Fabrication of an Organic Redox Capacitor with a Neutral Aqueous Electrolyte Solution

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ABSTRACT

Organic redox capacitors using neutral aqueous electrolyte solutions are environmentally friendly and safe. In this study, we report on the fabrication of an all-organic redox capacitor using NaCl solution. We used a 2,2,6,6-tetramethylpiperidiny-N-oxyl (TEMPO) benzene derivative (4-hydroxy TEMPO benzoate, HTB) and 9,10-anthraquinone (AQ) as active materials for the positive electrode and negative electrode, respectively. The former has a positive redox potential, and the latter reacts with two electrons, which enhances the energy density. The capacitor fabricated with HTB and AQ has an energy density of 8.36 Wh kg^{-1} at a rate of 10 C, which is nearly two times higher than that of the electric double-layer capacitor consisting of Ketjen black. The cycle test indicates that important factors affecting its performance are the ion diffusion and the dispersion of the active materials.

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Keywords : Organic Redox Capacitor, Neutral Aqueous Electrolyte, TEMPO, 9,10-Anthraquinone

1. Introduction

Great progress has been made in research on rechargeable energy-storage devices for realizing a sustainable society. Currently, mainly inorganic active materials such as lithium-ion are used as secondary batteries. These materials have a high energy density, but problems of inorganic secondary batteries include their resource constraints, environmental load, cost, and safety.^{1,2} Therefore, secondary batteries and capacitors based on organic compounds have been attracting attention in recent years.^{3–5} Organic energy-storage devices are significantly inferior to their inorganic counterparts in terms of their cycle characteristics owing to dissolution of the active material. Polymerization of the active material to prevent dissolution leads to a decrease in the conductivity and energy density.¹³ Thus, studies have been conducted to adsorb monomer-type active materials on porous carbon with a high surface area to prevent elution into electrolytes.^{14,15}

In addition, the safety of aqueous energy-storage devices is being researched.^{6–10} Aqueous energy-storage devices are non-flammable and safe; however, problems can arise with respect to their environmental compatibility, safety, and device durability because most water-based energy-storage devices use acidic and basic solutions.^{11,12} Therefore, it is desirable to use an aqueous solution with a neutral pH as the electrolytic solution. The improved environmental affinity and safety of neutral solutions in such energy-storage devices can lead to their use as power sources in wearable health monitoring devices and environmental monitoring devices (for soil and ecosystem analysis).

In this study, an organic redox capacitor was fabricated using a neutral aqueous solution and Ketjen black (KB), a commercially available carbon black, as the electrode material. The energy density can be enhanced by combining redox molecules with the electric double-layer (EDL) capacitor consisting of KB. As active materials for the positive and negative electrodes, 2,2,6,6-tetramethylpiperidiny-N-oxyl (TEMPO) benzene derivative (4-hydroxy TEMPO benzoate, HTB) and 9,10-anthraquinone (AQ) were used, respectively. The TEMPO derivatives have a positive redox potential.

Among different TEMPO derivatives, HTB has a low water solubility.^{16–20} The AQ was used as an active material because of its two-electron redox reaction and low solubility.^{5,14,21–24} These active materials with low water solubility were adsorbed onto KB to form electrodes to enhance the cycle characteristics. In addition, the impact of the neutral aqueous solution as the electrolyte was evaluated by aiming for an environmentally friendly, safe, and durable redox capacitor.

2. Experimental

2.1 Materials

The following materials were purchased from Fuji Film Wako Pure Chemical Industries, Ltd., Japan: 1-Methyl-2-pyrrolidone (NMP), potassium chloride, sodium chloride, sodium nitrate, and AQ. HTB was procured from Tokyo Chemical Industry Co., Ltd., Japan, and poly(vinylidene fluoride) [PVDF, 9305, 5 wt% in NMP] was obtained from Kureha Co., Ltd., Japan.

2.2 Electrode fabrication

For the electrode fabrication, 40 mg of KB EC300J (Ketjen Black International, Japan) was mixed with 5, 10, 20, or 30 wt% of the active material in a mortar. Subsequently, 200 μL of 5 wt% PVDF and 1 mL NMP were added as the binder and solvent, respectively, and stirred. This mixture was named the active material/KB ink.

