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Enhancement of the carbon electrode capacitance by brominated hydroquinones

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HIGHLIGHTS

- Brominated hydroquinone has been implemented as redox-active additive.
- Capacitance value has been improved by bromine redox activity.
- Specific energy of the device has been enhanced with no cycle life deterioration.

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ABSTRACT

This paper presents supercapacitors utilizing new redox-active electrolytes with bromine species. Two sources of Br specimen were investigated, i.e. dibromodihydroxybenzene dissolved in KOH and potassium bromide dissolved in KOH with hydroxybenzene additive. KOH-activated carbon, exhibiting a well-developed porosity, was incorporated as an electrode material. The tested systems revealed a capacitance enhancement explained by Br⁻ and partial BrO₃⁻ redox activity. The optimisation of the electrolyte concentration resulted in a capacitance value of 314 F g⁻¹ achieved at 1.1 V voltage range. Good cyclability performance (11% capacitance loss) combined with a high capacitance value (244 F g⁻¹) were obtained for the system operating in 0.2 mol L⁻¹ C₆H₄Br₂O₂ in 2 mol L⁻¹ KOH electrolytic solution.

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1. Introduction

The electric double-layer capacitors (EDLCs) (also known as supercapacitors) fill the gap between batteries and conventional capacitors in terms of specific power and energy delivered [1]. They represent complementary energy storage devices which exhibit several advantages, such as high power (both charge and discharge), high energy efficiency, long cycle life (counted in millions), no change in performance with cycling and high reliability [1,2]. The EDLCs store electrical charge in the electric double-layer formed at electrode/electrolyte interface [2,3]. High surface area electrode materials, such as activated carbons, can maximize this interface and result in an increase of capacitance value [4]. Since the energy density of the device is dependent on the capacitance and squared voltage (1), it is of significant importance to increase both

parameters.

$$E = \frac{1}{2}CU^2 \quad (1)$$

The voltage range of the EDLCs operating in the aqueous medium is thermodynamically limited by a decomposition of water at 1.23 V [5]. Therefore, an attractive way to improve capacitance of supercapacitor is to introduce the faradaic reactions accompanying typical EDL charging [6] as the electron transfer processes at the electrode/electrolyte interface improve the amount of the charge and the energy stored [7]. Aqueous electrolytes can induce faradaic reactions with carbon electrodes by a presence of functional groups (especially oxygen- and nitrogen-based), through hydrogen electro-sorption, and by redox reactions at the electrode/electrolyte interface [7]. In redox-based capacitors, the capacitance is governed by a reversible faradaic-type charge transfer process which can, however, be limited by an amount of active material or surface accessible [8]. Therefore, a developed mesoporosity of the electrode

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material plays a crucial role in a quick diffusion of redox species from the electrolyte to the surface or in the bulk of the solid electrode material [3,9]. An increase in charge capacity of the supercapacitors operating in a redox-active electrolyte is a result of either electro-adsorption of redox species in the porous carbon electrode material, or interaction with the reactive sites and functional groups on the surface of the carbon material [10–12]. The electrolytes enhancing the performance of the supercapacitor via redox reactions can be classified into: redox additive electrolytes in which redox active species are added to enable fast electron transfer redox reactions at the electrode/electrolyte interface (e.g. hydroquinones), and ‘core’ redox active electrolytes exhibiting redox activity itself without the supporting electrolyte [13,14]; iodides, bromides, as well as conjugated redox-couple systems based on iodide/vanadium, cerium/bromide and quinone/hydroquinone pairs [15–22] have been widely reported for this application.

In this research, we have investigated the brominated benzene derivative, i.e. dibromodihydroxybenzene and bromides, as the faradaic contributors to the double-layer capacitors. Bromine is a halogen element found naturally in the earth's crust and seawater in various chemical forms [23].

It is worth noting that the bromide species were previously investigated by Yamazaki et al. [16] as an organic salt, i.e. 1-ethyl-3-methylimidazolium bromide dissolved in 1-ethyl-3-methylimidazolium tetrafluoroborate. Moreover, the interactions between carbon-based electrode and bromine species have been studied in Ref. [24]. Here, we present the study of bromide compounds tested at different concentrations of KOH and aimed at optimizing the operating conditions of the system.

2. Experimental

2.1. Synthesis of dibromodihydroxybenzene

Dibromodihydroxybenzene (2,5-dibromobenzene-1,4-diol) compound was obtained according to the protocol described elsewhere [25]. Briefly, 9.2 mL of bromine in 20 mL of glacial acetic acid were added dropwise to a suspension of hydroquinone (benzene-1,4-diol) (10 g) in glacial acetic acid (90 mL) for 1 h at 0 °C. Afterwards, the mixture was warmed to a room temperature and stirred for 4 h. The solid product was filtered and washed with the glacial acetic acid and hexane before being dried in a vacuum. A yield of the reaction was noted to be 68% (16.5 g).

