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Title: Rechargeable-battery Chemistry Based on Lithium Oxide Growth through Nitrate Anion Redox

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Abstract:

Next-generation lithium-battery cathodes often involve the growth of lithium-rich phases, which enables specific capacities that 2-3 times higher than insertion cathode materials such as lithium cobalt oxide (LiCoO₂). Here, we investigate battery chemistry previously deemed irreversible in which lithium oxide (Li₂O), a lithium-rich phase, grows through reduction of the nitrate anion in a lithium nitrate-based molten salt at 150 °C. Using a suite of independent characterization techniques, we demonstrate that a Ni nanoparticle catalyst enables the reversible growth and dissolution of micron-sized Li₂O crystals through the effective catalysis of nitrate reduction and nitrite oxidation, resulting in high cathode areal capacities (~12 mAh/cm²). These results enable a rechargeable battery system that has a full-cell theoretical specific energy of 1579 Wh/kg, in which a molten nitrate salt serves as both active material and electrolyte.

Main Text:

State of the art commercial Li-ion batteries use cathodes such as lithium cobalt oxide (LiCoO₂), which rely on insertion and removal of Li ions from a host material during electrochemical cycling¹. Such insertion cathode materials are limited in their capacity by the electrochemically inactive components in their crystal structure; replacing them with a cathode that facilitates growth and dissolution of Li-rich solid phases could significantly increase a battery's energy density². For example, oxygen and sulfur cathodes have been widely researched due to their large theoretical energy density, with both involving the growth of a lithium-rich compound on a current collector/catalyst support³⁻⁶. However, these two chemistries suffer from practically low cathode areal capacities and severe electrolyte decomposition during cell operation. Here we propose a cell chemistry based on a solution-controlled mechanism that allows cathode areal capacity greater than 10 mAh/cm², 5-10x higher than current commercial Li-ion insertion cathodes, as well as an alkali metal nitrate based-electrolyte stable to both anode and cathode chemistries.

Similar to Li/O₂ and Li/S electrochemical systems, we consider a phase-forming conversion chemistry, in which a lithium nitrate-based molten salt serves as both an active material and the electrolyte. Molten nitrate salts have been studied as an active material in a primary Li battery, where Li₂O forms irreversibly when nitrate reduces to nitrite⁷⁻¹⁰. In this study, we introduce a metal nanoparticle catalyst that enables a reversible cell chemistry. A eutectic composition of LiNO₃ – KNO₃ electrolyte (42 – 58 mol %) has a melting point of 125 °C, which allows its use as a liquid electrolyte at ~150 °C. The chemical formulation, the Gibbs free energy, and the thermodynamic potential for this reaction at 150 °C are



The nitrate reduction chemistry of Eq. 1 has a theoretical capacity of 647 mAh/g based on the total mass of reactants (left side of Eq. 1) paired with a 1579 Wh/kg full cell theoretical specific energy. We confirm reversible molten nitrate battery chemistry by combining electrochemical measurements with spectroscopic analyses (Raman, UV-visible, X-ray Photoelectron), anion exchange chromatography, scanning and transmission electron microscopy, and *in situ* cell pressure monitoring coupled with residual gas analysis.

Results and Discussion

Mechanistic investigations. Previous work using this chemistry as a primary battery used a high surface area carbon as the cathodic current collector, which necessitates a large overpotential of ~500 mV on discharge¹⁰. Attempts to reverse the chemistry after discharge revealed that this significant overpotential was accompanied by gas evolution, which suggests the irreversibility of this reaction (Supplementary Fig. 1). Using a cathodic current collector that catalyzes the reaction in Eq. 1 would enable reversibility of the reaction, which would allow its use in a secondary battery¹¹, shown schematically in Fig. 1A. Finding such a catalyst for nitrite oxidation is particularly important because Li_2O oxidizes directly to O_2 at potentials above 2.8 V. We explored a variety of different metal nanoparticle catalyst candidates (Supplementary Table 1). Fig. 1B shows their first cycle overpotentials and clearly demonstrates that 50 nm-diameter Ni nanoparticles are particularly effective for catalyzing both the reduction of nitrate and the oxidation of nitrite, with 50 mV overpotential¹¹. The 50 micron-diameter Ni particles exhibit a large overpotential of ~600 mV and a low capacity, which highlights the importance of using a high surface area catalyst. Reaction in Eq. 1 also suggests that lithium metal anode reacts spontaneously with nitrates to form lithium oxide and nitrites. The formation of a thin Li_2O film

