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ORIGINAL ARTICLE

Hydroquinone-substituted polyallylamine: redox capability for aqueous polymer–air secondary batteries and recyclability

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Abstract

Organic redox polymers, composed of earth-abundant elements, offer rapid charge storage and are promising electrode-active materials for aqueous batteries, potentially replacing metals and overcoming their resource and performance limitations. However, the hydrophobicity of many organic redox molecules hinders their application using aqueous electrolytes. This necessitates molecular designs that impart hydrophilicity while immobilizing redox-active moieties onto electrodes. Polyallylamine, with its high density of hydrophilic amino groups, serves as an effective backbone. In this work, functionalizing it with hydroquinone enabled the use of the polymer in aqueous batteries. While hydroquinone provides high theoretical capacity, irreversible quinhydrone formation limits its reversible and thorough charge storage. We addressed this by covalently attaching hydroquinone to polyallylamine via condensation. The resulting polymer exhibited reversible and thorough charge storage, which was attributed to electrostatic repulsion between amino groups that suppressed quinhydrone formation. A polymer–air secondary battery was fabricated with the polymer, Pt/C, and a 0.5 M H_2SO_4 aqueous solution as the anode, cathode, and electrolyte, respectively, without any separator. This polymer–air secondary battery displayed a constant discharge voltage with high cyclability (>99% capacity retention after 100 cycles) and high-rate capability. Moreover, the polymer demonstrated recyclability, as raw materials were generated simply by acid treatment. This work demonstrates a polymer design strategy for integrating typically hydrophobic organic redox molecules into recyclable aqueous batteries.

Introduction

Organic redox polymers are bearing organic redox molecules that can reversibly store electric charge by reduction and oxidation [1]. Organic redox polymers are composed of abundant elements and are characterized by the ability to store charges quickly and thoroughly based on the fast charge transport phenomenon in their condensed layers [1, 2]. Therefore, these polymers have attracted attention as electrode-active materials capable of storing electric charge at high current densities and have been the subject of vigorous research [3–12]. In addition, batteries utilizing these polymers for their electrode-active materials are called organic batteries, and many organic batteries have been proposed as next-generation batteries for a sustainable society [13, 14].

In recent years, to overcome the weaknesses of metal electrodes (e.g., decreases in cycle performance due to dendrite formation [15, 16]) in aqueous batteries, research into replacing metal electrodes with organic electrodes has proceeded [14, 17, 18]. However, the organic redox molecules responsible for storing electric charge are often hydrophobic. Therefore, to apply organic redox polymers to aqueous batteries, a molecular design strategy is essential that imparts hydrophilicity to organic redox molecules

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while immobilizing them on the electrode to prevent dissolution in the electrolyte.

To apply organic hydrophobic and functional molecules to aqueous environments, we have focused on polyallylamine, which has a high density of hydrophilic amino groups. We have demonstrated that grafting organic redox molecules onto polyallylamine endows them with hydrophilic properties [19–24]. Polymers in which these organic functional molecules are substituted into polyallylamine have been applied as hydrophilic dyes [19], hydrogen storage materials [21, 24], and electrode-active materials for aqueous batteries [20, 22, 23]. Recently, we developed a novel quaternized polymer by substituting butanediol into polyallylamine. Furthermore, we demonstrated that the high hydrophilicity and electrostatic repulsion of the resulting polymer improved the reactivity of butanediol [24]. In other words, we confirmed that the substitution of organic functional molecules into polyallylamine can not only increase their hydrophilicity but also enhance their reactivity.

In the current work, we focused on hydroquinone. Although hydroquinone has a high theoretical capacity based on its small molecular weight, it is usually challenging to store charge reversibly and thoroughly due to the formation of quinhydrone, which hinders its application as an electrode-active material [25]. We hypothesized that by substituting hydroquinone into polyallylamine (Fig. 1), the resulting organic redox polymer can reversibly and thoroughly store charge with high capacity based on the improved hydrophilicity and electrostatic repulsion. Furthermore, we also investigated the decomposition of polyallylamine substituted with functional organic molecules into raw materials (recyclability, Fig. 1).

