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Aqueous Electrochemistry of Poly(vinylanthraquinone) for Anode-Active Materials in High-Density and Rechargeable Polymer/Air Batteries

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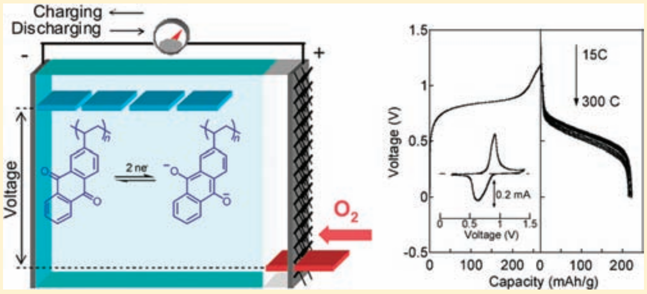
Supporting Information



ABSTRACT: A layer of poly(2-vinylanthraquinone) on current collectors underwent reversible electrode reaction at −0.82 V vs Ag/AgCl in an aqueous electrolyte. A repeatable charging/discharging cycles with a redox capacity comparable to the formula weight-based theoretical density at the negative potential suggested that all of the anthraquinone pendants in the layer was redox-active, that electroneutralization by an electrolyte cation was accomplished throughout the polymer layer, and that the layer stayed on the current collector without exfoliation or dissolution into the electrolyte during the electrolysis. The charging/discharging behavior of the polymer layer in the aqueous electrolyte revealed the capability of undergoing electrochemistry even in the nonsolvent of the pendant group, which offered insight into the nature of the anthraquinone pendants populated on the aliphatic chain. Charging/discharging capability of air batteries was accomplished by using the polymer layer as an organic anode-active material. A test cell fabricated using the conventional MnO_2/C cathode catalyst exhibited a discharging voltage at 0.63 V corresponding to their potential gap and a charging/discharging cycle of more than 500 cycles without loss of the capacity.

INTRODUCTION

Reversible and high-density storage of negative charge is required for an anode-active material in a rechargeable air battery which offers high energy density by employing oxygen in the atmosphere as a cathode-active material.[1] Primary and secondary (or rechargeable) air batteries have been investigated by using various metals. While conventional primary air batteries have been dominated by the Zn/air battery,[2] the rechargeable air battery is still under development because of low cycle performance as a result of the formation of dendrites on the metal anodes. In addition, oxygen reduction catalysts usually require strongly basic or acidic aqueous electrolytes to reduce oxygen at positive potentials,[3] which have limited the materials available for the anodes.[4]

A new strategy to design organic electrode-active materials has emerged recently,[5] based on the discovery of poly(2,2,6,6-tetramethylpiperidin-1-oxy-4-yl methacrylate) as a cathode-active material in rechargeable batteries.[6] Charge storage by the so-called radical battery[7] is accomplished by the ultimate charging of the neutral radical to an oxoammonium cation which is populated on the aliphatic backbone in a large density (ca. 4×10^{-3} mol unit/g).[8] The reversible and exhaustive charging of the pendant redox site in a slab of the polymer requires electroneutralization throughout the polymer layer,[9] which is made feasible by employing the swellable backbone to allow facile counterion migration.[10a] What has been learned from the studies on the rapid charging/discharging properties of the radical batteries is the capability of the highly populated redox sites to transport charges by successive electron self-exchange reactions driven by redox gradient,[11] giving rise to a large current density of ~0.1 mA/cm^2.[12] The efficient redox mediation has been found for many types of organic robust radical pendants that undergo reversible electrode reactions with heterogeneous electron transfer rate constants in the order of 10^{-1} cm/s and large bimolecular rate constants for the exchange reaction in the order of 10^7 $M^{-1}s^{-1}$, by virtue of the high population and thus of the small site-to-site distance.[13]

