Organic Proton Battery Employing Couple of Redox-Active Quinones Trapped Inside 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.

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 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. **Figure 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 **Figure 1b** consisting of one unit cell of ZTC framework. **Figure 1c** presents the ZTC model *stuffed* with 36 AQ molecules, where in **Figure 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.

Figure 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.

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).

3. Results and Discussion

Cyclic voltammograms (CVs) of the quinone-doped ZTCs, 3AQ-7ZTC, and 3TCHQ-7ZTC, which are the composites with the quinone:ZTC ratio of 3:7 (**Figure 2**), reveal the redox peaks at -0.16 and 0.45 V (vs. Ag/AgCl), which correspond to the redox reaction of AQ and of TCHQ, respectively. Note that the potential of TCHQ is slightly lower than those previously reported (0.5 V vs. Ag/AgCl) [19]. This might be due to the degradation of TCHQ, which can be air-oxidized to form the hydroxyquinone, during the experiments. These results confirm that both of AQ and TCHQ were successfully introduced into ZTC. Power XRD patterns of the composites, bulk AQ, and ZTC, are shown in **Figure 3a**, where the spectrum of ZTC only shows a sharp peak at $2\theta \sim 6^\circ$, representing (1 1 1) plane originated from the zeolite Y template with a periodicity of 1.4 nm. By introducing AQ into ZTC framework, the intensity of this sharp peak is decreased, indicating that the ordered structure of ZTC is distorted, which instead results in the present of a broad peak at 2θ around 23° , representing a carbon (0 0 2) structure. Up to 60 wt% of AQ loading, the peaks corresponding to AQ cannot be observed. However, at 70 wt%, we can clearly see such the peaks of AQ. These indicate that AQ would form large crystalline particles, and below this value, it would be held in the nanochannels of ZTC with a less crystalline and/or nanocrystalline structure. XRD patterns of TCHQ-doped ZTC also give the same tendency, where TCHQ loading amount can be increased up to 60 wt% (see Supplementary Data **Figure S1**).

^1H -NMR studies also support the results from XRD analyses. NMR signals for the solid samples are generally broader than that of the liquid samples, which can be attributed to the restricted motion of the sample. As can be in **Figure 3b**, AQ held in the nanopores of ZTC shows a sharp signal, which indicates that AQ in these narrow pores has a less-ordered structure, whose degrees of freedom (such as rotation and vibration) would be allowed compared with the bulk AQ, which only shows a broad signal. TCHQ trapped in ZTC also exhibits the same phenomenon; it shows a sharp NMR signal. Additionally, the chemical shift can be observed, which could be assigned to the charge-transfer between TCHQ molecules and the nanographene plane of ZTC (see Supplementary Data **Figure S2**).

We have also found that the amount of AQ loaded into ZTC can be increased up to 60 wt%, as can be seen in **Figure 3c**, where the AQ capacity of the functionalized electrodes reach their maximum resulting from the AQ adsorbed inside the nanochannels of ZTC (see Supplementary Data for the calculation of AQ capacity). This loading amount is two-fold higher than that of the activated carbon (Maxsorb) recently reported [19], which is only 30 wt%. Moreover, the maximum AQ capacity of the functionalized-ZTC is higher than that of the Maxsorb, as can be clearly seen in **Figure 3c**. Beyond the maximum loading value, AQ would form large crystals adsorbed at the external surface of the ZTC particles (since the pores of ZTC is fully filled with AQ at this point), which will be described later. This would lead to a reduction of the utilization rate of redox reaction and its capacity. These results clearly indicate that a large amount of AQ can be introduced into the ZTC framework, and adsorbed inside its 1.2-nm pore. The TCHQ-functionalized ZTC also gives a similar result (see Supplementary Data **Figure S4**). The maximum loading value is 70 wt%, however, based on the XRD analysis, we suggest that 60 wt% would be more preferable for ZTC as previously described, which is still higher than that of Maxsorb (50 wt%). Surprisingly, these values match the maximum AQ and TCHQ, which can be stuffed inside the ZTC framework

previously shown in **Figure 1c-d**. These clearly make ZTC a desirable support for the redox-active molecules, AQ and TCHQ, with a large loading amount, thanks to the unique pore characteristics of ZTC; uniform pore size at 1.2 nm with a large micropore volume. These molecules are redox-active, thus lead to the energy storage through the redox reactions upon the charge/discharge process in the sulfuric electrolyte.

Figure 2. Cyclic voltammograms (CVs) of the quinone-doped ZTCs (1 mV s^{-1} , fourth scan), 3AQ-7ZTC (solid line), and 3TCHQ-7ZTC (dotted line), together with the corresponding redox reactions.

