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Received 00th January 20xx, Accepted 00th January 20xx **Storage Capability in Rechargeable Acidic Polymer-air Batteries** Kouki Oka,^a Shuhei Furukawa,^a Saki Murao,^a Tatsuya Oka,^a Hiroyuki Nishide^{a,b} and Kenichi Oyaizu

Poly(dihydroxybenzoquinone): Its High-density and Robust Charge

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A rechargeable acidic polymer-air battery was firstly fabricated with poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene) (PDBM) as the anode, the conventional Pt/C cathode catalyst, and acidic aqueous electrolyte (pH 1). This battery yielded a high discharging capacity of 349 mAh/g_{polymer} with a long-lifetime of >500 cycles and high rate capabilities (up to 10 C).

Recently, electrochemical energy storage devices have been intensively pursued for the future renewable energy-based society, to buffer the unpredictable energy generation, to facilitate the efficient use of the renewable energy sources, and to reduce the environmental impact of device materials¹⁻⁷. In spite of the great success of lithium-ion batteries^{8, 9}, aqueous metal-air batteries have gained revived interest to achieve much larger energy density for the increasing demand of electricity consumption and lower environmental burden^{4,} ^{10, 11}. Aqueous metal-air batteries combine the design features of both conventional batteries and fuel cells ¹⁰, and are fabricated with a metal anode and an air-breathing cathode in a proper aqueous electrolyte. While primary Zn-air batteries are commercialized, the rechargeable air batteries are still under development due to the low cycle performance as a result of the formation of dendrites on the metal anodes^{4, 10, 12}. In addition, a very basic aqueous solution (e.g., 6-7 M KOH aqueous solution) is usually used as an electrolyte to achieve the optimum ionic conductivity¹³. The batteries often suffer from the carbonate clogging problem, which arises from the reaction of CO₂ in the air⁴.

Organic materials, with their inexpensive, abundant and readily available building blocks and tunable or designable properties, have been proposed as replacements for inorganic electrode-active materials¹⁴⁻¹⁷. Especially, organic redox polymers have progressed significantly, which are composed of redox-active groups as repeating units and are characterized by high charge transport and storage capabilities based on

their densely populated redox sites¹⁶⁻¹⁹. These redox polymers have been applied in sensors²⁰, electrochromic displays²¹, solar cells²²⁻²⁴, and also in rechargeable devices as anode- and cathode-active materials^{6, 25-33}. They are light-weight, flexible, moldable, and are easily processed by wet-fabrication.

Previously, we reported anthraquinone polymers as an anodeactive material for rechargeable air batteries^{30, 31}. The use of redox polymers, instead of metals, released the rechargeable air batteries from the dendrite problem and reduced the environmental impact by virtue of the heavy atom-free process. However, the carbonate clogging problem still remains due to the use of the strongly basic 10 M NaOH aqueous solution as the electrolyte. It is desirable that the rechargeable air batteries are composed of organic redox polymers and neutral or acidic electrolyte. Fortunately, bifunctional air electrodes for acidic aqueous electrolyte have been aggressively investigated for unitized regenerative proton exchange membrane fuel cells^{34, 35}.

In the current work, we focused on 2,5-dihydroxy-1,4benzoquinone (DHBQ), which is the major survivor of the bleaching treatment of cellulose products³⁶. DHBQ is readily formed from the breakdown of cellulose products and exhibits high resistance toward oxidants such as hydrogen peroxide, ozone, and oxygen by virtue of resonance stabilization³⁶. DHBQ undergoes redox reaction in basic aqueous electrolyte and organic electrolyte, and thus DHBQ and its polymer have been investigated as the electrode-active material for alkaline aqueous redox-flow, lithium, and sodium-ion batteries³⁷⁻⁴⁰. Aziz and coworkers revealed a two-electron, two-proton redox process of DHBQ in acidic aqueous solution³⁷. However, there have been no reports on the detailed electrochemical characteristics in acidic aqueous solution and performance in rechargeable air batteries. The polymeric extension of DHBQ and its electrochemical properties in acidic aqueous solution are described herein along with the molecular design of the anode-active redox polymer toward the fabrication of a rechargeable acidic polymer-air battery.