Experimental section

Preparation of hydroquinone-substituted polyallylamine (PDA)

2,5-Dihydroxybenzoic acid (2.54 mmol) and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) (2.54 mmol) were put in *N*,*N*-dimethylformamide (DMF) (10 mL). To this solution, a 15 wt% aqueous solution of polyallylamine (2.54 mmol) was added dropwise over 10 min, and the mixture was stirred for 10 h. The reaction mixture was subsequently poured into acetone, resulting in the formation of a precipitate. This precipitate was collected via filtration and washed with acetonitrile and acetone to obtain PDA as a brown powder. The degree of hydroquinone substitution into polyallylamine was calculated using ^{1}H-NMR spectroscopy. The polymer was confirmed to be PDA as follows (Figs. S1, S2): ^{1}H-NMR (400 MHz, dimethyl sulfoxide, δppm): 0.7−2.4 (CH_2, CH (polyallylamine)), 3.3–4.2 (CH_2, NH_2 (polyallylamine)), 6.5–7.5 (Ph (HQ)), 7.5–8.5 (NH (polyallylamine)), 8.8–9.3 (OH). FT-IR (ATR): $\nu = 2700-3500$ (br; ν(N-H, O-H)), 2917 (s; ν(C-H)), 1657 (s; ν(C = O)), 1585 (s; δ(NH_2)), 1446 (s; ν(C = C), 1356 (s; δ(C-H)).

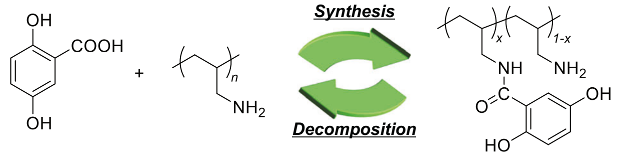


Fig. 1 Synthesis and decomposition of hydroquinone-substituted polyallylamine

Decomposition of hydroquinone-substituted polyallylamine

PDA (0.54 mmol) was added to a 15 M sulfuric acid or acetic acid aqueous solution (10.8 mmol) and stirred at 80 °C. After the reaction, the reaction mixture was poured into water, resulting in the formation of a precipitate. This precipitate was collected via filtration and washed with acetone to yield brown powder. The decomposition rate was calculated from the ratio of the substitution of hydroquinone into polyallylamine before and after the decomposition reaction.

Results and discussion

Synthesis of hydroquinone-substituted polyallylamine

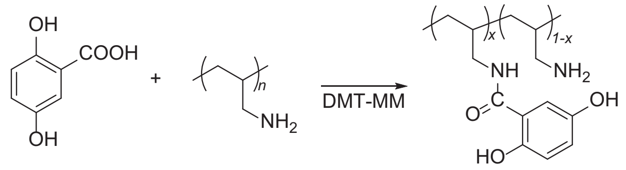
Facile condensation of 2,5-dihydroxybenzoic acid and polyallylamine produces hydroquinone-substituted polyallylamine (PDA) (Scheme 1). Increasing the temperature is considered to improve the reaction rate and, consequently, the incorporation rate. In other words, the degree of substitution could be easily adjusted in the range of 16–50% by changing the reaction temperature (Table 1). PDA could be purified by facile washing with acetonitrile and acetone, with high yields (e.g., 84% for Run 4). The resulting polymer was purified by simple washing with acetonitrile and acetone, with high yields (e.g., 84% for Run 2). All the PDAs were soluble in DMF, dimethyl sulfoxide, and NMP and were insoluble but swollen in water.

Electrochemical properties of hydroquinone-substituted polyallylamine

Chronoamperometric evaluation of the thin polymer film (610 nm) in 0.5 M H_2SO_4 aqueous solution (Fig. 2a) revealed that the diffusion coefficient of protons and electrons within the polymer layer was determined to be

1.7×10^{-13} cm^2 s^{-1} (with the rate constant for the electron self-exchange reaction estimated to be 3.5×10 M^{-1} s^{-1}). This is comparable to that of conventional organic redox polymers [26–28]. This result indicates that the polymer/carbon composite electrode is likely to perform at a moderate rate capability.

