Supporting Information

Electrochemical Energy Storage with an Aqueous Quinone-Air Chemistry

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Experimental Section

Sodium conductive solid state membrane (Na-SSM): Na^+-ion solid state membrane, $Na_3Zr_2Si_2PO_{12}$ (NZSP, σ = ~ 1.0 x 10^{-3} $S.cm^{-1}$), was purchased from 421 Energy Corporation (South Korea).

Preparation of anolyte and catholyte: An aqueous anolyte was prepared with 0.5 M sodium hydroxide (NaOH, Fisher Scientific) and 0.1 M hydroquinone (Fisher Scientific). An aqueous catholyte was prepared with 0.1 M H_2SO_4 (Fisher Scientific) + 0.1 M Na_2SO_4 (Fisher Scientific).

Preparation of IrO_2/Ti OER electrode: The IrO_2@TiO_2 catalyst was prepared according to a method presented in our previous literature.[1] The IrO_2 colloidal was prepared as follows. First, 0.2 mmol of K_3IrCl_6 (Fisher Scientific) and 1.0 mmol of oxalic acid ($H_2C_2O_2$, Fisher Scientific) were dissolved in 30 mL of deionized (DI) water. The pH of the mixture was adjusted to 9 – 10 by adding 5.0 mmol of K_2CO_3 (Fisher Scientific) followed by adding 20 mL of DI water. Then, the mixture was stirred at 35 °C for 10 days. A dark blue IrO_2 colloidal solution was formed. The IrO_2@Ti catalyst was prepared by an anodic deposition process with a three-electrode electrochemical cell. A piece of Ti mesh was used as the working electrode with a 1 cm × 1 cm area submerged into the IrO_2 colloidal solution. The reference and counter electrodes were, respectively, an SCE (saturated calomel electrode) and a piece of Pt mesh. A constant current of 35 µA was applied to the working electrode for 1.5 hours.

Preparation of Pt/C ORR electrode: ORR catalyst used in this study is a 40% Pt/C (40 wt. % Pt on carbon powder, supplied by Fuel Cell Store). The catalyst was dispersed in a mixture of deionized (DI) water and a certain volume of Nafion solution (5 %, DuPont®) by sonication for 15 min. The mass ratio of Nafion to the catalyst was 1 : 4 (mass ratio). The resulting ink was deposited onto a carbon fiber paper (Toray HP-60) and dried in air for 1 h at room temperature.

Characterization: The morphologies of the IrO_2@Ti catalyst and the carbon cloth (purchased from Fuel Cell Store, 1071 HCB) electrode matrix was studied with a Quanta 650 scanning electron microscope (SEM). The X-ray diffraction (XRD) patterns of the Ti mesh and the IrO_2@Ti catalyst were obtained with a Philips X-ray diffractometer equipped with CuK radiation at a scan step of 0.04 deg (^{o}). Ultraviolet-Visible (UV-Vis) spectra were collected with a Varian Cary 5000 UV-Vis-NIR Spectrophotometer.

Electrochemical experiments: Cyclic voltammetry (CV) experiments were conducted in a conventional three-electrode glass cell with a Pt mesh counter electrode and an SCE reference electrode. The working electrode was a strip of carbon paper (Toray HP-60). The CVs were collected with an Autolab PGSTAT302N potentiostat (Eco Chemie B.V.). To avoid any parasitic reactions between the hydroquinone (or diphenolate) and oxygen, all solutions were saturated with nitrogen before testing.

Quinone-air battery tests: The Quinone(alkaline) ‖ Na-SSM ‖ air(acid) cells were assembled and tested with an in-house designed cell in a layered cell mold as described in our previous publications.[1, 2] The negative electrode matrix was a piece of carbon cloth (purchased from Fuel Cell Store, 1071 HCB). The air cathodes were assembled with a dual-catalyst configuration as described in our previous publications.[1, 2] IrO_2@Ti was used as an OER electrode. The ORR electrode was prepared by spreading Pt/C nanopowder onto the carbon paper with a net Pt loading of 1.0 mg cm^{-2}. The surface area of the anode matrix, ORR electrode, and OER electrode is identially 1.0 cm^2. The NZSP membrane was used as a separator. Charge-discharge curves, as well as the polarization behavior of the cells, were recorded with an Arbin BT 2000 battery cycler. The charge and discharge data were alternatively collected with two separate channels on the Arbin instrument with a five-minute rest time between each discharge and charge cycle.