The cyclic voltammogram of DHBQ in acidic aqueous electrolyte (pH 1), shown in Figure 1, is dominated by the chemically reversible hydroquinone/quinone redox conversion peak centered at 0.2 V vs. Ag/AgCl. This peak has previously been assigned to the 2e⁻/2H⁺ redox conversion (see Figure 1

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Inset), and as expected the peak shows a linear negative shift of the formal potential with increasing pH ³⁷.



Figure 1. Cyclic voltammogram of 1 mM DHBQ in acidic aqueous electrolyte (pH 1) at a scan rate of 10 mV/s. Inset: Redox reaction of DHBQ.

The redox interconversion between quinone (Q) and hydroquinone (H₂Q) utilizes proton coupled electron transfer (PCET) in transferring redox equivalents with the transfer of both electrons and protons, to avoid high-energy intermediates ⁴¹⁻⁴⁵. From the previous literature ^{41, 44, 45}, the mechanical details of the electrochemical reduction from Q to H₂Q at pH 1 could be estimated: 1. The reduction from Q to semiquinone (HQ⁻) occurs by electron transfer followed by proton transfer. 2. HQ⁻ is highly unstable towards disproportionation to be Q and H₂Q. It should be noted that the interpretation of the Q/H₂Q interconversion is typically complicated by adsorption and mass-transfer effects.

The heterogeneous electron-transfer rate constant (k^0) of DHBQ was estimated using plots of the peak current and the square root of the sweep rate (the Nicholson method ⁴⁶) (Figure S1). The diffusion coefficient (*D*) of the reactant was determined from the diffusion-limited current using a rotating disc electrode (Figure S2). The k^0 and *D* values of DHBQ were 1.2 $\times 10^{-2}$ cm s⁻¹ and 4.1 $\times 10^{-5}$ cm² s⁻¹, respectively, which were similar to those of other typical redox molecules, such as anthraquinones and viologens ⁶, ³⁷, ⁴⁷, ⁴⁸. These kinetic results indicate that the charge-transfer from a current collector to DHBQ is sufficiently rapid.

We anticipated that the DHBQ unit with a one-step twoelectron reduction and fast electrode kinetics could be used as an electrode-active organic material with a high capacity and plateau output voltage. We designed a compact polymer via a simple polymerization method. Simple addition condensation of DHBQ yielded RDBM (Eigure 2a) ^{39, 40}. Cottrell plots were obtained 9/Difference the chronoamperogram of the PDBM layer over the potential range of 0.9 to 0.1 V (Figure 2b). In the region of pH around 1 -2, the electron exchange reactions tended to occur rather than the disproportionation because of the low concentration and instability of the semiquinone ⁴⁹. Since the reduction of DHBQ groups in the polymer layer was accompanied by the incorporation of protons that diffuse through the layer to restore electrical neutrality, the current observed in the experiment is likely limited by proton diffusion, or the proton diffusion should be of the same order of magnitude as the estimated electron exchange rates⁴⁹. From the linearity of the Cottrell plots (current density vs $t^{-1/2}$), at the early stage of the electrolysis, diffusion-limited behavior was observed and the diffusion coefficient for the diffusion of charge within the polymer layer by the electron self exchange was determined from the slope of the plots. The density of the original polymer was estimated to be 1 g/cm³ and the swelling degree for water was estimated to be 1.26 (See Supporting Information). The diffusion coefficient of $D = 3.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ was used to calculate the rate constant for the



Figure 2. a) Synthesis of PDBM. b) Chronoamperometric Cottrell plots for the cast layer of PDBM with the thickness of 10 nm in acidic aqueous solution (pH 1). Inset: Current decay of PFBM after application of potential (0 V vs. Ag/AgCl). c) Schematic image of proton exchange reaction in the polymer layer.



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Figure 3. a) Cyclic voltammogram of the PDBM/SWNT composite electrode in acidic aqueous solution (pH 1) at a scan rate of in mV/s. b) The charging (black) and discharging (red) curves of the battery at 10 C. c) Discharging curves of the bat terms at 10 C. c) Discharging curves of the battery at 10



Figure 4. a) Schematic image of the polymer-air secondary battery (charging). b) Schematic image of the battery (discharging). c) The charging (black) and discharging (red) curves of PDBM/air battery at 5 C. Inset: Capacity retention for 100 cycles upon galvanostatic charge and discharge of the battery at 10 C. d) Discharging curves of the battery at various discharging rates of 5, 10, 15, 20, and 30 C.

electron self-exchange reaction $k_{ex} = 1.1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ according to the relation $D = k_{ex}\delta^2 C/6$, where C and δ are the redox site concentration in the layer and the distance at the time of the electron (or proton) transfer approximated by $(N_A C)^{-1/3}$, respectively³³. These values were similar to those previously determined for redox polymers developed for facile charge storage such as anthraquinone polymers ^{30, 31}, indicating the fast electron (or proton) transport characteristics of the PDBM layer (Figure 2b). This result revealed the applicability of the PDBM anode to the thin-film rechargeable devices, using only a small amount of the current collector material.

