors and a glassy fibrous material as a separator. For comparison some experiments have been performed with stainless steel current collector. After examination of their electrochemical properties, those two electrolytes were combined in one system, where potassium iodide played a role of electrolyte for the positive electrode and vanadyl sulfate for the negative one. To preserve good condition of their separation and avoid mixing of them, Nafion® 117 membrane was used. The capacitance properties and other supercapacitor characteristics (expressed per active mass of a single electrode) were studied by applying different electrochemical techniques, i.e., galvanostatic cycling at current densities from 0.2 to 50 A g⁻¹, cyclic voltammetry at voltage scan rates from 1 to 100 mV s⁻¹ and electrochemical impedance spectroscopy in a frequency range from 1 mHz to 100 kHz using VMP3/Z Biologic, France. The modeling of the ions was performed with Gaussian® 03W software. An ionic behavior of iodine/iodide species was also investigated by in-situ Raman spectroscopy, using DXR dispersive Raman microscopy (ThermoFisher, USA) with 533 nm wavelength and 5 mW laser power. Fluorescence of the sample was linearly corrected with the background and prior to white light line.

3. Results and discussion

Fig. 1 shows nitrogen adsorption isotherms for all examined activated carbon materials. One can observe that the most different one is AAC 0 characterized by rather poorly developed microporosity, hence, the value of BET specific surface area is not high enough (only 718 m² g⁻¹) to satisfy electrochemical capacitor requirements. Therefore, this carbon has been chosen for activation by potassium hydroxide. As a consequence, activated carbon (AAC 2) with very promising characteristics was obtained and dedicated for supercapacitor applications. Nitrogen adsorption profile at very low relative pressure revealed microporous character of this material, however, there is also a significant contribution of mesopores. It is obvious that both kinds of those pores are very important in charge storage mechanism, because ions are accumulated in micropores during charging process and to ensure good access to them, the presence of mesopores is necessary. By applying mentioned activation step, we were able to develop specific surface area up to 1964 m² g⁻¹, which is incomparably higher value than for AAC 0.

In Fig. 1 one can observe that AAC 1 and AAC 3 samples demonstrate completely different porous structure than the AAC 0 and AAC 2. Whereas, the shape of their isotherms was quite similar to each other and the values of specific surface area were 1843 m² g⁻¹ and 2231 m² g⁻¹, respectively. Even if they have very well developed specific surface area it is worth noting that their applicability as the electrode material in proposed supercapacitor might be limited by the small contribution of mesopores. Lack of mesopores reduces efficiency in exploitation of such high amount of micropores to accumulate the charge by ion attraction. Insufficient quantity of small mesopores (2–5 nm) might cause difficulties in ion migration from electrolyte bulk to micropores, especially when considering very fast processes of charging–discharging, necessary to get very huge peak of power.

It is important to underline that electrodes prepared from carbons have definitively lower porosity than pure carbons. For example the specific surface area of pellets dropped for the best carbon AAC 2 from 1964 m² g⁻¹ to 1597 m² g⁻¹ whereas total micropore volume decreased from 1.344 cm³ g⁻¹ to 1.039 cm³ g⁻¹. On the other hand, microporous volume diminished from 0.873 cm³ g⁻¹ to 0.7158 cm³ g⁻¹ and mesoporous volume from 0.395 cm³ g⁻¹ to 0.2687 cm³ g⁻¹, respectively. Some pores are surely blocked by a binder. For this reason a small additive of carbon nanotubes (10% by mass) to electrode was very beneficial. It preserved mesoporosity of electrode (0.31 cm³ g⁻¹) and additionally greatly enhanced conductivity.

By using sodium/potassium iodide solution and vanadium species as the electrolytes in supercapacitor one needs to keep in mind that there is diversity of their possible oxidation states. All possible ions have

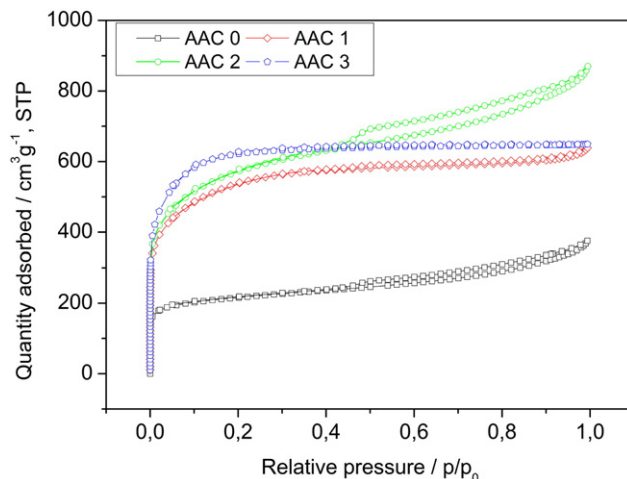


Fig. 1. Nitrogen adsorption isotherms (77 K) for different activated carbon materials.

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