PDA with a 43% degree of substitution, synthesized using the conditions of Table 1 (Run 4), was used in a carbon composite electrode, which exhibited a measurable current within the potential range of 0–+0.8 V in 0.5 M H_2SO_4 aqueous solution. The charge–discharge curves (Fig. 3b) indicated a potential plateau at + 0.4 V vs. Ag/AgCl and showed that the PDA electrode delivered a high capacity close to its theoretical capacity of 197 mAh/g (99% of the theoretical capacity, 199 mAh/g), which was calculated based on the molecular weight of the repeating unit (Columbic efficiency of >99%). This indicated that the improved hydrophilicity and electrostatic repulsion of PDA allowed the polymer/carbon composite electrode to reach almost full capacity. We also confirmed that PDAs with less than 43% substitution could achieve full capacity. Meanwhile, PDA with 50% substitution could not achieve the full capacity (143 mAh/g), presumably because of inadequate hydrophilicity. The polymer/carbon composite electrode demonstrated excellent rate capabilities (e.g., close to its theoretical capacity even at a high rate of 60 C), presumably because of a rapid electron (proton) exchanging reaction in the polymer (Fig. 2b). In addition, the excellent cyclability of the PDA electrode, with 99% of the initial capacity even after 100 cycles (Fig. 3b Inset), indicates the strong robustness of PDA. These results supported our hypothesis that by substituting hydroquinone into polyallylamine, the resulting organic redox polymer can reversibly and thoroughly store charge with high capacity based on the improved hydrophilicity and electrostatic repulsion.



Scheme 1 Synthesis of hydroquinone-substituted polyallylamine

Table 1 Conditions for the synthesis of hydroquinone-substituted polyallylamine.[a]

Run	Reaction temperature (°C)	Degree of substitution[b] (%)
1	40	16
2	50	29
3	60	34
4	65	43
5	80	50

[a] Reaction condition: Polyallylamine (2.54 mmol), 2,5-dihydroxybenzoic acid (2.54 mmol), and DMT-MM (2.54 mmol) in DMF (10 mL) for 10 h

[b] The degree of substitution was determined from the integration ratio of the peak derived from the main chain of PDA and the peak derived from substituted hydroquinone in ^{1}H-NMR

Polymer–air secondary battery

Air batteries that utilize an organic redox polymer as the anode and an acidic aqueous solution as the electrolyte have demonstrated the capability to achieve high cyclability [14]. Therefore, as an example of the application of PDA, a polymer–air secondary battery was fabricated with a PDA electrode as the anode, a conventional Pt/C catalyst as the cathode, and a 0.5 M H_2SO_4 aqueous solution as the electrolyte. (Fig. 4a, b). The anode was under inert gas, and the cathode was exposed to air. The battery was operated at

