Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplemental Information for:

A high-rate and high-efficiency molten-salt sodium-oxygen battery

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Contents:

Energy density calculation of alkali metal-oxygen batteries

1) Li-O_2 battery

Battery reaction: $2Li + O_2 = Li_2O_2$ (E^o = 2.96 V_{Li})

Electron transfer number: n = 2

We assume no binder, conductor or void in both Li metal negative and oxygen electrodes.

Charged state	**Starting Materials**	**Density, g/cm^3**	**Formula Weight, g/mole**	**Molar Volume, cm^3/mole**	**Stoichiometry, Moles/F**	**Faradaic Volume, cm^3/Ah**	**Faradic Weight, g/Ah**
Negative electrode	Li	0.53	6.94	13.09	1.00	**0.49**	**0.26**
Positive electrode	O_2	0.00	0.00	0.00	1.00	0.00	0.00

Discharged state	**Starting Materials**	**Density, g/cm^3**	**Formula Weight, g/mole**	**Molar Volume, cm^3/mole**	**Stoichiometry, Moles/F**	**Faradaic Volume, cm^3/Ah**	**Faradic Weight, g//Ah**
Negative electrode	-	0.00	0.00	0.00	1.00	0.00	0.00
Positive electrode	Li_2O_2	2.31	45.88	19.86	0.50	**0.37**	**0.86**

We used the smaller Faradaic volume and weight values to calculate the Specific energy (E_m) and volumetric density (E_{vol}):

E_m = 3458 Wh/kg

E_{vol} = 6059 Wh/L

2) Na-O_2 battery

Battery reaction: $Na + O_2 = NaO_2$ (E^o = 2.26 V_{Na})

Electron transfer number: n = 1

We assume no binder, conductor or void in both Li metal negative and oxygen electrodes.

Charged state	**Starting Materials**	**Density, g/cm^3**	**Formula Weight, g/mole**	**Molar Volume, cm^3/mole**	**Stoichiometry, Moles/F**	**Faradaic Volume, cm^3/Ah**	**Faradic Weight, g/Ah**
Negative electrode	Na	0.97	23.00	23.71	1.00	0.88	0.86
Positive electrode	O_2	0.00	0.00	0.00	1.00	-	-

Discharged state	**Starting Materials**	**Density, g/cm^3**	**Formula Weight, g/mole**	**Molar Volume, cm^3/mole**	**Stoichiometry, Moles/F**	**Faradaic Volume, cm$^{3/}$Ah**	**Faradic Weight, g/Ah**
Negative electrode	-	0.00	0.00	0.00	1.00	0.00	0.00
Positive electrode	NaO_2	2.20	55.00	25.00	1.00	0.93	2.05

We used the smaller Faradaic volume and weight values to calculate the Specific energy (E_m) and volumetric density (E_{vol}):

E_m = 1103 Wh/kg

E_{vol} = 2427 Wh/L

3) K-O_2 battery

Battery reaction: K + O_2 = KO_2 (E^o = 2.48 V_k)

Electron transfer number: n = 1

We assume no binder, conductor or void in both Li metal negative and oxygen electrodes.

Charged state	Starting Materials	Density, g/cm³	Formula Weight, g/mole	Molar Volume, cm³/mole	Stoichiometry, Moles/F	Faradaic Volume, cm³/Ah	Faradic Weight, g/Ah
Negative electrode	K	0.89	39.00	43.82	1.00	1.63	1.46
Positive electrode	O_2	0.00	0.00	0.00	1.00	0.00	0.00

Discharged state	Starting Materials	Density, g/cm³	Formula Weight, g/mole	Molar Volume, cm³/mole	Stoichiometry, Moles/F	Faradaic Volume, cm³/Ah	Faradic Weight, g/Ah
Negative electrode	-	0.00	0.00	0.00	1.00	0.00	0.00
Positive electrode	KO_2	2.14	71.10	33.22	1.00	1.24	2.65

We used the smaller Faradaic volume and weight values to calculate the Specific energy (E_m) and volumetric density (E_{vol}):

E_m = 935 Wh/kg

E_{vol} = 1517 Wh/L

Calculation of equilibrium potentials of Na-O_2 batteries

Citations for all thermodynamic values can be found in Table S3. $\Delta_f G^{443K}$ was calculated using:

$\Delta_f G^{443} = \Delta_f H^0 + (145\ K)C_p - (443\ K)(S^0 + C_p \ln(443\ K/298\ K))$

