Manuscript Number: CARBON-D-13-01863R1

Title: Carbon-carbon asymmetric aqueous capacitor by pseudocapacitive positive and stable negative electrodes

Article Type: Letter to the Editor

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Carbon-Carbon Asymmetric Aqueous Capacitor by Pseudocapacitive Positive and Stable Negative Electrodes

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Abstract

An asymmetric aqueous capacitor was constructed by employing zeolite-templated carbon (ZTC) as a pseudocapacitive positive electrode and KOH-activated carbon as a stable negative electrode. The asymmetric capacitor can be operated with the working voltage of 1.4 V, and exhibits an energy density that is comparable to those of conventional capacitors utilizing organic electrolytes, thanks to the large pseudocapacitance of ZTC. Despite relatively thick electrode (0.2 mm) configuration, the asymmetric capacitor could be well operated under a current density of 500 mA g⁻¹.

Zeolite-templated carbon (ZTC) [1] is an ordered microporous carbon which is synthesized by using zeolite as a hard template. ZTC has a very large specific surface area and exhibits a high electric double-layer capacitance with excellent rate capability in an organic electrolyte [2]. In addition, ZTC has a unique buckybowll-like framework [3] with a large amount of edges sites which can be easily functionalized by oxygen-functional groups, including pseudocapacitive quinone groups, thorough electro-oxidation in an aqueous electrolytes [4]. Herein, we demonstrate the construction of a carbon-carbon asymmetric capacitor using ZTC as a pseudocapacitive positive electrode and KOH-activated carbon (AC) as a negative electrode. Unlike other pseudocapacitive materials, such as metal oxides and conductive polymers, ZTC can be operated with a thick electrode configuration (0.2 mm) due to its intrinsic good conductivity.

ZTC and AC have very high BET surface areas ($P/P_0 = 0.01-0.05$): 3600 and 2600 m² g⁻¹, respectively. AC was prepared from a Spanish anthracite by its KOH-activation [5]. Details of the sample preparation and their porous texture characterizations are presented in the Supplementary data. Surface functionalities of ZTC and AC which were prepared by a protocol similar to the present work have been reported in our previous publications.[3, 6] Cyclic voltammograms (CVs) of the AC and ZTC electrodes in 1 M H₂SO₄ at positive potential range (0 to 0.8 V) using a three-electrode cell are shown in **Fig. 1a** and **b**, respectively. AC displays rectangular CV shape (**Fig. 1a**) which is typical for porous carbons showing double-layer capacitance. On the other hand, ZTC shows a large oxidation current above 0.5 V during the first positive potential scan (**Fig. 1b**), indicating that ZTC is greatly oxidized at the first anodic polarization. Moreover, broad redox peaks appear in the subsequent cycles around 0.20 V and 0.33 V, during the negative and positive potential sweeps, respectively. These redox peaks could be ascribed to the pseudocapacitance contributed from quinone groups [7], which are introduced in ZTC by the electro-oxidation [4]. The oxidized ZTC indeed owns a higher capacitance (measured by galvanostatic charge/discharge cycling; GC) than AC, as indicated in each graph of **Fig. 1**. Accordingly, ZTC was used as the positive electrode for the asymmetric capacitor. We also examined the electrodes against the lower potential region. Their voltammograms between -0.6 and 0.4 V are shown in

Fig. 2. In the case of ZTC, the hydrogen evolution occurs when the potential is below -0.50 V whereas that of AC takes place below -0.54 V, indicating its larger overpotential for hydrogen evolution, i.e., AC is more stable against negative polarization than ZTC. Furthermore, AC exhibits higher capacitance than ZTC in this region. Therefore, AC was selected as the negative electrode for the asymmetric capacitor.

The asymmetric ZTC/AC capacitor was constructed with the mass ratio ($ZTC/AC = 0.77$) of each electrode estimated based on the mathematical expression developed by Snook et al. [8] (see Supplementary data as for the details of cell assembling and the calculation of the mass ratio). **Fig. 3** shows CV patterns of the ZTC/AC capacitor measured within 1.4 V, whilst the addition of an auxiliary reference electrode (Ag/AgCl) allowed one to assess the potential of each electrode during the experiments. At the first CV scan, a great current can be observed when voltage surpasses 0.8 V. At the maximum voltage of 1.4 V, the potential of ZTC reached 0.94 V (vs. Ag/AgCl), and therefore, ZTC should be electrooxidized and an increase in pseudocapacitance is expected. This is confirmed by the subsequent CV scans, where the development of a broad peak can be found around 0.7 V, corresponding to the pseudocapacitance of the oxidized ZTC. We have previously studied that ZTC exhibits a large pseudocapacitance together with good cyclability as far as it is polarized below 1.1 V (vs. Ag/AgCl) [9]. Therefore, ZTC can work well at 0.94 V. Moreover, at the cell voltage of 1.4 V, the potential of AC reached -0.46 V (vs. Ag/AgCl), which is above the lower limit potential (-0.54 V) found in **Fig. 2**. Thus, the asymmetric capacitor is stably charge/discharged, as is found from almost the same CV patterns in the third and the fourth cycles in **Fig. 3**. At the cell voltage of 1.6 V, the ZTC/AC capacitor showed CV patterns similar to the case of 1.4 V, however, the potential of AC actually deviated from the limit (see Supplementary data). **This could be further improved by optimizing the mass ratio, which should be calculated from the capacitance of each electrode in the actual potential range in the two electrode system, and the resulting capacitor with this optimized mass ratio could be well-operated at 1.6 V.**