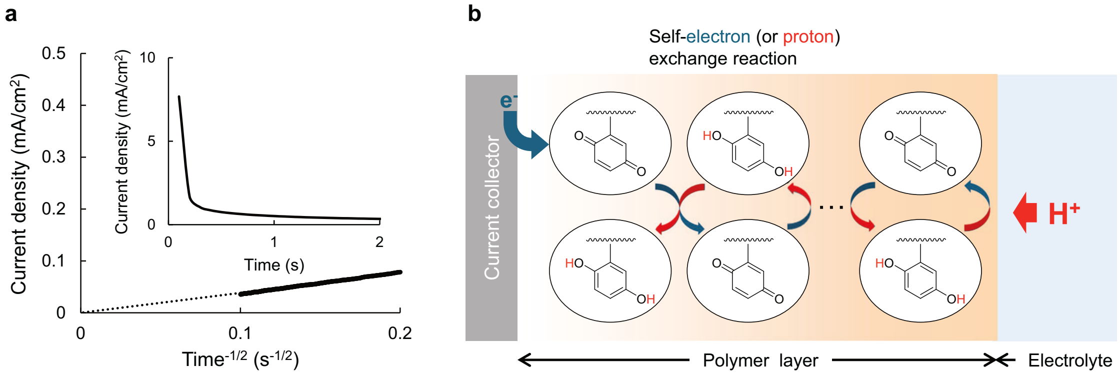


Fig. 2 **a** Chronoamperometric Cottrell plots for 610-nm PDA film in 0.5 M H_2SO_4 aqueous solution. Inset: PDA current decay after application of potential (–0.2 V vs. Ag/AgCl). **b** Schematic image of proton exchange reaction in PDA film

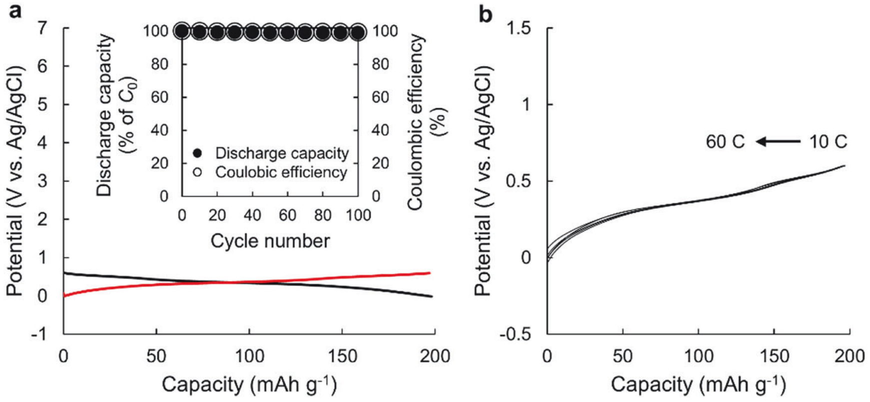


Fig. 3 **a** Charging (black) and discharging (red) curves of the electrode at 10 C. Inset: Capacity retention over 100 cycles of galvanostatic charge and discharge at 20 C. **b** Discharging curves at discharging rates of 10, 15, 20, 30, 40, and 60 C

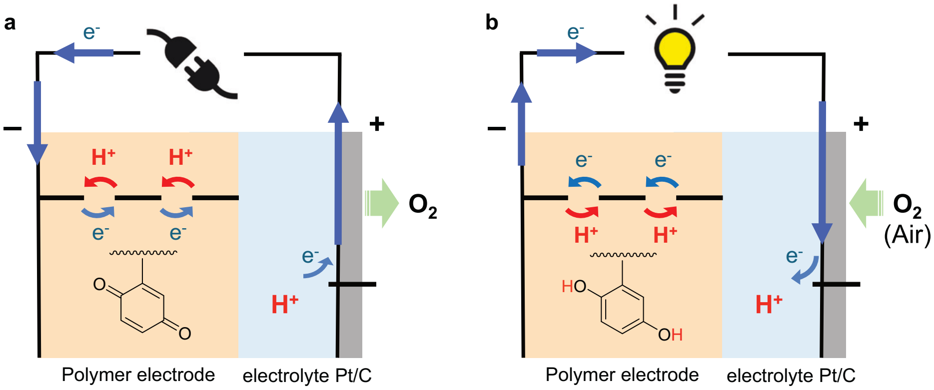


Fig. 4 Schematic images of the polymer–air secondary battery. **a** Charging. **b** Discharging

