



Carbon-based electrochemical capacitors with acetate aqueous electrolytes



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ABSTRACT

This paper reports on the performance of the supercapacitor operating in aqueous acetic acid salts. Lithium, sodium and magnesium acetate aqueous solutions at various concentrations have been selected as electrolytes. Maximum operational voltage and the overall capacitor performance have been determined by several electrochemical techniques. Floating and galvanostatic charge/discharge tests proved the promising performance at high voltages (1.5 V); the capacitance values have been retained at more than 80% of initial value for all tested electrolytes. Additionally, due to the ability to operate at high voltages, the maximum energy obtained in the system with $0.5 \text{ mol L}^{-1} \text{ CH}_3\text{COONa}$ is more than two times higher than with $6 \text{ mol L}^{-1} \text{ KOH}$, i.e., conventional aqueous capacitor. Taking into account a mild character of the electrolytes used, a novel concept of eco-friendly energy storage device has been proposed.

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1. Introduction

Supercapacitors are energy storage devices with charge/discharge time in the domain of seconds. Electrostatic type of charge accumulation preserves their long-term cyclability and high reliability with rare user maintenance [1–4]. They have found the application in several areas such as backup power systems, regenerative braking systems, mobile computers or even in emergency exits during aircraft evacuation [5–7]. Although electrostatic nature of charge accumulation preserves an excellent power rate, modern electrochemical capacitors suffer from the relatively low energy density [1–7]. For this reason, an industrial implementation of electrochemical capacitors very often requires their coupling with other devices, e.g., Li-ion batteries. The design of the hybrid (asymmetric) device can also be done by combining AC (as the negative electrode) with $\text{Ni}(\text{OH})_2$ or PbO_2 (as the positive electrode). It has to be noted here, that a synergistic effect is thereof obtained – the presence of the capacitor in the system (providing a peak of power on high-demand) improves the efficiency and prolongs the lifetime of the battery (supplying energy). Hence, an overall performance of both devices might be enhanced. Notwithstanding, capacitive performance can also be merged by introducing pseudocapacitive effects to the system.

There are numerous studies concerning asymmetric supercapacitors, where pseudocapacitive effects are present. It has been proved that utilization of nanostructured MnO_2 as positive electrode and AC as negative one provides higher capacitance values than traditional symmetric construction. However, as it was widely described, the symmetric system is more beneficial in terms of its efficiency and lifetime [8,9].

Since the energy density of the capacitor strongly depends on the operating voltage window and capacitance values [1–4], electrolytes with wide electrochemical stability are the main challenge for today scientists. However, one should note, that the final voltage output depends majorly on the kind of the electrolyte used but also on the electrode material applied. Until now, a great variety of the electrode materials combined with different electrolytes has been studied. Apart from organic electrolytes and ionic liquids, a lot of attention has been paid to supercapacitors operating in aqueous medium [10–13] because water-based electrolytes demonstrate several interesting features, at least, they are environment-friendly, safe and have relatively low price; cell assembling process does not require an inert atmosphere and thorough drying of particular components. Moreover, a high power rate of the device is preserved by the conductivity values remarkably higher than for organic medium (e.g. 70 mS cm^{-1} for $1.0 \text{ mol L}^{-1} \text{ Li}_2\text{SO}_4$ solution at 25°C but may reach even 600 mS cm^{-1} for $6.0 \text{ mol L}^{-1} \text{ KOH}$ solution). Unfortunately, the operating voltage in the aqueous medium is thermodynamically limited to 1.23 V [14] but in practice, for alkaline and acidic solutions this

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value is even lower; it has been accepted that highly defected structure of activated carbons may diminish potentials of hydrogen/oxygen evolution. Decomposition of the electrolyte is obviously harmful to capacitor performance in general (lack of electrolyte, internal pressure increase), but it has been demonstrated that hydrogen electrosorption on negative electrode allows the voltage and capacitance values to be slightly enhanced [15,16]. C.-C. Hu et al. recently published a paper concerning hydrogen adsorption/desorption in a carbon-based asymmetric supercapacitor. It has been proved that addition of buffer agent ($0.34 \text{ mol L}^{-1} \text{ NaH}_2\text{PO}_4$) to the electrolyte ($1.0 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$) stabilizes the local pH value at electrode/electrolyte interface. It can significantly improve proton supply and rate of hydrogen electrosorption within AC what can finally affect the higher pseudo-capacitive effect, but also change the potential of hydrogen evolution. However, the abovementioned study was performed in the three-electrode cell [17].