Reaction: Na + 1/2O_2 = 1/2Na_2O_2

Electron transfer number n = 1

Faraday constant F = 96485 C/mol

$\Delta_f G^{443K}$ (Na_2O_2) = -553.0 kJ/mol

$\Delta_f G^{443k}$ (Na) = -22.7 kJ/mol

$\Delta_f G^{443k}$ (O_2) = -90.9 kJ/mol

ΔG^{443k} = -208.4 kJ/mol

$E^{443k} = \Delta G^{443k}/ (n*F) = 2.16\ V_{Na}$

Reaction: 2Na + 1/2O_2 = Na_2O

Electron transfer number n = 2

Faraday constant F = 96485 C/mol

$\Delta_f G^{443K}$ (Na_2O) = -449.6 kJ/mol

$\Delta_f G^{443k}$ (Na) = -22.7 kJ/mol

$\Delta_f G^{443k}$ (O_2) = -90.9 kJ/mol

ΔG^{443k} = -358.7 kJ/mol

$E^{443k} = \Delta G^{443k}/ (n*F) = 1.86\ V_{Na}$

Reaction: Na + O_2 = NaO_2

Electron transfer number n = 1

Faraday constant F = 96485 C/mol

$\Delta_f G^{443K}$ (NaO_2) = -313.7 kJ/mol

$\Delta_f G^{443k}$ (Na) = -22.7 kJ/mol

$\Delta_f G^{443k}$ (O_2) = -90.9 kJ/mol

ΔG^{443k} = -200.1 kJ/mol

$E^{443k} = \Delta G^{443k}/ (n*F) = 2.07\ V_{Na}$

Reaction: $NaNO_3 + 2Na^+ + 2e^- = Na_2O + NaNO_2$

Electron transfer number n = 2

Faraday constant F = 96485 C/mol

$\Delta_f G^{443K}$ (Na_2O) = -447.5 kJ/mol

$\Delta_f G^{443K}$ ($NaNO_2$) = -404.7 kJ/mol

$\Delta_f G^{443k}$ (Na) = -22.7 kJ/mol

$\Delta_f G^{443K}$ ($NaNO_3$) = -519.5 kJ/mol

$E^{443k} = \Delta G^{443k} / (n*F) = 1.49\ V_{Na}$

Reaction: $NaNO_3 + Na^+ + e^- = NaNO_2 + 1/2Na_2O_2$

Electron transfer number n = 1

Faraday constant F = 96485 C/mol

$\Delta_f G^{443K}$ (Na_2O_2) = -553.0 kJ/mol

$\Delta_f G^{443K}$ ($NaNO_2$) = -404.7 kJ/mol

$\Delta_f G^{443k}$ (Na) = -22.7 kJ/mol

$\Delta_f G^{443K}$ ($NaNO_3$) = -519.5 kJ/mol

$E^{443k} = \Delta G^{443k} / (n*F) = 1.44\ V_{Na}$

Reaction: $Na_2O_2 + 2KNO_3 = K_2O_2 + 2NaNO_3$

$\Delta_f G^0$ (Na_2O_2) = -447.7 kJ/mol

$\Delta_f G^0$ ($NaNO_3$) = -367.0 kJ/mol

$\Delta_f G^0$ (K_2O_2) = -428.4 kJ/mol

$\Delta_f G^0$ (KNO_3) = -394.9 kJ/mol

ΔG = 75.1 kJ/mol (at 298.15 K)

Reaction: $Na_2O_2 + 2CsNO_3 = Cs_2O_2 + 2NaNO_3$

$\Delta_f G^0$ (Na_2O_2) = -447.7 kJ/mol

$\Delta_f G^0$ ($NaNO_3$) = -367.0 kJ/mol

$\Delta_f G^0$ (Cs_2O_2) = -327.0 kJ/mol

$\Delta_f G^0$ ($CsNO_3$) = -406.5 kJ/mol

ΔG = 199.7 kJ/mol (at 298.15 K)

Supplementary Figures and Tables

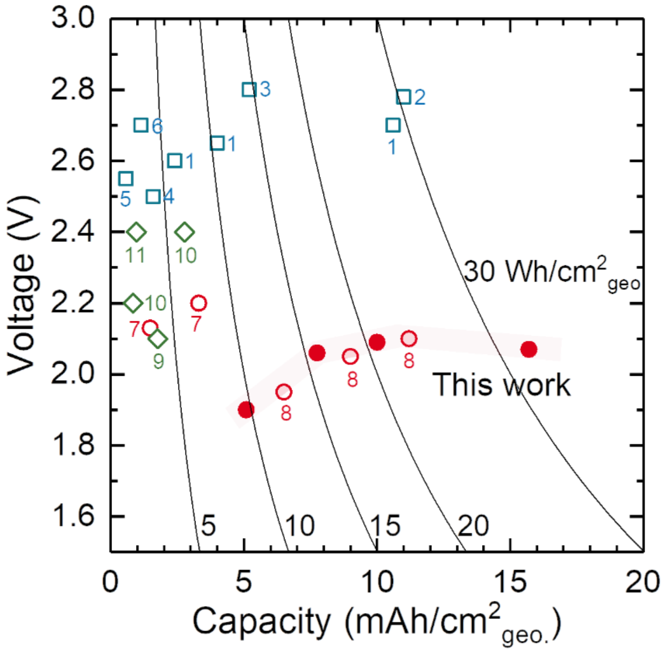


Figure S1. The comparison of capacity-voltage plot for alkali metal-oxygen batteries (Li-O_2 [1-6], Na-O_2[7, 8], K-O_2[9-11] batteries). The detailed information on the reported performance was shown in Table S1.

