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

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Alkali metal–oxygen batteries can provide greater specific energy than Li-ion batteries but often suffer from low power density, cycleability, and energy efficiency due to the sluggish kinetics of the oxygen electrode and parasitic reactions at both the oxygen and alkali metal electrodes. In this study, we demonstrated a molten-salt Na–O2 battery operating at 443 K with high areal energy (33 mW h cm−2 geo) and power densities (19 mW cm−2 geo), with high energy efficiency (~90% at 5 mA cm−2 geo), and stable cycling (400 cycles with no capacity loss). Raman, pressure tracking and titration measurements were used to show that the dominant discharge product is Na2O2. Moreover, the redox activity of nitrate anions in the molten salt was found to be critical to enable the formation of Na2O2. Through 18O-labeling experiments as well as discharging Na–Ar cells, we demonstrated that the discharge reaction occurs via the electrochemical reduction of NaNO3 to Na2O and NaNO2, where chemical reactions with O2 lead to the formation of Na2O2 from Na2O, and the regeneration of NaNO3 from NaNO2.

Introduction

Alkali metal–oxygen batteries have high theoretical energy densities and are promising electrochemical energy storage systems to enable the electrification of heavy-duty vehicles and aviation.4 For instance, Li–, Na–, and K–O2 batteries can deliver values of specific energy of 3458 W h kg−1 (Li, O2/active Li2O2), 1103 W h kg−1 (Na, O2/active NaO2), and 935 W h kg−1 (K, O2/active KO2) at room temperature, respectively (where calculation details can be found in the ESI†). However, the formation of dendrites5 and the high reactivity of alkali metals has hindered the development of metal-based batteries, including metal–oxygen batteries.6 Recently, research effort has focused on modifying the alkali metal negative electrode to increase rechargeability and stability, especially that of lithium metal.4,5 Moreover, the sluggish kinetics of the oxygen reduction and evolution reactions (ORR and OER)7 can increase the overpotentials at the positive electrode of metal–oxygen batteries, leading to poor energy efficiencies.8,9 To reduce the overpotentials of metal–oxygen batteries, solid electrochemical catalysts8 and redox mediators8,9 have been intensely investigated. Unfortunately, the (electro)chemical stability of the electrodes10 and electrolyte11–14 against reaction intermediates and products as well as the operating voltages remain a big challenge.

Recently, a molten-salt Li–O2 battery has been reported by Giordani et al.15 in 2016, showing high electrolyte stability and...
high-energy efficiency (≈95%) at an operating temperature of 423 K. Unfortunately, the formation of Li₂CO₃ from the oxidation of carbon in the oxygen electrode led to poor cycling stability (<50 cycles, ~2.6 mA h cm⁻²geo at ~0.6 mA cm⁻²geo, normalized based on the geometric area of the positive electrode). Subsequently, Xia et al. have demonstrated a molten-salt Li–O₂ battery with a four-electron conversion of O₂ to Li₂O using NiO in the oxygen electrode, showing stable cycling performance (150 cycles, 0.5 mA h cm⁻²geo at 0.2 mA cm⁻²geo) with a Coulombic efficiency of ~100%. Koo and Kang have reported that iron(II, III) oxide can also serve as an effective catalyst to produce Li₂O in nitrate molten-salt Li–O₂ batteries. Most recently, we have shown that Li₂O in nitrate molten-salt Li–O₂ batteries is enabled by the redox activity of nitrate anions and by studying different 3d transition metal oxides have found that NiO has the lowest overpotential during discharge due to its optimal binding of nitrate and nitrite anions. Nitrate molten salts have also been used as the O₂ reservoir for a closed Li–O₂ battery system and molten-salt electrolytes have been used with other metal–oxygen batteries besides Li such as Fe, Zn, and Mg, showing long cycling life and high rate capability. A schematic of the structure of a molten-salt Li–O₂ battery is shown in Fig. 1a. Solid-state electrolytes are needed in molten-salt Li–O₂ batteries to prevent crossover of soluble Li₂O that can form due to the reaction between Li metal and the electrolyte. A molten-salt buffer layer was used to provide a highly Li⁺ conducting interface between the Li metal electrode and solid-state electrolyte in order to achieve high rate and energy efficiency in molten-salt Li–O₂ batteries. Replacing Li by Na provides an opportunity to increase the power of the system due to low interfacial resistance between liquid Na and the solid-state electrolyte at an operating temperature of 443 K.

In this work, a molten-salt Na–O₂ battery was developed with a liquid Na negative electrode and Ni oxygen electrode with a NaNO₃/KNO₃/CsNO₃ eutectic salt electrolyte and a β-Al₂O₃ membrane, where the stable interface between liquid Na and β-Al₂O₃ can be advantageous relative to molten-salt Li–O₂ batteries. Such molten-salt Na–O₂ batteries showed high energy (33 mWh cm⁻²geo) and power densities (19 mW cm⁻²geo) as well as stable cycling (400 cycles, 0.5 mA h cm⁻²geo at 5 mAh cm⁻²geo). Using Raman, pressure tracking and titration measurements, we show that the dominant discharge product is Na₂O₂. Moreover, the redox of nitrate anions is identified as being critical to enable the formation of Na₂O₂ upon discharge. Molten-salt Na–Ar cells show the electrochemical reduction of NaNO₃ to Na₂O and NaNO₂. On the other hand, in an O₂ environment the formed Na₂O and NaNO₂ can further react with O₂ to yield Na₂O₂ and regenerate NaNO₃, respectively. Finally, using ¹⁸O-labeling experiments, we demonstrate that the oxygen reduction reaction in molten-salt Na–O₂ batteries occurs via a nitrate-mediated mechanism whereby NaNO₃ facilitates an apparent 2e⁻/O₂ overall reaction to form Na₂O₂. The presented nitrate-mediated molten-salt Na–O₂ battery provides a novel approach to develop alkali metal–O₂ batteries with high energy and power densities, with a cell architecture that can stabilize the alkali metal electrode.