PDBM was coated on a glassy carbon plate with a thickness of ca. 10 μ m in the presence of a small amount (20 wt%) of single-walled carbon nanotube (SWNT)50 as the conductive additive. The PDBM electrode displayed a reversible redox response at 0.2 V vs. Ag/AgCl (Figure 3a). Reducing-oxidizing or charging-discharging curves of the PDBM electrode exhibited a plateau voltage at 0.2 V, and their coulombic efficiencies (the ratio of discharging vs. charging capacity) were nearly 100% (Figure 3b). The capacity of the PDBM electrode was 352 mAh/g_{polymer}, suggesting that almost all of the DHBQ moieties contributed to charge storage (the theoretical capacity of PDBM was calculated to be 352 mAh/g_{polymer}). Cycle performance of the PDBM electrode (Figure 3b Inset) revealed that 96% of the initial capacity was maintained after 100 cycles, which was robust compared to other n-type redox materials having a similar high density (>200 mAh/g_{\text{polymer}}), such as $\pi\text{-}$ conjugated and nonconjugated redox polymers ^{19, 51}. The rate performance of the discharging process is shown in Figure 3c. The PDBM electrode exhibited a small voltage drop but kept the full discharging capacity of 352 $mAh/g_{polymer}$ which was almost 100% of the theoretical capacity even at a rapid discharging of 10 C which corresponded to the full discharging within 360 s. Furthermore, the cell kept the high discharging capacity of 250 mAh/g_{polymer} (85% of the theoretical capacity) even at a rapid discharging of 60 C. These results clearly demonstrated that PDBM was a high capacity electrode-active material with the redox potential at 0.2 V vs. Ag/AgCl.

A rechargeable acidic polymer-air battery was fabricated with the PDBM electrode as the anode, the conventional Pt/C

cathode catalyst, and acidic aqueous electrolyte (pH 1). (Figure 4a and 4b). The charging-discharging curves of the battery at 5 C exhibited a plateau voltage at 0.5 V and their coulombic efficiencies were >99%. (Figure 4c), demonstrating the reversible charge storage property of the cell. The capacity for the anode used in the battery was 349 mAh/g_{polymer}, suggesting that almost all of the DHBQ moieties contributed to charge storage. The rate performance of the discharging process is shown in Figure 4d. The battery kept the almost full discharging capacity of 348 mAh/g_{polymer} even at a rapid discharging of 10 C which corresponded to the full discharging within 360 s. Furthermore, the battery kept the discharging capacity of 209 mAh/g_{polymer} (60% of the theoretical capacity) even at a rapid discharging of 30 C. The high capacities of 93% after 100 charging-discharging cycles and 88% after 500 cycles were still maintained (Figure 4d), which demonstrated the long-life ability of the rechargeable acidic polymer-air battery.

Conclusions

PDBM was prepared via simple addition condensation, and was characterized as an anode-active material in acidic aqueous electrolyte (pH 1). The polymer displayed a reversible redox response at 0.2 V vs. Ag/AgCl, and showed remarkably high capacity (>300 mAh/g_{polymer}) and good cycle performance (>500 cycles). For the first time, a rechargeable acidic polymerair battery was fabricated with a PDBM anode, an air cathode, and acidic aqueous electrolyte (pH 1) displayed reversible charging-discharging curves at an output voltage of 0.5 V and the active part of the anode showed a moderate energy density of 172 mWh/ganode. In future studies, by developing polymeric anode-active materials, the fabrication of the rechargeable acidic polymer-air battery with a high voltage of ~1.5 V and a higher energy density will be pursued. Furthermore, exploring the catalyst for air electrode^{34, 35, 52} should enable us to fabricate a rechargeable acidic polymer-air battery made from abundant sources.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