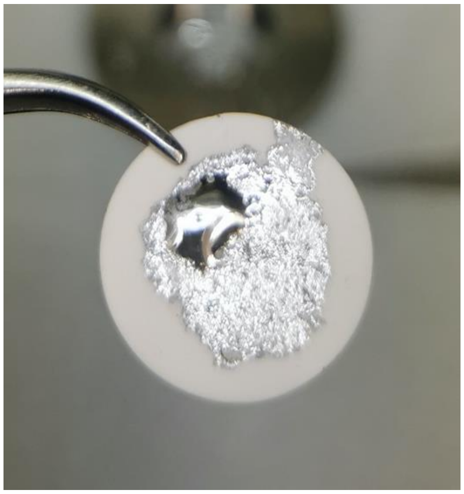


Figure S2. Photo of a β-Al_2O_3 membrane after 2 hours of resting in a Na-O_2 cell.

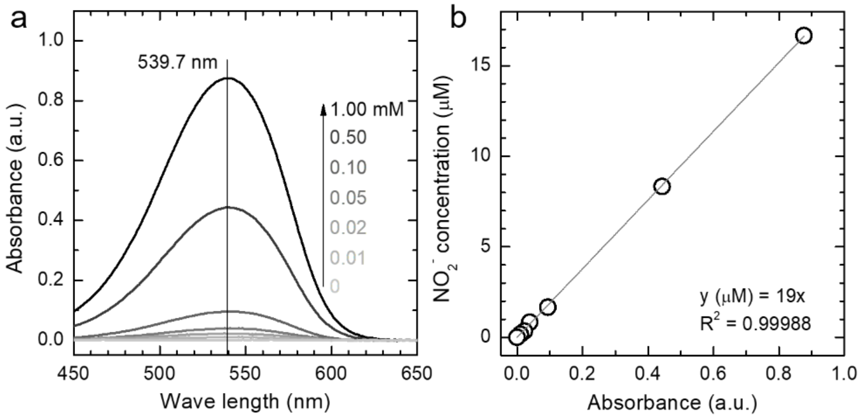


Figure S3. UV-Vis spectra (a) and calibration curve (b) for nitrite (NO_2^-) titration via the Griess method[2]. The standard NO_2^- solutions (0, 0.01, 0.02, 0.05, 0.1, 0.5, 1 mM) were used for obtaining the calibration curve (b).

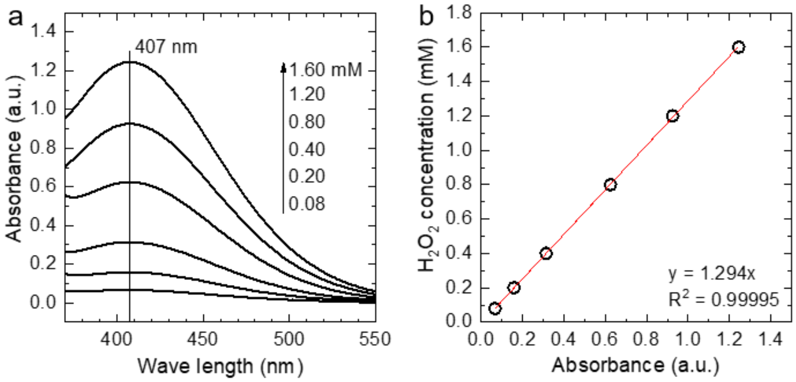


Figure S4. UV-Vis spectra (a) and (b) calibration curves of the titration of H_2O_2 with a standardized Ti^{4+}oxysulfate solution. The detailed information of standard samples is shown in the method section.

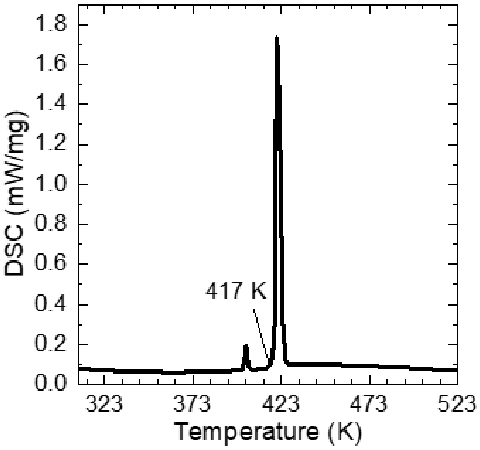


Figure S5. The differential scanning calorimetry (DSC) result of the eutectic salts ($NaNO_3$ 26.4 w%, KNO_3 27.3 w%, and $CsNO_3$ 46.3 w%). The onset of the melting point of the eutectic salts was ~417 K.