Experimental

Materials

Nickel metal powder (325 mesh, 99.8%, Fisher Scientific Co. LLC.) was used for electrode preparation. NaNO₃ (99.999%, Fisher Scientific Co. LLC.), KNO₃ (99.99%, Fisher Scientific Co. LLC.), CsNO₃ (99.99%, Fisher Scientific Co. LLC.), NaNO₂ (>97%, Fisher Scientific), NaTFSI (sodium trifluoromethanesulfonimide, 97%, Sigma Aldrich), KTFSI (potassium trifluoromethanesulfonimide, 97%, Sigma Aldrich) were used to prepare the eutectic molten-salt electrolytes and electrodes. Na–β-Al₂O₃ discs (Ionotec Ltd.) were used as Na-ion conductors for molten-salt Na–O₂ batteries. Na₂O₂ (97%, Sigma Aldrich), NaO₂ (Thermo Scientific™), Na₂CO₃ (99.5%, Sigma Aldrich), and K₂CO₃ (99.0%, Sigma Aldrich) were used as standard samples for Raman spectroscopy. Standardized titanium(IV) oxysulfate solution (Aldrich, ~15 wt% in dilute sulfuric acid, 99.99% trace metals basis) was used to quantify Na₂O₂ in discharged electrodes. Hydrochloric acid (0.01 N, VWR) was used for acid–base titration experiments for Na₂O and Na₂O₂ from discharged electrodes. A Griess reagent system (Promega) was used for nitrite titration for discharged electrodes.

Preparation of the Ni/NaNO₃/KNO₃/CsNO₃ electrodes

2 g of Ni powder (325 mesh, 99.8%, Fisher Scientific Co. LLC.) was added into 5 mL of a NaNO₃ (26.4 w%)/KNO₃ (27.3 w%)/CsNO₃ (46.3 w%) solution (0.25 g mL⁻¹ in Deionized water, DIW). Then the above suspension was sonicated for 10 min and transferred into an oven for drying at 453 K for 2 hours.

![Fig. 1](image-url)
Next, the composite powder was ground for half an hour and pressed as an electrode (0.2 g and 12.7 mm in diameter) onto stainless steel mesh (120 mesh) with 2 tons of pressure for 1 min in an Ar-filled glove box. These electrodes were transferred into a vacuum Buchi glass oven at 473 K for two days and then stored in an Argon-filled glove box. After preparation, there is a small amount of NO₂⁻ in the Ni/NaNO₃/KNO₃/CsNO₃ eutectic molten salt, which can be attributed to at least one of the following reactions:\(^{33} \text{Ni} + \text{NaNO}_3 \rightarrow \text{NiO} + \text{NaNO}_2 (\Delta G^0 = -128.7 \text{ kJ mol}^{-1})\) from thermodynamic data in Table S3, ESI†. Ni + KNO₂ → NiO + KNO₂ (\(\Delta G^0 = -122.8 \text{ kJ mol}^{-1}\)) from thermodynamic data in Table S3, ESI† or Ni + CsNO₂ → NiO + CsNO₃ (\(\Delta G^0 = -118.4 \text{ kJ mol}^{-1}\)) from thermodynamic data in Table S3, ESI†.

Preparation of Ni/NaTFSI/KTFSI electrodes
2 g of Ni powder (325 mesh, 99.8%, Fisher Scientific Co. LLC.) was added into 5 mL of a NaTFSI (31.9 w%)/KTFSI (68.1 w%) solution (0.25 g mL⁻¹ in DIW). Then, the above suspension was sonicated for 10 min, transferred into an oven, and dried at 453 K for 2 hours. Next, the composite powder was ground for half an hour and compressed as a 12.7 mm electrode (0.2 g) on stainless steel mesh (120 mesh) with 2 tons of pressure for 1 min in an Ar-filled glove box. These electrodes were transferred into a vacuum Buchi glass oven at 473 K for two days and then stored in an Ar-filled glove box prior to use.

Synthesis of Na₃ONO₂
Na₂O (Fisher Scientific) and NaNO₂ (> 97%, Fisher Scientific) with a 1 : 1 molar ratio was ground for 20 min, and then 50 mg of the mixture was pressed as a pellet. After that, the pellets were sealed in an air-tight stainless-steel (SS) reactor under an Ar environment. The reactor was put in the oven at 573 K for 30 h. The produced yellow pellet (Na₃ONO₂) was transferred into an Ar-filled glove box for characterization.

Assembly of Na molten-salt cells
All parts of Na–O₂ cells were dried in a vacuum oven at 353 K for 12 h before use. The liquid Na negative electrode and the Ni/salt positive electrode (12.7 mm in diameter) were separated by a piece of β-Al₂O₃ conductor. A schematic structure of the Na molten-salt cell is shown in the inset of Fig. 2a. After assembly, the cells were charged with O₂ or Ar. The charged O₂ or Ar pressure ranged from ~70 to 280 kPa at room temperature. There was good wetting between liquid Na and β-Al₂O₃ membrane after resting for 2 hours in Na–O₂ cells (Fig. S2, ESI†).

Characterization of the reaction between Na₂O and O₂
10 mg of Na₂O was added to 200 mg of Ni/salt powder (8/5 weight ratio) and then pressed as a pellet under a pressure of 2 tons. After that, the pellet was put into an air-tight cell with 275 kPa of O₂ or Ar at 443 K for 48 h. After the reaction, the pellet was characterized in an air-tight cell using Raman spectroscopy.

Quantification of the solubility of Na₂O₂ in molten salts
The solubility of Na₂O₂ in NaNO₃ (26.4 w%)/KNO₃ (27.3 w%)/CsNO₃ (46.3 w%) eutectic molten salt was measured via an acid–base titration method. 2 w% of Na₂O₂ in the above molten salts was stirred at 443 K for two days, and then rest for three days at the same temperature. After that, the top, clear molten salt was collected for acid–base titration.

Electrochemical measurements
Molten-salts Na–O₂ cells were measured on a temperature-controlled hot plate. The temperature was set at 443 K. The operation voltage window was set between 1.8 to 2.8 V. The applied current density ranged from 0.1 to 10 mA cm⁻². The battery tests were conducted using a Biologic VMP3 electrochemical workstation. The areal capacity, energy density and power density obtained from the electrochemical measurements were normalized by the area of the positive electrode.

