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Rechargeable-battery chemistry based on lithium oxide growth through nitrate anion redox

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Supplementary Information

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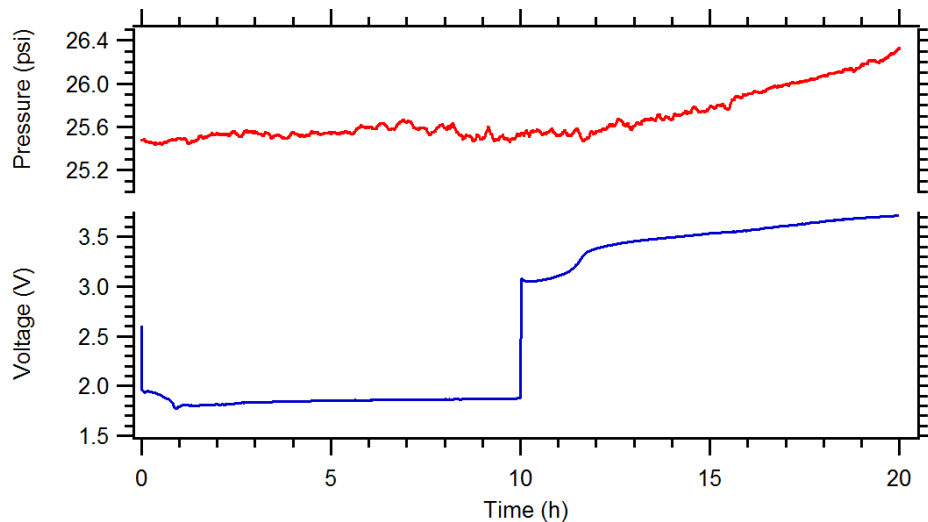
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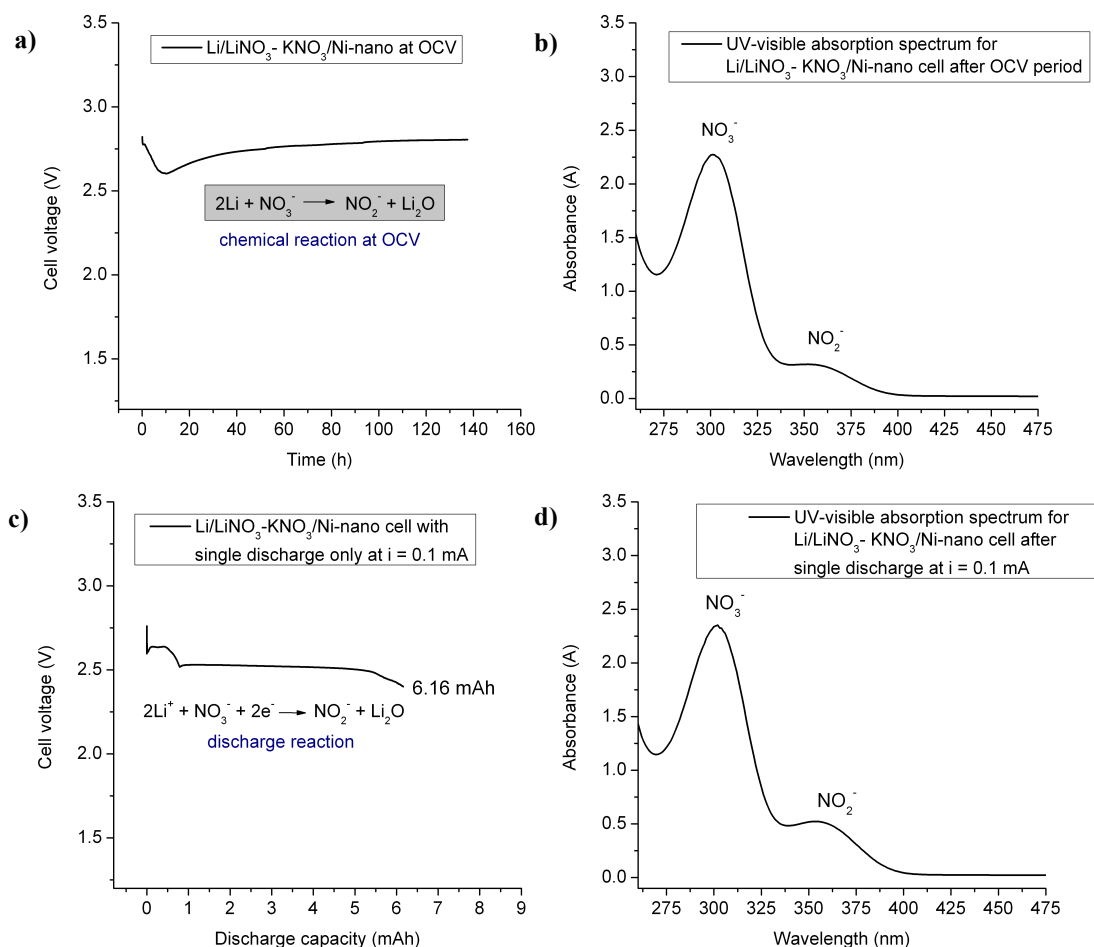
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Supplementary Fig. 1. Voltage Profile of Carbon Electrode in Alkali Metal Nitrate Electrolyte with *in situ* Pressure Analysis. Discharge and charge of a $\text{Li}|\text{LiNO}_3:\text{KNO}_3$ molten salt cell with a Super P carbon cathode ($j = 0.25 \text{ mA cm}^{-2}$). The large overpotential demonstrates that carbon is a poor catalyst for nitrate reduction. Pressure monitoring of the head space of the cell shows the generation of a gas side product upon charge.