allows lithium metal to be used as negative electrode in alkali metal nitrate melts. However slow corrosion of Li metal due to solubility of the Li₂O surface layer, leading to the production of nitrites, has been observed⁷. UV-visible spectroscopy was used to quantify the amount of nitrites generated by both the anode chemical reaction and the cell discharge reaction (Supplementary Fig. 2). The concentration of “electrochemically formed” nitrites in the cell following discharge was found to be in good agreement with the discharge capacity. Symmetric Li-Li cells employing a molten LiNO₃-KNO₃ eutectic electrolyte cycling at 150 °C showed a slight increase in Li plating/stripping overpotential after 70 cycles or ca. 700 hours (Supplementary Fig. 3). To confirm electrochemical reversibility and to determine the Open Circuit Voltage (OCV) when using Ni nanoparticles as a cathode catalyst, we employ Galvanostatic Intermittent Titration Technique (GITT) across a single discharge/charge cycle with two different electrolyte compositions: (1) an all-nitrate LiNO₃ – KNO₃ electrolyte (dashed line) and (2) a nitrate/nitrite LiNO₃ – KNO₂ electrolyte (solid line) (Fig. 1C). By interrupting the discharge and charge processes with extended periods of open circuit, this technique allows measuring the reaction potential of the occurring electrochemistry. Fig. 1C shows a stable OCV of ~2.47 V for the LiNO₃ – KNO₂ electrolyte, which agrees with the calculated standard potential of 2.44 V. The consistency of the OCV on discharge and charge suggests the reversibility of the reaction. For the LiNO₃ – KNO₃ electrolyte, the OCV was initially ~2.55 V and gradually decreased on discharge and increased on charge. This process agrees with what we would expect from the Nernst equation (Eq. 2), since the concentration of nitrite, the reduced species, is initially negligible.

$$E = E^0 - \frac{RT}{zF} \ln \left(\frac{\alpha_{Red}}{\alpha_{Ox}} \right) \quad (2)$$

R is the gas constant, T is temperature, z is the number of electrons transferred in the reaction, F is Faraday's constant, and a is the species activity. When assuming an initial nitrate-to-nitrite ratio of 100:1, this corresponds to a Nernstian potential shift of 84 mV, in agreement with the measured potential shift between the two electrolyte concentrations. As the concentration of nitrite increases throughout discharge, its activity approaches unity, and thus the OCV approaches the equilibrium potential. Without the presence of nitrates (i.e. an all nitrite eutectic) the cell discharges according to the following cell reaction: $\text{Li} + \text{LiNO}_2 \rightarrow \text{NO}\uparrow + \text{Li}_2\text{O}$, which takes place at ca. 2.1 V vs. Li^+/Li^0 (Supplementary Fig. 4).

The role of Ni nanoparticle cathode current collector. We performed *ex situ* characterization of the Ni nanoparticle electrode and various electrolyte compositions. Fig. 2(A,B) shows Scanning Electron Microscope (SEM) images of a discharged cathode, which reveals the solid discharge product to consist of octahedral, micron-sized crystals and a thin film growing over the bed of Ni nanoparticles (Supplementary Fig. 5 shows SEM of bare Ni nanoparticles). Energy Dispersive X-ray Spectroscopy (EDS) of a discharged cathode reveals only oxygen to be present in these crystals (Supplementary Fig. 6); identifying Li is beyond the detection limits of EDS. Fig. 2C shows Transmission Electron Microscope (TEM) analysis of a representative octahedron, with the inset containing an electron diffraction pattern of the marked selected area (indexed pattern and corresponding bright field image are shown in Supplementary Fig. 7). This diffraction pattern corresponds to single crystalline antifluorite crystal structure, consistent with Li_2O . The faceted octahedral morphology of these single crystals are consistent with what would be predicted by a lowest surface energy (Wulff) construction of Li_2O ¹². We conjecture that Li_2O grows according to its Wulff construction due to enhanced kinetics from the elevated operation

temperature and discharge product solubility, similar to that reported for a Li-O₂ battery using this electrolyte^{13,14}.