Differential electrochemical mass spectrometry (DEMS) measurements were conducted on a custom-made DEMS setup which has been detailed previously.\(^{32}\) O₂ (16O16O), \(^32\)O₂ (16O18O), \(^34\)O₂ (18O18O), and \(^36\)O₂ (18O18O) were detected during charging with 10 min of accumulation time for each point. O₂ pressure was measured during the discharge process to quantify the O₂ consumption. Helium (Ultra High Purity 5.0 Grade, Airgas) was used as the carrier gas in DEMS measurements. The effective area of electrodes was 0.785 cm² for DEMS measurement. The operation temperature was 443 K. The applied discharge and charge current densities ranged from 0.1 to 0.4 mA cm⁻².

Quantification of discharge products
NO₂⁻ was quantified using the Griess method.\(^{18}\) NO₂⁻ titration was conducted on a UV-vis spectrophotometer (Genesys 180, Thermofisher Scientific). The NO₂⁻ calibration curve was generated using titration of the standard NO₂⁻ solutions (0, 0.01, 0.02, 0.05, 0.1, 0.5, 1 mM). 50 μL of standard NO₂⁻ solution and 50 μL of sulfamic acid (10 mg mL⁻¹ solution in 5% phosphoric acid, Promega) were added into a 1.2 mL plate deep well and then was kept in a dark environment for 3–5 min. Next, 50 μL of \(N(1\text{-naphthyl})\text{ethylenediamine dihydrochloride}\) (1 mg mL⁻¹) solution (Promega) was added to the above solution and was kept in a dark environment for another 3–5 min. After that, 100 μL of the above solution was transferred into a quartz cuvette (10 mm path length, VWR) with 1.9 mL of deionized water (DIW). The solution in the cuvette was tested immediately using UV-vis with a scanning rate of 1 nm s⁻¹ from 450 to 700 nm. The curve of absorbance vs. NO₂⁻ concentration was linearly fit, as shown in Fig. S3 (ESI†). For quantification of electrolytes, the samples were dispersed in 50 mL of DIW, and then a clear solution was obtained by centrifugation. The clear solution was diluted ranging from 1/50 to 1/100. The diluted solution was then titrated using the above procedure.

Na₂O₂ was quantified using titanium oxysulfate titration. Discharged electrodes were extracted from discharged molten-
salt Na–O₂ or Na–Ar cells in an Ar-filled glove box. Then, the electrode was removed from the glovebox and immediately dispersed in 50 mL of cooled DIW (stored in a refrigerator at 278 K) and stirred for 4 min. During this time, the following reaction occurred: Na₂O₂ + 2H₂O → 2 NaOH + H₂O₂. There is a side reaction Na₂O₂ + H₂O → 2NaOH + 0.5O₂, which can be neglected based on literature findings.²⁸ Next, 1 mL of the solution was filtered using a 0.2 μm filter and was added to 1 mL of cooled DIW and titrated with 0.5 mL standardized titanium(v) oxysulfate solution (Aldrich, ~15 wt% in dilute sulfuric acid, 99.99% trace metals basis). This step allows the fast reaction between H₂O₂ and Ti⁴⁺ oxysulfate to form yellow pertitanic acid. The reaction is Ti⁴⁺ + H₂O₂ + 2H₂O → H₂TiO₄ + 4H⁺. The concentration of the yellow pertitanic acid was determined using UV-vis spectroscopy (Genesys 180, Thermo Fisher Scientific) with a scanning rate of 1 nm s⁻¹ from 350 to 650 nm. The UV-vis spectra of the titration of standardized H₂O₂ solutions (Certified ACS 31.7%, Fisher Chemical) at various concentrations (0.08, 0.2, 0.4, 0.8, 1.2, 1.6 mM) and the corresponding calibration curve are shown in Fig. S4 (ESI†).

Acid-based titrations for Na₂O quantification were done using a pH meter (PH 700 meter, VWR) and 0.01 N of HCl standard solution (VWR). All discharged electrodes were first dispersed in 20 mL of DIW, and then clear solutions were collected via centrifugation and filtration using a 0.2 μm filter. The reaction of Na₂O in the electrode and DIW is Na₂O + H₂O = 2NaOH.²² 1 mL of the filtered solution was diluted to 10 mL for acid–base titration. The titration reaction is NaOH + HCl = NaCl + H₂O.²¹ The end point of the titration was determined by the pH reaching ~7 (6.5–7.5). In the event that Na₂O₂ was detected, the contribution from Na₂O₂ was deducted from the value determined from acid–base titration to determine the contribution from Na₂O.

Characterization of electrodes

Ni electrodes were characterized through X-ray diffraction (XRD, Bruker D2), scanning electronic microscopy (SEM, Zeiss Merlin), and Raman spectroscopy (HORIBA Scientific LabRAM HR800). In the measurements of XRD and Raman spectra, the electrodes were sealed in air-tight cells. In XRD measurements, the applied voltage and current were 30 kV and 10 mA, respectively, using Cu-Kα radiation (λ = 1.54178 Å). In Raman spectroscopy measurements, a red laser (λ = 632.8 nm) was used with 50-fold magnification. An exposure time of 15 s with a 600 grating was used, and each spectrum was accumulated five times.

Results and discussion

Electrochemical performance of molten-salt Na–O₂ cells

Molten-salt Na–O₂ cells discharged at 443 K exhibited discharge voltages of 1.9–2.1 V at rates up to 10 mA cm⁻²geo where the cells consisted of a liquid Na negative electrode, β-Al₂O₃ membrane and Ni/NaNO₃/KNO₃/CsNO₃/stainless steel (SS) oxygen electrode (inset of Fig. 2a). A ternary NaNO₃ (26.4 w%)/KNO₃ (27.3 w%)/CsNO₃ (46.3 w%) eutectic molten-salt electrolyte was selected due to its lower melting temperature (427 K in Fig. S3, ESI†) compared to NaNO₃/KNO₃ (494 K) and NaNO₃/CsNO₃ (464 K) binary eutectics (Table S2, ESI†). Critically, all three nitrate salts show thermal stability up to 600 K,³³ which is significantly higher than the operating temperature of 443 K in this study. By investigating different weight ratios of Ni to NaNO₃/KNO₃/CsNO₃ salts, an optimal ratio of 8/5 was identified, which yielded a discharge capacity of ~16 mA h cm⁻²geo at 0.2 mA cm⁻²geo (Fig. S6, ESI†). Increasing current density from 0.2 to 10 mA cm⁻²geo was accompanied by an exponential decrease in areal capacity suggesting that the discharge process could be limited by O₂ diffusion at high rates (Fig. 2a and Fig. S7, ESI†). On the other hand, the discharge voltages decreased linearly with increasing current densities in Fig. 2a and Fig. S7 (ESI†), which was consistent with the overpotential being governed by the cell’s resistance of ~10 Ω from the slope in Fig. S7 (ESI†). Further support came from electrochemical impedance spectroscopy (EIS) in Fig. S8 (ESI†) which revealed low Ohmic resistance (R1) of ~7 Ω, charge transfer resistance
between β-Al2O3, and the electrodes (R2) of ~8 Ω, and low ionic resistances from β-Al2O3 (R3) of ~2 Ω. These resistances add up to a total cell resistance of ~17 Ω which is similar in magnitude to the slope of discharge voltage vs. current from Fig. S7 (ESI†) (~10 Ω). Moreover, galvanostatic intermittent titration technique (GITT) measurements in Fig. S9a (ESI†), showed small overpotentials (~10 mV, the inset of Fig. S9a, ESI†) for the discharge plateau, with 3–4 mV of the overpotentials came from charge/discharge IR drop (Fig. S9, ESI†).

