Electronic Supplementary information

Hybrid Na-Air Flow Batteries using an Acidic Catholyte: Effect of the Catholyte pH on the Cell Performance

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Table S1. Calculated maximum molar concentrations of Li and Na salts

Products	Molar mass [g/mol]	Solubility in water [g/100 ml]
LiOH	23.95	12.8 (20°C)
NaOH	40.00	111 (20°C)
Li_2CO_3	73.89	1.29 (25°C)
Na_2CO_3	105.99	50.31 (29.9°C, monohydrate)

Supplementary Note 1. Calculation of theoretical energy density of hybrid Li-air and hybrid Na-air cells using an alkaline catholyte

The overall charge/discharge reactions for hybrid metal-air cells using an alkaline catholyte are expressed as

$$Li + 0.25O_2 + 0.5H_2O \leftrightarrow LiOH\ (aq)\ \text{for Li-air},$$
$$Na + 0.25O_2 + 0.5H_2O \leftrightarrow NaOH\ (aq)\ \text{for Na-air}$$

The above reactions are effective when the discharge products are soluble in the aqueous catholyte, according to the typical hybrid metal-air concept based on a highly soluble discharge product. Thus, the theoretical specific capacity (energy density) of a hybrid metal-air cell based on an alkaline catholyte is determined by the solubility of the discharge product (metal hydroxide) in water.

(i) For Li-air, considering the solubility of LiOH (12.8 g/100g H_2O at 20 °C), in order to make LiOH soluble in water, at least 10.39 mol of H_2O per 1 mol LiOH is required, as follows.

$$x = \frac{\frac{100g}{M_{H2O}}}{\frac{12.8g}{M_{LiOH}}} = \frac{100g \times 23.95g/mol}{12.8g \times 18g/mol} = 10.39$$

Thus, the overall reaction can be expressed as

$$Li + 0.25O_2 + 0.5H_2O + 10.39H_2O \leftrightarrow Li^+ + OH^- + 10.39H_2O,$$
$$Li + 0.25O_2 + 10.89H_2O \leftrightarrow Li^+ + OH^- + 10.39H_2O$$

The specific capacity (Q) including O_2 is calculated as

$$Q = \frac{n \times F}{M_{Li} + 0.25M_{O2} + 10.89M_{H2O}} = \frac{1 \times \frac{96485C}{mol}}{\frac{6.94g}{mol} + 0.25 \times \frac{32g}{mol} + 10.89 \times \frac{18g}{mol}}$$
$$= 457C/mol = 127Ah/kg$$

When the cell voltage (V) is assumed to be 3.44 V using an alkaline catholyte (pH=14), the theoretical energy density (E) including O_2 is estimated as ~437 Wh/kg.

$$E = Q \times V = 437 \text{ Wh/kg}$$

(ii) For Na-air, similarly, considering the solubility of NaOH (111 g/100g H_2O at 20 °C), at least 2 mol of H_2O per 1 mol NaOH is required to keep LiOH soluble in water.

$$x = \frac{\frac{100g}{M_{H2O}}}{\frac{111g}{M_{NaOH}}} = \frac{100g \times 40g/mol}{111g \times 18g/mol} = 2.00$$

$$Na + 0.25O_2 + 0.5H_2O + 2H_2O \leftrightarrow Na^+ + OH^- + 2H_2O$$

The specific capacity (Q) including O_2 is calculated as

$$Q = \frac{n \times F}{M_{Na} + 0.25M_{O2} + 2.5M_{H2O}} = \frac{1 \times 96485C/mol}{22.99g/mol + 0.25 \times 32g/mol + 2.5 \times 18g/mol} = 1270C/mo$$

When the cell voltage (V) is assumed to be 3.11 V using an alkaline catholyte (pH=14), the theoretical energy density (E) including O_2 is estimated as ~1098 Wh/kg.

$$E = Q \times V = 1098 \text{ Wh/kg}$$

Supplementary Note 2. Reaction of LiOH (or NaOH) (aq) with ambient CO_2 (g)

CO_2 (*g*) is absorbed by a LiOH (or NaOH) solution to form dissolved sodium carbonate (air capture process).[S1]

$2LiOH\ (aq) + CO_2\ (g) \rightarrow Li_2CO_3\ (aq) + H_2O\ (l)$
$2NaOH\ (aq) + CO_2\ (g) \rightarrow Na_2CO_3\ (aq) + H_2O\ (l)$

Supplementary Note 3. Theoretical calculation of the cell voltage of hybrid Na-air batteries using an aqueous catholyte.

The electrochemical reactions in hybrid Na-air batteries involve the redox reactions of Na^+ ions on the anode and the OER/ORR on the cathode during charge/discharge process. As described in 'Introduction', the overall reactions can be expressed according to the pH of catholyte as follows.

$4Na^+ + O_2\ (g) + 4H^+ + A^* + 4e^- \leftrightarrow Na_4\text{–}A^*\ (aq) + 2H_2O$
(based on 4-electron transfer in acidic solutions; pH<7)

$4Na^+ + O_2\ (g) + 2H_2O\ (l) + 4e^- \leftrightarrow 4NaOH\ (aq)$
(based on 4-electron transfer, in neutral and alkaline solutions; pH≥7),

where A^* and Na_4-A^* indicate the conjugate base of an acid (A) and its Na complex, respectively.

