Supplementary Information

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A Strategically Managed Rechargeable Battery System with a Neutral Methyl Viologen Anolyte and an Acidic Air-Cathode Enabled by a Mediator-ion Solid Electrolyte

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EXPERIMENTAL METHODS

Sodium-ion conductive solid-state electrolyte (Na-SSE) was purchased from 421 Energy Corporation (South Korea). This material exhibits an ionic conductivity of ca. 1.0 x 10^-3 S.cm^-1 at room temperature with a stoichiometric composition of Na_3Zr_2Si_2PO_12. The thickness of the Na-SSE is ca. 0.7 mm. The oxygen reduction reaction (ORR) catalyst was a 40 wt.% Pt/C (40 wt. % Pt on carbon powder) purchased from Fuel Cell Store. The powder catalyst was first dispersed in a mixture of water and Nafion solution (DuPont®). Then, the resulting slurry was deposited onto a carbon fiber paper (Toray HP-90). The catalyst loading was 2 mg cm^-2. The oxygen evolution reaction (OER) catalyst was prepared in the lab by depositing an IrO_2 colloidal on a Ti mesh substrate according to our previous report.1 The neutral anolyte used in this study was prepared with 0.1 M methyl viologen dichloride ([C_6H_7N]_2Cl_2, Sigma Aldrich) and 0.5 M Na_2SO_4 (Fisher Scientific). The acidic catholyte was prepared with 0.1 M H_3PO_4 (Fisher Scientific) and 1.0 M NaH_2PO_4 (Fisher Scientific).

The MV (neutral) \| Na-SSE \| air (acid) cells were fabricated with a layered cell mold as described in our previous report.1,2 A piece of carbon cloth (supplied by Fuel Cell Store, 1071 HCB) was used as the anode matrix. A dual-catalyst configuration was designed for the air
cathode as described in our previous report,\textsuperscript{1,2} which employs an IrO$_2$@Ti OER electrode and a Pt/C ORR electrode. The cells were fabricated with a piece of Na-SSE membrane as a separator. The areas of the anode matrix, ORR electrode, OER electrode, and the Na-SSE membrane exposed to the anolyte/catholyte are identically 1.0 cm$^2$. Discharge-charge profiles and the polarization behavior of the cells were tested with an Arbin BT 2000 instrument.

Electrochemical experiments (cyclic voltammetry, CV) were conducted in a conventional three-compartment cell with a standard SCE reference electrode and a Pt mesh counter electrode. A strip of Pt foil was used as the working electrode. The CV profiles were recorded with an Autolab PGSTAT302N potentiostat.

The morphologies of the carbon cloth matrix and the IrO$_2$@Ti catalyst were imaged with a Quanta 650 scanning electron microscope (SEM). Ultraviolet-Visible (UV-Vis) analysis was conducted on a Varian Cary 5000 UV-Vis-NIR spectrophotometer.

**Fig. S1.** (a) A picture of a piece of carbon cloth matrix purchased from Fuel Cell Store. (b) Scanning electron microscopy (SEM) image of the carbon cloth matrix.
Fig. S2. (a) Picture of a piece of a titanium mesh supported iridium oxide (IrO$_2$/Ti) catalyst. (b) Scanning electron microscopy (SEM) image of the IrO$_2$/Ti catalyst. The wire diameter of the Ti mesh is $ca.$ 100 µm. The inset shows the high-magnification image of the IrO$_2$/Ti catalyst with a small patch of the IrO$_2$ layer being intentionally scratched off in order to show the contrast between the Ti substrate and the IrO$_2$ coating.
Fig. S3. The color change of the anolyte during charging an MV (neutral) | Na-SSE | air (acid) cell. For the convenience of observation, the anolyte chamber was specially designed with a crescent-shape groove in the lower right corner. A piece of Ti mesh (alternative to the carbon cloth) was used as the anode current collector.
Fig. S4. Consecutive discharge-charge curves of the MV (neutral) | Na-SSE | air (acid) cell at current densities of (a) 0.5 mA cm$^{-2}$ and (b) 2.0 mA cm$^{-2}$.
**Fig. S5.** Scanning electron microscopy (SEM) image of a cycled (after 50 cycles) carbon cloth matrix.