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All-Solid-State Rechargeable Air Batteries Using Dihydroxybenzoquinone and Its Polymer as the Negative Electrode

Makoto Yonenaga, Yusuke Kaiwa, Kouki Oka, Kenichi Oyaizu, and Kenji Miyatake*

Abstract: A proof-of-concept study was conducted on an all-solid-state rechargeable air battery (SSAB) using redox-active 2,5-dihydroxy-1,4-benzoquinone (DHBQ) and its polymer (PDBM) and a proton-conductive polymer (Nafion). DHBQ functioned well in the redox reaction with the solid Nafion ionomer at 0.47 and 0.57 V vs. RHE, similar to that in acid aqueous solution. The resulting air battery exhibited an open circuit voltage of 0.80 V and a discharge capacity of 29.7 mAh g_{DHBQ}^{-1} at a constant current density (1 mA cm⁻²). With PDBM, the discharge capacity was much higher, $176.1 \text{ mAh } g_{\text{PDBM}}^{-1}$, because of the improved utilization of the redox-active moieties. In the rate characteristics of the SSAB-PDBM, the coulombic efficiency was 84 % at 4 C, which decreased to 66 % at 101 C. In a charge/discharge cycle test, the capacity remaining after 30 cycles was 44 %, which was able to be significantly improved, to 78%, by tuning the Nafion composition in the negative electrode.

Batteries with high capacity, durability, environmental compatibility, and low cost are in great demand.^[1] Compared to the existing, commercially available secondary batteries, including lead-acid batteries, nickel-cadmium batteries, and lithium-ion batteries,^[2] air batteries using oxygen from ambient air as an active material in the positive electrode have generated great interest due to their potentially high

[*] M. Yonenaga, Prof. Dr. K. Miyatake Clean Energy research Center, Fuel Cell Nanomaterials Center, University of Yamanashi 4 Takeda, Kofu, Yamanashi 400-8510 (Japan) E-mail: miyatake@yamanashi.ac.jp Y. Kaiwa, Dr. K. Oka, Prof. Dr. K. Oyaizu, Prof. Dr. K. Miyatake Department of Applied Chemistry, Research Institute for Science and Engineering, Waseda University Tokyo 169-8555 (Japan) Dr. K. Oka Current address: Center for Future Innovation (CFI) and Department of Applied Chemistry, Graduate School of Engineering, Osaka University Osaka 565-0871 (Japan) 🕤 © 2023 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used

energy density.^[3] For typical air batteries, metals such as Li, Ca, Al, Mg, Cd, and Zn have been used as active materials for the negative electrodes. Among these, Li-air and Zn-air batteries have been most actively studied.^[4] For example, a recent study revealed that a rechargeable Li-air battery using GaO_x/Li_xLM/LiM exhibited a maximum capacity of ca. 1100 mAhg⁻¹, a coulombic efficiency of 100%, and a capacity of 70% remaining after 350 charge/discharge cycles at 0.2 C.^[5] A rechargeable Zn-air battery using a ZnO/C negative electrode exhibited a maximum discharge capacity of 207 mAhg⁻¹ and a coulombic efficiency of 83% without dendrite formation.^[6]

In most cases, rechargeable metal-air batteries utilize liquid electrolytes (in the above cases, lithium salts in dimethoxyethane and KOH aqueous solution, respectively) accompanied by inherent issues of high ohmic resistance, leaching and/or combustion. Furthermore, metal-air batteries often have to use protective films and separators to mitigate the dendrite formation and growth peculiar to metal materials and to avoid exposure to the atmosphere.^[4,7]

Recently, in place of metals, redox-active organic molecules have also been investigated for use as negative electrodes, in which protons or hydroxide ions participate in the redox reactions.^[8] In those previous studies, quinone- or amine-based molecules or polymers were used with acidic or basic aqueous solution. The resulting rechargeable air batteries exhibited high performance, close to the theoretical maximum capacity. The maximum capacity could be higher than ca. 200 mAhg⁻¹ with >60 000 charge/discharge cycle capability.^[9] The use of redox-active organic molecules releases rechargeable air batteries from the problems associated with metals, including dendrite formation and negative environmental impact. Nevertheless, these types of batteries still use liquid electrolytes, with their attendant safety concerns.