1. Li, L. J.; Manthiram, A. Long-Life, High-Voltage Acidic Zn-Air Batteries. *Adv. Energy Mater*. 2016, 6, 1502054.
2. Li, L. J.; Manthiram, A. Decoupled bifunctional air electrodes for high-performance hybrid lithium-air batteries. *Nano Energy*, 2014, 9, 94-100.

Table S1. Concentrations of diphenolate species in the anolyte of the Quinone(alkaline) ‖ Na-SSM ‖ air(acid) cell at different charge-discharge states.

	Before discharge	Half-way discharge	Full discharge	Half-way charge	Full charge
Concentration of diphenolate, M	0.100	0.058	0.015	0.059	0.100

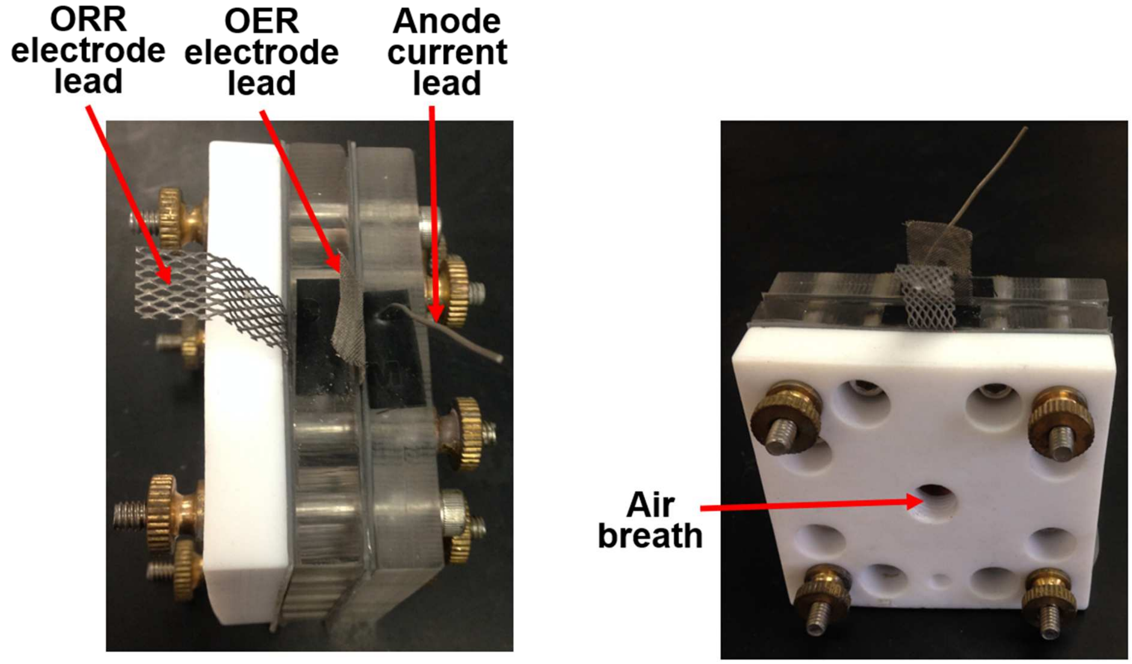

Figure S1. Picures of a quinone (alkaline) ‖ Na-SSM ‖ air (acid) cell showing the layouts of electrodes.