Catalyst	Specific Surface Area (m²/g)	Particle Size (nm)
Pt	45-52	5-7.5
Ni micro	<1	50 (μm)
Pd	40-48	6-10
Fe	40-60	80
Co	40-60	28
Cu	30-50	50
Ni nano	40-60	50

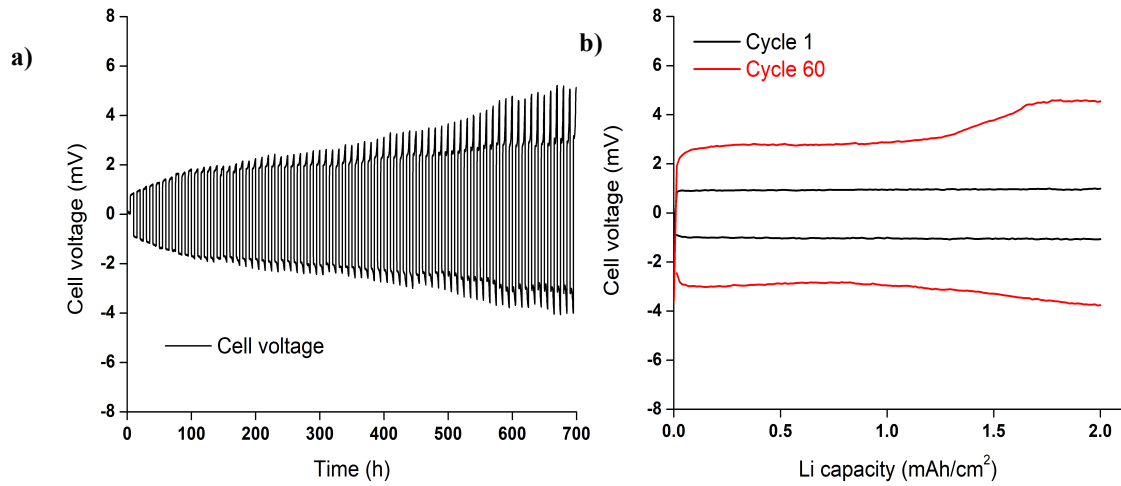
Supplementary Table 1. Structural properties of catalysts used in this study.



