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Quinone-introduced oligomeric supramolecule for supercapacitor

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Abstract

A new generation of energy storage material based on electroactive oligomeric supramolecule has been proposed as a proton battery or an aqueous electrochemical capacitor material. A crystalline supramolecular oligomer of 1,5-diaminoanthraquinone (DAAQ) was successfully prepared as a thin film by electrochemical oxidation from an acidic non-aqueous medium. The resulting DAAQ oligomer film exhibited a specific capacity as high as 45–50 Ah kg⁻¹ in 4 M H₂SO₄ aq. The redox reaction involves those of the quinone and the π -conjugated system in the DAAQ oligomer which occur separately and/or cross over with exchanging three protons per monomer unit. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 1,5-Diaminoanthraquinone; Supramolecules; Electrochemical capacitor materials

1. Introduction

Electrochemical capacitors based on conducting polymers have been proposed. Among them, n- and p-dopable polythiophene derivatives are good candidates [1–4]. The maximum energy and power densities of these polymer materials ranged from 30 to 50 Wh kg⁻¹ and 2 to 20 kW kg⁻¹, respectively [5,6]. The specific capacities of these polymers (10–15 Ah kg⁻¹) are higher by a factor of 5–6 than those of high surface area (over 2000 m² g⁻¹) carbon materials, such as activated carbon and carbon fibers which are devised in electric double layer capacitors (EDLC). However, compared with cathode materials of lithium secondary batteries, such as LiCoO₂ or LiNiO₂ (around 100 Ah kg⁻¹), the specific capacity of the polythiophene derivatives is one order of magnitude lower.

The authors have been attempting to design polymeric or oligomeric new materials with even higher specific capacity and higher cycleability. We used aniline moiety to build up a new category of the material because of its relatively high specific capacity, its high electrocatalytic activity, and electrochemical durability. Furthermore, to increase specific capacity, we have focused on 3-electron π -conjugated system by hybridizing polyaniline backbones with other redox organic moieties of even higher specific capacity than the host matrices [7]. The moieties which shall be hybridized with polyaniline matrix are, for example, -SH/S-S (837 Ah kg⁻¹)

and BQ/HQ (496 Ah kg⁻¹). As one such material with high electrocatalytic activity and high theoretical specific capacity, we focused on a crystalline oligomer of 1,5-diaminoanthraquinone (DAAQ) (theoretical specific capacity: 338 Ah kg⁻¹). In this study, the redox response and cyclability of the film in acidic aqueous solutions were investigated.

2. Experimental

A DAAQ oligomer was prepared by electrooxidation at +1.5 V versus Ag/AgCl in a propylene carbonate (PC) solution containing 10 mM DAAQ monomer + 0.1 M TEAClO₄ + 0.5 M CF₃COOH. Other details on the preparation conditions are described in our previous report [8]. The molecular weight and crystallinity of the obtained product were characterized by GPC and XRD analyses. All electrochemical experiments were carried out in aqueous solution of 4 M H₂SO₄. The ion-exchange characteristics were evaluated during the redox reaction using in situ quartz crystal microbalance (QCM) gravimetry by monitoring resonance frequency change (Δf).

3. Results

3.1. Characterizations

From the result of GPC analysis, the average molecular weight of the electrooxidized DAAQ was found to be ca.

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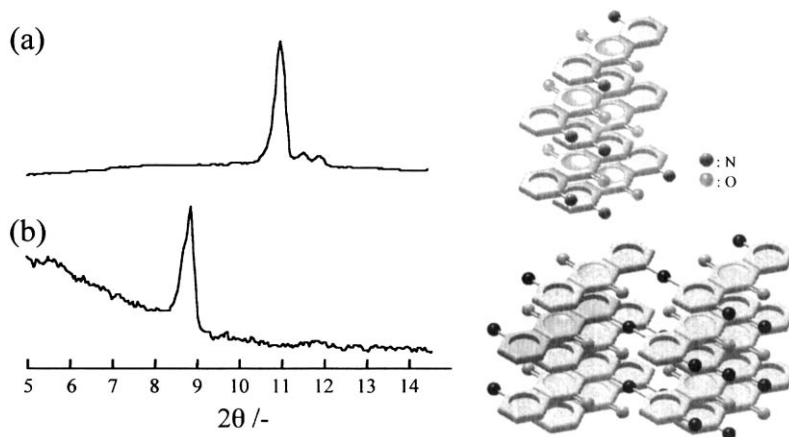


Fig. 1. XRD patterns and schematic illustrations of the crystal structure for (a) DAAQ monomer, and (b) DAAQ oligomer.