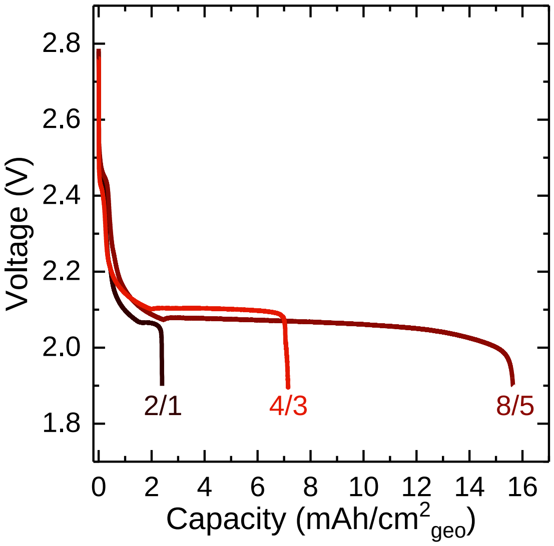


Figure S6. The discharge profiles of molten-salt Na-O₂ batteries with Ni/salts electrodes with the different ratios of Ni/salts (2/1, 8/5, and 4/3). The discharge current is 0.2 mA/cm$^2_{geo}$. The operation temperature was 443 K. The O_2 pressure in the cell is ~280 kPa at room temperature. The salts were the mixture of $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%).

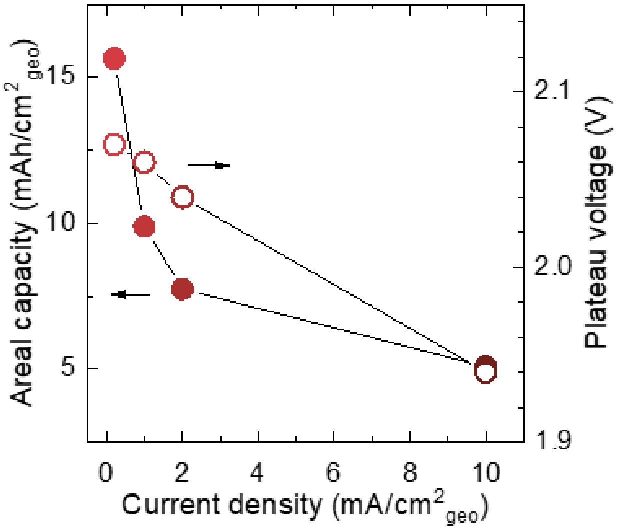
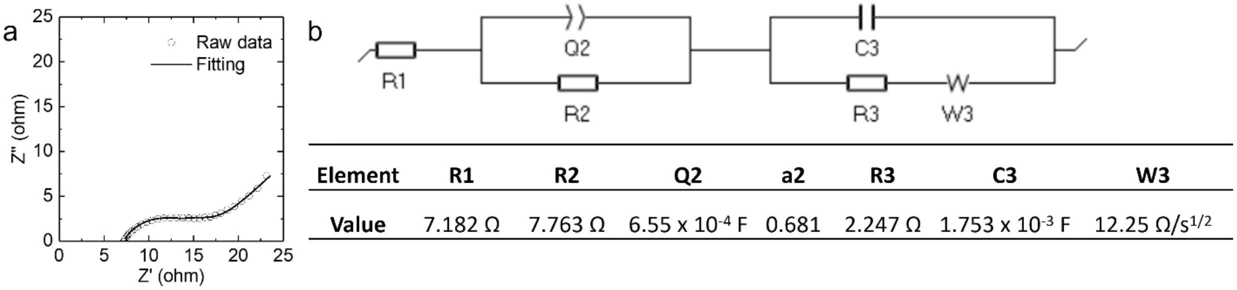


Figure S7. The change of the areal capacities and plateau voltages with increasing discharge currents (0.2, 1.0, 2.0, 10.0 mA/cm$^2_{geo}$).



Element	R1	R2	Q2	a2	R3	C3	W3
Value	7.182 Ω	7.763 Ω	6.55 x 10^{-4} F	0.681	2.247 Ω	1.753 x 10^{-3} F	12.25 Ω/$s^{1/2}$

Figure S8. (a). Electrochemical impedance spectroscopy (EIS) measurements of a molten-salt Na-O_2 battery, including the contact resistance and the resistance from β-Al_2O_3 and the interface between β-Al_2O_3 and liquid Na or Ni/$NaNO_3$/KNO_3/$CsNO_3$/SS oxygen electrode. (b) Fitting details from the electrochemical impedance spectroscopy (EIS) spectra in (a). R1: ohmic resistance, R2: charge transfer resistance, R3: ionic resistance of β-Al_2O_3 membrane, W3: Warburg constant, Li^+ diffusion in β-Al_2O_3 membrane.

