

Original Research

Hybrid aqueous capacitors with improved energy/power performance

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Abstract

This work reports on a high-voltage, hybrid capacitor involving two separate redox reactions. Aqueous solutions of $Mg(NO_3)_2$ and KI have been used for negative and positive electrode, respectively. Adjusting $pH=2$ for electrode (+) with KI solution and modifying $Mg(NO_3)_2$ solution to $pH=9$ for negative side play a crucial role for a stable long-term operation of capacitor at enhanced voltage. A benefit from such a construction is a pseudocapacitive contribution from hydrogen sorption reaction on the negative electrode and high iodine/iodide activity on the positive electrode, enhancing the energy with no remarkable impact on the power profile. Proposed solution allows a high voltage (1.8 V) to be reached and thereby high power and energy performance (~ 20 W h/kg at 1 kW/kg) to be obtained. High long-term stability has been confirmed by floating and galvanostatic tests.

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1. Introduction

Electrochemical capacitors are high power devices designed to fill the gap between batteries and electrolytic capacitors. Application of activated carbon electrodes with high surface area significantly improves the energy performance of these devices over classical capacitor design [1,2]. Electrochemical capacitors can be classified into several groups, depending either on the electrolyte used or the electrodes design; thus, one can distinguish water [3–8], organic [9–13] and ionic liquid [14–16] based supercapacitors. On the other hand, if one will look at the electrode configuration [17] there are two groups, i.e. symmetric AC/AC [18,19] and hybrid capacitors [20–25]. Nevertheless, in all of these groups one always struggles in a compromise between power, energy and cycle life of the final device.

The major disadvantage of AC/AC supercapacitors working in aqueous electrolytes is their low maximum operating voltage (~ 1 V for H_2SO_4 and KOH solutions) which directly limits the energy output of these devices at ca. 5 W h/kg [26]. With the

energy density at such a moderate level, water-based devices will always be less attractive than organic ones, reaching 2.7 V and characterized by maximum energy at the level of ca. 20 W h/kg [27]. Hence, an enhancement of operating voltage is required. To list the benefits of aqueous systems, one can mention typical technological aspects such as easier assembly process (no need for inert atmosphere, material purification processes, and expensive drying steps), user safety and environmental friendliness. Another advantage of the aqueous electrolytic solution is remarkably higher conductivity leading to better power performance.

Recently, in pursuit of improving energy in aqueous-based capacitors, the system operating up to 2.2 V in alkali metal sulfate solution has been reported [8]. However, such extremely high voltage value was achieved on gold current collectors that exclude the parasitic effect of corrosion. Recently, a maximum operational voltage of Li_2SO_4 -based electrolyte is reported as 1.5 V [28]. Higher voltages lead to water decomposition and current collectors corrosion. Unfortunately, even at 1.5 V the energy output is still lower than for devices operating in organic solutions. On the other hand, high values of capacitor voltage were achieved by involving redox active transition metal oxide and carbon electrodes. Such asymmetric configurations are

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characterized by high energy efficiency and operation in the voltage range from 1.7 V up to 2.4 V in aqueous electrolytes [29–31].

As the energy of capacitor depends on the amount of charge accumulated, another possibility of energy density improvement is an introduction of fast redox reactions originating either from electrolyte solution like halide ions [24,32,33], hydroquinones [34,35] or electrode material with pseudocapacitive effects [36,37]. In such a hybrid configuration, two different charge storage phenomena are combined: an electrostatic on one electrode with significant potential change during charging/discharging whereas redox-couple determines constant potential of the second electrode with only moderate changes when the voltage of the device is extended. Moreover, electrochemical hydrogen storage has to be considered as a source of additional capacitance on negative electrode [38–42]. An advantage of this phenomenon is the shift of the hydrogen evolution potential; it can be exploited to increase the maximum electrochemical window of aqueous-based supercapacitors.

In this work a high voltage hybrid, aqueous capacitor involving two separate redox reactions is presented. The idea of such device was described in our previous report, where KOH and KI electrolytes were used, and system reached 1.6 V [25]. In this construction, the KOH was replaced by $\text{Mg}(\text{NO}_3)_2$ and KNO_3 served as an electrolyte for the separator soaking. The novelty of our present system is an additional pH change of electrolyte solution to acidic one for the positive side and into alkaline pH on the negative side. The purpose of such a construction is to benefit from hydrogen sorption reaction on the negative electrode and high iodine/iodide activity on the

positive electrode. Proposed solution allows a high voltage to be reached and thereby high power and energy performance to be obtained.