In the present paper, we took on the challenge of constructing an all-solid-state rechargeable air battery (SSAB) consisting of redox-active organic molecules and a proton-conductive polymer electrolyte (Nafion). To the best of our knowledge, there have not been such air batteries using organic electrodes and acidic polymer without liquid electrolyte. 2,5-Dihydroxy-1,4-benzoquinone (DHBQ) and poly(2,5-dihydroxy-1,4-benzoquinone-3,6-methylene)

(PDBM) were chosen as the negative electrode active materials since they exhibit stable and reversible redox reaction in acidic conditions. Nafion is the most common proton-conductive membrane, with a conductivity of up to $10^{-1} \,\mathrm{S \, cm^{-1}}$ in humidified air. Charge/discharge performance,

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for commercial purposes.

rate characteristics, and cyclability of the SSABs were investigated.

Figure 1 depicts detailed configuration of the all solidstate air battery used in the present study (see Figure S1 for photos). For the oxygen electrode, a gas diffusion electrode (GDE) attached to the membrane, typically used for polymer electrolyte membrane fuel cells (PEMFCs), was adopted. A minor difference was the separator made of platinum-coated titanium plate for anti-corrosion at high potential. The negative electrode containing the redox active organic molecules was directly coated onto the protonconductive solid polymer electrolyte (Nafion) membrane. Another GDE with reference hydrogen electrode (RHE) was attached onto the Nafion membrane through the gas diffusion layer to measure each electrode potential, independently.

Figure 2 shows the CV curves of the negative electrodes with solid polymer electrolyte in SSAB-DHBQ and SSAB-PDBM. DHBQ is known to exhibit reversible redox peak at 0.2 V vs. Ag/AgCl (or ca. 0.46 V vs. RHE) in sulfuric acid aqueous solution (pH = 1) based on two-electron hydroquinone/quinone redox reaction. In the present case, DHBQ exhibited a set of two broad peaks at ca. 0.47 and 0.57 V vs RHE, indicative of two-step one-electron redox reaction with the solid electrolyte (Figure 2a). From the electric charge of the oxidation peak, the utilization of DHBQ (=



Figure 1. Configuration of the all solid-state air battery containing redox-active organic negative electrode, GDEs (for oxygen electrode and RHE), and solid polymer electrolyte (Nafion) membrane. GDE and GDL refer to gas diffusion electrode and gas diffusion layer, respectively.



Figure 2. Cyclic voltammograms (CVs) of redox-active organic negative electrodes in a) SSAB-DHBQ and b) SSAB-PDBM before charge/ discharge cycles (solid line) and after charge/discharge cycles (dashed line). The CVs were obtained at 40 °C at a scan rate of 20 mV s⁻¹ supplying fully humidified hydrogen to the positive electrode at 100 ml min⁻¹ and no gases to the negative electrode, respectively.

electric charge divided by the moles of DHBQ loaded in the electrode assuming the two-electron redox reaction) was merely 5.7%. With the polymeric (PDBM) electrode, similar but more distinct redox peaks were observed at similar potentials (Figure 2b), where the utilization of PDBM was as high as 45.8%. Much higher utilization with PDBM than that with DHBQ is probably because the polymeric PDBM would have better affinity with the polymeric proton conductive electrolyte achieving better-connected and more efficient triple phase boundary with the electron conductive carbon in the electrode (this issue is discussed below with Figure 4c and d).

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Figure 3 shows the configuration and cell reactions of SSAB-DHBQ. In order to minimize the overpotential at the oxygen electrode and the ohmic resistance of Nafion membrane, the system was maintained at 100% relative humidity (RH) during the charge/discharge experiments.