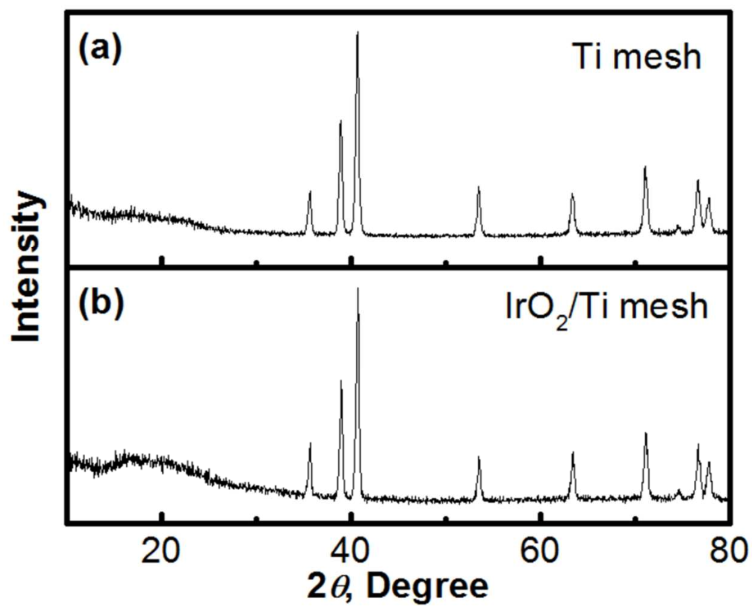

Figure S2. X-ray diffraction (XRD) patterns of (a) the titanium mesh substrate and (b) the titanium mesh supported iridium oxide (IrO_2/Ti) catalyst. There was no difference between the two samples, indicating the amorphous structure of the IrO_2 coating.

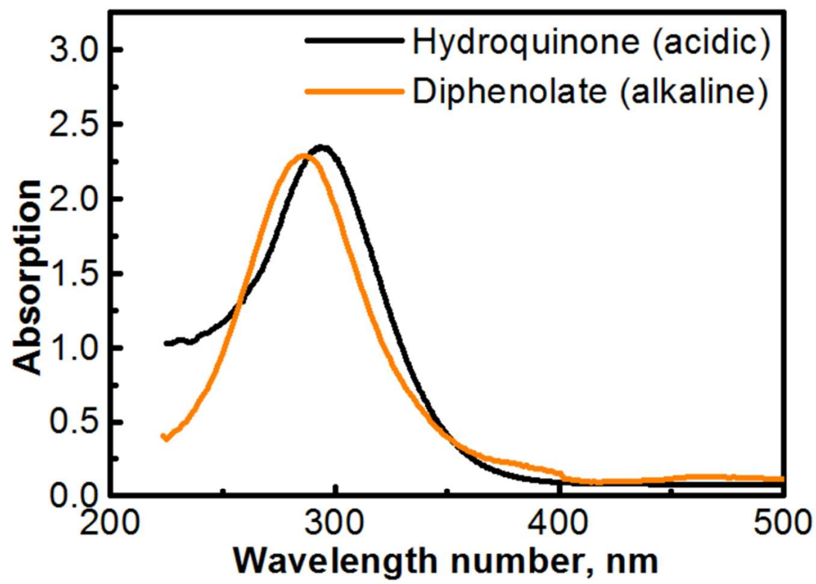

Figure S3. UV-Vis spectra of the hydroquinone in a weakly acid solution and that in an alkaline solution (existing as diphenolate).