Remarkably, these results suggest fast oxygen redox kinetics in molten-salt Na–O2 cells in contrast to reported room temperature Na–O2 batteries using organic aprotic solvents for the electrolytes and carbon nanotube electrodes44 which had a discharge overpotential of ~1 V at a rate of 1 mA cm−2geo.

Molten-salt Na–O2 cells also demonstrated low overpotentials during charging, as well as high cycling stability (400 cycles), and high Coulombic (~100% at 5 mA cm−2geo) and energy (~90% at 5 mA cm−2geo) efficiencies. Molten-salt Na–O2 cells were discharged and charged with capacities limited to 1 mA h cm−2 geo at rates from 1 mA cm−2 geo to 10 mA cm−2 geo (Fig. 2b). Remarkably, even at high rates of 10 mA cm−2 geo the overpotential on charge remained small (~300 mV) for most of the charging process, only increasing sharply after 0.8 mA h cm−2 geo. Moreover, molten-salt Na–O2 cells could be stably cycled at 5 mA cm−2 geo to 0.5 mA h cm−2 geo for 400 cycles (Fig. 2c) with negligible increase in overpotential, as well as stable Coulombic (CE) and energy efficiencies (EE) of ~100% and ~90%, respectively (Fig. 2d). Moreover, increasing the cut-off capacity during cycling to 1.0 mA h cm−2 geo the molten-salt Na–O2 cell still showed low overpotentials, long cycling life (100 cycles), and high CE (~100%) and EE (~90%) (Fig. S10, ESI†). Such molten-salt Na–O2 cells exhibited higher energy (33 mW h cm−2 geo) and power densities (19 mW cm−2 geo) as compared with even the highest performing nonaqueous Na–O2 cells with 24 mW h cm−2 geo and 1.0 mW cm−2 geo.45 Significantly, when compared to reported Li–O2 batteries,18,36 these molten-salt Na–O2 cells can also provide comparable areal energy density (33 mW h cm−2 geo vs. 30 mW h cm−2 geo)18 and higher areal power density (19 mW cm−2 geo vs. 6 mW cm−2 geo)18 than the highest performing cells reported to date. Please see Fig. 1c, Fig. S1, and Table S1 (ESI†) for a detailed comparison of the reported performance of alkalai metal–oxygen batteries vs. the molten-salt Na–O2 cells reported in this work.

Discharge products of molten-salt Na–O2 cells

The discharge of molten-salt Na–O2 cells mainly produces Na2O2. Discharge of Ni/NaNO3/KNO3/CsNO3/SS electrodes was accompanied by the emergence of four Raman bands from 700 to 800 cm−1, which can be assigned to the O–O stretching vibration (Fig. 3a). For instance, the Raman bands at 737 and 792 cm−1 are consistent with those reported for the A′1 and A′2 vibration modes of Na2O2,44 while those at 756 and 781 cm−1 can be attributed to O–O stretching of Cs2O2 (Ag mode)45 and K2O2 (Ag mode),44 respectively. The presence of K2O2 and Cs2O2 was unexpected because it is thermodynamically uphill to replace the Na+ ions in Na2O2 with K+(Na2O2 + 2KNO3 → K2O2 + 2NaNO3, ΔG = 75.1 kJ mol−1) or Cs+(Na2O2 + 2CsNO3 → Cs2O2 + 2NaNO3, ΔG = 199.7 kJ mol−1) from the molten nitrate electrolyte (please see ESI† for calculation details). We therefore hypothesize that the K2O2 and Cs2O2 observed in the discharged electrode came from soluble O2−2 in the molten-salt electrolyte that, upon cooling of the electrodes, became kinetically trapped out of equilibrium. This hypothesis is in agreement with the Raman spectra of an electrode that was cooled slowly (~1 K min−1), which shows very weak Raman bands for K2O2 and Cs2O2 (Fig. S11, ESI†). Interestingly, Raman spectra of discharged electrodes that had not been washed in aprotic solvents between discharge and characterization (Fig. S12, ESI†) showed evidence of some Na2O formation, which will be discussed below. Further support that the dominant discharge product was Na2O2 came from XRD patterns of washed, discharged electrodes (Fig. 3b) that showed clear peaks from Na2O2 ((220), (112), and (300)), but none from K2O2 or Cs2O2 or...
Na2O, where small amounts of amorphous Cs2O2 and K2O2 formed during cooling of the electrode would not be detectable using XRD. SEM images (Fig. 3c and d) reveal Na2O, large faceted crystals (5 to 30 μm) produced in the discharged electrode, which may be attributed to the high solubility of Na2O2 (65 mM, detailed method in ESI†) in NaN03/KNO3/CsNO3 molten-salts.