- 1. Z. Yang, J. Zhang, M. C. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon and J. Liu, *Chem. Rev.*, 2011, **111**, 3577-3613.
- 2. J. Lu, L. Li, J. B. Park, Y. K. Sun, F. Wu and K. Amine, *Chem. Rev.*, 2014, **114**, 5611-5640.
- 3. M. R. Palacin and A. de Guibert, *Science*, 2016, **351**, 1253292.
- L. Li and A. Manthiram, *Advanced Energy Materials*, 2016,
 6.
- M. Sterby, R. Emanuelsson, X. Huang, A. Gogoll, M. Strømme and M. Sjödin, *Electrochim. Acta*, 2017, 235, 356-364.
- 6. K. Oka, R. Kato, K. Oyaizu and H. Nishide, *Adv. Funct. Mater.*, 2018, **28**.
- K. Oka, C. Strietzel, R. Emanuelsson, H. Nishide, K. Oyaizu, M. Strømme and M. Sjödin, *Electrochem. Commun.*, 2019, 105.
- M. Winter, B. Barnett and K. Xu, Chem. Rev., 2018, 118, 11433-11456.
- G. L. Zhu, C. Z. Zhao, J. Q. Huang, C. He, J. Zhang, S. Chen,
 L. Xu, H. Yuan and Q. Zhang, *Small*, 2019, **15**, e1805389.
- 10. Y. Li and J. Lu, ACS Energy Letters, 2017, **2**, 1370-1377.
- 11. J. Lu, Z. Chen, Z. Ma, F. Pan, L. A. Curtiss and K. Amine, *Nature Nanotechnology*, 2016, DOI: 10.1038/nnano.2010.207.
- 12. E. L. Dewi, K. Oyaizu, H. Nishide and E. Tsuchida, *J. Power Sources*, 2003, **115**, 149-152.
- 13. J. Zhang, Z. Zhao, Z. Xia and L. Dai, *Nat Nanotechnol*, 2015, **10**, 444-452.
- 14. H. D. Abruña, Y. Kiya and J. C. Henderson, *Physics Today*, 2008, **61**, 43-47.
- B. Huskinson, M. P. Marshak, C. Suh, S. Er, M. R. Gerhardt, C. J. Galvin, X. Chen, A. Aspuru-Guzik, R. G. Gordon and M. J. Aziz, *Nature*, 2014, **505**, 195-198.
- 16. H. Nishide and K. Oyaizu, *Science*, 2008, **319**, 737-738.
- 17. K. Oyaizu and H. Nishide, in *Conjugated Polymers*, CRC Press, 2019, pp. 587-594.
- 18. K. Oyaizu, Y. Ando, H. Konishi and H. Nishide, *J. Am. Chem. Soc.*, 2008, **130**, 14459-14461.
- K. Oyaizu and H. Nishide, *Adv. Mater.*, 2009, **21**, 2339-2344.
- 20. S. W. Thomas, 3rd, G. D. Joly and T. M. Swager, *Chem. Rev.*, 2007, **107**, 1339-1386.
- 21. P. M. Beaujuge and J. R. Reynolds, *Chem. Rev.*, 2010, **110**, 268-320.
- 22. F. Kato, A. Kikuchi, T. Okuyama, K. Oyaizu and H. Nishide, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 10177-10180.
- 23. L. Rostro, L. Galicia and B. W. Boudouris, *J. Polym. Sci., Part B: Polym. Phys.*, 2015, **53**, 311-316.
- 24. W. Okada, T. Suga, K. Oyaizu, H. Segawa and H. Nishide, ACS Applied Energy Materials, 2019, **2**, 2848-2853.
- 25. H. Nishide, S. Iwasa, Y.-J. Pu, T. Suga, K. Nakahara and M. Satoh, *Electrochim. Acta*, 2004, **50**, 827-831.