Figure 4a shows charging curves of SSAB-DHBQ and SSAB-PDBM cells at a constant current density of 0.227 mA cm⁻² which corresponded to 7.63 C for SSAB-DHBQ and 1.09 C for SSAB-PDBM, respectively. During the charging, the potential of the oxygen electrode increased rapidly from ca. 0.70 V to ca. 0.90 V and then gradually to over 1.10 V, where the water oxidation reaction took place to produce oxygen (Figure 4b). Accordingly, the potential of the redox active organic electrode decreased from ca. 0.70 V to 0.1 V reducing DHBQ and PDBM (Figure 4c). The charging time was much longer for SSAB-PDBM than for SSAB-DHBQ. The charge capacity was 29.7 mAhg_{DHBO}⁻¹ for SSAB-DHBQ and 208 mAh g_{PDBM}^{-1} for SSAB-PDBM, respectively. Based on the loading amount of the redox active molecules in the electrode, the utilization of DHBQ and PDBM for the charging was 8 % and 59 %, respectively, assuming the two-electron redox reaction. It is noted the



Figure 3. Simplified cell configuration and cell reactions of SSAB-DHBQ. The temperature and humidity were set at 40 $^{\circ}$ C and 100% RH, respectively, throughout the experiment.

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Figure 4. Charging curves of SSAB-DHBQ and SSAB-PDBM at 0.227 mA cm⁻². a) cell voltage, b) oxygen electrode potential, c) redox active electrode potential and d) ohmic resistance. The curves were obtained at 40 °C and 100% RH.

redox active polymer, PDBM, participated much more in the redox reaction than the small molecule DHBQ presumably because PDBM and proton-conductive polymer Nafion would have formed better-connected ionic and electronic channels with carbon. The hypothesis was supported by smaller ohmic resistance of SSAB-PDBM ($0.22 \,\Omega \text{cm}^2$) than that of SSAB-DHBQ ($0.51 \,\Omega \text{cm}^2$) (Figure 4d).

When discharging, the cell voltage was initially ca. 0.80 V (OCV) and decreased with time at a constant current density of 1 mA cm⁻² (Figure 5a). The discharging time was much longer for SSAB-PDBM than for SSAB-DHBQ, similar to the charging time. For SSAB-DHBQ, since the oxygen electrode potential was nearly constant at 0.89 V after the initial drop from 1.02 V (Figure 5b), the cell voltage was mostly dominated by the DHBQ electrode. In fact, the

n electrode potential (V vs. RHE) 9.0 8.0 7.0 7.0 8.0 included) (V) SAB-DHBC 1.0 0.8 (IR 0.6 voltage (0.4 Oxygen SSAB-DHBQ SSAB-PDBM 0.2 0.2 Cell 0 100 150 250 100 150 200 0 50 0 50 Discha 250 Discha ge can ty (mAh g⁻¹) city (mAh g⁻¹) c (1.2 □ (1.2 □ (1.0) □ (1.0) d 1.2 resistance ($\Omega~\text{cm}^2)$ --- SSAB-DHBQ 1.0 0.1 . S 8.0 ≤ 28: 8.0 ≤ 0.8 a potential 9 potential 9 0.0 0.6 0.4 Redox octrode F Ohmic SSAB-DHBQ SSAB-PDBM 0.2 0 50 100 150 200 Discharge capacity (mAh g ⁻¹) 50 100 150 200 Discharge capacity (mAh g⁻¹) 200 250 250

Figure 5. Discharging curves of SSAB-DHBQ and SSAB-PDBM at 1 mA cm⁻². a) cell voltage, b) oxygen electrode potential, c) redox active electrode potential and d) ohmic resistance. The curves were obtained at 40 °C and 100% RH.

potential of the DHBQ electrode increased from 0.24 V to 0.89 V with the discharging time (Figure 5c). For SSAB-PDBM, although both electrode potentials behaved similarly, the oxygen electrode became constant at somewhat lower potential (ca. 0.76 V). The increase in the negative electrode was much smaller for PDBM than for DHBQ. The ohmic resistance was constant for both cells during discharging at the same values as that during the charging (Figure 5d).

