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COMMUNICATION

A Low Temperature Iron Molten Air Battery

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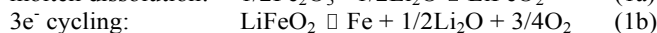
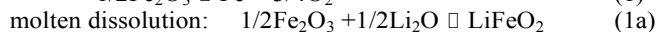
The Molten Air Battery is demonstrated at temperatures more compatible with EV applications. Molten Air is a new class of highest storage energy density, rechargeable, batteries discharging air cathode, molten electrolyte and multi-electron anode. Soluble LiFeO₂ in eutectic electrolyte and cell configuration optimization lower battery temperatures by >100°C. At 600°C in the eutectic, Iron Molten Air battery-cycling averages 1.3V charge and 1.0V constant load discharge at 60% efficiency, or at 92% coulombic efficiency to a lower 0.5V cut-off.

Higher energy density batteries are urgently needed for today's medical and consumer electronics, and to functionalize low CO₂ emitting technologies.¹⁻⁴ This latter category includes higher capacity batteries to reduce range anxiety of electric vehicles and to improve storage for wind and solar generated electricity.

Recently, we introduced a new class of rechargeable batteries, Molten (Electrolyte) Air Batteries, with amongst the highest reversible electrical energy storage capabilities. When discharging these batteries, each utilizes an air cathode, a molten electrolyte and a high capacity multi-electron anode.¹ Discharge of rechargeable Molten Air batteries couples cathodic reduction of O₂ from the air with anodic multi-electron/molecule oxidation yielding an intrinsic storage capacity on the order of 10⁴ Wh/liter, which is greater than Li-air and over tenfold greater than Li-ion.¹

To date, Molten Air Battery chemistries were demonstrated at temperature of 730°C to 800°C using anodes discharging (i) the 11e⁻ oxidation of VB₂ (with a vanadate/borate electrolyte), (ii) the 4e⁻ Carbon or (iii) the 3e⁻ Iron (each with carbonate electrolyte).¹ Lower temperature battery chemistries would greatly expedite their utility for EV (electric vehicle) applications (as discussed in the Electronic Supplementary Information).

In this study we probe one example, Iron Molten Air batteries. We will probe sustainable current densities and discharge efficacy, and then demonstrate a pathway to lower temperature rechargeable Iron Molten Air. The Iron Molten Air battery is represented by Eq. 1, including the Eq. 1a dissolution of Fe₂O₃ with Li₂O to form lithiated iron oxide, LiFeO₂,⁵ followed by quasi-reversible charge/discharge of LiFeO₂ to iron, Eq 1b. global 3e⁻ Iron Molten Air charge/discharge:



Various Iron Molten Air cell battery configurations are shown in the top of Fig. 1, each photographed prior to insertion of the molten electrolyte. Each of the cells exhibits similar, reproducible charge/discharge behaviour. A sampling of the repeated charge/discharge cycling behaviour is shown below the photos for the nickel crucible configuration battery, and the measured full cell voltage is presented as Voltage (V). In the left-hand photo the crucible is nickel. In the adjacent alumina configuration

the upper electrode is McMaster 200 pure Ni shim perforated with holes to facilitate oxygen escape, and the electrolyte is contained in a (white) alumina crucible, while in the other configurations electrolyte is retained by a Ni or Ni alloy container that also functions as the air electrode. Rather than pure Ni as the cell case and air electrode, the U or V shaped configurations shown use Inconel Ni alloy, which results in the same battery voltage, cycling performance and stability, and exhibits better stability in contact with external heated oxygen.

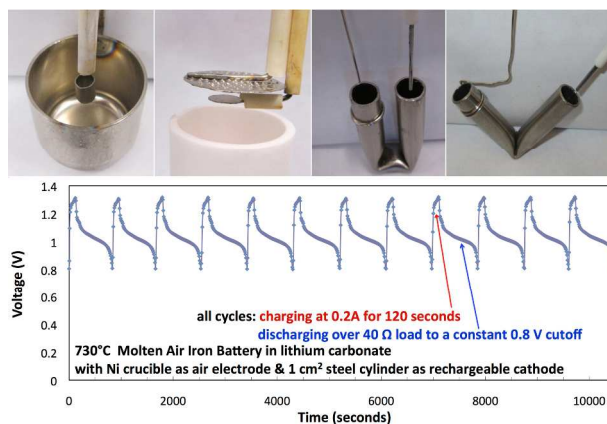


Fig. 1 Cycled charge/discharge of the 730°C Iron Molten Air Battery with 1.5m Fe₂O₃, 3m Li₂O in Li₂CO₃ electrolyte. The photographed batteries utilize a 1 cm² stainless steel 316 electrode located inside Ni (left) or inconel (right) or under Ni (2nd photo). In all but the 2nd photo, the encasement also acts as the air electrode. In the 2nd photo the encasement is a AdValue AL-2100, OD 40 mm, height 95 mm alumina crucible. The inconel is McMaster 600 1.1 cm id tubing. The left Ni crucible is a 20 ml Alfa 35952. On the right, the “U” or “V” shape seals the cell bottom and provides contact to the inner wall air electrode.