Figure 2D shows X-ray Diffraction (XRD) analysis of a Ni cathode held at OCV, after discharge, and after a full cycle, with a reference scan of Li₂O. The peaks at $2\theta = 45^\circ$ and 52° that correspond to Ni and those at $2\theta = 39^\circ$, 45° , and 65° that correspond to Al (current collector) are present in each scan; the additional peaks at $2\theta = 34^\circ$, 56° , and 67° in the discharged cathode align with the reference peaks for Li₂O. These results suggest the formation of crystalline Li₂O upon discharge and its oxidation upon charge. The absence of any diffraction peaks besides Li₂O and the cathode materials confirms that no other crystalline products were formed. Fig. 2E contains Raman spectra of a nitrate electrolyte held at OCV, after discharge, and after a full cycle, with “as-prepared” nitrate and nitrite eutectics provided for comparison. These spectra demonstrate the formation of nitrite upon discharge and its oxidation upon charge. Broadening of the nitrate eutectic Raman bands at 720 and 740 cm⁻¹ during cycling is thought to originate from melt structural changes as nitrite ions are introduced^{15,16}. Raman analysis of discharged Nickel electrode surface did not allow us to detect lithium oxide, most probably due to excess molten nitrate electrolyte currently used in these cells (150 μL/cm²). KNO₃ (58 mol.% in the eutectic) has limited solubility in most organic solvents commonly used for Li battery electrode rinsing. Minimizing nitrate electrolyte volume for accurate detection of Li₂O by XPS depth profiling analysis is an ongoing effort.

A reversible process. Figure 2F demonstrates an attempt to charge newly constructed cells.

When using an all-nitrite electrolyte and a clean cathode, the cell polarized due to the absence of Li₂O. The other three cells contained a cathode harvested from another cell that was discharged to 2.3 V, effectively pre-loading the cathodes with Li₂O. Those cells with at least some nitrite in

the electrolyte and a discharged cathode were able to charge, and those with a purely nitrate electrolyte polarized because the absence of nitrite disallows the charging reaction. These results demonstrate that Li_2O and a nitrite-containing electrolyte must coexist to allow the charging reaction ($\text{Li}_2\text{O} + \text{LiNO}_2 \rightarrow 2\text{Li} + \text{LiNO}_3$) to occur.

These results qualitatively confirm the formation of both nitrite and Li_2O on discharge, and now we use a quantitative technique that can be corroborated with electrochemical data. In a similar vein, differential electrochemical mass spectrometry (DEMS) found use in the Li-O_2 battery field to directly quantify the amount of oxygen consumed and produced, whereas before a simple qualitative confirmation of Li_2O_2 was seen as sufficient^{17,18}. To this end, we use ion exchange chromatography to measure the ratio of nitrate to nitrite anions in the electrolyte. This allows a direct comparison between the electrochemical data (Fig. 2F) and the amounts of nitrate and nitrite present in the electrolyte.

All three of the electrolyte compositions whose electrochemical performance is shown in Fig. 2F were examined via ion exchange chromatography, with the purely nitrite electrolyte proving to be most revealing (detailed explanation in Supplementary Fig. 8). After accounting for the small impurity amounts found in nitrite, all of the nitrate can be attributed to the charging reaction.

Considering this reaction transfers $2e^-/\text{mol}$ nitrite generated, we converted the number of moles of produced nitrate to the equivalent number of mAh passed due to this reaction. We passed 2 mAh of charge based on the electrochemical data in Fig. 2F, and the ion exchange chromatography data revealed that 2.09 mAh equivalent of nitrate is present in the electrolyte.

This suggests that the charge process is consistent with the chemical reaction described in Eq. 1.

To better understand the role of Ni nanoparticles as a catalyst in this system, we performed TEM analysis on Ni nanoparticles after their exposure to the molten nitrate salt and observed a ~ 5 nm

thick surface layer on each particle (Supplementary Fig. 9). X-ray Photoelectron Spectroscopy (XPS) depth profile of a Ni nanoparticle electrode exposed to molten salt demonstrates that this surface layer is nickel oxide (NiO), which contains both Ni²⁺ and Ni³⁺ states, and upon depth profiling, a transition to metallic Ni (Fig. 3A, B). This mixed oxidation state surface suggests a Ni deficient NiO layer. While a native oxide layer with a small Ni vacancy concentration forms on Ni surfaces exposed to air¹⁹, we conjecture that the exposure of Ni to a molten nitrate salt further enhances this Ni deficiency by introducing Li substitutions at Ni sites in their rock salt crystal lattices, as supported by other work using LiNO₃ to dope NiO particles²⁰.