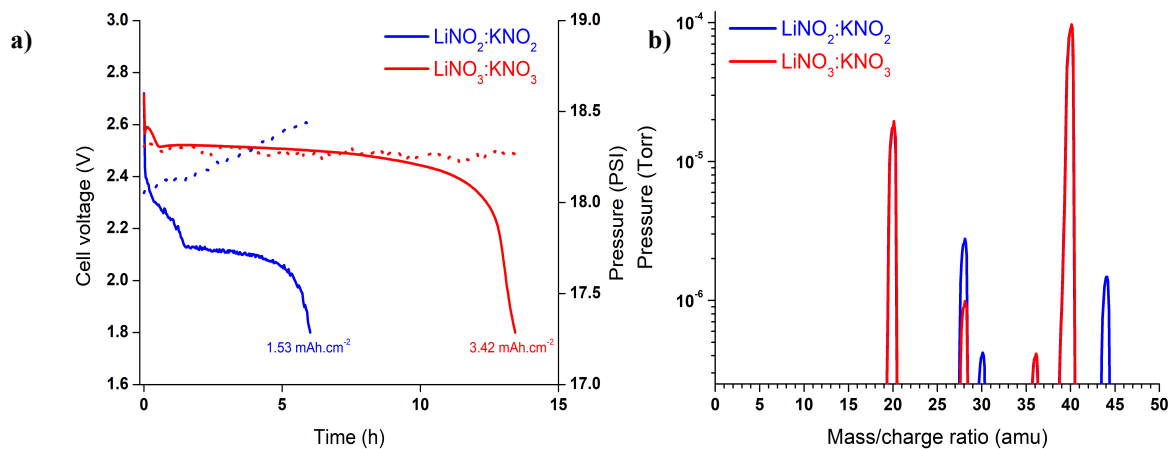
Supplementary Fig. 2. Li/LiNO₃-KNO₃/Ni-nano cells used for UV-visible spectroscopy and nitrite quantification. (a) Cell kept under OCV at 150 °C (b) UV-visible data of the water solution of electrolyte and cathode of the OCV cell (c) Single discharge cell at 150 °C (d) UV-visible data of the water solution of electrolyte and cathode of the discharged cell.

All UV-visible spectrometry measurements were performed using a Perkin Elmer Lambda 25 Spectrophotometer with quartz SUPRASIL[®] cells. To prepare samples for this UV-vis analysis, two cells were assembled identically in sealed Swagelok fixtures under argon using Li disc (8 mm diameter) as anode, and Ni nano-powder (20 mg/cm² loading, 0.785 cm² electrode, MTI, 50 nm particle size) as cathode and eutectic mixture of LiNO₃-KNO₃ (200 mg) as electrolyte. Both cells were kept at 150 °C for 5 days 17 hours 16 min - one under OCV only and the other one under discharged condition at 0.1 mA/cm² to 2.4 V cutoff. Both cells were stopped at the same time, cooled to room temperature, and disassembled. After disassembly, we separated the

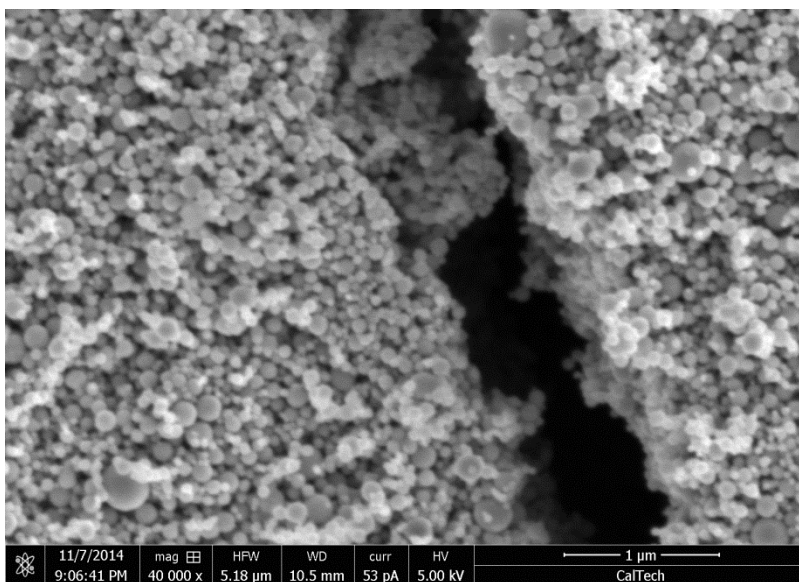
cathodes from separator-pellets and placed them in 5 mL of ultra-pure H₂O in a separate volumetric flask before filtering out the Ni nano-powder. The volume of H₂O was adjusted to 10 mL in each volumetric flask. The UV-visible spectra of both solutions were taken separately with the same UV-visible spectrophotometer scanning from wavelengths 800 – 200 nm. Pure H₂O was used as a reference sample for each measurement. We generated a calibration curve by making a series of solutions with varying concentrations of NO₂⁻ in ultra-pure H₂O with a known concentration of NO₃⁻ (200 mM). The UV spectra indicate that the amount of NO₂⁻ generated during the OCV period was 0.1213 mmol, and that generated during the discharge period is 0.2273 mmol, which represents the combined amount of NO₂⁻ from the electrochemical discharge reaction and the chemical reaction. Therefore, the amount of NO₂⁻ generated only from the electrochemical discharge reaction is 0.1057 mmol. According to the Faraday's law, 0.1057 mmol of NO₂⁻ is equivalent to the capacity of 5.67 mAh. The discharge capacity obtained from the cell is 6.16 mAh (fig. S2c), which renders the error for quantification of NO₂⁻ from the discharged cell <8%.