For cyclic voltammetry, 2 μL of the active material/KB ink was dropped onto a glassy carbon (GC) electrode (outer diameter 6.0 mm, inner diameter 3.0 mm; ALS, Japan) and dried at 60 °C overnight. The weights of the active materials adsorbed on the GC electrode were 3.1, 6.2, 12, and 25 μg for 5, 10, 20, and 30 wt%, respectively. For the charge/discharge test, 500 μL of active material/KB ink was dropped on a 1 cm $\times$ 4 cm $\times$ 2 mm carbon felt (CF, GF-20; Nippon Carbon, Japan) and dried at 60 °C overnight. This procedure was repeated until a total of 1 mL of the ink had been dropped onto the CF. Finally, 1.5 mg of the active material was deposited on both electrodes.

2.3 Electrochemical measurement

Cyclic voltammetry was performed with a three-electrode system

consisting of a KB electrode with an active material as the working electrode, a home-made Ag/AgCl/saturated KCl reference electrode, and a platinum wire (0.5 mm ϕ , 10 cm) counter electrode. A 2.0 mol L⁻¹ (M) aqueous solution of NaCl, KCl, and NaNO₃ was used as the electrolyte solution, and each aqueous solution was dissolved in distilled water or a 0.1 M phosphate buffer. A scan rate of 10 mV/s was used for 100 cycles. The adsorption amount of the active material was calculated from the Faradaic process of the cathodic peak area of HTB and anodic area of AQ of the resultant cyclic voltammogram (CV) using the following equation:

$$Q = nFN \quad (1)$$

where Q is the charge (C), n is the number of reacting electrons, and N is the amount of adsorption (mol).

In the charge/discharge measurement, a CF modified with active material and KB was used as the electrode material. A 2.0 M NaCl aqueous solution dissolved in distilled water was used as the electrolyte for the positive electrode, and a 0.1 M phosphate buffer + 2.0 M NaCl solution was used as the electrolyte for the negative electrode. A cation exchange membrane (CSE; ASTOM, Japan) was placed between the two electrodes. In total, 1000 cycles of charge/discharge experiments were performed under the following conditions: maximum voltage of 2 V; cutoff voltage of 0.5 V; and current of 10, 20, or 30 C. In this study, 1 C is the current value at which charge/discharge is completed in 1 h. All measurements were carried out under argon gas bubbling, and the capacity and energy densities were calculated using the total mass of KB, PVDF, and the active materials used in the positive and negative electrodes.

3. Results and Discussion

3.1 Electrochemical performance of HTB on KB in a neutral aqueous solution

Figure 1a shows the CVs of the electrode in which the weight ratio of HTB to KB is 5 %. The scan rate is 10 mV/s, and the potential ranges from 0.5 to 1.0 V during 100 cycles. A 2.0 M NaCl

Scheme 1. Redox reaction of HTB.

aqueous solution was used as the electrolyte solution. The oxidation peak indicates a one-electron oxidation reaction from nitroxide to oxoammonium cations (Scheme 1). The midpoint potentials of the anodic and cathodic peak currents in the 1st and 100th cycles are 0.770 and 0.755 V, respectively. The potential differences between the anodic and cathodic peaks in the 1st and 100th cycles were both 30 mV, which indicates that the redox reaction of HTB is electrochemically quasi-reversible and stable. Positively charged oxoammonium cations form oxoammonium salts with anions (chloride ions) in the solution.⁸ Positively charged molecules such as oxoammonium cations have a higher solubility in water than neutral reduced forms and are desorbed from the electrode surface. In this system, desorption from KB can be prevented by the formation of an oxoammonium salt with an anion. In addition, the peak current densities of this electrode were proportional to the scan rate (from 2 s to 20 mV/s), indicating that HTB was adsorbed on KB (Fig. S1).