We anticipated that such an efficient redox mediation should also be found for organic redox-active molecules other than the robust radicals, such as quinones,[14] imides,[15] and viologen derivatives,[10] based on their reversible $2e^-$ redox processes of the pristine benzenoids to give the corresponding quinoids. Especially, anthraquinone have been shown to possess a large heterogeneous rate constant for the electrode reaction ($>10^{-2}$ cm/s) at a moderately negative potential near −0.8 V[14] and a noticeable chemical stability among quinones due to the absence of the α-hydrogen atom which is the most susceptible to degradation. The electrochemical properties suitable for the anode-active materials, together with the particular stability

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which has been demonstrated from the H_2O_2 production process,[16] prompted us to examine anthraquinone as the pendant group. On the basis of the design principles established in the studies of the radical batteries,[7,17] we focused on poly(2-vinylanthraquinone) (PVAQ)[18] in which the $2e^-$ redox sites are directly bound to the aliphatic backbone to maximize the formula weight-based theoretical density (229 mAh/g). While most of the anthraquinone-containing polymers in the previous reports possess π-conjugated backbones designed for semiconductor applications,[19] studies on the aliphatic polyanthraquinones have been limited by the low molecular weights and the poor solubility or swellability ascribed to the crystallization of the pendant groups during the polymerization.[20] Indeed, the crystalline domain due to the fused ring moieties which is unequilibrated in electrolyte solutions is undesirable for the charge transport and storage, because it significantly lowers the capacity and the rate performance and leads to exfoliation from the electrode.[21] Here we report the synthesis of PVAQ with a sufficiently high molecular weight to accomplish both swelling and yet insoluble properties in the electrolyte solution, and the excellent charging/discharging properties of the polymer layer allowing the application to the organic anodes.[22] The cyclability exceeding 300 exhaustive charging/discharging cycles without loss of the capacity from the formula weight-based theoretical density in the basic electrolyte conditions allowed fabrication of the first organic rechargeable air battery, which suggested a new type of charge storage configuration in secondary batteries.

EXPERIMENTAL SECTION

Electrochemical Measurements. Electrochemical measurements were performed using an ALS electrochemical analyzer Model 660D. All measurements were performed under an atmosphere of dry argon. A one-component cell with a glassy carbon plate electrode, a platinum wire and a Ag/AgCl electrode as the working, the counter and the reference electrodes, respectively, were employed to obtain the voltammograms. Aqueous electrolytes were prepared using deionized water after distillation. The electrolytes at various pH values from pH 13.7 to pH 8.9 were prepared using 2.5 M NaOH and NaCl electrolyte which was thoroughly degassed by argon bubbling. The pH was monitored using a HORIBA F-51 pH meter. Effect of pH on the cyclic voltammograms of the polymer layer was examined by varying the pH of the bathing electrolyte. The formula weight-based theoretical density (or capacity) (in mAh/g) was calculated according to 1000 nFM^{-1} $(3600)^{-1}$, where n, F, and M are stoichiometric number of electrons, the Faraday constant, and the molar mass of the repeating unit, respectively. The redox capacity (in mAh/g) was obtained employing 1000 Qm^{-1} $(3600)^{-1}$, where Q and m are charge passed in electrolysis and the loading weight of the anode-active material which was determined by weighing the anode or using the concentration of PVAQ in dropcast solution.

Preparation of the Coin-Type Cell. A punched coin-type case (Hosen Co.) was employed as an electrochemical cell. A PVAQ solution in $CHCl_3$ was dropcast on a disk electrode and dried under the saturated solvent vapor to form a layer, which was put into the case as anode. An oxygen reduction catalyst composed of vapor-grown carbon fibar (Showa Denko Co.), MnO_2, and poly(vinylidene fluoride) (90:5:5 in w/w/w) was molded on a Ni grid, which was placed on a Teflon substrate and employed as cathode. The cell was filled with 30 wt % of NaOH or KOH electrolyte. The schematic structure of the coin-type cell was shown in Figure S4, Supporting Information.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 or Bruker AVANCE 600 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectra were obtained using a JASCO FT-IR 410 spectrometer using potassium bromide pellets. Molecular weight measurements were done by gel permeation chromatography using TOSOH HLC 8220 instrument with $CHCl_3$ as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. Two parallel analyses were performed for each sample. Mass spectra were obtained using a JMS-SX102A or Shimadzu GCMS-QP5050 spectrometer. Thermal analyses were performed using a Seiko DSC220C and TG/DTA 220 thermal analyzer under nitrogen.