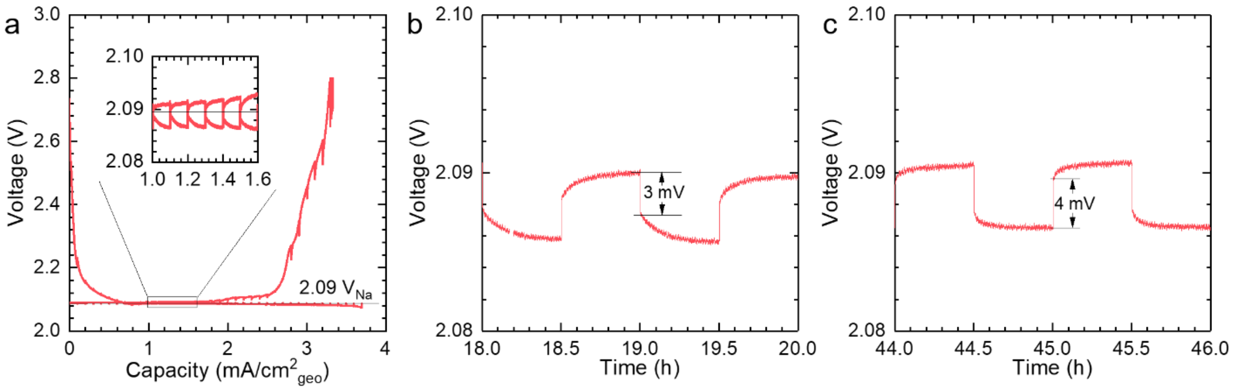


Figure S9. The voltage profiles of a molten-salt Na-O_2 cell using the galvanostatic intermittent titration technique (GITT) measurement. (a) The voltage profiles with time in galvanostatic intermittent titration technique (GITT) measurements. The two selected steps from discharge (b) and charge (c) in the GITT process. The scenario of GITT in the discharge was 30 min of discharge at a current density of 0.2 mA/cm^2_{geo} and then 30 min of rest. The scenario of GITT in the charge at a current density of 0.2 mA/cm^2_{geo} was 30 min of charge and then 30 min of rest. The molten-salt Na-O_2 cell were tested at 443 K. The salts were a mixture of $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%).

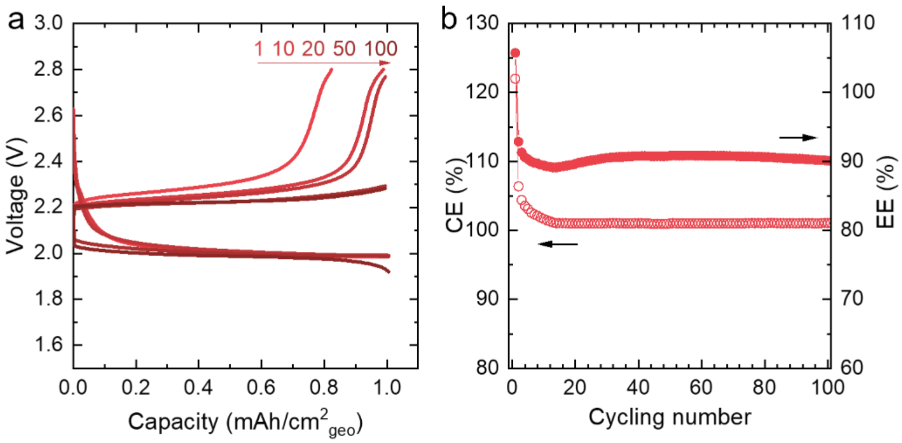


Figure S10. (a) Charge-discharge profiles of a molten-salt Na-O_2 battery at a current density of 5 mA/cm$^2_{geo}$ (1st, 10th, 20th, 50th, and 100th cycles) with a limited discharge capacity of 1.0 mAh/cm$^2_{geo}$. (b) The Coulombic (CE) and energy efficiencies (EE) of a molten-salt Na-O_2 battery at a current density of 5 mA/cm$^2_{geo}$ for 100 cycles. The Na-O_2 cell were tested at 443 K. The salts were a mixture of $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%).

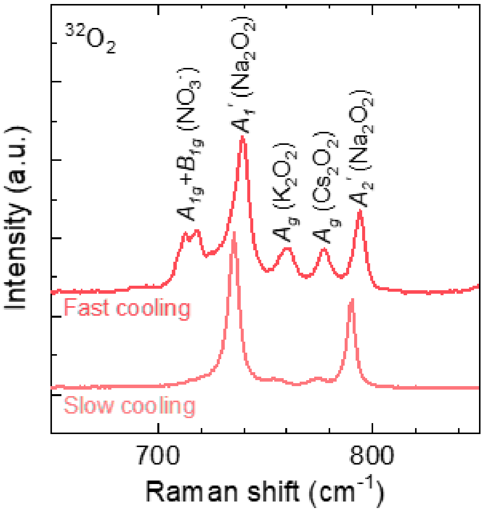


Figure S11. The Raman spectra of Ni/salts electrodes (8/5 in weight) with the addition of Na_2O before and after reaction in 280 kPa (RT) of $^{32}O_2$ at 443 K. The cells were cooled down with fast (~20 K/min) and slow rates (1 K/min).