Figure 1b shows the active amount of HTB adsorbed on the electrode calculated from the cathodic peak area of the CV (Eq. (1)) shown in Fig. 1a. The retention ratio is defined as the ratio of each cycle to the first cycle. In this study, 2.0 M KCl, NaCl, and NaNO₃ were tested as aqueous electrolyte solutions. Compared with the first cycle, HTB retention on the electrode in KCl, NaCl, and NaNO₃

Figure 1. Cyclic voltammograms of HTB/KB (4-hydroxy TEMPO benzoate/Ketjen black) and ratios of electrochemical HTB on the electrode. (a) Cyclic voltammograms of HTB/KB on the glassy carbon (GC) electrode in 2 M NaCl at 10 mV/s after 1, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 cycles. (b) Electrochemically active HTB on the electrode during the first cycle in 2 M KCl (red circle), 2 M NaCl (blue square), and 2 M NaNO₃ (green diamond). (c) Ratio of electrochemically active HTB on the electrode for each cycle for different weight ratios of HTB to KB (5 %, red circle; 10 %, blue square; 20 %, green diamond; 30 %, purple triangle) in 2 M NaCl.

Figure 2. Cyclic voltammograms of AQ/KB (9,10-anthraquinone/Ketjen black) and ratios of electrochemical AQ on the electrode. (a) Cyclic voltammograms of AQ/KB on the glassy carbon (GC) electrode in 2 M NaCl at 10 mV/s after 1, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 cycles. (b) Ratio of electrochemically active AQ on the electrode for each cycle in 2 M KCl (red circle), 2 M NaCl (blue square), 2 M NaNO₃ (green diamond) at a weight ratio of AQ to KB of 5 %. (c) Ratio of electrochemically active AQ on the electrode for each cycle for different weight ratios of AQ to KB (5 %, red circle; 10 %, blue square; 20 %, green diamond; 30 %, purple triangle) in 2 M NaCl.

solutions during the 100th cycle is 78, 71, and 62 %, respectively (Fig. S2). This suggests that chloride ions are superior to nitrate ions with respect to the formation of oxoammonium salts with oxoammonium cations. The diffusion coefficient of NaNO₃ is lower than that of NaCl.²⁵ This could have affected the formation of an oxoammonium salt from HTB, leading to its desorption from the working electrode. Compared with the 10th cycle, the HTB retentions on the electrode in KCl and NaCl solutions during 100th cycle are 78 and 81 %, respectively. Therefore, NaCl is expected to be a better electrolyte. The same experiment was performed with a solution in which each electrolyte was dissolved in 0.1 M phosphate buffer (pH 7.0). The redox peak disappeared in several cycles for all electrolytes. As mentioned above, it is assumed that the diffusion resistance increases with increasing size of the phosphate ion, which prevents the formation of an oxoammonium salt. Therefore, we used 2 M NaCl in distilled water for HTB.

Figure 1c shows the retention of the electrochemically active HTB on the electrode after 100 cycles, which was calculated from the cathodic peak area of the CV (Eq. (1)) by changing the weight ratio of HTB to KB from 5 to 30 % (Fig. S3). The amount of electrochemically active HTB increases, but the stability decreases with increasing HTB loadings. At HTB/KB weight ratios of 5, 10, 20, and 30 %, 70.5 ± 0.9, 65 ± 5, 52 ± 5, and 47 ± 2 % remains on the electrode after 100 cycles, respectively. The retention decreases with increasing HTB amounts. When the amount of HTB is large, HTB aggregation prevents the mass transfer of the counter anion to the oxoammonium cation, resulting in the elution of HTB during the potential scan. An excess amount of HTB might be eluted from the electrode, but the amount of HTB remaining on the electrode is limited by the effective surface area.