Catalyzed cathode conversion reaction. We propose that it is this cation deficient NiO surface, and not metallic Ni, that serves as the catalyst for reversible nitrate reduction. These point defect sites in the form of a Ni vacancy or Li substitution serve as an oxide ion transfer catalyst enabled by the neighboring Ni atom's ability to cycle between 2⁺ and 3⁺ oxidation states. To test this hypothesis, we synthesized Li-doped NiO (L-NiO) particles for use as a cathode catalyst in nitrate reduction (Supplementary Fig. 10). Such a doped NiO displays p-type conductivity, allowing its use without a conductive additive^{21,22}. Fig. 3C demonstrates its performance on charge and discharge, which is nearly identical to that of the cell with Ni nanoparticles, and confirms that it is this doped NiO which serves as the catalyst for this reaction. While a pure NiO is not conductive, and thus makes a poor choice of electrode material, a doped NiO could potentially be a better choice than Ni nanoparticles if one were to more optimally design this system going forward.

With a good understanding of the reversibility of Eq. 1 afforded by the catalysis of L-NiO, we probed the cycling behavior of the system. To de-couple studying the chemistry's reversibility from the cathode's ability to accommodate Li₂O growth, we cycled these cells with a capacity

limitation of 1.27 mAh/cm² on discharge (i.e. ~10% of total discharge capacity 12 mAh/cm², Supplementary Fig. 11), and to avoid O₂ evolution at higher potentials, we cycled with a potential limitation of 2.75 V on charge. Fig. 4A shows that the pressure in the headspace of the cell remained constant over 1000 hours of cycling, which suggests that no side reactions with gaseous evolution occurred. The cycling profile remains unchanged over 100 cycles except for the gradual drop in potential due to accumulating nitrite and the increase in coulombic efficiency as the electrolyte and cathode saturate with nitrite and Li₂O (Fig. 4A, B). The initially poor coulombic efficiency can be attributed to the diffusion of nitrite away from the cathode and to the sparing solubility of Li₂O in molten nitrate^{13,14,23}. The current design allows only ~10% nitrate utilization which is caused by Li₂O clogging the cathodic current collector. This is not a limitation of the chemistry but a cell engineering problem, which is the subject of our ongoing work.

Conclusions

While the implementation of this chemistry is hindered by the long term stability of a Li anode, an issue in most “beyond Li-ion” chemistries, the cycling stability of the cathodic reaction stands in contrast to similar systems such as the Li-O₂ battery which is plagued by degrading side reactions²⁴. The absence of carbonaceous species in the cell removes many of the typical side reaction mechanisms found in other chemistries^{25,26}. While the elevated temperature operation may impact the development of molten nitrate batteries for certain applications (e.g. electric vehicles), the implementation of low melting point ternary or quaternary molten salt electrolytes allowed us to reduce the cycling temperature to 110 °C²⁷. Through careful characterization of nitrate reduction, we have demonstrated the ability of a Ni nanoparticle catalyst to enable the

reversibility of a previously irreversible system, creating a new, high capacity secondary battery chemistry in which the electrolyte also serves as the active material.

Methods

Cell Design and Construction

All alkali metal nitrate salts were purchased from Sigma-Aldrich, vacuum dried at 120 °C for 1 week and stored inside an Ar-filled glovebox. Typically, a 12 mm diameter glass microfiber separator (Whatman) was impregnated with 200 mg of eutectic mixture and then vacuum dried at 200 °C (above the eutectic melting point) for 1 day using an oven (LC Technology Solutions) inside the glovebox. For trace amounts of water in the electrolyte, Karl Fischer titration was performed using dry N-methyl acetamide solvent (NMA, 5 ppm H₂O, Sigma-Aldrich), showing a typical water content of 10 ppm. The positive electrode, except for the catalyst search, consisted of Nickel nanopowder (MTI Corporation, 50 nm particle size, 40-60 m²/g specific surface area). The nanopowder was used as received with no pretreatment or surface activation and dry pressed on a 10 mm diameter stainless steel or aluminum mesh. Typical Nickel loading in these batteries was 5-20 mg/cm² and that of the electrolyte ~150 μL/cm². Cathode surface area was 0.785 cm². Platinum and Palladium nanoparticles were obtained from Fuel Cell Store. Cobalt, Iron, and Copper nanoparticles were obtained from MTI Corporation. Micron-sized Nickel was obtained from Sigma-Aldrich. All powders were vacuum dried inside an Ar-filled glovebox at 120 °C for 3 days prior to use. Particle size and specific surface area were all provided by suppliers and are listed in Supplementary Table 1. Cathode loading for catalyst search experiment was 5 mg/cm².