Figure 3. (a) Powder XRD patterns of (from bottom to top) ZTC, AQ, and the AQ-ZTC composites with the AQ:ZTC ratio varied from 3:7 to 7:3. (b) ¹H-NMR spectra of bulk AQ (lower dotted line) and AQ held in the nanopores of ZTC (6AQ-4ZTC, upper solid line), obtained with a spin rate of 8 kHz at room temperature. (c) Specific discharge capacities derived from AQ on the basis of the AQ amount as a function of AQ content.

Specific surface areas calculated from N₂-sorption measurements using the Brunauer-Emmett-Teller (BET) method of the pristine ZTC and the quinone-doped ZTC with 60 wt% loading, 6AQ-4ZTC and 6TCHQ-4ZTC, are shown in **Table 1** together with their total pore, micro and mesopore volumes. ZTC is generally characterized by its very high specific surface area, total and micropore volumes. However, 60 wt% of quinones loading makes ZTC almost lost its surface area and micropore volume. These clearly indicate that the quinone molecules (AQ and TCHQ) are adsorbed inside the micropores of ZTC. Moreover, pore size distributions of ZTC before and after the quinone introduction further emphasize

that the 1.2 nm pore of ZTC is fully filled by the quinones (AQ and TCHQ) at 60 wt% of loading (**Figure 4**). Note that the theoretical quinone loading values calculated from the total pore volume of ZTC and the density of AQ (1.31 g cm^{-3}) and TCHQ (1.85 g cm^{-3}) are 68 wt% of AQ and 75 wt% of TCHQ. Considering the experimental loading amount of 60 wt%, the quinones would have lower density than that of the crystallites. We thus calculated the actual density of quinone inside the pores from the experimental value and it is 0.91 g cm^{-3} , which is lower than the crystallite density previously mentioned. This indicates the less crystalline structure of quinones inside the pores of ZTC and further supports the results from XRD and $^1\text{H-NMR}$ analyses.

It is also crucial to point out how the redox process takes place even the pores are fully filled. This makes the electrolyte cannot penetrate into the pores. However, it has been reported that single-layer graphene is highly permeable to protons and the transport rate is very high [20]. Additionally, the nanographenes would exhibit the proton transfer process reversibly from the aqueous phase and across the framework [21,22]. Since ZTC can be considered as one of the nanographene family [14], it is therefore reasonable to expect such behaviors and protons could transport throughout the ZTC framework without the penetration of electrolyte into the pores. Additionally, this transport process would probably lead to a considerably large capacity arising from charge-discharge of electric double-layer (106 out of 310 mAh g^{-1} -AQ, see Supplementary Data for details) regardless of the small surface area.

Table 1. Specific surface area (S_{BET}) of ZTC and the quinone-doped ZTC with 60 wt% of quinone loading together with their total pore volume (V_{total}), micropore (V_{micro}) and mesopore (V_{meso}) volumes.

	$S_{\text{BET}}^{\text{a}} / \text{m}^2 \text{g}^{-1}$	$V_{\text{total}}^{\text{b}} / \text{cm}^3 \text{g}^{-1}$	$V_{\text{micro}}^{\text{c}} / \text{cm}^3 \text{g}^{-1}$	$V_{\text{meso}}^{\text{d}} / \text{cm}^3 \text{g}^{-1}$
ZTC	3400	1.65	1.54	0.11
6AQ-4ZTC	11	0.064	0.006	0.058
6TCHQ-4ZTC	6	0.053	0.002	0.051

^a Determined at $0.01 < P/P_0 < 0.05$. ^b Determined at $P/P_0 = 0.96$. ^c Determined by DR method.

^d $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$.

Figure 4. DFT pore size distribution of ZTC and the quinone-functionalized ZTC, 6AQ-4ZTC and 6TCHQ-4ZTC. An inset represents the enlarged distribution regarding the y-axis.

We then assembled an **organic proton battery** using the quinone-functionalized ZTC, 6AQ-4ZTC and 6TCHQ-4ZTC, as a negative and positive electrodes, respectively. **Figure 5a** shows the typical galvanostatic cycle and the positive and negative electrodes in 0.5 M H₂SO₄ electrolyte. The plateau potentials of the negative and positive electrodes correspond to the redox peaks of AQ (-0.15 V vs. Ag/AgCl) and TCHQ (0.45 V vs. Ag/AgCl), as previously described in the CVs (**Figure 2**). **Considering the battery behaviors together with the protons involved coming from the organic molecules, we thus classified our device as the organic proton battery rather than the hybrid capacitor (regardless its considerably large capacity arising from charge/discharge of electric double layer), which generally requires one electrode acting as a battery whereas another as a capacitor [23,24].** The plateau potential in the galvanostatic cycle at ~0.6 V thus corresponds to their difference. These clearly indicate that the proton extraction/insertion reaction of AQ takes place at the negative electrode simultaneously with that of TCHQ at the positive electrode, and the energy is stored based on the *proton rocking-chair* mechanism. The rechargeable energy density of this **device** is as high as 30.6 Wh kg⁻¹ (see Supplementary Data for the calculation of energy density), based on the total weight of both electrodes at a current density of 0.045 A g⁻¹ with an operating voltage of 1.4 V. This value is higher than that of the **device** using Maxsorb as a support (20.3 Wh kg⁻¹) [19] and the asymmetric aqueous capacitor assembled from ZTC and activated carbon (24.5 Wh kg⁻¹) [25], recently reported. Furthermore, this also exceeds that of the RuO₂-based aqueous capacitor (26 Wh kg⁻¹) [26] and is even superior to the activated carbon-based capacitors working in an organic electrolyte [27-29] and is in the same range of lead acid batteries (20-40 Wh kg⁻¹). Additionally, since the volumetric performance is recently a focus of capacitor materials [30-33], the volumetric density of the device was also calculated based on the average density of the electrodes (see Supplementary Data for details). The obtained value is 22.6 Wh L⁻¹, which is higher than those of carbon-based (13-15 Wh L⁻¹