The formation of Na2O2, as well as some Na2O during discharge of molten-salt Na–O2 cells is further supported by the equilibrium potential from cyclic voltammogram (CV) measurements as well as pressure tracking and titration measurements. CVs collected using a molten-salt Na–O2 cell at 0.2 mV s−1 (Fig. S13, ESI†) showed a cathodic peak at 2.00 V, and anodic peak at 2.26 V. Significantly, the equilibrium potential estimated by E1/2 was 2.12 V, which is similar to that obtained from GITT measurements (≈2.09 V (Fig. S9a, ESI†)), as well as the calculated thermodynamic potential of the 2Na1+ + O2 + 2e− → Na2O at 443 K (2.15 V, see ESI† for details), but different from the formation Na2O (2.07 V, see ESI† for details) and Na2O (1.86 V, see ESI† for details), in agreement with the overall reaction being the formation of Na2O from O2.

Interestingly, pressure tracking measurements (Fig. 3e) of molten-salt Na–O2 cells during discharge showed two distinct regions corresponding to a 2.0 e−/O2 process at early discharge (0–4.5 mA h cm−2geo) and a 2.8 e−/O2 process later in discharge (4.5–12 mA h cm−2geo). The transition between the 2.0 e−/O2 and 2.8 e−/O2 processes at a discharge capacity of ≈4.5 mA h cm−2geo was accompanied by a transition from a sloped discharge voltage profile to a flat voltage profile once the discharge voltage reached ≈2.10 V. While the 2.0 e−/O2 in early discharge is consistent with the formation of Na2O2, the 2.8 e−/O2 process later in discharges suggests the formation of both Na2O2 (2 e−/O2) and Na2O (4 e−/O2). The origin of these two regions during cell discharge will be discussed later. Further evidence that the discharge product contained both Na2O2 and Na2O came from quantifications of a Ni/NaNO3/KNO3/CsNO3/SS electrolyte reacted at 6.0 mA h cm−2geo via the acid–base titrations method (details in the Experimental section). As shown in Fig. 4a, the pristine Ni/NaNO3/KNO3/CsNO3/SS electrolyte showed a cathodic peak at 1.46 V and anodic peak at 1.89 V, corresponding to an equilibrium potential of 1.68 V, which is in good agreement with the thermodynamic potential of NaNO3 + 2Na1+ + 2e− → Na2O + Na2O2 at 443 K (E° = 1.49 V, see ESI† for details). Further support that the discharge of Ni/NaNO3/KNO3/CsNO3/SS electrolytes in Na–Ar cells forms equilibrium Na2O and Na2O2, as shown by the acid–base titrations (details in the Experimental section). CV measurements of Na–Ar cells (Fig. S19, ESI†) showed a cathodic peak at 1.46 V and anodic peak at 1.89 V, corresponding to an equilibrium potential of 1.68 V, which is in good agreement with the thermodynamic potential of NaNO3 + 2Na1+ + 2e− → Na2O + Na2O2 at 443 K (E° = 1.49 V, see ESI† for details).

Nitrate anions are redox active in molten-salt Na–O2 batteries

Discharging Ni/NaNO3/KNO3/CsNO3/SS electrodes in Na–Ar cells resulted in the formation of Na3ONO2 (from equimolar Na2O and NaNO3) with a discharge voltage of ≈1.6 V (Fig. S15 and S16, ESI†). Ni/NaNO3/KNO3/CsNO3/SS electrodes could be discharged to capacities of >12 mA h cm−2geo in Na–Ar cells (Fig. S17, ESI†). Na–Ar cells with Ni/NaNO3/KNO3/CsNO3/SS electrodes could be discharged stably at rates up to 5 mA h cm−2geo (Fig. S17, ESI†) and after the first cycle, could be cycled with Coulombic efficiency (CE) of ~104% for 5 cycles (Fig. 4b and Fig. S18, ESI†). Raman spectra of the discharged electrode (Fig. 4c) showed bands at 810, 1056, 1064, 1319 cm−1, which come from a chemical reaction between Na and nitrate salts (please see details in the Experimental section), but instead 22.2 μmol of Na2O and 99.9 μmol of Na2O2 were detected, which combined, accounts for 5.2 mA h cm−2geo comparable to the actual capacity of 6.0 mA h cm−2geo. The mechanism for the formation of both Na2O2 and Na2O will be discussed later in detail.

**Fig. 4** The electrochemical performance and characterization of molten-salt Na–Ar batteries. (a) Titration results of pristine and discharged Ni/NaNO3/KNO3/CsNO3/SS electrodes in O2 and Ar (see Fig. S15, ESI† for the discharge profiles of the electrode). The amounts of NO2− measured via the Griess method (Fig. S3, ESI†), Na2O via the acid–base method, and Na2O2 via the titanium oxysalt titration method (Fig. S4, ESI†). The pristine electrode showed a small amount of NO2−, which was attributed to the electrode preparation process (see Experimental section for details). (b) The charge–discharge profiles of a molten-salt Na–Ar cell at a current density of 1 mA h cm−2geo (1st to 5th cycles) with a limited discharge capacity of 2.0 mA h cm−2geo at a temperature of 443 K. (c) The Raman spectra of positive electrodes before and after discharge from Na–Ar cells. Raman spectra of commercial Na2O and NaN03 as well as synthetic Na3ONO2 as a reference (see Experimental section for preparation details). (d) The charge–discharge profiles of molten-salt Na–Ar cells with eutectic salt of NaTFSI (31.9 w%)/KTFSI (68.1 w%) in 32O2 and Ar at current density of 0.2 mA h cm−2geo at temperature of 483 K.
5.77 mA h cm$^{-2}$$_{\text{geo}}$ and is close to the actual capacity of 6.0 mA h cm$^{-2}$$_{\text{geo}}$. The small amount of Na$_2$O$_2$ can be attributed to the direct formation of Na$_2$O$_2$ from NaNO$_2$ given by NaNO$_3$ + Na$^+$ + e$^-$ → NaNO$_2$ + 2Na$_2$O$_2$ with $E$ = 1.44 V$_{\text{NHE}}$ at 443 K. The redox activity of nitrate anions in molten-salt Na–Ar cells is in agreement with recent work on molten-salt Li–Ar cells.19