3.2 Electrochemical performance of AQ on KB in a neutral aqueous solution

Cyclic voltammetry was performed in a 2.0 M aqueous solution

Scheme 2. Redox reaction of AQ.

of NaCl, KCl, or NaNO₃ dissolved in distilled water. The results show that the redox peak disappears after a few cycles. As protons are involved in the redox reaction, it is necessary to prevent pH changes using a buffer solution. Therefore, the electrolytes NaCl, KCl, or NaNO₃ were dissolved in a 0.1 M phosphate buffer. Figure 2a shows the CVs of the electrode in which the weight ratio of AQ to KB is 5 % in the 0.1 M phosphate buffer + 2.0 M NaCl solution (pH 7.0). The scan rate is 10 mV/s, and the potential ranges from −0.1 to −0.7 V during 100 cycles. The reduction peak corresponds to the two-electron–two-proton reduction reaction from the −C(=O)− group to the −C(OH)− group (Scheme 2). The redox potential of the 1st cycle is −0.475 V and that of the 100th cycle is −0.485 V. The redox potential differences during the 1st and 100th cycles are 50 mV, indicating the very stable redox response of AQ on the KB electrode. In addition, the peak current densities of this electrode were proportional to the scan rate (from 2 to 20 mV/s), indicating that AQ was adsorbed on KB (Fig. S4).

Figure 2b shows the active amount of AQ on the KB electrode calculated from the anodic peak area of the CV (Eq. (1)), similar to Fig. 1b. To determine the optimal electrolyte, 2.0 M of KCl, NaCl, and NaNO₃ was used. Compared to the first cycle, the active amounts of AQ on the KB electrode in the KCl, NaCl, and NaNO₃ solutions during the 100th cycle are 90, 94, and 84 %, respectively

Scheme 3. The organic redox capacitor with a neutral aqueous electrolyte solution.

Figure 3. Constant current charge and discharge energy density. (a) Constant current charge (open)/discharge (filled) curves in 2 M NaCl at different rates: 10 C (red circle), 20 C (square), 30 C (diamond). (b) Discharge energy density for a full-cell cycle of a redox capacitor (red circle) and a EDL capacitor (gray circle) in 2 M NaCl. (c) Discharge energy density for a full-cell cycle in 2 M NaCl at different rates: 10 C (circle), 20 C (square), 30 C (diamond).

(Fig. S5). AQ can be strongly adsorbed on carbon materials through π - π interactions between AQ and the carbon materials.²⁴ Similarly, in this case, AQ was adsorbed stably on KB and did not desorb even after repeated cycles. NaCl shows high retention based on the comparison of the 10th and 100th cycles. Therefore, the 0.1 M phosphate buffer + 2.0 M NaCl solution was used as the electrolyte solution for the experiments.

Figure 2c shows the residual amount of electrochemically active AQ on the KB electrode calculated from the anodic peak area of the CV (Eq. (1)) after changing the weight ratio of AQ to KB from 5 to 30 % (Fig. S6). At 5 % AQ, 100 ± 10 % remains on the KB electrode after 100 cycles, whereas the AQ retention is 73 ± 3 % at 30 % AQ. At AQ/KB weight ratios of 10 and 20 %, the electrodes have high retention rates (97 ± 7 and 96 ± 2 % after 100 cycles, respectively). In addition, two redox peaks were observed in the case of the electrodes for AQ to KB weight ratios ranging from 10 to

30 %. This indicates aggregation of AQ.²⁴ When the amount of AQ is increased, AQ aggregation prevents the mass transfer of phosphate ions such that the delay in the supply of protons causes a decrease in the retention of the electrochemical response of AQ. Besides, the peak current densities observed in the CVs were not linear to the weight ratios of AQ to KB (Fig. S6). This may be due to the stacking of AQ and ion diffusion, but this aspect needs to be studied further.

3.3 Charge and discharge test

Scheme 3 shows a schematic of the redox capacitor fabricated in this study. Figure 3a shows a full-cell charge/discharge profile using HTB (5 % weight to KB) in a 2.0 M NaCl electrolyte solution for the positive electrode and AQ (5 % weight to KB) in the 0.1 M phosphate buffer + 2.0 M NaCl solution for the negative electrode. A plateau region can be observed at 1.3 to 1.5 V, which is due to the

Table 1. Organic redox capacitors.