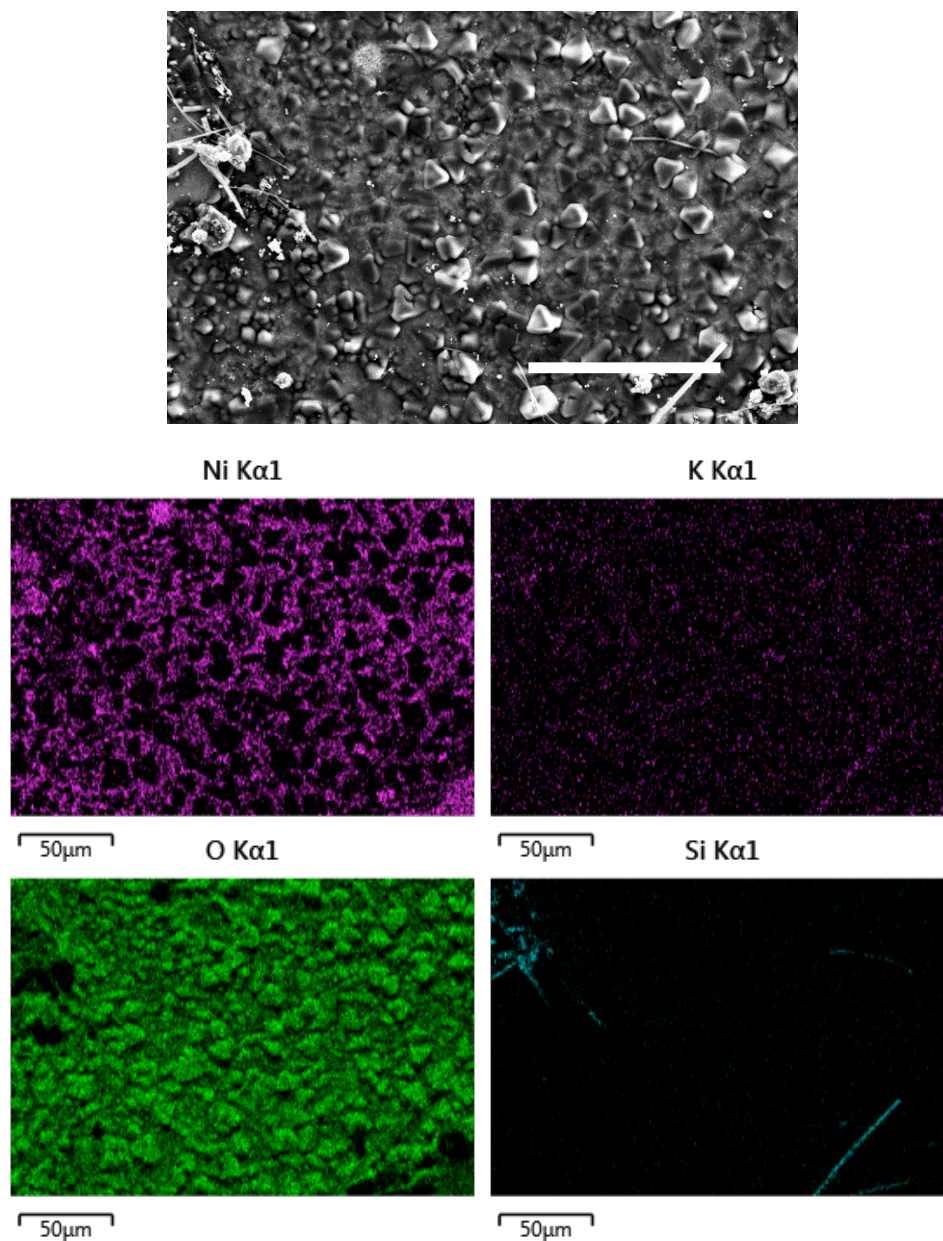
Supplementary Fig. 3. Electrochemistry of Li/Li Cell in Alkali Metal Nitrate Electrolyte. a) Li-Li symmetric cell comprising 200 mg LiNO₃:KNO₃ molten salt cycled under Ar at 150 °C at 0.4 mA/cm² and 2 mAh/cm² per half-cycle. b) Comparison between 1st and 60th cycle.