The presence of redox active nitrate anions in the electrolyte is essential to enable molten-salt Na–O$_2$ cells that form Na$_2$O$_2$ during discharge. Given the observed redox activity of nitrate anions in molten-salt Na–Ar cells, molten-salt cells were constructed where nitrate anions were replaced with redox inactive bis(trifluoromethanesulfonyl)imide anions (TFSI$^-$) by using NaTFSI/KTFSI (31.9/68.1 w%) eutectic salt50 with a melting temperature of 453 K as the electrolyte. The redox inactivity of TFSI$^-$ anions was confirmed by the negligible capacity of molten-salt Na–Ar cells with Ni/NaTFSI/KTFSI/SS electrodes (Fig. 4d). Molten-salt Na–O$_2$ cells with Ni/NaTFSI/KTFSI/SS electrodes discharged at 483 K showed a much higher discharge voltage of $\sim$2.6 V (Fig. 4d) compared to Ni/NaNO$_3$/KNO$_3$/CsNO$_3$/SS electrodes. Significantly, Raman spectra of the discharged Ni/NaTFSI/KTFSI/SS electrode (Fig. S20a, ESI†) indicated the formation of Na$_2$CO$_3$ (1080 cm$^{-1}$, $A'_g$ ($\text{CO}_3^{2-}$)) and K$_2$CO$_3$ (1055 cm$^{-1}$, $A'_g$ ($\text{CO}_3^{2-}$)), but not Na$_2$O$_2$. The formation of Na$_2$CO$_3$ and K$_2$CO$_3$ could be attributed to the decomposition of the TFSI$^-$ anion, the only major source of carbon in the electrode. Acid–base titration measurements confirmed that negligible amounts of Na$_2$O, Na$_2$O$_2$ or Na$_2$O$_3$ were present in discharged Ni/NaTFSI/KTFSI/SS electrodes. The formation of parasitic Na$_2$CO$_3$ and K$_2$CO$_3$ during the discharge of Ni/NaNO$_3$/KNO$_3$/CsNO$_3$/SS electrodes is consistent with negligible capacity ($<0.03$ mA h cm$^{-2}$$_{\text{geo}}$) upon charging to 3 V (Fig. S20b, ESI†). Through comparison of NaNO$_3$/KNO$_3$/CsNO$_3$ and NaTFSI/KTFSI electrolytes, it is clear that nitrate anions are critical for highly cyclable molten-salt Na–O$_2$ batteries. We next examine the chemical reactions between O$_2$ and the Na$_2$O and NaNO$_3$ that can form from the electrochemical reduction of NO$_3^-$.

Chemical oxidation of Na$_2$O and NaNO$_2$ by O$_2$

Na$_2$O$_2$ can be oxidized chemically by O$_2$ to form NaNO$_3$, while Na$_2$O can react with O$_2$ to form Na$_2$O$_2$ in Ni/NaNO$_3$/KNO$_3$/CsNO$_3$/SS electrodes. In order to assess the reaction between Na$_2$O and O$_2$, Ni/NaNO$_3$/KNO$_3$/CsNO$_3$/SS electrodes were prepared with added Na$_2$O, and held at 443 K in both an O$_2$ and Ar environment for 48 hours. Following 48 hours in an Ar environment, the Raman spectra of the Ni/NaNO$_3$/KNO$_3$/CsNO$_3$/SS electrode with added Na$_2$O was largely unchanged, retaining a strong signal at 237 cm$^{-1}$ from Na$_2$O (Fig. 5a). On the other hand, following the reaction in an O$_2$ environment, the Raman peak for Na$_2$O at 237 cm$^{-1}$ disappeared and new Raman peaks at 733 ($A'_g$ (Na$_2$O$_2$)), 754 ($A_g$ (Cs$_2$O$_2$)), 773 ($A_g$ (K$_2$O$_2$)), and 789 cm$^{-1}$ ($A'_g$ (Na$_2$O$_2$)) appeared.44,45 The disappearance of Na$_2$O and appearance of Na$_2$O$_2$ can be attributed to the reaction given by Na$_2$O + $\frac{1}{2}$O$_2$ → Na$_2$O$_2$, which is supported by the fact that Na$_2$O is thermodynamically more stable than Na$_2$O and Na$_2$O$_2$ at 443 K, as shown in Fig. 5b. We also noticed that the two distinct Raman peaks at 1052 and 1068 cm$^{-1}$ associated with the overlapping $A_{1g}$ modes of KNO$_3$51 and the $A_{1g}$ mode of NaNO$_3$,52 respectively, in the pristine electrode became a single broad peak at 1054 cm$^{-1}$ following the reactions in Ar and O$_2$, where this charge is attributed to the formation of a glassy NaNO$_3$/KNO$_3$/CsNO$_3$ state53 following fast cooling of the cell. We further examined the chemical reactions of Na$_2$O and NaNO$_3$ with O$_2$ by exposing a Ni/NaNO$_3$/KNO$_3$/CsNO$_3$/SS electrode discharged to 7.6 mA h cm$^{-2}$$_{\text{geo}}$ in a He environment, to O$_2$ at 443 K for 7 hours. Pressure tracking measurements upon the introduction of O$_2$ showed an initial, very rapid decrease in pressure, following which the pressure slowly stabilized over $\sim$6 hours [Fig. S21, ESI†]. By fitting the O$_2$ consumption curve over the first 3 min we determined a rate of $\sim$0.18 mmol h$^{-1}$, corresponding to a current density of 25 mA cm$^{-2}$.$_{\text{geo}}$ and indicating that the reactions of Na$_2$O and/or NaNO$_3$ with O$_2$ can be very fast. This finding is in agreement with previous work54 that indicates that NO$_2^-$ can be oxidized by O$_2$ to form NO$_3^-$ in bulk NaNO$_3$/KNO$_3$ molten salt at temperatures over 573 K.