In the Fig. 1 photos, the counter electrode is always 1 cm² of 316 stainless steel shim (McMaster), either flat or curved into the indicated cylindrical shape, and is situated in the middle of and/or below, the air electrode. In the absence of Fe(III), the cell acts as a Carbon Molten Air Battery and charging results in a graphite deposition on the steel. Carbon Molten Air discharges in the 0.3 to 0.7V domain (and is

capable of being charged at potentials as low as 1 V).¹ It is only when Fe(III) is added for the Iron Molten Air Battery, that the charging product in molten carbonate becomes a loose, electrodeposited iron layer on the steel.⁶ This discharges in the 0.8 to 1.2 V domain. When Iron Molten Air is discharged to a lower cut-off voltage; after this high voltage plateau it can also approach a second, low, voltage graphite discharge plateau.

We have previously demonstrated that the Iron Molten Air Battery exhibits a high degree of reversibility.¹ Fig. 2 includes the discharge voltage for the Iron Molten Air battery in a 730°C Li₂CO₃ electrolyte. The battery exhibits 5-100 mA cm⁻² discharge current density, evident by comparing the voltage to the load as normalized by the steel electrode area. These moderate currents, combined with the high intrinsic Molten Air battery capacity (approaching 10⁴ mAh/g), can lead to days or weeks discharge times that are a challenge to compare in a reasonable time frame.

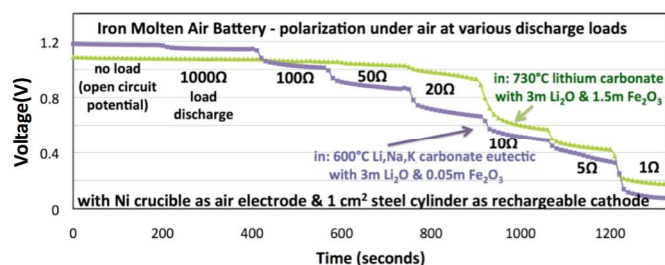


Fig. 2 Comparison of the Iron Molten Air Battery potential at open circuit and the discharge potential under load, of the 600°C Li_{0.87}Na_{0.63}K_{0.50}CO₃ electrolyte or the 730°C Li₂CO₃ electrolyte battery.

As predicted by our prior thermodynamic calculations (ESI), temperature decrease should increase open circuit potential for the (endothermic iron oxide reduction) Iron Molten Air Battery. Pure Li₂CO₃ melts at 723°C. Li_{0.87}Na_{0.63}K_{0.50}CO₃ eutectic melts at ~393°C permitting the Iron Molten Air Battery study in low temperature molten electrolytes. Fig. 2 compares the measured battery potential for similar Iron Molten Air batteries, but one contains lithium carbonate at 730°C as the electrolyte, and the second a lower working temperature battery using the eutectic carbonate at 600°C as the electrolyte. As predicted, the lower temperature battery has a higher open circuit potential. The 600°C compared to 730°C battery also exhibits higher polarization losses, as lower temperature will increase electrolyte resistivity and impede charge transfer kinetics.

Originally we studied 1.5 m LiFeO₂ (m=moles/kg carbonate) batteries.¹ For this study we probe the opposite domain, a low concentration of dissolved Fe(III) to accelerate discharge probes of the cell. When the dissolved iron is decreased to 0.05m Fe₂O₃ in the molten Li₂CO₃ electrolyte, the intrinsic capacity in the battery is lowered to 333 coulombs of Fe(III). This is a sufficiently small storage capacity that the cell may be charged/discharged in hours, rather than days or weeks.

Each of the Fig. 1 Iron Molten Air battery configurations exhibit highly invariant charge/discharge curves. Other factors observed probed in Fig. 3 will impact the battery chemistry. The coulombic efficiency is measured by comparing the extent of discharge as a percentage of the constant charge input during each cycle, and compares cells purposely discharged to a lower cut-off voltage (to 0.5V rather than 0.8 V) to effectuate comparison of the charge efficiency. During charge iron oxide is converted back to iron metal and oxygen. During this charging, we observe oxygen forming at the air electrode (the nickel or monel wall), rising and leaving the cell. As seen in Fig. 3A if the steel electrode is too near the air electrode then charge is lost. The Iron Molten Air Charge Coulombic

Efficiency decreases from 100% to < 70% if the iron electrode is located too near to the air cathode. The chemical self discharge loses stored charge as: $3\text{Fe} + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$ (2)