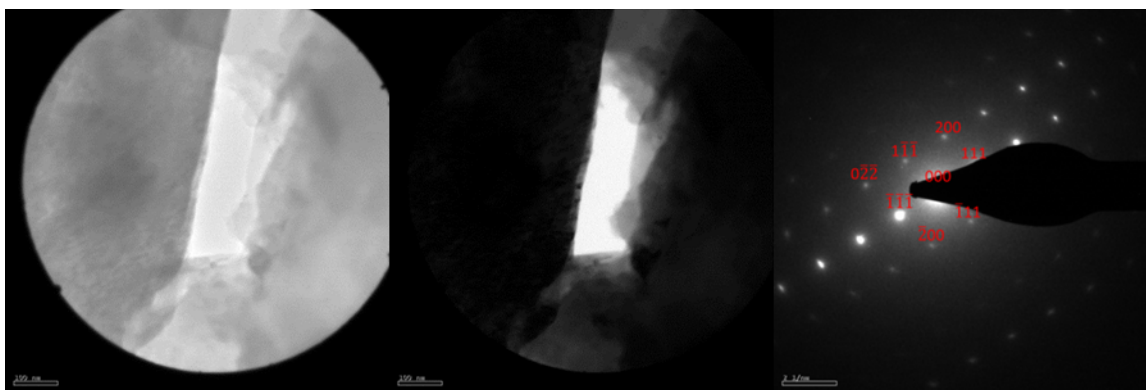
Supplementary Fig. 4. Comparison between an all nitrate and an all nitrite based electrolyte. (a) Ni nano-powder cathode (15 mg/cm²) discharged in (red) LiNO₃-KNO₃ melt and (blue) LiNO₂-KNO₂ melt with in-situ pressure analysis (dotted lines). Both cells used a 200 mg molten salt electrolyte and were discharged under Ar at 150 °C at 0.25 mA/cm² to a 1.8 V vs. Li⁺/Li⁰ cut-off. (b) Corresponding ex-situ gas analysis recorded at the end of discharge. Cells were allowed to cool down to room temperature, connected to a calibrated mass spectrometer (RGA 100, Stanford Research Systems) for gas analysis of the cell's headspace (argon carrier gas).



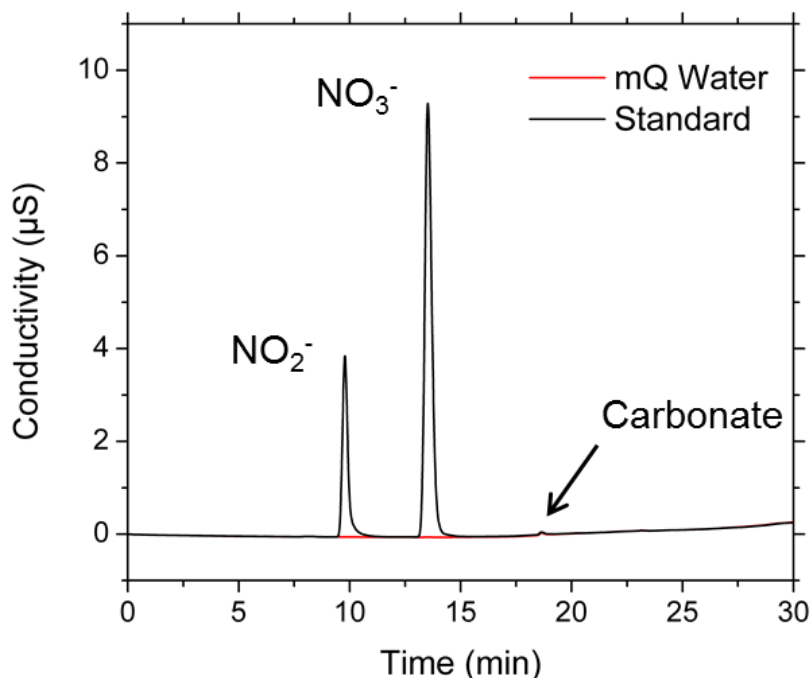
Supplementary Fig. 5. SEM of bare Ni nanoparticles as pressed onto on Al grid after exposure to molten nitrate salt.



Supplementary Fig. 6. Microscopic observation and chemical analysis of a discharged porous nickel cathode in $\text{LiNO}_3\text{-KNO}_3$ eutectic molten salt electrolyte. SEM and EDS elemental map of a discharged cell with Ni nanoparticle cathode (scale bar: 30 μm). The only element observed in the large crystals is oxygen. Considering that lithium is too light to be seen with EDS, this serves as additional confirmation of the discharge product being Li_2O .