Nitrate-mediated oxygen reduction reaction in Na–O$_2$ batteries

The oxygen reduction reaction in molten-salt Na–O$_2$ batteries occurs via a nitrate-mediated mechanism whereby NaNO$_3$ is first reduced electrochemically to form Na$_2$O and NaNO$_2$ (reaction (1)), following which Na$_2$O reacts with O$_2$ to form Na$_2$O$_2$ (reaction (2)), and NaNO$_3$ is oxidized by O$_2$ to regenerate NaNO$_3$ (reaction (3)), resulting in an apparent 2 e$^-$/O$_2$ overall reaction given by 2Na$^+$ + O$_2$ + 2e$^-$ → Na$_2$O$_2$ (reaction (4)). We note in the proposed reaction scheme that nitrate anions are not consumed during discharge such that the entire discharge capacity comes from the overall 2e$^-$/O$_2$ reduction of O$_2$ to Na$_2$O$_2$. Each step of the nitrate-mediated 2 e$^-$/O$_2$ reaction has been demonstrated above, where the electrochemical reduction of NaNO$_3$ to Na$_2$O and NaNO$_2$ was observed in Na–Ar cells (Fig. 4), and the oxidation of Na$_2$O and NaNO$_2$ by O$_2$ was shown through chemical experiments (Fig. 5 and Fig. S21, ESI†). Further evidence that the formation of Na$_2$O$_2$
from O₂ is facilitated by nitrate anions comes from ¹⁸O-isotopic labelling, where according to the proposed mechanism, discharge of Ni/NaNO₃/KNO₃/CsNO₃/SS electrodes in a 3⁶O₂ (¹⁸O¹⁸O) environment would proceed via:

\[
\begin{align*}
2\text{Na}^+ + \text{NaNO}_3 + 2\text{e}^- & \rightarrow \text{Na}_2\text{O}_2 + \text{Na}^{16}\text{O} \quad (1) \\
\text{Na}_2\text{O}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{Na}_2\text{O}_3 \quad (2) \\
\text{NaNO}_2 + \frac{1}{2} \text{Na}_2\text{O}_2 & \rightarrow \text{Na}_2\text{O}_3 \quad (3) \\
\text{Overall reaction: } 2\text{Na}^+ + 3\text{O}_2 + 2\text{e}^- & \rightarrow \text{Na}_2\text{O}_3 \quad (4)
\end{align*}
\]

Raman spectroscopy of a Ni/NaNO₃/KNO₃/CsNO₃/SS electrode discharged in a 3⁶O₂ (¹⁸O¹⁸O) environment showed evidence of red-shifted Raman peaks associated with ¹⁸O-enrichment of both NaNO₃ (reaction (2)) and Na₂O₂ (reaction (3)). As shown in Fig. 6a, ⁴⁰O₂ discharged electrodes showed several new red-shift peaks at 693, 713, and 768 cm⁻¹ in the O–O stretching region relative to those of ¹⁶O-substituted peroxides at 733, 754, 773, and 789 cm⁻¹, which could be attributed to ¹⁸O-substituted peroxides. Such red shifts of ¹⁸O-substituted Na₂O₂ are supported by the density functional theory (DFT) computed Raman spectra for Na₂¹⁸O₂ and Na₂¹⁶O₂, where the bands of Na₂¹⁸O₂ are shifted by 46 cm⁻¹ relative to Na₂¹⁶O₂ (Fig. 6a). Of significance is to note that while red-shifted Raman bands appeared in the 3⁶O₂ discharged electrode, the band at 789 cm⁻¹ attributable to Na₂¹⁶O₂ remained, suggesting the discharge product was a mixture of Na₂¹⁸O₂ and Na₂¹⁶O₂. In addition, in the NO₃⁻ symmetric stretching region, there are also red-shift peaks at 1010, 1013, 1018, 1029, 1033, 1037, 1045, and 1057 cm⁻¹, consistent with the formation of ¹⁸O-substituted NaNO₃, KNO₃ and CsNO₃ (Fig. 6b). Such red shifts in the NO₃⁻ symmetric stretching region due to ¹⁸O-enrichment is supported by simulated wavenumber of symmetric stretching as a function of ¹⁸O-substituted-N¹⁶O₃⁻ (Fig. 6b) obtained from DFT calculations of the isolated anion in vacuum at the B3LYP/6-31G(d,p) level, where greater red-shifts in the symmetric stretching were correlated with greater ¹⁸O substitution in N¹⁶O₃⁻. The presence of ¹⁸O-substituted-N¹⁶O₃⁻ can be attributed to the oxidation of N¹⁶O₂⁻ by ³⁶O₂ given by reaction (3).

Further evidence of a nitrate-mediated, apparent 2 e⁻/O₂ oxygen reduction reaction came from different electrochemical mass spectroscopy (DEMS) ¹⁸O-isotopic labelling experiments that showed that evolved oxygen came primarily from nitrate anions, as opposed to the O₂ discharge environment. DEMS measurements were conducted using a symmetric molten-salt Na–O₂ cell discharged in ³⁶O₂ (Fig. 6c). The negative electrode used in the DEMS cell was prepared in a Na–Ar cell with discharge capacity of 1.6 mA h cm⁻² to achieve a flat discharge plateau (Fig. S16, ESI†). Upon charging at 0.2 mA cm⁻², three types of molecular oxygen (i.e., ³₂O₂ (¹⁶O¹⁶O), ³⁴O₂ (¹⁶O¹⁸O), and ³⁶O₂ (¹⁸O¹⁸O)) were detected, consistent with the decomposition of Na₁⁶O₆O, Na₃¹⁶O⁴O and Na₅¹⁸O₈O, respectively. Remarkably, the amount of ³⁶O₂ evolved was very small (<2%), which indicates only a small amount of Na₃¹⁸O₈O was formed during discharge in ³⁶O₂, consistent with a nitrate-mediated reaction, as opposed to the direct reduction of O₂ to Na₂O₂. The high proportion (90%) of ³²O₂ (¹⁶O¹⁴O) detected during charge is in disagreement with reactions (1)-(4), which can be attributed to either (1) that the electrochemical reduction of NaNO₃ to Na₂O₂ given by NaNO₃ + Na⁺ + e⁻ → NaNO₂ + 1/2Na₂O₂ can contribute more significantly to the discharge process in Na₂O₂ cells as opposed to that observed in Na–Ar cells in Fig. 4a, (2) that the lower O₂ pressure for ³⁶O₂ cells ~ 100 kPa as opposed to ³²O₂ cells ~ 410 kPa slowed reactions (2) and (3), resulting in a higher proportion of Na₁⁶O in the discharged electrode, which could evolve ³₂O₂ (¹⁶O¹⁴O) or (3) that the nitrate-mediated reaction pathway is more complex than that given by reactions (1)-(4). Although this discrepancy motivates additional research into the detailed mechanism, we note that the high ratio of ¹⁶O¹⁸O ~ 3 in