positive electrode negative electrode	electrolyte	voltage /V	energy density /W h kg ⁻¹	ref
LiMn ₂ O ₄ poly(pyrene-4,5,9,10-tetraone)	2.5 M Li ₂ SO ₄	1.13	92	10
LiCoO ₂ polypyrrole	saturated Li ₂ SO ₄	0.85		11
poly(2,3-dithino-1,4-benzoquinone) Zn	4 M zinc trifluoromethanesulfonate	~1.25	190.1	12
1,4-napthoquinone,tetrachlorobenzoquinone AQ	1 M H ₂ SO ₄	0.65	23.5	3
tetrachlorohydroquinone (TCHQ) AQ	0.5 M H ₂ SO ₄	~0.8	30.6	15
PTAm poly(antraquinone-substituted ethyleneimine)	3 M NaCl	1.1		14
poly(TEMPO-substituted norbornene) poly(galvinoxystyrene)	0.5 M (C ₄ H ₉) ₄ NClO ₄	0.66		7
HTB bipyridinium-naphthalene oligomer	8 M NaClO ₄	0.96	35	16

redox reactions of HTB and AQ. In general, water-based organic redox capacitors have a low cell voltage compared to those of capacitors based on organic electrolytes. However, the redox capacitor in our study realizes a high cell voltage (Table 1) owing to the combination of HTB and AQ. The difference between the charge and discharge plateau regions is due to the resistance of the electrolyte and overvoltage of the redox reactions. The capacity densities are 7.16 mAh/g at 10 C, 6.36 mAh/g at 20 C, and 6.02 mAh/g at 30 C. They are enhanced by the redox reactions of the active materials.

Figures 3b and S7 show the discharge energy density of the redox capacitor and the capacitor consisting of KB at different currents. The energy density of the redox capacitor at 10 C (8.36 Wh kg⁻¹) is nearly two times higher than that of the EDL capacitor (4.33 Wh kg⁻¹). The capability of the redox capacitor for a high current density is similar to that of the EDL capacitor. This indicates that the fast redox reaction of the active materials contributes to this capability, thus making it comparable to that of the EDL capacitor.

Figures 3c and S8 show the discharge energy density depending on the charge/discharge cycle numbers. The energy densities of the 1st and 1000th cycles are 8.36 and 4.94 Wh kg⁻¹, respectively. The energy density decreases during 200 cycles of charge and discharge and subsequently remains constant. The main cause of the decrease in the energy density might be the elution of HTB from the CV, as shown in Fig. 1. The energy density stabilizes when the diffusion of counter anions is balanced by the electrochemical reaction. The higher the charge/discharge current, the lower the energy density. This might be because the diffusion of the counter anion is insufficient in the short charge/discharge time. Strong adsorption of the electrochemically active material (especially in the case of active material with low molecular weight) on the electrode with good dispersion (almost monolayer form) is necessary. Owing to aggregation, excess active material suppresses the electrochemical reaction rate owing to its low conductivity. In this study, the strength of the π - π interaction between HTB and KB, and between AQ and KB is sufficiently large for 1000 charge/discharge cycles. On the other hand, the dispersion of the active material and adsorption mechanism of the active material on the electrode surface must be improved to further enhance the stability.

4. Conclusions

In this study, HTB was used as the active material for the positive electrode and AQ was used as the negative electrode to fabricate a redox capacitor that operates in a neutral aqueous solution. The KB was used as the electrode material. The HTB/KB electrode is more stable in NaCl and KCl electrolyte solutions than in NaNO₃ solution, but the phosphate ions interrupt the electrochemical reaction. In the case of AQ, a stable electrochemical response was achieved in the presence of a phosphate buffer system with 2.0 M KCl or NaCl. The results showed that the responses of the HTB and AQ electrodes were most stable when the weight ratios of HTB and AQ to KB were 5 %. During a constant current charge/discharge test with a full cell, the energy density decreases to 61.5 % after the initial 200 cycles and subsequently remains stable up to 1000 cycles. The cell voltage ranges from 1.3 to 1.5 V, which is higher than that of other aqueous organic redox capacitors. Therefore, an organic redox capacitor based on a neutral aqueous electrolyte solution is characterized by properties such as environmental affinity, safety, and high cell voltage. The performance of the redox capacitor can be enhanced by improving the dispersion of active material on the electrode surface.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.21-00004>.

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