- T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu and H. Nishide Adv. Mater., 2009, 21, 1627-1630 DOI: 10.1039/D0CC00660B
- L. Åkerlund, R. Emanuelsson, S. Renault, H. Huang, D. Brandell, M. Strømme and M. Sjödin, *Advanced Energy Materials*, 2017, 7.
- 28. R. Emanuelsson, M. Sterby, M. Stromme and M. Sjodin, *J. Am. Chem. Soc.*, 2017, **139**, 4828-4834.
- 29. A. Wild, M. Strumpf, B. Häupler, M. D. Hager and U. S. Schubert, *Advanced Energy Materials*, 2017, **7**.
- T. Kawai, K. Oyaizu and H. Nishide, *Macromolecules*, 2015, 48, 2429-2434.
- W. Choi, D. Harada, K. Oyaizu and H. Nishide, J. Am. Chem. Soc., 2011, 133, 19839-19843.
- R. Kato, K. Oka, K. Yoshimasa, M. Nakajima, H. Nishide and K. Oyaizu, *Macromol. Rapid Commun.*, 2019, DOI: 10.1002/marc.201900139, e1900139.
- K. Oyaizu, W. Choi and H. Nishide, *Polym. Adv. Technol.*, 2011, **22**, 1242-1247.
- 34. M. Hunsom, D. Kaewsai and A. M. Kannan, *Int. J. Hydrogen Energy*, 2018, **43**, 21478-21501.
- J. Lee, B. Jeong and J. D. Ocon, *Current Applied Physics*, 2013, 13, 309-321.
- 36. T. Hosoya, A. French and T. Rosenau, *Mini-Reviews in Organic Chemistry*, 2013, **10**, 309-315.
- Z. Yang, L. Tong, D. P. Tabor, E. S. Beh, M.-A. Goulet, D. De Porcellinis, A. Aspuru-Guzik, R. G. Gordon and M. J. Aziz, Advanced Energy Materials, 2018, 8.
- 38. Z. Zhu, H. Li, J. Liang, Z. Tao and J. Chen, *Chem Commun* (*Camb*), 2015, **51**, 1446-1448.
- 39. T. Le Gall, K. H. Reiman, M. C. Grossel and J. R. Owen, *J. Power Sources*, 2003, **119-121**, 316-320.
- N. Oyama, T. Sarukawa, Y. Mochizuki, T. Shimomura and S. Yamaguchi, J. Power Sources, 2009, 189, 230-239.
- N. Song, C. J. Gagliardi, R. A. Binstead, M. T. Zhang, H. Thorp and T. J. Meyer, *J. Am. Chem. Soc.*, 2012, **134**, 18538-18541.
- 42. F. Muh, C. Glockner, J. Hellmich and A. Zouni, *Biochim. Biophys. Acta*, 2012, **1817**, 44-65.
- 43. P. D. Astudillo, J. Tiburcio and F. J. González, J. Electroanal. Chem., 2007, **604**, 57-64.
- 44. K. Sasaki, T. Kashimura, M. Ohura, Y. Ohsaki and N. Ohta, *J. Electrochem. Soc.*, 1990, **137**, 2437-2443.
- N. Gupta and H. Linschitz, J. Am. Chem. Soc., 1997, 119, 6384-6391.
- 46. S. Takeo, P. Yong-Jin, O. Kenichi and N. Hiroyuki, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 2203-2204.
- K. Lin, Q. Chen, M. R. Gerhardt, L. Tong, S. B. Kim, L.
 Eisenach, A. W. Valle, D. Hardee, R. G. Gordon, M. J. Aziz and M. P. Marshak, *Science*, 2015, **349**, 1529-1532.
- T. Janoschka, N. Martin, M. D. Hager and U. S. Schubert, Angew. Chem. Int. Ed. Engl., 2016, 55, 14427-14430.
 F. LAVIRON. J. Electrograph Chem
 - E. LAVIRON, J. Electroanal. Chem.
 K. Hatakevama-Sato, H. Wakamatsu, R. Kata
- 50. K. Hatakeyama-Sato, H. Wakamatsu, R. Katagiri, K. Oyaizu and H. Nishide, *Adv. Mater.*, 2018, **30**, e1800900.
- 51. S. Muench, A. Wild, C. Friebe, B. Haupler, T. Janoschka and U. S. Schubert, *Chem. Rev.*, 2016, **116**, 9438-9484.
- M. Liu, L. Wang, K. Zhao, S. Shi, Q. Shao, L. Zhang, X. Sun, Y. Zhao and J. Zhang, *Energy & Environmental Science*, 2019, DOI: 10.1039/c9ee01722d.

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A rechargeable acidic polymer-air battery was firstly fabricated, which exhibited a long-lifetime of >500 cycles and high rate capabilities.

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