



An organic proton battery employing two redox-active quinones trapped within the nanochannels of zeolite-templated carbon



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ABSTRACT

For the first time, we present in this work a simple method to achieve high energy density device by functionalizing zeolite-templated carbon (ZTC) with quinone molecules. Two types of quinone, anthraquinone and tetrachlorohydroquinone, which have different redox potential, were introduced into ZTC framework by a wet impregnation method, and were characterized in a sulfuric acid. An organic proton battery was assembled from two different functionalized-ZTC electrodes in the sulfuric acid, where the energy is stored by a *proton-rocking-chair* mechanism resulting from a quinone couple trapped inside the nanopores of ZTC with a less crystalline or nanocrystalline structure. The assembled device possesses an energy density as high as 30.6 Wh kg⁻¹, which is superior to the activated-carbon-based capacitors working in the organic electrolytes and lead batteries.

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1. Introduction

One potential strategy to increase an energy density of the aqueous capacitors, which work in the aqueous electrolytes, is to use an electrode containing the redox-reactive materials. Among them, quinones are well known to show rapid redox reactions facilitating two protons and electrons. Taking these into account, the use of quinonic compounds in energy storage devices is a good promising for achieving high energy and power densities. Therefore, many studies were done using the quinones as active materials in electrochemical capacitors [1–5]. However, there were some drawbacks resulting from the dissolution of quinones into the electrolyte and their low electrical conductivity. Highly porous carbon supports, which can prevent such dissolution and provide high electrical conductivity, are thus of interest [6,7]. We have previously investigated the use of zeolite-templated carbon (ZTC), which is an ordered microporous carbon having a very high specific surface area and ordered pore structure replicated from the zeolite template [8–10], as a promising electrode for electrochemical capacitor [12,13]. Since ZTC has a unique molecular structure

consisting of a bucky bowl-like framework [14], it thus contains a large amount of edge sites, which can be functionalized via an electrochemical oxidation in the sulfuric acid [15] and even in an organic electrolyte [16]. As a result, the oxygen-containing functional groups including quinones can be introduced at the edge sites of ZTC, which lead to the pseudocapacitance induced from the quinone/hydroquinone redox reaction in the sulfuric acid electrolyte [17].

However, variety of quinones can exhibit different redox potentials, both in aqueous and organic electrolytes [18]. We have recently reported the study of anthraquinone (AQ) and tetrachlorohydroquinone (TCHQ), which have redox potentials of –0.16 and 0.50 V in the sulfuric acid (vs. Ag/AgCl), supported on the activated carbon (Maxsorb, MSC-30) [19]. Assembling these electrodes into an energy storage device, the energy will be stored based on the redox reactions of AQ and TCHQ, where protons are shuttled back and forth upon charge and discharge process, so called a *proton-rocking-chair* mechanism. Additionally, we have previously found that the quinone molecules are favorably adsorbed into the nanopores (pore size ~ 1 nm) [19]. Maxsorb activated carbon unfortunately has random pore architecture and the nanopores of Maxsorb are not enough for a large introduction of quinones. Therefore, carbon support having a large amount of nanopores with a uniform pore size is preferable for the quinones

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adsorption. ZTC meets these requirements with its uniform pore size of 1.2 nm together with a large micropore volume [10].

This work thus presents the introduction of a large amount of AQ and TCHQ into the nanopores of ZTC by a simple method, wet impregnation. Fig. 1a shows a macroscopic model of ZTC having a three-dimensional ordered micropore structure replicated from the zeolite Y template. The enlarged model of ZTC is shown in Fig. 1b consisting of one unit cell of ZTC framework. Fig. 1c presents the ZTC model *stuffed* with 36 AQ molecules, where in Fig. 1d, the nanochannels of ZTC are *stuffed* with 31 TCHQ molecules. Note that AQ and TCHQ molecules were introduced into the ZTC framework considering the van der Waals radii of AQ, TCHQ and ZTC framework so that these models are reasonably realistic. These numbers of quinone molecules correspond to 60 wt% of quinones inside the ZTC/quinone composite (See [Supplementary Data](#) for the detail of calculation). The quinone-functionalized ZTCs are fully characterized physico-chemically and electrochemically in sulfuric acid. The ZTC electrodes with the optimized quinones loading will be assembled as an organic proton battery, and electrochemically characterized in sulfuric acid.