Then, the rate characteristic of the SSAB-PDBM was investigated. Figures 6 shows discharging curves at different rate, where the charging rate was constant at 4 C $(0.705\ mA\ cm^{-2})$ for all cases (see Figure S2 for the charging curves). The OCV was ca. 0.8 V. At any discharging rate from 4 C to 101 C, the initial loss in the cell voltage from OCV to ca. 0.5 V was similar (Figure 6a). The discharge capacity was 146.1 mAh $g_{\text{PDBM}}{}^{-1}$ at 4 C and decreased with the discharging rate to $115.6 \text{ mAh} g_{\text{PDBM}}^{-1}$ at 101 C. The oxygen electrode potential decreased faster at higher discharging rate (Figure 6b) and the redox active electrode potential was much less dependent on the discharging rate (Figure 6c), indicating that the oxygen reduction reaction became sluggish probably because the product water became liquid at 40°C and was not effectively exhausted from the electrode at high discharging rate (so-called flooding) resulting in the insufficient supply of oxygen. The coulombic efficiency was substantially high (84%) at 4 C and decreased gradually to 66 % at 101 C without significant drop (Figure 6d). Since the oxygen electrode was exposed to high potential (>1.1 V) during the charging, the Pt/C catalysts might have degraded to cause deteriorated catalytic activity.

Cycle test of SSAB-PDBM was performed at 15 C (2.268 mA cm⁻²). As shown in Figure 7a and Figure 8, the discharge capacity was initially 109.6 mAh g_{PDBM}^{-1} and decreased to 47.9 mAh g_{PDBM}^{-1} after 30 cycles where the



Figure 6. Discharging curves and coulombic efficiency of SSAB-PDBM at 4 (0.705), 10(1.763), 20(3.528), 40(7.054), 61(10.58), 81(14.11), and 101 (17.63) C (mA cm⁻²). a) cell voltage, b) oxygen electrode potential, c) redox active electrode potential and d) coulombic efficiency. The curves were obtained at 40°C and 100% RH.

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Figure 7. Discharging curves of SSAB-PDBM during cycle test at 15 C (2.268 mA cm⁻²). a) cell voltage, b) oxygen electrode potential and c) redox active electrode potential. The curves were obtained at 40 °C and 100 % RH.



Figure 8. Change of the discharge capacity (black) and Coulombic efficiency (red) of SSAB-PDBM at 15 C (2.268 mAcm⁻²) during the cycle test.

capacity remaining was 44 % (see Figure S3 for the charging curves). The decrease of the capacity was due both to the oxygen (Figure 7b) and PDBM electrodes (Figure 7c). The oxygen electrode was probably deteriorated during the repeated charging where the potential exceeded over 1.50 V vs. RHE causing the corrosion of the carbon support. To identify the cause of the performance loss in the PDBM electrode, the CV curve was measured after 30 cycles. As shown in Figure 2b, the redox peaks of the PDBM became smaller with the utilization of PDBM from 46% (initial) to 13% (after 30 cycles). Some PDBM molecules might have become electrochemically inactive probably because of leaching out from the triple phase boundary during the cycle tests since PDBM is a highly hydrophilic molecule with four hydroxy groups per phenylene unit in the reduced form. Although the capacity decreased, the coulombic efficiency was initially 77 % and was kept relatively high at 61 % after 30 cycles (Figure 8), indicating that the remaining PDBM molecules participated well in the redox reactions.

To improve cyclability of the SSAB-PDBM, the mass ratio of Nafion ionomer to the carbon (I/C) in the PDBM electrode was increased from 0.7 to 2.0 aiming at making more PDBM electrochemically active and preserving the polymer in the active site for longer time. As shown in Figures 9a and 10, the initial discharge capacity was



Figure 9. Discharging curves of SSAB-PDBM (I/C=2.0) during cycle test at 15 C (2.967 mA cm⁻²). a) cell voltage, b) oxygen electrode potential and c) redox active electrode potential. The curves were obtained at 40°C and 100% RH.