Activated carbon (AC) with the well-developed surface area (S_{BET} in the range $1000\text{--}2500 \text{ m}^2 \text{ g}^{-1}$) [18,19] are the materials being the most often used for supercapacitor application. As the capacitance is proportional to the electrode surface area accessible for ions, the higher the surface area, the higher the capacitance. However, one should note that this trend is not straightforward and is limited; definitely, specific surface area S_{BET} does not equal to the accessible surface of the material for electrolyte ions and some boundary conditions could be determined. In regard to the literature [20,21] concerning the influence of specific surface area and porosity of applied electrode material on capacitance, it can be concluded that textural characteristics of activated carbons limit the overall electrochemical performance. Apart from the electrolyte concentration, ions have to match the porosity of the electrode; too narrow pores, which significantly increase the specific surface area (S_{BET}) could not be fully used during ions adsorption; one of the several reasons is connected to the inability of relatively large ions to penetrate micropores or smaller nanopores. Hence, not only the type of pores is important but also the accessible pore volume should be considered. A detailed study done by M. D. Levi et al. [22] with the use of electrochemical quartz microbalance concerning the ions movement into the bulk of electrolyte and electrode material during polarization of the electrode surface confirms such a statement. Accordingly, one may conclude that solvent, electrolyte concentration, possible desolvation phenomenon and textural characteristic of the electrode affect each other; thus, one should consider that interaction of the

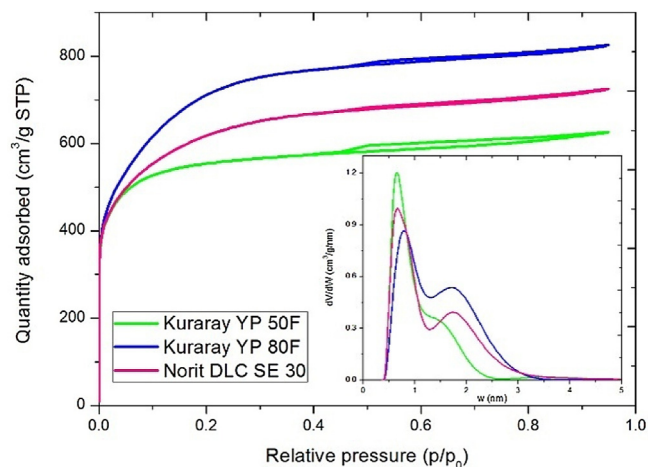


Fig. 1. Nitrogen adsorption/desorption isotherms for activated carbons. Inset: pore size distribution (PSD) calculated by 2D-NLDFT method.

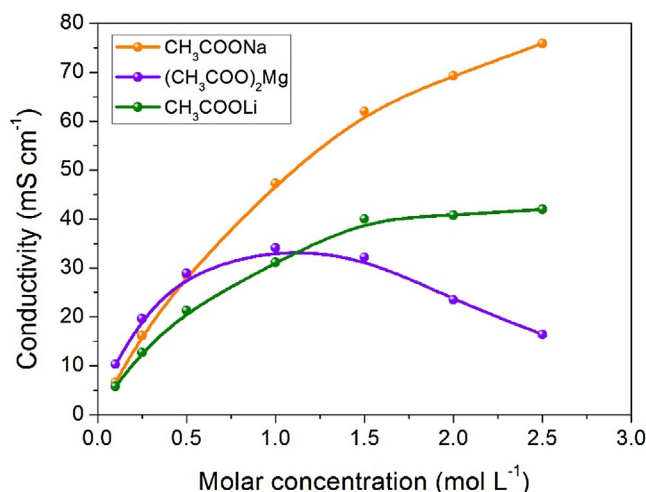


Fig. 2. Conductivity values vs. molar concentration of selected acetate salts (298 K).

species in the electrochemical system are a complex matter, where all factors should be considered holistically. Nevertheless, a typical electric double-layer (EDL) capacitance from electrostatic attractions of ions may be enhanced by the introduction of redox-active species in the electrode material or/and in the electrolyte, which are supposed to be capable of fast electron transfer during ongoing reaction [8]. The presence of the reversible redox reactions remarkably increase the capacitance values and thus improve the energy density. Faradaic processes come either from the surface functionalities of carbon (oxygen- or nitrogen-based) or from the presence of transition metal oxides [23–25]. Moreover, the redox-active electrolytes with pseudocapacitance effects originating from the electrolyte solution have also been reported [24]. Usually, either inorganic salts based on iodine, bromine, cerium or organic compounds with well-defined redox chemistry like hydroquinones or ferrocene are applied.

On the other hand, the aqueous organic salts have not been so widely investigated to date. W. Sugimoto et al. reported on the ruthenium oxide-based electrodes operating in a buffer solution of acetic acid and sodium acetate [26,27]. Interestingly, an application of buffer solution allowed to exploit an enormous capacitance of RuO_2 , however, ruthenium oxide because of high price and toxicity has rather limited application. Y. Gogotsi et al. reported on ‘green’ capacitor assembled from fully eco-friendly materials (especially without fluorine-based binders) with sodium acetate as the electrolyte [11]. Authors claimed an interesting behavior of the capacitor within electric double-layer range at 1 V. Notwithstanding, the scope of this research concerns mainly selection of environmentally friendly components; the overall behavior could be still improved – the capacitor has been tested in the mild range of electrochemical voltage window (lower than theoretical water decomposition).

Our motivation of this work was to develop new class of ‘green’ AC/AC supercapacitor with enhanced parameters and excellent lifetime. Additionally, we investigated the influence of moderate conductivity of acetic salts with various cations (Li^+ , Na^+ , and Mg^{2+}) at the different concentration ($0.1\text{--}2.0 \text{ mol L}^{-1}$) on the performance of the carbon-based electrochemical capacitor. We expected that moderate conductivity value of acetates affects the maximum operating voltage and allows the voltage of the system to be extended. Finally, the aqueous acetate-based system could be an ideal and relatively cheap energy storage device. Our research leads to the invention of an eco-friendly carbon-based capacitor with improved energy output.

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