3000, indicating that DAAQ monomer was electrooxidized to form an oligomer-level (composed of ca. 10 monomer units) of macromolecule. As previously reported, the bonding manner of the DAAQ oligomer was found to be mainly 1,4 and 5,8 positions, which is similar to that of an electroactive polyaniline having head-to-tail structure [8]. The FTIR analysis also indicated that the quinone structure (C=O) in the DAAQ oligomer was maintained after electrooxidation. The DAAQ oligomer maintained sufficiently high electronic conductivity ($0.3\text{--}2.0\ \Omega^{-1}\ \text{cm}^{-1}$) within a wide potential range (from -2.0 to 0.8 V where the film is electrochemically active) [8]. In other words, the electronic conductivity is less potential dependent than those of other conducting polymers, like polyaniline.

Fig. 1 shows the obtained XRD pattern of DAAQ monomer and the DAAQ oligomer. In the spectrum of the DAAQ monomer (Fig. 1a), a major peak is observed at $2\theta = 11.06$. From the angle of the peak, the interstitial distance (d) is calculated to be $7.99\ \text{\AA}$ which is consistent with a plausible π - π stacking structure as illustrated in Fig. 2a [9]. In the spectrum of the DAAQ oligomer (Fig. 1b), the peak at $2\theta = 8.88$ ($d = 9.95\ \text{\AA}$) is observed. The appearance of the peak in Fig. 1b suggests that DAAQ maintains its crystal structure even after oligomerization and that the interstitial

distance of monomer–monomer stacking extends (see Fig. 2b). It is important and interesting to note that the DAAQ oligomer is in the category of “supramolecule” with π - π stacked structures that is rarely observed for the conventional conducting polymers. With such a peculiar feature of the crystalline structure possessed by this DAAQ oligomer, an enhanced electrical conductivity, which is potential-independent as mentioned above, is well explained by its 3D-extended π -conjugated structure. Also, it is expected to show better cyclability and potential thermal durability as described below.

3.2. Redox response

Fig. 2 shows a cyclic voltammogram (CV) and Δf profile (QCM) for the crystalline oligomeric DAAQ film in $4\ \text{M}\ \text{H}_2\text{SO}_4$ aq. The voltammogram shows a single redox couple around 0.7 V with the peak separation of $22\ \text{mV}$, indicative of a reversible system with three-electron exchange. From the CV, it was calculated that the DAAQ oligomer exhibited a specific capacity as high as $45\text{--}50\ \text{Ah}\ \text{kg}^{-1}$ (13–15% of the theoretical one). The value may not seem to be much higher than that of the conventional conducting polymers reported in other paper [3]. However, it is much higher than those for

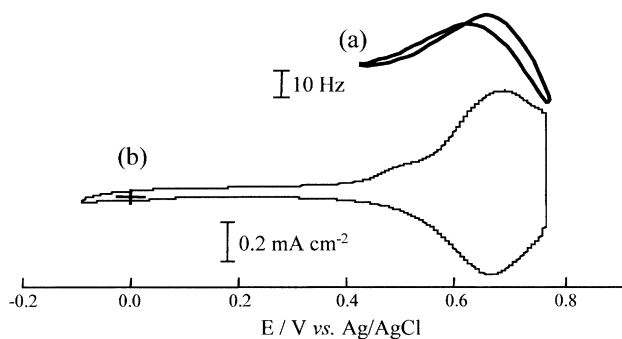


Fig. 2. (a) change of resonance frequency (Δf) vs. potential, and (b) cyclic voltammogram for the oligomeric DAAQ film in $4\ \text{M}\ \text{H}_2\text{SO}_4$ (scan rate: $10\ \text{mV}\ \text{s}^{-1}$).