We expected that the introduction of bromine to the hydroquinones should change their physicochemical properties (conductivity, reactivity, mobility, etc.) and for a comparison purpose molecular calculations based on DFT theory have been performed. Fig. 1 presents the molecules of quinone, hydroquinone and 2,5-dibromobenzene-1,4-diol. The modelling of the molecules was performed with Gaussian® 03W software using DFT models with B3LYP functional and 3-21G basis set.

Computational study of the charge distribution provided an important information about the possible electrochemical activity of the aforementioned species. Quinone molecule has symmetric charge distribution, with negligible changes of charge density close to carbonyl groups, however, no dipole moment can be observed (0.0003 Debye). Hydroquinone has a dipole moment dependently on the arrangements of hydroxyl groups (2.92–2.94 Debye). An incorporation of halide specimen (bromine) significantly changes the charge distribution around the molecule but the dipole moment seems to be not affected (2.96 Debye). This tendency has a real reflection in solubility of these compounds – quinone is almost insoluble in polar solvents (like KOH solution used in the study) while hydroquinone and 2,5-dibromobenzene-1,4-diol are greatly soluble. Moreover, it seems that the molecule is prone to the

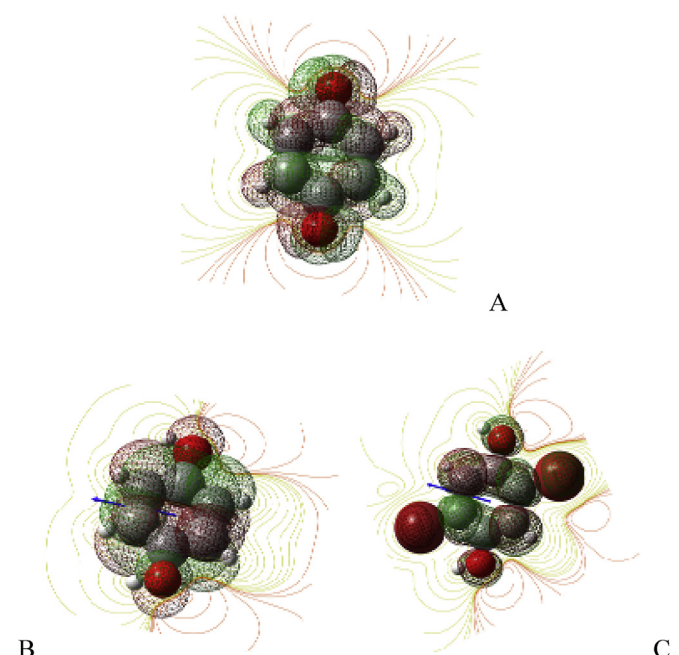


Fig. 1. Comparison of the molecule structures: a) quinone and b) hydroquinone and c) 2,5-dibromobenzene-1,4-diol.

nucleophilic attack (e.g. oxidation) from the bromide side, and the molecule tends to decrease or equilibrate the negative charge but on the other hand, the free energy for the molecule is significantly lower for brominated species. This might explain a superior capacitance values observed for electrolytes containing brominated hydroquinones when compared to a control solution of hydroquinone with an equivalent concentration of bromides.

It has been also found that the addition of 2,5-dibromobenzene-1,4-diol might slightly enhance the conductivity of the electrolyte solution; a HOMO/LUMO gap calculated (unoccupied and occupied orbitals are presented in Fig. 1) is the highest for brominated hydroquinone molecule and the lowest for quinone.

2.2. Electrode preparation

The experimental work on 2,5-dibromobenzene-1,4-diol, as a source of redox reactions in the electrolyte, was conducted with an application of carbon Norit SX2 which was a subject to KOH activation in 1:4 ratio of precursor to activating agent [26,27], labelled as AAC.

The electrodes for the Swagelok system® were prepared by mixing the KOH-activated carbon AAC (85 wt%), poly(vinylidene fluoride) (PVdF) Kynar HSV900 from Arkema, France, (10 wt%) and carbon black Timcal C65 (5 wt%) in a mortar by adding approx. 10 mL of acetone to a mixture of all the constituents and mixing until its evaporation. The obtained powder was pressed under 5 ton cm⁻² in order to form the pellets which then were dried under a vacuum at 120 °C for 2 h. The ready-to-use electrodes were in a form of pellets of a diameter of 10 mm and a thickness of ca. 0.2 mm.

2.3. Physico-chemical characterisation of the carbon materials

Hitachi Model S-3400 N Scanning Electron Microscope equipped with quad-type semiconductor backscattered electron (BSE) detector was used to investigate the surface morphology of the carbons. The energy-dispersive spectrometry (EDS) enabled a

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