When considering the electrochemical reactions of a hybrid Na-air cell using an acidic catholyte, the half-reactions of the anode and cathode can be described as follows.

Anode: $Na^+ + e^- \leftrightarrow Na\ ;\ -2.71\ V\ vs.\ SHE$

$$e_{anode} = e^{o}_{Na^+/Na} + \frac{RT}{F} ln\left(\frac{a_{Na^+}}{a_{Na}}\right) = e^{o}_{Na^+/Na} + \frac{RT}{F} ln\left(\frac{[Na^+]}{[Na]}\right) + \frac{RT}{F} ln\left(\frac{\gamma_{Na^+}}{\gamma_{Na}}\right)$$
$$= -2.71 + 0.059 \log [Na^+] + 0.059 log(\gamma_{Na^+})$$

Cathode: $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O\ (pH < 7)$

$$e_{cathode} = e^{o}_{O_2/H_2O} + \frac{RT}{4F} ln\left(\frac{a_{O_2} a_{H^+}^4}{a_{H_2O}^2}\right) = e_{O_2/H_2O}^{o} + \frac{RT}{4F} ln\left(\frac{[O_2][H^+]^4}{[H_2O]^2}\right) + \frac{RT}{4F} ln\left(\frac{\gamma_{O_2}\gamma_{H^+}^4}{\gamma_{H_2O}^2}\right)$$
$$= 1.229 + \frac{0.059}{4} log\left([O_2][H^+]^4\right) + \frac{0.059}{4} log\left(\frac{\gamma_{O_2}\gamma_{H^+}^4}{\gamma_{H_2O}^2}\right)$$
$$= 1.229 + \frac{0.059}{4} log(P_{O_2}) + 0.059 log[H^+] + 0.059 log(\gamma_{H^+})$$
$$= 1.229 + \frac{0.059}{4} log(P_{O_2}) + 0.059 pH + 0.059 log(\gamma_{H^+})$$

$$e_{overall} = e_{cathode} - e_{anode}$$

$$= 3.939 + \frac{0.059}{4} log(P_{O_2}) + 0.059pH + 0.059\log\left[Na^+\right] + 0.059log(\frac{\gamma_{H^+}}{\gamma_{Na^+}})$$

Since hybrid Na-air cells operate in ambient air, the oxygen partial pressure (P_{O_2}) is approximately 0.2 [atm]. Thus, the overall cell voltage is dependent on Na^+ concentration in catholyte and the mean activity coefficients of H^+ and Na^+, as well as largely on the catholyte pH.

Supplementary Note 4. Significance of open-circuit voltage (OCV) of an electrochemical cell

The open-circuit voltage (OCV) represents the quasi-equilibrium potential where the cathodic and anodic currents of an electrochemical cell are equal under no external electric current, and it is also referred to as a mixed potential or an electromotive force (*emf*). Thus, the OCV roughly reflects the practical cell voltage of a cell; however, the practical charge and discharge voltages are determined by overpotentials (η) occurred under an applied current condition, resulting in deviations from the OCV.