Typical electrochemical cells consisted of hermetically sealed stainless steel fixtures (Swagelok[®]) of known volume (~10 mL) containing a pressure sensor (Omega) and a valve (Valco Instruments) that can easily be connected to a mass spectrometer for qualitative and quantitative gas analysis. Batteries were routinely leak-tested with helium gas at 150 °C prior to

use. The anode consisted of an 8 mm diameter lithium metal disc (250 microns thick) used as received (MTI Corporation). Once electrolyte and cathode were added into the battery, a stainless steel spring was used to accommodate volume changes upon electrolyte. All battery construction was performed in an Ar-filled glovebox with O₂ and H₂O levels maintained below 0.1 ppm. Batteries were purged with pure Argon at room temperature and maintained under positive pressure, typically around 1-3 atm. Batteries were then transferred to an oven kept at 150 °C. Open-circuit voltage was applied for 12 hours to ensure both the battery voltage and the pressure reached equilibrium.

For cathode and electrolyte characterization measurements, cells having completed their electrochemical protocol were collected inside an Ar-filled glove box for disassembly and harvesting. Typically, positive electrodes were extracted from batteries after reheating to melt the electrolyte and rinsed with ultra-dry NMA solvent (3x 30 minutes) in order to remove excess nitrate salts.

Characterization

Scanning Electron Microscopy (SEM) analysis was performed in a Versa 3D DualBeam focused ion beam (FIB) microscope (FEI) and the elemental analysis with a ZEISS 1550VP FESEM microscope equipped with an Oxford X-Max SDD X-ray energy dispersive spectrometer.

Transmission Electron Microscopy (TEM) analysis was performed using a FEI Tecnai F30ST (300kV). X-ray Diffraction (XRD) was performed in a PANalytical X'Pert Pro with Cu K α 1 radiation. Raman spectroscopy was performed on a Renishaw M1000 Mirco Raman

Spectrometer System with an Ar ion laser at 514.5 nm. X-ray Photoelectron Spectroscopy (XPS)

was performed with a Surface Science Instruments M-Probe XPS system under monochromatic Al K α X-ray (1486.6 eV) illumination.

Ion Exchange Chromatography

Batteries of varying electrolyte compositions were assembled and discharged to a 2.3 V cutoff. The cells were taken to the glovebox and disassembled, separating the electrolyte and cathode. For some cells, the cathode was cleaned using the procedure above and then put into another cell with new lithium anode and electrolyte. These cells with discharged cathodes (containing Li₂O) were then charged a fixed amount (2 mAh) and similarly disassembled. All electrolytes of interest were collected and dissolved in mQ water of known volume. Following a dilution procedure, the ion concentration was in the 10-500 μ M range which is appropriate for ion exchange chromatography. A Dionex ICS-2000 Ion Chromatography System was used for all experiments, and a calibration procedure for both NO₂⁻ and NO₃⁻ was performed before each set of samples. A ratio of NO₃⁻ to NO₂⁻ anions was calculated from the measurements (typical data in Supplementary Fig. 8), and using the initial mass of electrolyte in the cell, the number of moles of each could be calculated.

Li-doped NiO Synthesis

2.0 mL of H₂O:iso-propanol (2:1) was added to a mixture of Ni(OH)₂ (1.0 g, 10.79 mmol) and LiOH (12.93 mg, 0.54 mmol) in a vial. The suspension was sonicated at room temperature for 2 hours to make it a homogeneous mixture. Water and iso-propanol were then removed using a rotary evaporator under vacuum. The resulting wet slurry was dried in an oven at 50 °C for overnight. The Ni(OH)₂-LiOH solid mix was then heated to 300 °C in a furnace for 3 hours to

give nano-particles of Li-doped NiO. BET surface area measurements were performed using a Micromeritics TriStar II Plus surface area analyzer. A BET surface area of 120 m²/g was measured, following a 17-hour degassing at 120 °C under N₂ flow. SEM and TEM data is shown in Supplementary Fig. 10.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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Author Contributions

D.A., G.V.C., V.G., and J.U. conceived of the project. V.G., J.U., D.T., and H.T. collected electrochemical data. D.T. performed electron microscopy, diffraction, and chromatography. H.T. performed Raman spectroscopy. D.T. and B.M.G. performed x-ray photoelectron spectroscopy. J.U. performed UV-visible spectroscopy and synthesized lithium doped Ni oxide. B.D.M. and J.R.G. assisted with data analysis. D.T. and V.G. wrote manuscript with input from all authors.