Figure 10. Change of the discharge capacity (black) and Coulombic efficiency (red) of SSAB-PDBM (I/C=2.0) at 15 C (2.967 mAcm⁻²) during the cycle test.

183.8 mAh g_{PDBM}^{-1} and much higher than that of the abovementioned cell with I/C = 0.7 (see Figure S4 for the charging curves). The discharge capacity decreased to 143.4 mAh g_{PDBM}^{-1} after 30 cycles with capacity remaining of 78% which was also much higher than that (44%) of the cell with I/C=0.7. Although the oxygen electrode was deteriorated similarly during the cycle test (Figure 9b), the PDBM electrode was rather stable for 30 cycles with minor changes in the discharging curves (Figure 9c). The coulombic efficiency was initially 83% and decreased to 64% (Figure 10), similar to that of the cell with I/C=0.7. The results suggest that the increased Nafion ionomer in the PDBM electrode was effective in improving the performance and durability of the negative electrode and accordingly, those of the SSAB-PDBM. After the test, the catalyst coated membrane was recovered from the cell and subjected to the SEM analyses. The surface images of the PDBM electrode and the cross-sectional images did not provide evidences of structural and morphological degradation (Figure S5).

As a conclusion, we have successfully operated an allsolid-state rechargeable air battery (SSAB) composed of redox-active organic molecules as the negative electrode, a proton-conductive polymer as the electrolyte, and an oxygen-reducing, diffusion-type positive electrode. Unlike typiGDCh

cal air batteries using a metallic negative electrode and an organic liquid electrolyte, the SSAB did not deteriorate in the presence of water and oxygen (on the contrary, water is essential for the redox reaction and proton conduction). Compared to the small redox-active molecule (2,5-dihydroxy-1,4-benzoquinone (DHBQ)), its polymeric counterpart (PDBM) functioned better as the negative electrode, with higher utilization. Accordingly, the respective discharge capacities at a constant current density (1 mA cm⁻²) were 29.7 $mAh g_{DHBQ}^{-1}$ for SSAB-DHBQ and 176.1 $mAh g_{PDBM}^{-1}$ for SSAB-PDBM. In examining the rate characteristics of the SSAB-PDBM, even though the PDBM electrode potential was not dependent on the discharge rate, the oxygen electrode potential decreased faster with increasing discharge rate. Thus, the coulombic efficiency gradually decreased from 84 % at 4 C to 66 % at 101 C. The charge/ discharge cyclability of the SSAB-PDBM was not very satisfactory, with a discharge capacity of only 44 % remaining after 30 cycles. The remaining capacity was able to be significantly improved, to 78%, by tuning the negative electrode composition (by increasing the proton-conductive polymer content). Thus, while the present study proved the concept of the SSAB experimentally, its performance was still somewhat primitive. The instability of the oxygenreducing diffusion electrode and the relatively high redox potential of the organic molecules are priority issues that we plan to address in our near-future agenda.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Electrochemistry · Hydroxybenzoquinones · Ionomers · Polymer Membranes · Solid-State Air Batteries

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Solid-state Air Batteries

M. Yonenaga, Y. Kaiwa, K. Oka, K. Oyaizu, K. Miyatake* _____ e202304366

All-Solid-State Rechargeable Air Batteries Using Dihydroxybenzoquinone and Its Polymer as the Negative Electrode



All-solid-state rechargeable air battery has been achieved using a redox-active organic molecule (dihydroxybenzoquinone, DHBQ) as the negative electrode active material and a proton exchange membrane as the electrolyte. The high redox activity of DHBQ with the polymer electrolyte made the concept of the device possible and furthermore, use of polymeric DHBQ improved significantly the discharge capacity with reasonable cyclability.