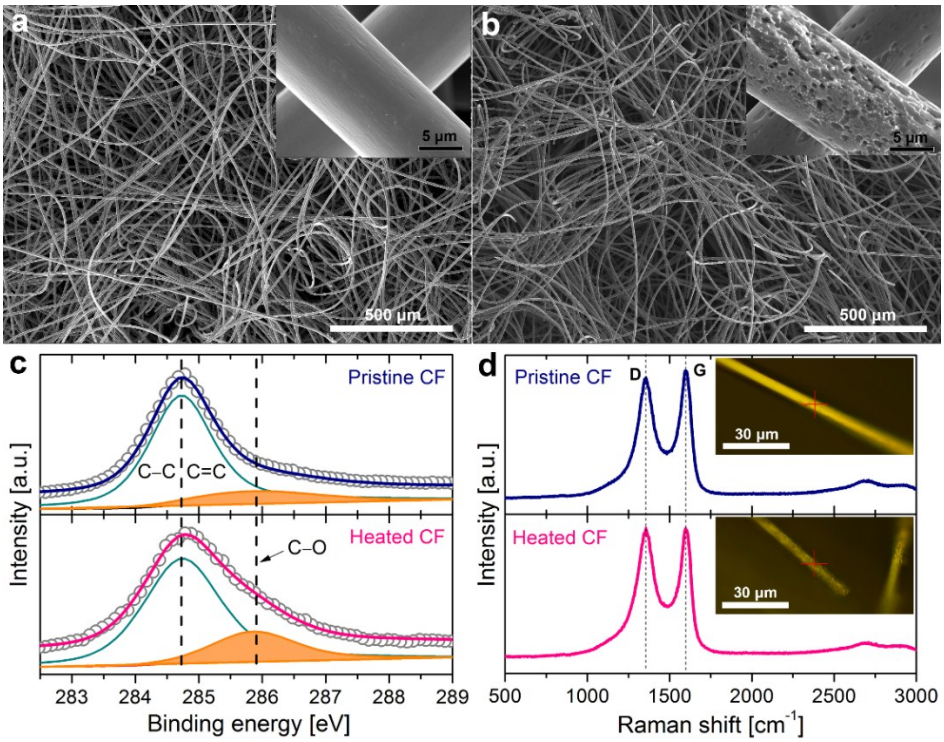

Fig. S1. Morphological and structural characteristics of carbon felt before and after heat-treatment at 500 °C in ambient air. SEM images (a,b); XPS spectra (c); and Raman spectra (d) of the pristine carbon felt (a) and heated carbon felt (b). The insets in (a) and (b) display magnified images of the carbon fiber surface. The insets in (d) show the optical images of the irradiated carbon fiber surface. The intensity ratios of the D and G bands (I_D/I_G) of the pristine and heated carbon felts were 0.96 and 1.00, respectively.

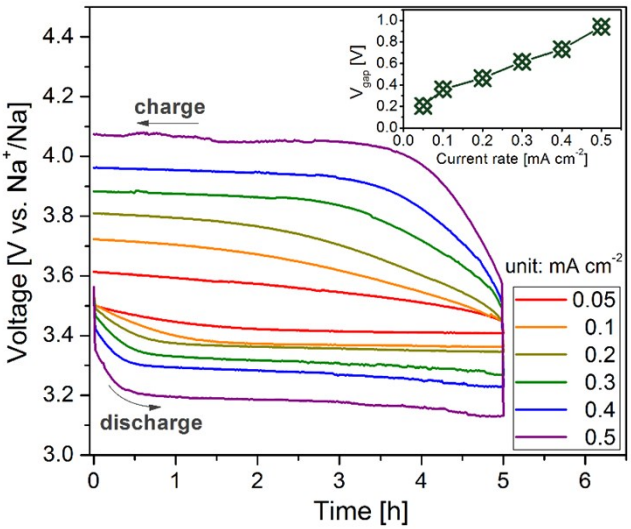

Fig. S2. Discharge-charge voltage profiles of the cell using Pt/C- and IrO_2-loaded HCF at current rates of 0.05-0.5 mA cm^{-2}. The inset shows the variation in the voltage gap between the charge and discharge curves.

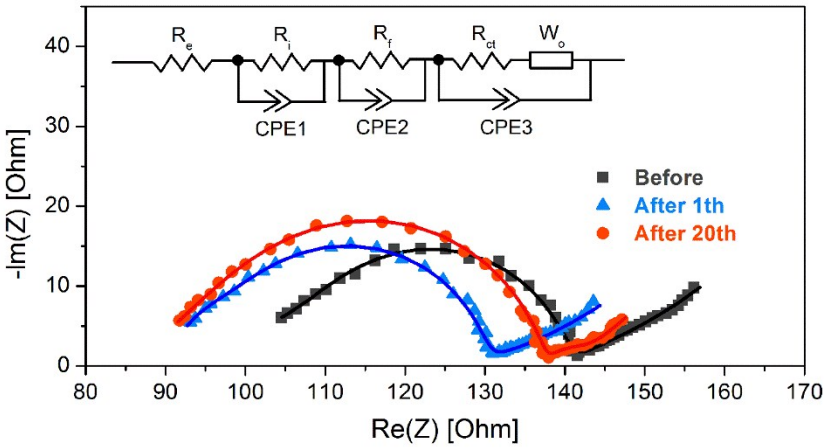

Fig. S3. Nyquist plots of the Pt/C-IrO_2 cell before and after cycling at a current rate of 0.1 mA cm^{-2}. The inset indicates the equivalent circuit used to fit the experimental data.[S2,S3] R_e indicates the resistance of two liquid electrolytes and the bulk (intragrain) resistance of the NASICON; R_i is due to the grain boundary (intergrain) resistance of the NASICON and the interfacial resistances between the NASICON and liquid electrolytes; R_f represents the resistance of a solid-electrolyte interphase layer on the Na anode; R_{ct} and W_o correspond to the charge-transfer resistance in an air-electrode and the finite-length Warburg element related to a diffusion behavior in the air-electrode, respectively; CPE1, CPE2, and CPE3 are the associated constant-phase elements. The fitted parameters are summarized in Table S2.

Table S2. Simulated results for the elements of equivalent circuit of cells before and after cycling

Sample	R_e [Ω]	R_i [Ω]	R_f [Ω]	R_{ct} [Ω]	Z_w [Ω]
Before cycling	95.10	26.81	18.90	24.12	4.23
After 1^{th} cycle	89.57	6.28	32.19	30.55	5.38
After 20^{th} cycle	86.07	17.77	34.30	4.85	2.47

Reference

S1. F. Zeman, *Environ. Sci. Technol.*, 2007, **41**, 7558.

S2. F. Liang and K. Hayashi, *J. Electrochem. Soc.*, 2015, **162**, A1215

S3. P. He, Y. Wang and H. Zhou, *J. Power Sources*, 2011, **196**, 5611.