¹) and polyaniline/carbon-based aqueous capacitor (17.8 Wh L^{-1}) and is comparable with the organic capacitor [33-35]. This further highlights the performance of our **organic proton battery** and is clearly a result from the large amount of quinones introduced into the nanochannels of ZTC together with a benefit from the *proton rocking-chair* system.

To fully characterize the performances of this **device**, we investigated the rapid responsibility at several current densities and the cyclability at 0.225 A g^{-1} . As can be seen in **Figure 5b**, which is the discharge profile at 0.045 , 0.45 , and 4.5 A g^{-1} , the profiles exhibit the plateau-like regions derived from the redox reactions of the quinones introduced into the nanochannels of ZTC. These mean that the proton insertion/extraction via the *proton rocking-chair* mechanism also takes place even at high current density. We suggest that the separation between the plateau of charge and discharge profiles might due to the electrolyte resistance and the overpotential of the redox reaction, which lead to the decreasing of energy density. Along 500 cycles of charge/discharge measurement at 0.225 A g^{-1} , the energy density of the **device** decreases from its maximum of 26.0 to 18.4 Wh kg^{-1} (Supplementary **Figure S6**), which is higher than the Maxsorb-based **device** previously reported [19]. However, the retention of ZTC-based **device** (71%) is slightly lower than that of the Maxsorb one (79%), but both of them are still relatively high regardless of their battery-like behavior. **This might be due to the higher quinone loading amount in the ZTC. When the ZTC electrode is fully filled with the quinone, the molecules located near the external surface or pore mouth would be easily dissolved back to the electrolyte.** Generally, durability becomes a critical issue when using organic compounds (i.e. quinones) as the redox-active materials, because of their solubility. In this case, AQ and TCHQ would adsorb inside the nanochannels of carbon framework by π - π interaction between the benzene ring of the quinones and the framework [36]. This interaction is fairly strong enough to make the quinone molecules not to dissolve into the electrolyte solution upon several charge/discharge cycles. However, development

regarding this issue is still that of a challenge to have the capacitor with high energy density together long life cyclability. One possibility would be the optimization of quinone structure i.e. the attachment of a chloro group, which can suppress the solubility of quinone in the aqueous solution [19].

Figure 5. (a) Galvanostatic cycle of the organic proton battery and the evolution of the potential corresponding to the negative (6AQ-4ZTC) and positive (6TCHQ-4ZTC) electrodes in 0.5 H₂SO₄ electrolyte at 0.045 A g⁻¹. (b) Galvanostatic charge (solid line) and discharge (dotted line) profiles of the device at 0.045 (1C, black lines), 0.45 (10C, red lines), and 4.5 (100C, blue lines) A g⁻¹.

4. Conclusion

In summary, we have succeeded for the first time the introduction a large amount of quinones, AQ and TCHQ, into the confined nanochannels of ZTC by using a simple impregnation method thanks to the unique characteristics of ZTC having a uniform pore size of 1.2 nm together with a large micropore volume. The maximum loading content was 60 wt%, where the capacity of the quinone-functionalized ZTC electrode reaches its maximum. At this stage, the nanopores of ZTC with a pore size of 1.2 nm were fully filled with the

quinones molecules. XRD and ^1H -NMR analyses suggested that the quinones held inside these nanopores would have a less-crystalline or nanocrystalline structure. The **organic proton battery** was assembled using two types of electrode, AQ- and TCHQ-functionalized ZTC, which have different redox potentials. The assembled **device** exhibited high energy density induced by the AQ/TCHQ couple held inside the nanochannels of ZTC, where the energy is stored through the *proton rocking-chair* mechanism, together with a rapid response at high current density and reasonable energy retention upon charge/discharge cycles. Therefore, this work is promising for large stationary applications in electrical energy storage systems for the energy grid.

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Appendix A. Supplementary Data

Supplementary Data associated with this article can be found in the online version.

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