Synthesis. 2-Vinylanthraquinone was synthesized by two steps from 2-aminoanthraquinone via the Stille coupling reaction as follows. See Supporting Information for the details of the reagents.

*2-Iodoanthraquinone (**2**).* Sulfuric acid (20 g, 20 mmol) and $NaNO_2$ (5 g, 72 mmol) were slowly added to 2-aminoanthraquinone (5 g, 22 mmol) which was stirred for 2 h at 0 °C. The mixture was poured into ice−water (1 L) and stirred for further 1 h. The resulting mixture was filtered, and KI (2.5 g, 15 mmol) was added to the filtrate which was left for 3 h at room temperature. After removal of the precipitate by filtration, KI (2.5 g, 15 mmol) was added again to the filtrate. This operation was repeated until the total amount of the added KI reached 12.5 g. All of the collected precipitate was purified by silica gel column chromatography using CH_2Cl_2 as an eluent to yield **2** (2.6 g). FAB-MS (m/z): M^+ 334.0. Found 335. IR (KBr, cm^{-1}): ^1H NMR ($CDCl_3$, 600 MHz, ppm, TMS): δ 7.81 (t, 1H), 7.82 (t, 1H), 7.99 (d, 1H), 8.15 (d, 1H), 8.30 (m, 2H), 8.65 (d, 1H).

*2-Vinylanthraquinone (**1**).* To a strictly dried vessel purged with pure argon were purged **2** (201 mg, 0.60 mmol), 2,6-di-*tert*-butyl-*p*-cresol (1.02 mg, 4.6 μmol), and $Pd(PPh_3)_4$ (32.2 mg, 28 μmol). Anhydrous benzene (4.65 mL) and tri-*n*-butylvinyltin (0.46 mg, 1.9 mmol) were added via syringe to the mixture under argon. The resulting mixture was stirred at 80 °C for 14 h. After cooling to room temperature and evaporating the solvent, the mixture was extracted with CH_2Cl_2 and purified by silica gel column chromatography using dichloromethane/hexane (1:1 in v/v) as an eluent. The obtained solid was recrystallized from benzene/methanol to yield a white needle like crystal. Yield: 62%. FAB-MS (m/z): M^+ 234.2. Found 235. IR (KBr, cm^{-1}): 1676 ($\nu_{C=O}$). Anal. Calcd for $C_{16}H_{10}O_2$: C, 81.9; H, 4.30%. Found: C, 81.9; H, 4.01%. ^1H NMR ($CDCl_3$, 600 MHz, ppm, TMS): δ 5.54 (d, 1H), 6.05 (d, 1H), 6.87 (dd, 1H), 7.80 (m, 3H), 8.28 (d, 1H) 8.32 (m, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm, TMS): δ 183.2, 182.6, 143.2, 135.4, 134.1, 134.0, 133.8, 133.6, 133.5, 132.5, 131.4, 128.3, 127.8, 127.2, 124.8, 118.4.