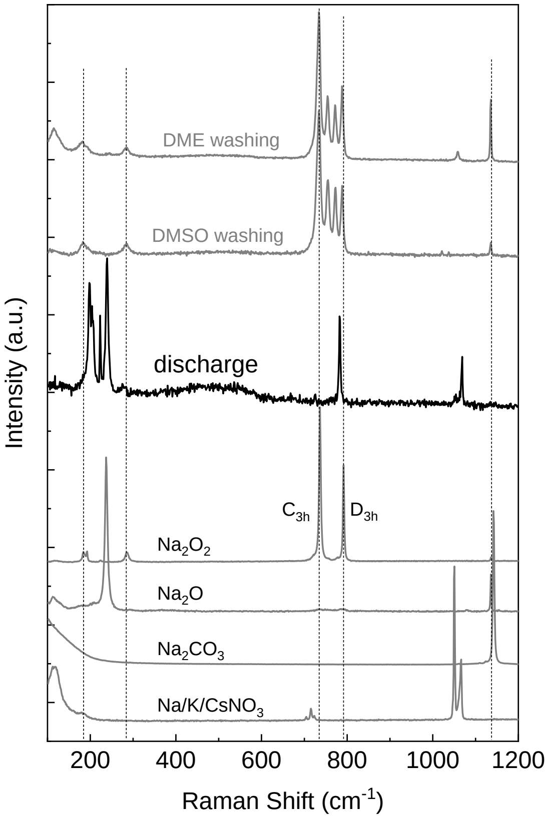


Figure S12. The Raman spectra of Ni/$NaNO_3$/KNO_3/$CsNO_3$/SS electrode after discharge with different washing procedures. Raman spectra of commercial Na_2O_2, Na_2O, Na_2CO_3 and eutectic salts (Na/K/$CsNO_3$) were used as the references

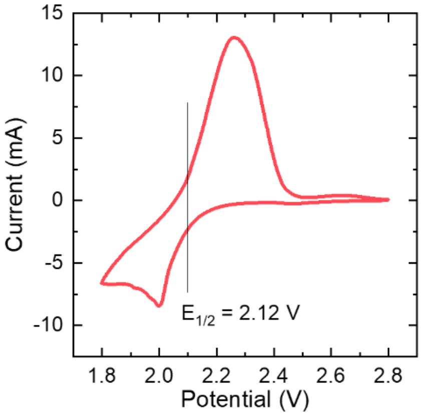


Figure S13. The CV of a molten salt Na-O_2 cell in O_2 atmosphere ranging from 1.8 to 2.8 V. The scanning rate was set as 0.2 mV/s. The molten-salt Na-O_2 cell contains liquid Na negative electrode, β-Al_2O_3 membrane, Ni/salts positive electrode, 280 kPa O_2 (RT), Stainless steel (SS) plate. The salts are a mixture of $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%).

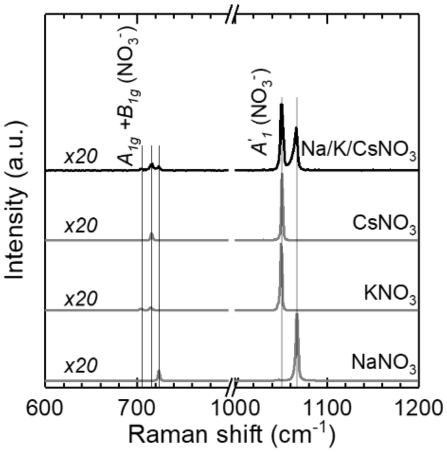


Figure S14. The Raman spectra of commercial Na_2O_2, $NaNO_3$, KNO_3, $CsNO_3$ and eutectic salts (Na/K/$CsNO_3$). The eutectic salts were prepared by mixing the $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%) salts at 473 K for 12 h in an Ar-filled glove box. All these Raman spectra were collected at room temperature in an air-tight cell with Ar environment.

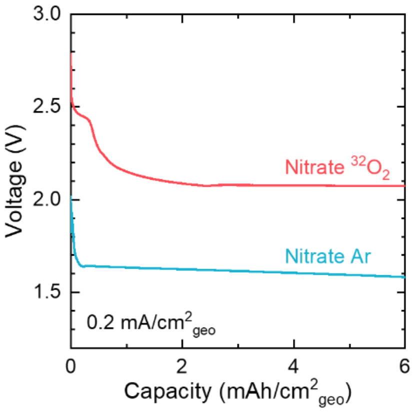


Figure S15. Discharge profiles of molten salt Na-O_2 and Na-Ar cells for quantifications in Figure 4a.

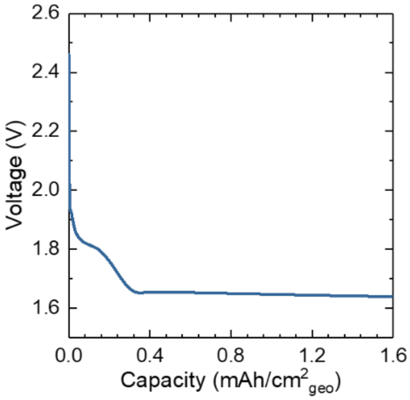


Figure S16. The discharge profile of a molten-salt Na-Ar battery at a current of 0.4 mA/cm$^2_{geo}$ for 1.6 mAh/cm$^2_{geo}$.