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**Fig. 6** (a and b) The Raman spectra of discharged Ni/NaNO₃/KNO₃/CsNO₃/SS electrodes of Na–O₂ cells in ³⁶O₂ and ³²O₂ and DFT calculated Raman spectra. (c) The rate of oxygen evolution of ³²O₂, ³⁴O₂, and ³⁶O₂ as detected by DEMS measurements during charging a symmetric molten-salt Ni/NaNO₃/KNO₃/CsNO₃/SS battery at 0.2 mA cm⁻² to 2.8 V at 443 K with He carrier gas. Prior to the DEMS measurements, a Na–O₂ cell with Ni/NaNO₃/KNO₃/CsNO₃/SS was discharged to 8 mA h cm⁻² at 0.2 mA cm⁻² and the positive electrode was collected to serve as the counter electrode for the DEMS measurement. In the DEMS experiments, the battery was kept at OCV for 5 hours at 443 K to ensure full melting of the mixture of NaNO₃ (26 w%), KNO₃ (27 w%), and CsNO₃ (47 w%). The electrode geometric area was 0.785 cm². The ratio of ³⁶O₂/³²O is ~ 3 in the first charging plateau at ~2.1 V and the ratio increased in the second charging plateau at 2.5 V. The redox potential of nitrate reduction in Ar was ~1.65 V (vs. Na negative electrode) and was used to convert the measured cell potential to the voltage (vs. Na negative electrode) scale (Fig. S16, ESI†).
Fig. 6c strongly supports the hypothesis of a nitrate-mediated oxygen reduction reaction instead of direct O₂ reduction in molten-salt Na–O₂ cells.

In this work, we have reported a molten-salt Na–O₂ battery where the formation of Na₂O₂ is mediated by the electrochemical activity of nitrate anions. Such findings are similar to our recent work on molten-salt Li–O₂ batteries where the redox activity of nitrate anions can enable the formation of Li₂O upon discharge at 423 K. However, in molten-salt Li–O₂ cells, the Li₂O formed from the reduction of NO₃⁻ to NO₂⁻ is thermodynamically preferred to Li₂O₂ whereas in Na–O₂ cells, NaO can further react with O₂ to form Na₂O₂. The mediation of the oxygen reduction reaction by nitrate anions in molten-salt Li–O₂ and Na–O₂ cells has a number of interesting implications on the cell design and performance. First, the catalytic activity of the electrode surface towards nitrate redox is critical to enable high rates and low overpotentials. In molten-salt Li–O₂ cells, we identified NiO as having high catalytic activity due to its optimum binding of NO₃⁻ and NO₂⁻, whereas weaker binding catalysts like Cu₂O were limited by NO₃⁻ adsorption whereas stronger binding catalysts like Mn₃O₄ were limited by the oxidation of NO₂⁻ by O₂. The high performance of Ni-based catalysts for nitrate redox is in agreement with previous reports for Li–Ar cells. Second, the high weight of Ni-based electrodes limits the achievable specific energy of the positive electrode, necessitating the development of novel electrode materials with high catalytic activity for nitrate redox with lower weight, such as Ni-coated carbon.

Third, while the electrolyte is not consumed in the overall reaction where nitrate anions can participate in multiple catalytic cycles over the span of a single discharge (reactions (1)–(3)), the role of nitrate’s redox activity in the oxygen reduction reaction may introduce limitations in the lean-electrolyte regime needed to achieve high cell level specific energy, warranting additional research. Fourth, the blocking of O₂ within the electrode due to accumulation of the discharge product may shift the discharge product towards the formation of Na₂O at deeper discharges, which may be responsible for the presence of minor Na₂O in addition to major Na₂O₂ in deep discharge observed in Fig. 3e. Finally, the temporary formation of NO₂⁻ in the electrolyte during discharge may locally alter the physicochemical properties of the molten-salt electrolyte, such as its melting point, viscosity or ionic conductivity. During charging, our recent work has shown that the 2 electron oxidation of bulk Na₂O₂ to O₂ is limited by the last step (Na₂O₂ → O₂ + Na⁺ + e⁻), which is known to occur with small overpotentials in Na–O₂ cells with aprotic solvents, rationalizing the small charging overpotentials observed in this work. However, further work is needed to confirm the reaction pathway upon charging in molten-salt Na–O₂ batteries. While this work has shown that molten-salt Na–O₂ batteries can achieve promising areal energy (33 mW h cm⁻²) and power densities (19 mW cm⁻²) as well as stable cycling (400 cycles) and high energy efficiencies ~90%, further research efforts are needed to achieve commercially viable cell level performance.

Conclusions

In summary, we report high-performance molten-salt Na–O₂ batteries with a simple structure, utilizing a nitrate-mediated reaction to achieve >2e⁻ /O₂. First, we investigated the electrochemical performance of these molten-salt Na–O₂ batteries, showing high power density (19 mW cm⁻²) at 10 mA cm⁻² and high-energy efficiency (~90%) at a high current density of 5 mA cm⁻², with long cycle life (400 cycles). Next, using Raman, pressure tracking and titration measurements, we showed that the dominant discharge product was Na₂O₂. We further studied the redox activity of nitrate anions in Na–Ar cells, showing that NaNO₃ could be electrochemically reduced to Na₂O and NaNO₂, where Na₂O and NaNO₂ could further react chemically with O₂. Finally, using ¹⁸O-labeling experiments, we showed that the oxygen reduction reaction in molten-salt Na–O₂ batteries occurred via a nitrate-mediated mechanism whereby NaNO₃ was first electrochemically reduced to form Na₂O and NaNO₂, following which NaO reacted with O₂ to form Na₂O₂, while NaNO₂ was oxidized by O₂ to regenerate NaNO₃, resulting in an apparent 2 e⁻ /O₂ overall reaction to form Na₂O₂. Such nitrate-mediated molten-salt Na–O₂ batteries provide a novel approach to develop alkali metal–O₂ batteries with high energy and power density.

Author contributions

Y. G. Z., G. L. and Y. S. H. conceived and designed the study. Y. G. Z., G. L., A. A., K. G., Y. Z. and Y. S. H. conducted experiments, computation, and analysis. Y. G. Z., G. L. and Y. S. H. wrote the manuscript, and all authors edited the manuscript. There is no competing interest. All data and materials used in the work are available in the manuscript or supplementary materials.

Conflicts of interest

Y. G. Z., G. L. and Y. S. H. have applied for a patent related to this work.

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