*Polymerization of **1***. The monomer **1** was polymerized to PVAQ using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. Polymers obtained from the reactions in toluene, benzene, and THF were all oligomers due to precipitation in the course of the polymerization. A sufficiently large molecular weight (vide infra) was accomplished by employing 1,2-dichloroethane as the solvent, in which the polymerization proceeded without any precipitation. After the polymerization, the solution was poured into methanol to precipitate the product which was purified by reprecipitation from chloroform to methanol to yield PVAQ as a light green powder. Yield: 92%. GPC (chloroform eluent, polystyrene standard): $M_w = 7.8 \times 10^4$, $M_w/M_n = 1.6$, Anal. Calcd for $C_{16}H_{10}O_2$: C, 81.9; H, 4.30%. Found: C, 80.7; H, 4.08%. ^1H NMR ($CDCl_3$, 600 MHz, ppm, TMS): δ 8.30−7.01 (br, 7H, Ar), 2.88−1.71 (br, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm, TMS): δ 183.5−179.0, 152.5−148.8, 134.9−129.7, 128.5−124.3, 45.2−37.8. DSC (10 °C/min, under argon): T_g = 160 °C. TG-DTA (10 °C/min, under argon): $T_{d10\%}$ (temperature for 10% weight loss) = 379 °C. Results of the polymerization are summarized in Table S1, Supporting Information.

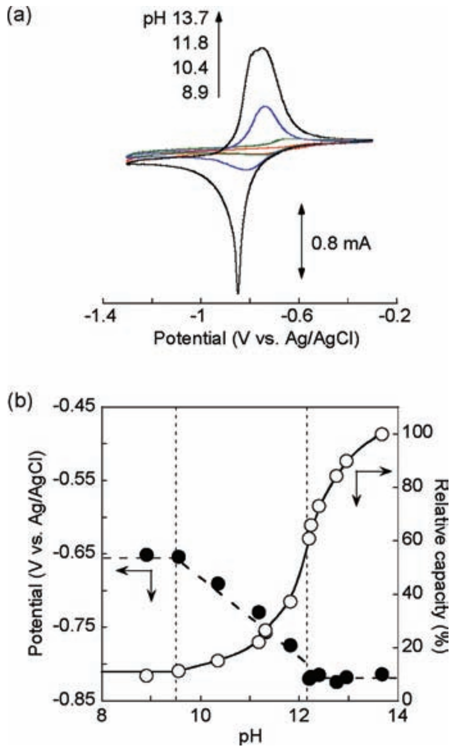

Figure 1. (a) Cyclic voltammograms of PVAQ in 2.5 M aqueous NaCl at pH 8.9 (red), 10.4 (green), 11.8 (blue), and 13.7 (black) at a scan rate of 10 mV/s. The pH values were controlled by 2.5 M NaCl and NaOH electrolyte. (b) Dependence of $E_{1/2}$ and redox capacity on the pH value. The redox capacity was calculated from the integrated area of the cyclic voltammograms.

RESULTS AND DISCUSSION

A $CHCl_3$ solution of PVAQ was dropcast on electrode and dried under the solvent vapor to form a thin layer of PVAQ. Effect of pH on the cyclic voltammogram of the polymer layer is illustrated in Figure 1a. The cyclic voltammogram was examined on a same layer by varying the pH of the bathing electrolyte. Under weakly basic conditions near pH 8, the cyclic voltammogram showed a single redox couple at $E_{1/2} = -0.65$ V, but the peak current and the redox capacity determined by integrating the redox waves were less than 10% of the theoretical density, suggesting low swellability of the layer due probably to the strong $\pi-\pi$ stacking of the pendant group in the aqueous electrolyte. On the other hand, all of the anthraquinonyl pendants underwent the redox reaction at pH 13.7. The negative shift of $E_{1/2}$ with increasing the pH (Figure 1b) indicated the destabilization of the reduced polyanion under the basic conditions with a rough magnitude of $\Delta G = -nF\Delta E = 16$ kJ/mol. At pH 13.7, the integrated redox capacity was equal to the formula weight-based density, and a highly reversible charging/discharging cycle was accomplished. Plots of the relative capacity versus the pH of the electrolyte revealed the presence of two sudden increases in the capacity at pH 9.5 and 12.1 (Figure 1b), which agreed well with the protonation constants pK_{a1} and pK_{a2} for anthraquinone expressed by eqs 1 and 2.