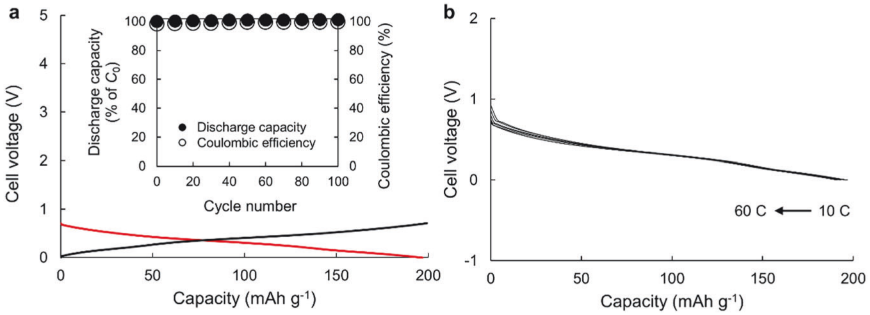
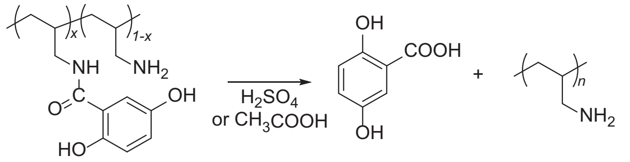


Fig. 5 **a** Charging (black) and discharging (red) curves of the polymer–air secondary battery at 10 C. Inset: Capacity retention for 100 cycles upon galvanostatic charge and discharge of the battery at 20 C. **b** Discharging curves at discharging rates of 10, 15, 20, 30, 40, and 60 C

0.5 V during discharge and demonstrated a discharge capacity of 197 mAh/g (more than 99% of the theoretical capacity) with a high Coulombic efficiency of 99% (Fig. 5a), a high capacity close to its theoretical capacity even at a high rate of 60 C (Fig. 5b), and high cyclability (more than 99% of the initial capacity even at 100 cycles, Fig. 5a inset). Therefore, functionalizing polyallylamine with hydroquinone enables the use of the polymer in aqueous batteries.

Decomposition of hydroquinone-substituted polyallylamine into raw materials

To prevent plastic pollution, the design of polymer materials must consider their recycling after use [29, 30]. As shown in Scheme 2, we demonstrated that PDA was decomposed to the raw materials by acid hydrolysis (see also Fig. S3). As a representative example, the decomposition rates of PDA (Table 1, Run 4) for each decomposition condition were investigated and are summarized in Table 2. A comparison of Runs 1 and 2 indicates that a reaction time of 48 h is insufficient for decomposition, whereas nearly complete decomposition is achieved in 72 h. A comparison of Runs 2 and 3 indicates that sulfuric acid is better than acetic acid for PDA decomposition. Therefore, acid hydrolysis using 15 M sulfuric acid can almost completely decompose PDA to its raw materials, which is the first time that material recycling has been demonstrated in polymer design using polyallylamine. This work demonstrates a polymer design strategy for integrating typically hydrophobic organic redox molecules into recyclable aqueous batteries.



Scheme 2 Decomposition of hydroquinone-substituted polyallylamine

Table 2 Conditions for the decomposition of hydroquinone-substituted polyallylamine.[a]

Run	Type of 15 M acid	Reaction time (hours)	Decomposition rate[b] (%)
1	Sulfuric acid	48	76
2	Sulfuric acid	72	91
3	Acetic acid	72	60

[a] Reaction condition: PDA (0.54 mmol) in 15 M sulfuric acid or acetic acid aqueous solution (10.8 mmol) at 80 °C

[b] The decomposition rate was calculated from the ratio of the degree of substitution before and after the decomposition reaction

Conclusion

The substitution of hydroquinone into polyallylamine allowed the redox polymer (PDA with a degree of substitution below 43%) to achieve almost full capacity (99% of the theoretical capacity) due to the improvement in hydrophilicity and electrostatic repulsion. The polymer–air battery discharged at a constant output voltage and displayed high cyclability (more than 100 cycles) and rate capability (up to 60 C). In addition, we also investigated the decomposition (recyclability) of PDA into raw materials. The current work demonstrates a polymer design strategy that enables not only the application of hydrophobic organic redox molecules that typically aggregate in aqueous environments but also their recycling after use.

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Author contributions All the authors have approved the final version of the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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