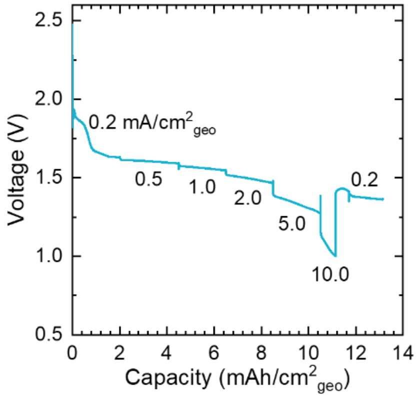


Figure S17. Discharge of a molten-salt Na-Ar cell with increasing discharge currents from 0.2 mA/cm$^2_{geo}$ to 10.0 mA/cm$^2_{geo}$.

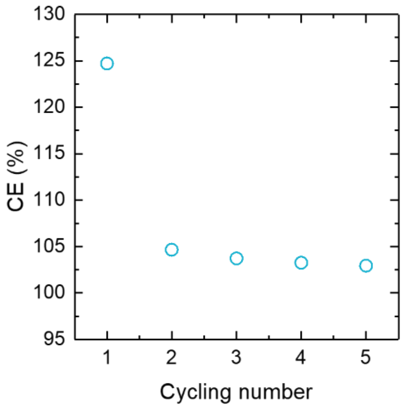


Figure S18. The Coulombic efficiencies of a molten-salt Na-Ar battery at a current density of 1 mA/cm$^2_{geo}$ for 5 cycles with a limited discharge capacity of 2.0 mA/cm$^2_{geo}$ at the temperature of 443 K.

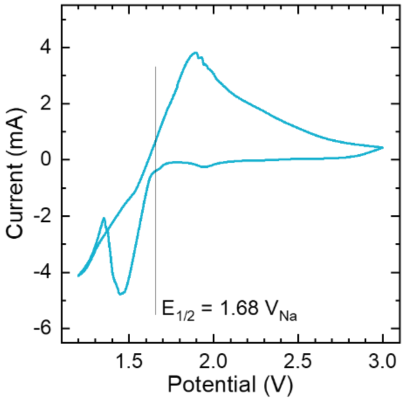


Figure S19. The CV of a molten-salt Na-Ar cell at scanning rate of 0.2 mV/s in the potential range from 1.2 to 3.0 V. The molten-salt Na-Ar cell contains liquid Na negative electrode, β-Al_2O_3 membrane, Ni/salts positive electrode, Stainless steel (SS) plate. The salts are a mixture of $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%).

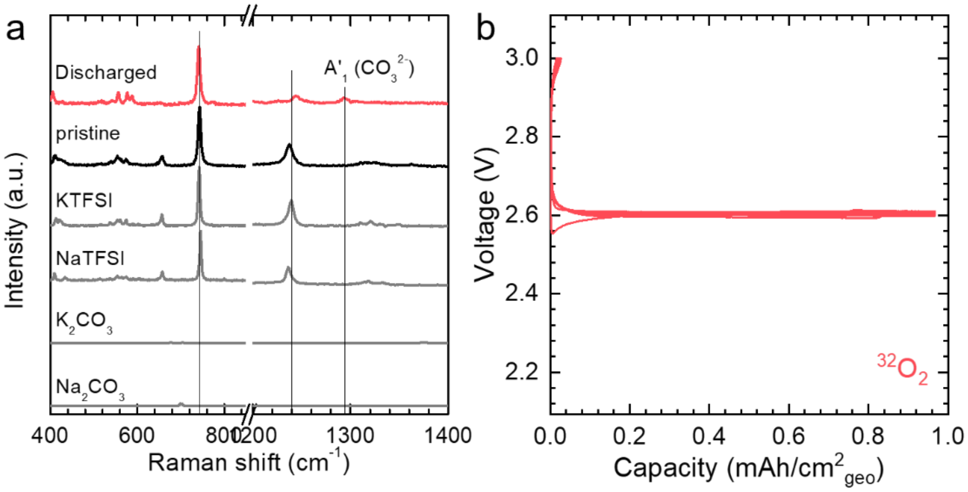


Figure S20. (a) The Raman spectra of pristine and discharged electrode of a molten-salt Na-O_2 cell in $^{32}O_2$ and the standard samples (Na_2CO_3, K_2CO_3, NaTFSI, and KTFSI). (b) The charge/discharge profiles of a molten-salt Na-O_2 cell in $^{32}O_2$ at current density of 0.2 mA/cm$^2_{geo}$. All the above cells were tested at 483 K. The salts in the above cells were a mixture of NaTFSI (31.9 w%)/KTFSI (68.1 w%).