2. Experimental

2.1. Electrode and electrolyte preparation

The electrode material was prepared by mixing of 85 wt% activated carbon AC (Kuraray[®] YP-80), 10 wt% of poly (tetrafluoroethylene) PTFE (60% water dispersion from Sigma Aldrich[®]) as a binder and 5 wt% of carbon black (Super C65, Timcal[®]) used to improve the electrode conductivity. The activated carbon has a typical microporous character and BET specific surface area of ca. $2429 \text{ m}^2 \text{ g}^{-1}$, measured by nitrogen adsorption/desorption technique at 77 K with ASAP 2460 Micromeritics[®] (Fig. 1).

Isopropanol was added to electrode components, and the mixture was stirred with heating until all excess of solvent was removed, and homogenous pulp of electrode material was obtained. The material was then calendared to form the self-standing film afterwards. The electrodes for electrochemical investigation were cut in the form of pellets (10 mm diameter, mass 11–13 mg, thickness ca. 0.25 mm). Glass microfibrinous Whatman[®] GF/D filter paper was used as a separator. Electrolytes used were prepared from KNO_3 (99% purity), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99% purity), KI (> 99% purity), KOH (99% purity) and H_2SO_4 (98% purity); all chemicals were supplied by AVANTOR POLAND[®].

For investigation several electrolytes were prepared: 1 M KNO_3 , 1 M $\text{Mg}(\text{NO}_3)_2$, 1 M KI, 1M $\text{Mg}(\text{NO}_3)_2/\text{KOH}$ and 1 M KI/ H_2SO_4 . Mixtures of electrolytes with adjusted pH were made adding drop-by-drop respective 6 M KOH and 0.01 M H_2SO_4 into 1 M solutions with on-line pH control until the desired pH has been obtained. The pH and conductivity of electrolytes were measured by Mettler Toledo[®] pH meter and conductivity meter (Table 1).

2.2. Cell configuration

All investigations were performed in two- and three-electrode Swagelok[®] cell configuration with stainless steel current collectors. The experiments were conducted in two configurations, AC/AC symmetric cells and AC/AC hybrid electrolyte cell. In all cases, firstly the electrodes were immersed in the electrolyte solution and left under vacuum for 1 h. In the case of symmetric cells, both electrodes and separator were immersed in the same electrolyte. In the case of hybrid electrolyte system, the positive electrode was immersed

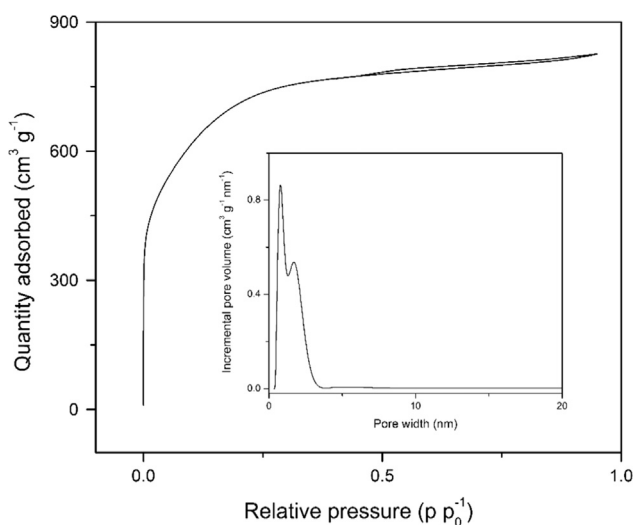


Fig. 1. Nitrogen adsorption/desorption isotherms and pore size distribution of carbon Kuraray[®] YP80F.

Table 1

Conductivity and pH of used electrolytes.

	$\text{Mg}(\text{NO}_3)_2$	KNO_3	KI	$\text{Mg}(\text{NO}_3)_2/\text{KOH}$	KI/ H_2SO_4
Conductivity (mS/cm)	111	91	114	111	114
pH	3.4	5.7	5.7	9	2

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