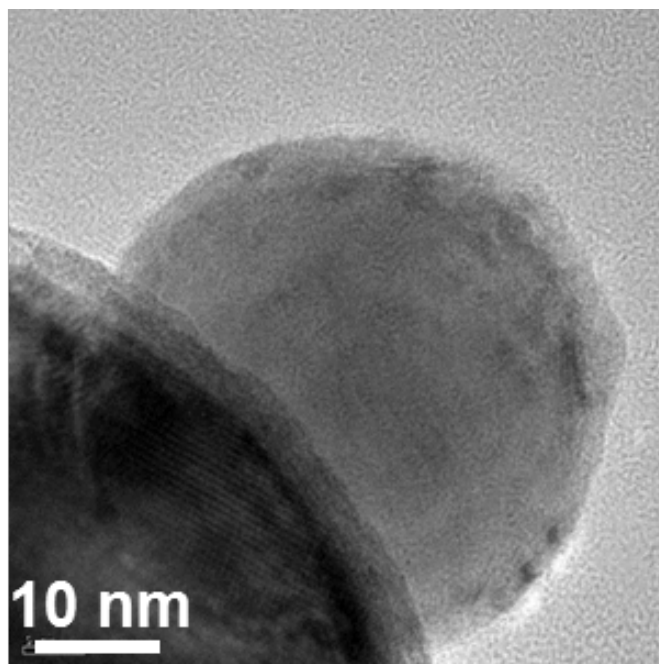


Supplementary Fig. 7. TEM Analysis of discharged cathode. Standard image (left), bright field (middle), and indexed selected area diffraction (right) of material from a discharged cathode. The indexed pattern corresponds to the [01-1] orientation of antifluorite Li_2O .

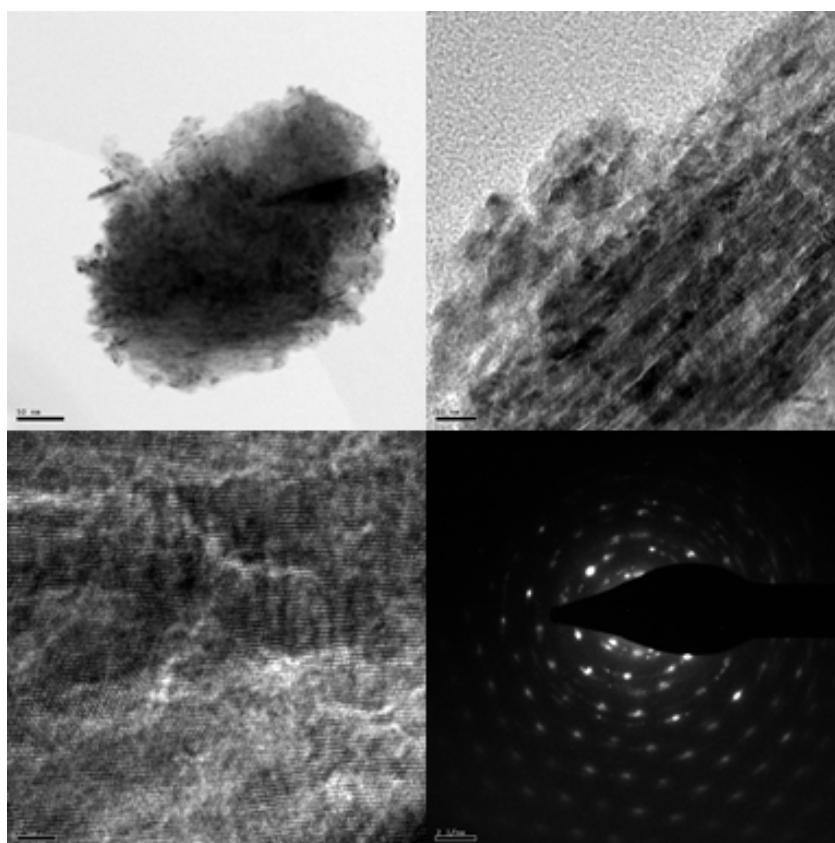
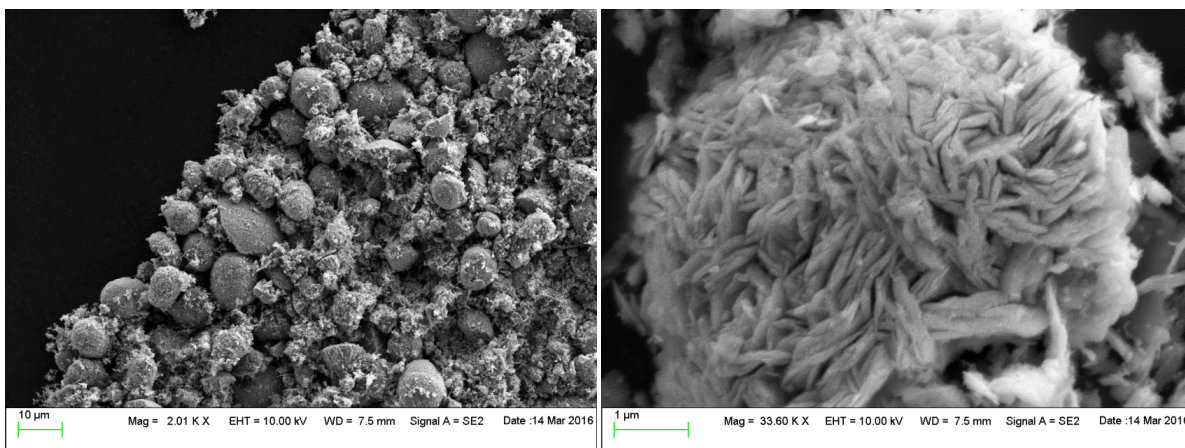