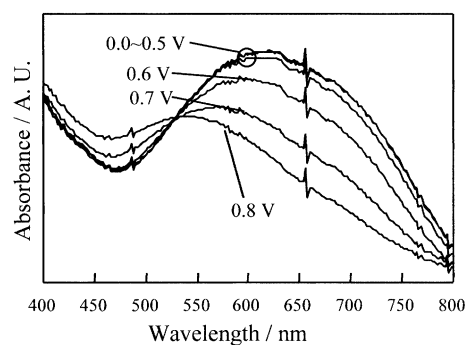
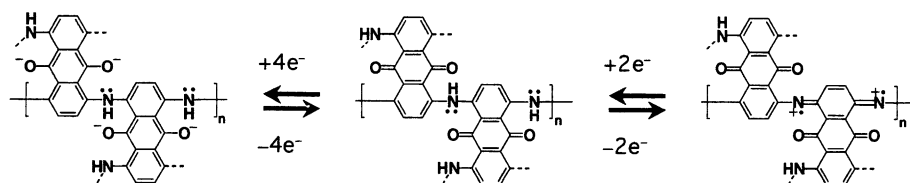
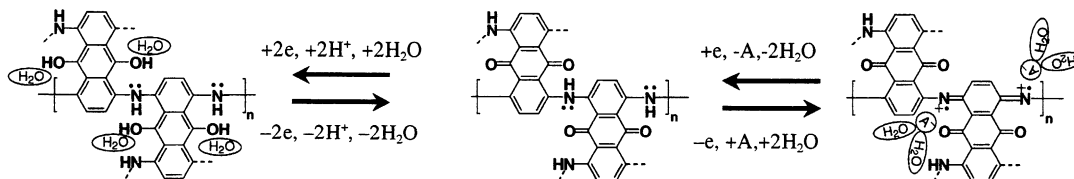


Fig. 3. In situ UV–VIS spectra for the DAAQ oligomer in the potential range from 0.0 to 0.8 V vs. Ag/AgCl.



Scheme 1.



Scheme 2.

the conventional conducting polymers, such as polyaniline (25 Ah kg^{-1}) and polypyrrole (2 Ah kg^{-1}), which were prepared on the same kind of substrate.

Fig. 3 shows in situ UV–VIS spectra for the DAAQ oligomer at several applied potentials. At 0 V, there can be observed a peak at 620 nm (benzenoid structure in the π -conjugated system), and a shoulder at 670 nm (quinone dianion) [10]. With respect to the peak at 620 nm, there was no change in absorbance when the potential was scanned from 0 to 0.5 V. When the potential was further scanned anodically from 0.5 up to 0.8 V, the intensity of the peak decreased. The shoulder at 670 nm showed a similar intensity decrease against potential (0–0.8 V) to that of the peak at 620 nm. The shoulder disappeared beyond 0.7 V. The above in situ UV–VIS spectroscopic analysis together with CV suggests the following scheme (Scheme 1):

To investigate ion-switching characteristics during such redox reactions, a mass change per electron (M_{eq}) was calculated from the Δf values (Fig. 2a) using the charge passed during the redox reactions. In the potential range from 0.45 to 0.65 V, the M_{eq} value was 19 g mol^{-1} which is considered to be equivalent to the molecular weight of H_3O^+ . While the M_{eq} value was 106 g mol^{-1} that is possibly equivalent to the molecular weight of ClO_4^- plus H_3O^+ in the potential range from 0.65 to 0.75 V.

From the above discussions, the following scheme is proposed for the redox reactions of the DAAQ oligomer (Scheme 2): in the potential range from 0.45 to 0.65 V, the DAAQ oligomer exchanges two electrons by quinone/hydroquinone (Q/HQ) redox reactions, while two protons with hydrated water are exchanged. In the potential range from 0.65 to 0.75 V, the redox of the π -conjugated system (emeraldine/quinone diimine) occurs to exchange one electron and two anions hydrated with two molecules of water.

4. Conclusion

As a member of a new category of material with high specific capacity, high electrocatalytic activity, and electrochemical durability, the authors investigated the oligomeric DAAQ film in acidic aqueous solutions. The DAAQ oligomer was found by XRD analysis to have high crystallinity, the features of which cannot be observed in the conventional conducting polymers. From the cyclic voltammetric response, it is found that the DAAQ oligomer has an electrochemically reversible redox system, and that it exhibited higher specific capacity as high as $40\text{--}50 \text{ Ah kg}^{-1}$ because of the 3-electron π -conjugated redox reaction. The CV together with in situ UV–VIS spectroscopic analyses suggests that the two-redox reactions responsible for the quinone group and the π -conjugated system occur in overlapping potential range.

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