2. Experimental section

A preparation method for ZTC is described in detail elsewhere [8,9]. As a comparison, KOH-activated carbon (Maxsorb[®], MSC-30, Kansai Coke and Chemicals Co., Ltd.) was also used. To prepare the quinone-carbon composite, the as-received organic compounds (AQ and TCHQ, Tokyo Chemical Industry Co., Ltd.) were firstly dissolved in acetone to get the solution of 5.77 mmol L⁻¹. Then, the carbon (ZTC or Maxsorb) was dispersed into the solution by

sonication. The weight ratios of the quinones to ZTC were varied from 3:7 to 7:3. By the evaporation of acetone at 70 °C, the quinones would be introduced into the carbon materials. For a better understanding, ZTC prepared by the weight ratio of AQ to ZTC of 3:7 will be labeled as 3AQ:7ZTC, and so on. Some of the composites were subjected to N₂-sorption and solid-state ¹H NMR analyses.

The electrodes were prepared in the form of pressed pellets (7 mm in diameter) using the quinones-carbon composite and polytetrafluoroethylene (PTFE) as a binder. The weight ratio of the composite to the binder was 9:1. The electrodes were attached onto Au mesh current collector by pressing at 450 N twice. They were characterized in 0.5 M H₂SO₄ electrolyte using a three-electrode configuration, where Ag/AgCl electrode was used as a reference. Note that before the characterization, the cell was evacuated for 1 h, where the electrolyte was well vacuum-impregnated into the electrodes. Cyclic voltammetry and galvanostatic charge/discharge measurements were performed at room temperature with the N₂ gas bubbling using a potentiostat/galvanostat (VMP3, Bio-Logic). The current density and the energy density were based on the total weight of both electrodes. Note that the device was constructed with the optimized mass ratio (AQ/TCHQ = 0.91) based on the theoretical capacity of each quinone using the expression developed elsewhere [11].

Molecular modeling software, ChemBio3D Ultra 12.0 (Cambridge Soft Co.), was used for constructing a molecular model of the ZTC and the quinone-functionalized ZTC. For the ZTC framework, the geometry optimization calculation of the model was performed using the semi-empirical Hamiltonian PM5 with the MOZYME algorithm in MOPAC, which is available in Scigress Explorer 7.6 software (Fujitsu Limited).

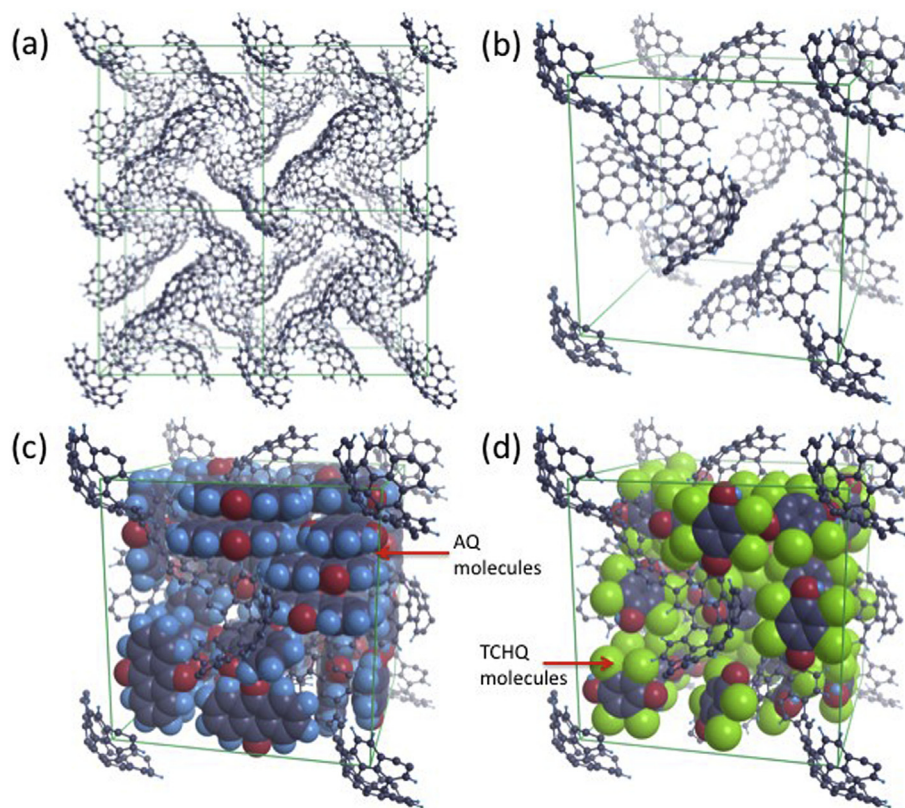


Fig. 1. (a) A macroscopic model of ZTC showing the three-dimensional ordered micropore structure originated from the zeolite Y template. (b) The enlarged model of ZTC consisting of one unit cell of ZTC framework. The ZTC model *stuffed* with (c) 36 AQ molecules and (d) 31 TCHQ molecules. The dark-grey, blue, red, and green balls represent the carbon, hydrogen, oxygen, and chlorine atoms, respectively. (A colour version of this figure can be viewed online.)

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