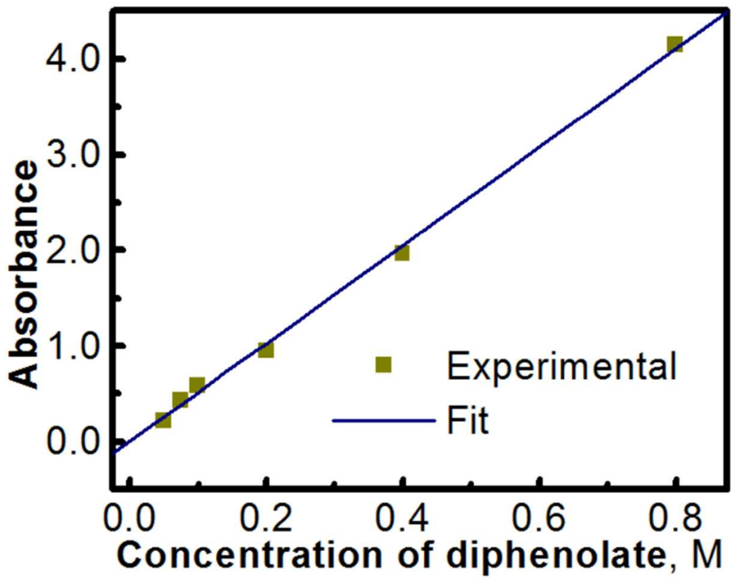

Figure S4. UV-Vis calibration curve of the diphenolate solutions.

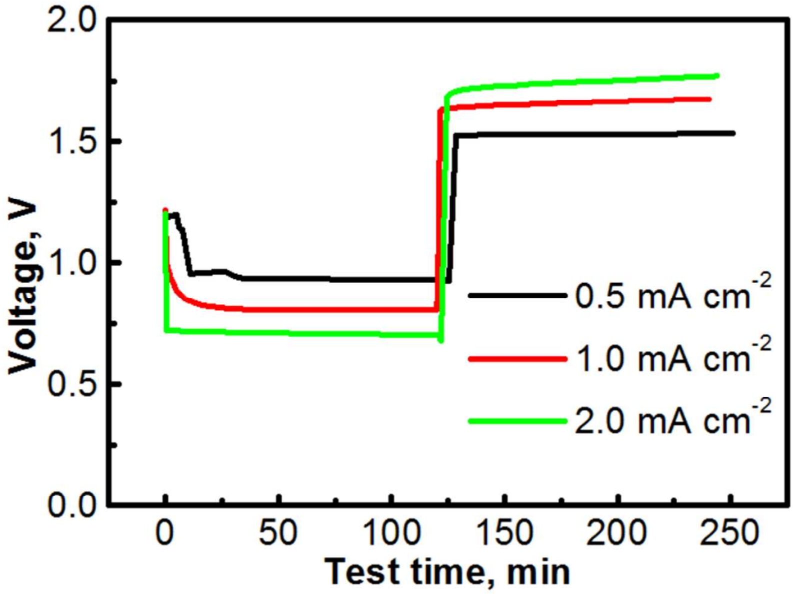

Figure S5. Polarization behavior of the Quinone(alkaline) ‖ Na-SSM ‖ air(acid) cell at different operating current densities.

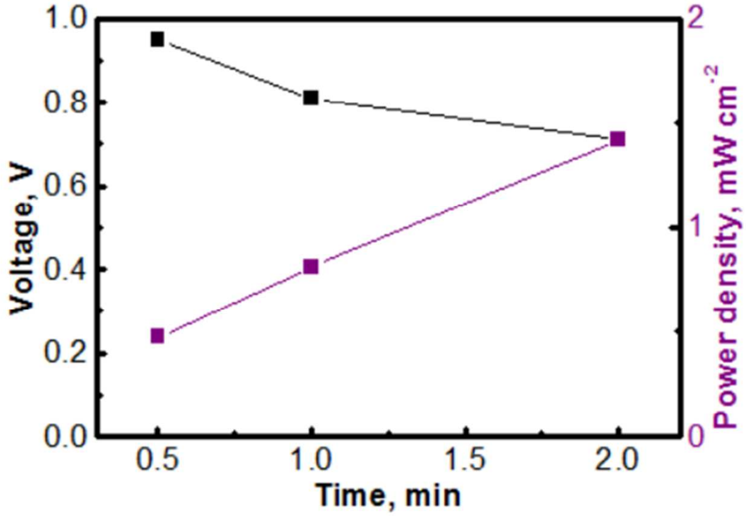

Figure S6. Discharge voltages and power densities of the Quinone(alkaline) ‖ Na-SSM ‖ air(acid) cell at different operating current densities.