$$AQH_2 \rightarrow AQH^- + H^+ \qquad K_{a1} \tag{1}$$

$$AQH^- \rightarrow AQ^{2-} + H^+ \qquad K_{a2} \tag{2}$$

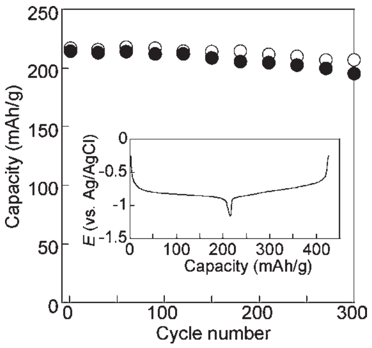

Figure 2. Cycle performance of PVAQ for charging (○) and discharging (●) capacity. Inset: charging and discharging curves of PVAQ in 30 wt % NaOH electrolyte (pH 14) at a current density of 5 A/g with a layer thickness of 80 nm.

Smith et al. reported that the reduced state of anthraquinone produced by the overall $2e^-$ reaction (AQ^{2-}) exists as an equilibrated mixture of the dianion AQ^{2-}, the protonated anion AQH^-, and hydroanthraquinone AQH_2 and that their distribution depended on the pK_a of hydroanthraquinone and the total concentration of the species.[23] In electrolytes at the pH below pK_{a2}, the species should be dominated by AQH^- and AQH_2, resulting in the low swellability and the poor redox properties due to the strong hydrogen-bonding interaction between the pendant groups. At the pH larger than pK_{a2}, AQ^{2-} becomes the major species which is free from the intersite interaction. Based on the reported values of $pK_{a1} = 9$ and $pK_{a2} = 12.05$ for the eqs 1 and 2,[23c] the fully reduced state of anthraquinone at pH 13.7 should be composed of 97.8% of AQ^{2-}, 2.2% of AQH^-, and 0.0% of AQH_2.[23] While the backbone of the polymer was still insoluble in the aqueous electrolyte, the anionic pendant groups underwent swelling to accommodate H_2O and counterions to allow the exhaustive charging/discharging cycle.

Dependence of $E_{1/2}$ on pH provided added support for the interpretation of the redox activity of the PVAQ layer. Plots of $E_{1/2}$ versus pH in Figure 1b obtained under strongly basic conditions (pH > 12.1) revealed the negative redox potential near $E_{1/2} = -0.82$ V. In the range of $9.5 < \text{pH} < 12.1$, $E_{1/2}$ shifted positively with a slope of −54 mV/pH. At pH less than 9.5, $E_{1/2}$ was almost constant near −0.65 V, which suggested the slow kinetics of the protonation in the polymer compared to the electrode reaction. The constantly narrow peak-to-peak separation (75−190 mV) in the range of pH 9.6−13.7 in Figure 1a compared to the case of hydroquinone (>300 mV) revealed the rapid self-exchange reactions between the pendant groups which was independent of the protonation equilibrium.

The charging/discharging property of the PVAQ layer was investigated in 30 wt % NaOH electrolyte. Figure 2 (inset) demonstrates the presence of a plateau region between −0.75 and −0.85 V obtained for the galvanostatic electrolysis of the PVAQ layer, which coincided with the $E_{1/2}$ of PVAQ in Figure 1a. The reversible charging/discharging capacity of 217 mAh/g was achieved with a 100% Coulomb efficiency, which agreed with the theoretical capacity of 229 mAh/g, indicating that all of the pendant anthraquinone groups underwent the reversible $2e^-$ redox reaction to AQ^{2-} without undesired reactions such as electrophilic attack, dimerization, and irreversible binding of electrolyte cations. Cycle performance of the polymer layer (Figure 2) revealed that 91% of the initial capacity was