Specific capacitance of the ZTC/AC capacitor operated at 1.4 and 1.6 V was calculated from the

galvanostatic charge/discharge measurement for 200 cycles (**Fig. 4**). **Note that the specific capacitance is defined based on the total weight of the active material included in both electrodes.** The data of the symmetric AC/AC [6] and ZTC/ZTC capacitors are also plotted in **Fig. 4**. From the comparison between ZTC/AC and AC/AC systems, the benefit of the pseudocapacitive positive electrode (**Fig. 1b**) in ZTC/AC could be clearly understood from its higher capacitance. In the case of ZTC/ZTC capacitor, despite a large capacitance of the positive electrode, the poor capacitance of the negative electrode (**Fig. 2**) lowers the total capacitance of the whole capacitor. **Fig. 4** thus emphasizes an excellent combination of the good positive and negative electrodes, i.e. ZTC and AC, respectively, for achieving a high performance asymmetric capacitor. The energy density of the ZTC/AC capacitor (1.4 V) is calculated to be 24.5 Wh kg^{-1} (based on the electrode mass), and this value is comparable or higher than those of conventional capacitors utilizing organic electrolytes (see Supplementary data). It can be seen in **Fig. 4** that the operating voltage of 1.4 V is more appropriate than 1.6 V in ZTC/AC to achieve a good cyclability, as was presumed. At 1.4 V, the capacitance drops from 100 to 90 F g^{-1} at the first 20 cycles and becomes stable at the following cycles, whereas at 1.6 V operation, the capacitance continuously decreases to 83% of the initial value after 200 cycles. Moreover, the ZTC/AC asymmetric capacitor showed reasonably high stability at the longer period durability test within 1.4 V over 5000 cycles (Supplementary data).

Generally, pseudocapacitors suffer from a drawback of high inner resistance due to poor electric conductivity of the active materials, such as metal oxides and conductive polymers. Though a lot of papers reported fantastic energy and power densities, in most cases, the electrochemical characterization is performed with a very small amount of active materials, and/or an extremely thin active-material layer. In this work, we demonstrated that the ZTC/AC capacitor can be constructed with reasonably thick (0.2 mm) electrode layers including enough large weight (ca. 10 mg) of active materials, thanks to the advantage of ZTC, i.e., high pseudocapacitance like conductive polymers together with high conductivity as carbon. **We have indeed confirmed that the ZTC-containing electrode sheet has a higher conductivity than that of AC**

(Supplementary data). In addition, the appropriate combination with AC, which is a good negative electrode, further enhances the performance of the resulting ZTC/AC asymmetric capacitor. The present work thus demonstrates that it is possible to construct asymmetric aqueous capacitors having comparable performance to conventional organic capacitors, by using carbon materials, for both electrodes.

The authors would like to thank the Spanish MINECO, FEDER funds (Project MAT2010-15273 and PRI-PIBJP-2011-0766). This research was also supported by Strategic International Cooperative Program, Japan Science and Technology Agency. We also thank Hitachi Chemical Co., Ltd. for kindly supplying Hitasol.

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Fig. 1 Cyclic voltammograms of (a) AC and (b) ZTC electrodes using a three-electrode configuration in 1 M H_2SO_4 at 5 mV s^{-1} . The first and fourth patterns are shown. The specific capacitances described are calculated from GC measurements after the fourth CV scans.

Fig. 2 Cyclic voltammograms (fourth scan) of the AC (dotted line) and ZTC (plain line) electrodes using the three-electrode configuration in 1 M H₂SO₄ at 5 mV s⁻¹.

Fig. 3 Cyclic voltammograms of the asymmetric ZTC/AC capacitor in 1 M H₂SO₄, with a scan rate of 5 mV s⁻¹. The first, third, and fourth patterns are shown.

Fig. 4 Plots of specific capacitance versus the cycle number for the asymmetric ZTC/AC capacitor and symmetric capacitors of AC/AC and ZTC/ZTC in 1 M H_2SO_4 . Each of operating potential is described in the figure. A current density is 500 mA g^{-1} . Data for AC/AC are taken from ref. [9].

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