Supplementary Fig. 8. Characteristic raw ion exchange chromatography data for a solution containing nitrate and nitrite anions. From the peak area and a proportionality constant found through a calibration procedure, the concentration in solution is obtained.

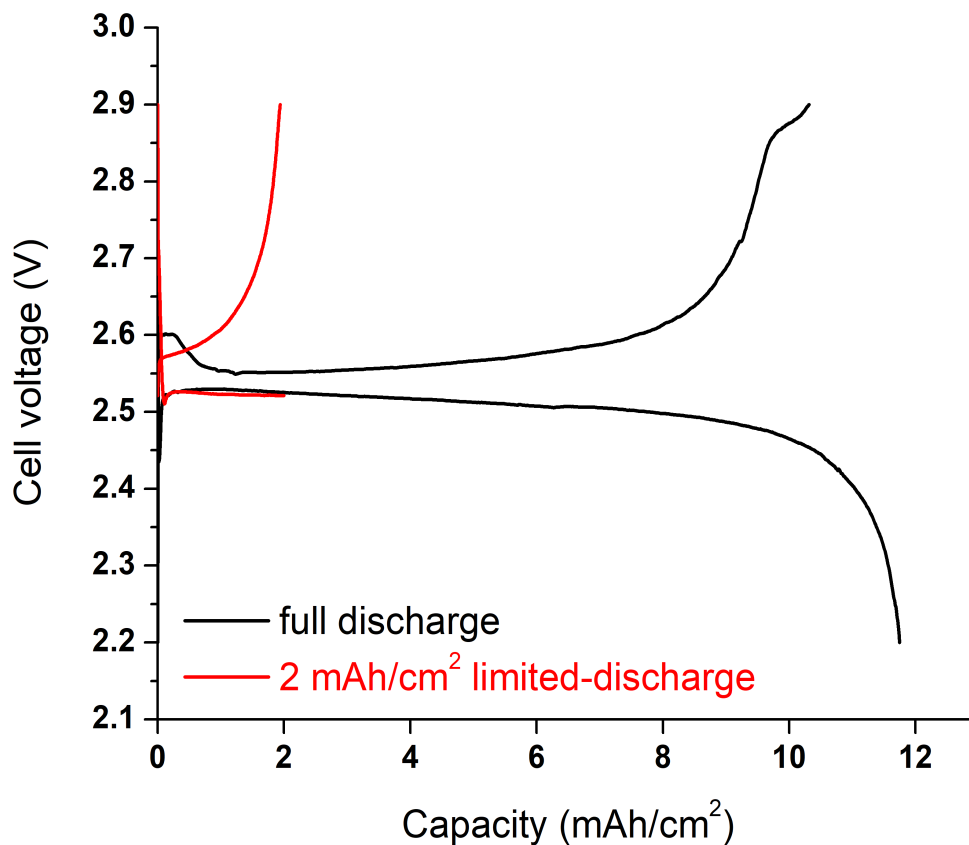
Due to impurities in the electrolyte salts (i.e. NO_2^- salt containing NO_3^- impurity), correction factors calculated from ion exchange chromatography data were applied to give final values. When calculating the number of moles of NO_3^- and NO_2^- to attribute to electrochemical behavior, several factors need to be considered. First, when using an electrolyte that contains significant NO_3^- , it is important to note that the reaction described in Eq. 1 also occurs on the lithium anode as the SEI forms. This process can be seen in cells that sit at OCV and is difficult to account for, so it is hard to make an accurate correction for it when calculating moles of NO_3^- consumed in an electrochemical process. However, working with a NO_2^- electrolyte avoids this issue, so studying a purely NO_2^- electrolyte with a cathode previously discharged is most appropriate for accurate calculations. Second, NO_2^- is not generally pure, but it is thermodynamically favorable for $\sim 1\%$ to convert to NO_3^- in air. This is constant though, and it is therefore easy to account for in calculations.