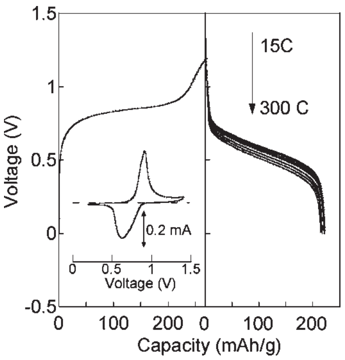

Figure 3. Charging and discharging curves of a PVAQ/air cell at various discharging rates of 3, 7, 10, 14, 20, 27, and 34 A/g (15—300 C) in 30 wt % KOH electrolyte. The PVAQ layer was 30 nm in thickness. Inset: cyclic voltammogram of the cell at a scan rate of 5 mV s^{-1}.

maintained after 300 cycles, which was strikingly robust compared to other n-type redox materials having similar high density (>200 mAh/g) such as π-conjugated[24] and nonconjugated polymers.[5,25] While the high solubility of the reduced state is usually the problem for those polymers and the polysulfide analogue,[26] no significant elution of PVAQ was observed during the repeated charging/discharging cycles.

An air battery was fabricated by employing the PVAQ anode and the oxygen cathode placed in a coin-type cell assembly containing a 30 wt % NaOH solution (see Supporting Information). The linear sweep voltammogram of the cathode showed onset of the O_2 reduction current at −0.1 V.

The cyclic voltammogram of the cell is shown in Figure 3 (inset). The charging and discharging voltages were 0.92 and 0.63 V corresponding to the potential gap between the anode and the cathode (Figure 3a). The charging curve obtained for the electrolysis at 3 A/g (15 C) showed a plateau voltage near 0.75 V, and the discharging curve at the same current density appeared near 0.5 V with the Coulomb efficiency of 91% (Figure 3), demonstrating the reversible charge storage property of the cell. The rate performance of the discharging process is shown in Figure 3. The cell exhibited a small voltage drop but kept the discharging capacity of 214 mAh/g which was 93% of the theoretical capacity even at a rapid discharging of 34 A/g (150 C) which corresponded to the full discharging within 24 s. The discharging capacity was maintained for 500 cycles (Figure S3, Supporting Information). It may be noted that once the electrolyte was degassed by argon before the fabrication process, the cell operated without additional supply of O_2 during 500 cycles, which suggested the possibility of fabricating air batteries in a closed system. Exposure of the cell to O_2 always brings about the unfavorable possibility of the autoxidation of the reduced polyanion through the cathode, so that one usually has to consider the use of O_2-blocking electrolyte layer. The preliminarily established mass balance for AQ^{2-} with the amount of O_2, which is produced by the oxidation of OH^- during the initial charging, supported the effectiveness of the test cell (Figure S4, Supporting Information) which accomplished more than 500 charging/discharging cycles. This stability may also result from the fact that O_2 is sparingly soluble in the aqueous electrolyte and effectively consumed on the hydrophobic surface of the cathode. Exploring the electrode configuration to optimize the cell performance is the topic of our continuous investigation.

■ CONCLUSION

The radical polymerization of 2-vinylanthraquinone in 1,2-dichloroethane yielded PVAQ with a sufficiently high molecular weight to allow application to organic anode-active materials that must be insoluble but swellable and equilibrated in electrolyte solutions. The amorphous PVAQ layer underwent redox reaction in aqueous electrolytes, which allowed the pursuit of the electrochemistry of anthraquinone in H_2O. The robustness of the anthraquinonyl skeleton and the ion-permeating properties of the polymer layer were demonstrated by the fully redox-active pendant groups to allow the exhaustive $2e^-$ charging per repeating unit at the negative potential near −0.85 V for 300 cycles. The swelling property of the polymer depended on pH, which offered a clear insight into the solvation of AQ^{2-} in the polymer matrix. The PVAQ layer was employed as the anode-active material with the highest charging/discharging density to fabricate the first rechargeable polymer/air battery, which accomplished the large energy density of 123 mWh/g by virtue of the relatively large output voltage and the use of O_2 as the external cathode-active material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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