Competing Interests

D.A., G.V.C., V.G., and J.U. are inventors on patent application US 2016/0204418.

Materials and Correspondence

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Figure Captions

Fig. 1. Electrochemical Reduction of Nitrate Anions and Reversible Formation of Lithium Oxide Discharge Product. a, Schematics of the discharge and charge processes in a nitrate reduction chemistry, with molten nitrate electrolyte shown in blue and Li_2O formed on the conductive catalyst cathode support shown in yellow. The discharge reaction involves the

reduction of nitrate to produce nitrite and lithium oxide while the charge reaction is the reverse process. The nitrate-based molten salt is used as both the electrolyte and the cathode active material. **b**, First discharge/charge cycle of 1.0 mAh capacity limited nitrate reduction using various nanoparticle cathode current collectors, (0.1 mA/cm², ~5 mg/cm² catalyst loading, 0.785 cm² cathode area). Both discharge and charge voltages are highly dependent on the nature of cathode surface, with Ni nanoparticles showing the highest energy efficiency. **c**, Galvanostatic Intermittent Titration Technique (GITT) of nitrate reduction with Ni nanoparticle cathode in an all-nitrate (dotted line) and nitrate/nitrite (solid line) electrolyte, which demonstrates the reversibility of the reaction. The cell equilibrium voltage is measured during open circuit voltage and found consistent with the available thermodynamic data for the battery reaction: $2\text{Li}^+ + \text{NO}_3^- + 2\text{e}^- = \text{Li}_2\text{O} + \text{NO}_2^-$.

Fig. 2. Elucidation and Characterization of Battery Discharge and Charge Mechanisms. **a**, and **b**, SEM images of Ni nanoparticle cathodes extracted in the discharged state, showing the growth of large crystals of Li₂O (scale bars: 20 μm and 5 μm, respectively). **c**, Transmission Electron Microscopy (TEM) of octahedral discharge product harvested from the extracted Ni nanoparticle cathode after discharge. Inset contains the electron diffraction pattern of the shown selected area (scale bar: 200 nm). **d**, XRD of Ni nanoparticle cathodes extracted after rest at OCV, after discharge, and after one full discharge-charge cycle, with Li₂O reference scan (65-2972 JCPDS card#) provided for comparison. Peaks not attributed to Li₂O are from the Ni nanoparticles and Al grid they are pressed onto. **e**, Raman spectroscopy of extracted nitrate electrolyte after rest at OCV, after discharge, and after one full discharge-charge cycle, with measured nitrate and nitrite eutectics provided for comparison. **f**, Charging profile of newly

constructed cells with 2.0 mAh capacity limitation. The clean cathode has a $\text{LiNO}_2 - \text{KNO}_2$ electrolyte. The other three cells contain a Ni nanoparticle cathode harvested from a discharged cell and put into a new cell containing the labelled electrolyte composition (0.25 mA/cm^2 , $\sim 5 \text{ mg/cm}^2$ Ni loading).

Fig. 3. Cathode Surface Catalysis Promoting Reversible Nitrate Electrochemistry. XPS depth profiles of a Ni nanoparticle electrode exposed to molten nitrate for the **a**, Ni 2p and **b**, O 1s binding energies. **c**, Full cycle of cells containing Ni nanoparticle and Li-doped NiO cathodes (0.1 mA/cm^2 , $\sim 5 \text{ mg/cm}^2$ catalyst loading).

Fig. 4. Molten Nitrate Cell Using Ni Nanocatalyst with Long Cycle Life. **a**, Pressure of cell headspace with evolution of cycling profile. *In situ* pressure monitoring during battery cycling show no variation in gas profile over 1000 hours, consistent with the cell chemistry and demonstrating very stable system with no side reactions typically associated with electrolyte interfacial degradations at both anode and cathode materials. **b**, discharge/charge capacity with coulombic efficiency for a cell using a Ni nanoparticle cathode (0.25 mA/cm^2 , 1.27 mAh/cm^2 capacity limitation, 15 mg/cm^2 Ni loading).