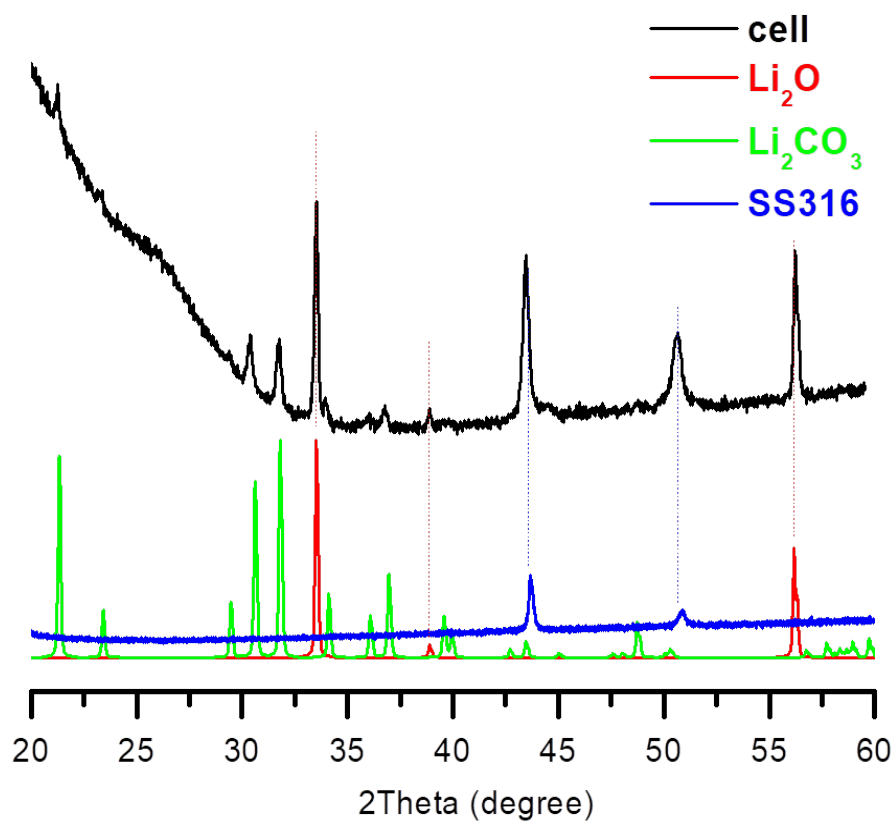
Supplementary Fig. 9. High Resolution Transmission Electron Microscopy (HRTEM) of Ni nanoparticles after exposure to molten nitrate.



Supplementary Fig. 10. SEM/TEM analysis of as-made Li-doped NiO nanoparticles.



Supplementary Fig. 11. Effect of deep cycling. Voltage profile comparison of replicate Li metal|LiNO₃:KNO₃ cells using 200 mg LiNO₃:KNO₃ eutectic electrolyte and nanopowder Ni cathode (Ni loading: 20 mg/cm²). Cells were cycled at 0.25 mA/cm² under argon and at 150 °C. Deep cycling cell was discharged and charged between 2.2 V and 2.9 V vs. Li metal anode, respectively.



Supplementary Fig. 12. XRD of Super P carbon cathode discharged ($\sim 5 \text{ mAh/cm}^2$) in $\text{LiNO}_3\text{-KNO}_3$ eutectic under Ar at $150 \text{ }^\circ\text{C}$ at 0.25 mA/cm^2 showing co-precipitation of lithium carbonate on electrode surface during electrochemical cycling.