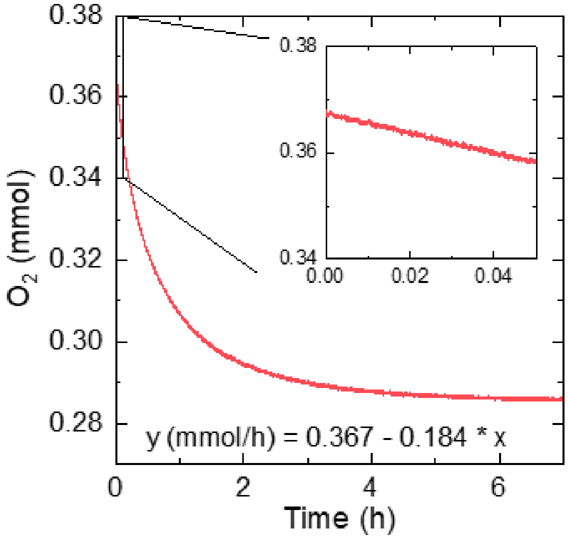


Figure S21. The O_2 pressure tracking of the cell after the symmetric molten-salt Na-He battery was discharged for ~6 mAh. The negative electrode was a Ni/salts electrode discharged in Ar for 8 mAh. The cathode was a pristine Ni/salts electrode. After discharging, the cell was evacuated and purged O_2. The inset showed that the linear fitting of the O_2 consumption rate in the first 3 mins. The electrode geometric area was 0.785 cm$^2_{geo}$. The fitting function is y (mmol) = 0.367 – 0.184*x. Note: salts are the mixture of $NaNO_3$ (26.4 w%), KNO_3 (27.3 w%), and $CsNO_3$ (46.3 w%).

Table S1. The detailed performance of reported Li-O_2, Na-O_2, and K-O_2 batteries.

System	Discharge voltage (V)	Current (mA/cm$^{2}_{geo}$)	Capacity (mAh/cm$^{2}_{geo}$)	Energy density (mWh/cm$^{2}_{geo}$)	Power density (mW/cm$^{2}_{geo}$)	Reference
Li-O_2	2.7	0.2	10.6	28.62	0.54	[1]
	2.65	1	4	10.6	2.65	[1]
	2.6	2	2.4	6.24	5.2	[1]
	2.78	0.1	11	30.58	0.278	[2]
	2.8	0.32	5.2	14.56	0.896	[3]
	2.5	2.5	1.6	4	6.25	[4]
	2.55	0.129	0.57	1.4535	0.32895	[5]
	2.7	1.142	1.142	3.0834	3.0834	[6]
Na-O_2	2.2	0.12	3.3	7.26	0.264	[7]
	2.13	0.2	1.48	3.1524	0.426	[7]
	2.1	0.1	11.2	23.52	0.21	[8]
	2.05	0.2	9	18.45	0.41	[8]
	1.95	0.5	6.5	12.675	0.975	[8]
K-O_2	2.1	0.2	1.76	3.696	0.42	[9]
	2.4	0.16	0.96	2.304	0.384	[11]
	2.4	0.0885	2.77	6.648	0.2124	[10]
	2.2	0.664	0.84	1.848	1.4608	[10]
***This work**	**1.9**	**10**	**5.09**	**9.671**	**19**	
	2.06	**2**	**7.75**	**15.965**	**4.12**	
	2.09	**1**	**10**	**20.9**	**2.09**	
	2.07	**0.2**	**15.7**	**32.499**	**0.414**	

Table S2. The potential nitrate eutectic salts used for Na-O_2 batteries

$NaNO_3$ (w%)	KNO_3 (mol%)	$CsNO_3$ (mol%)	Melting point (K)	Reference
45.7	54.3	-	494	[12]
35.7	-	64.3	464	[12]
26.4	27.3	46.3	427	[12]

Table S3. Thermodynamic data used in the work

Compound	**Δ_fH^0 (kJ/mol)**	**S^0 (J/mol·K)**	**C_p (J/mol·K)**	**Δ_fG^0 (kJ/mol)**
Na	0[13]	51.3[13]	28.2[13]	0[13]
NaO_2	-260.2[13]	115.9[13]	72.1[13]	-218.4[13]
Na_2O_2	-510.9[13]	95.0[13]	89.2[13]	-447.7[13]
Na_2O	-414.2[13]	75.1[13]	69.1[13]	-375.5[13]
$NaNO_2$	-358.7[13]	103.8[13]	NA	-284.6[13]
$NaNO_3$	-467.9[13]	116.5[13]	92.9[13]	-367.0[13]
KNO_2	-369.8[13]	152.1[13]	107.4[13]	-306.6[13]
KNO_3	-494.6[13]	133.1[13]	96.4[13]	-394.9[13]
K_2O_2	-495.4[14]	110.1[14]	95.8[14]	-428.4[15]
$CsNO_2$	NA	NA	NA	-313.8[16]
$CsNO_3$	-506.0[13]	155.2[13]	NA	-406.5[13]
Cs_2O_2	NA	NA	NA	-327.0[17]
NiO	-239.3[18]	38.0[18]	67.7[18]	-211.1[18]
O_2	0[13]	205.2[13]	29.4[13]	0[13]
Ni	0[13]	29.9[13]	26.1[13]	0[13]

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