This loss in charge efficiency is avoided by evolving O₂ spatially removed from the iron deposited on the inner steel. The discharge plateau observed below 0.7V represents a loss of voltage efficiency but not charge efficiency. As previously delineated¹ and elaborated in the ESI, this is due to the competing formation and discharge of graphite from the carbonate electrolyte at lower potentials:

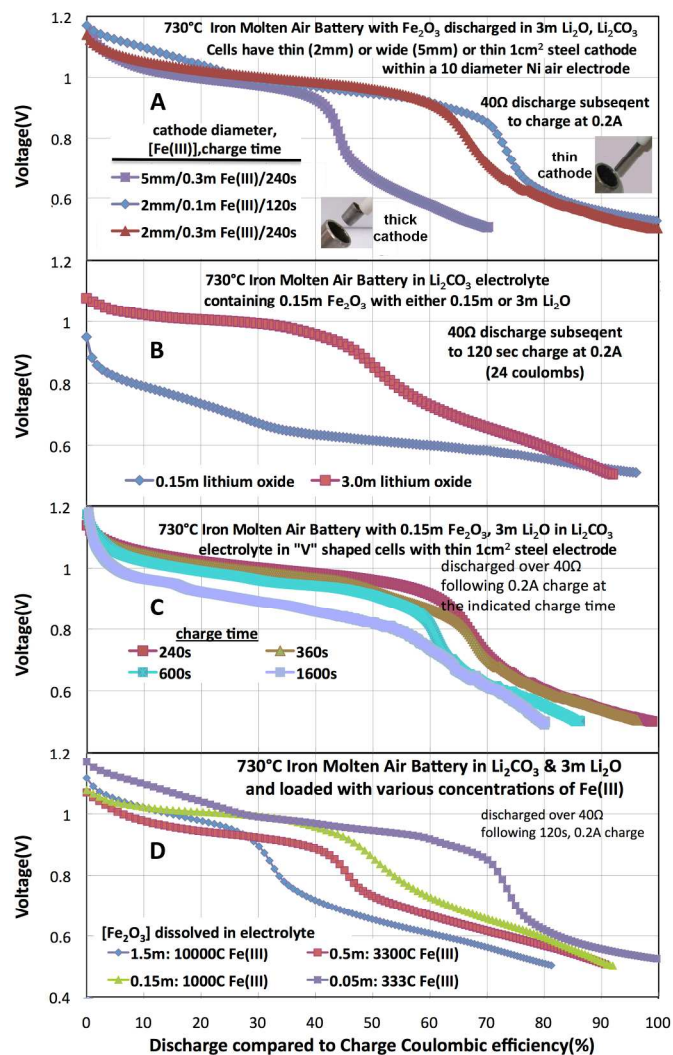
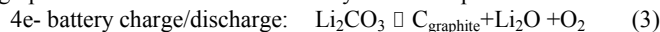


Fig. 3 730°C Iron Molten Air Battery variation of the discharge voltage with Charge Coulomb efficiency as affected by: (A) proximity of the inner steel electrode to the outer air electrode (using the Fig. 1 V shape configuration). (B) The [Li₂O] in the molten carbonate electrolyte. (C) The charge duration during battery cycling. (D) The [Fe(III)] in the molten carbonate electrolyte.

Dissolved iron represents a substantial electrical storage capacity, and the Iron Molten Air battery can contain a large fraction of rechargeable iron. A low concentration of Li₂O to Fe₂O₃ limits the molten carbonate solubility of the ferric species, Eq. 1a, and results in a discharge overpotential. Fig. 3B illustrates that the Li₂O concentration impacts the Iron Molten Air Battery; while 0.15m Fe₂O₃ dissolves in 0.15m Li₂O, the regeneration of iron oxide by oxidation of iron metal occurs at substantial overpotential losses during discharge. This loss does not occur when excess (3m) Li₂O is added to the electrolyte.

Fig. 3C compares the discharge, subsequent to constant current (0.2A) charge for different durations. Charges prior to each discharge range from $0.2A \times 1600s = 320$ coulombs down to 24 coulombs. The efficiency of discharge to a 0.5 V cut-off remains high, however the average upper plateau discharge voltage in diminishes from 1.1 V during the short duration (240 second) charge, down to 0.9V during the longer duration (1600 second) charge. Note, that the discharge time over the 40Ω load is quite long following the 1600s charge; in this case the discharge to the 0.5V cut-off occurs over $>13,000$ seconds.

We probe the effect of dissolved Fe(III) concentrations on coulombic efficiency in Fig. 3D. When concentration is decreased to $0.05m$ Fe_2O_3 , the intrinsic capacity in the battery is lowered to 333 coulombs of Fe(III). As shown, the discharge voltage improves as the intrinsic Fe(III) in the battery is lowered from 10,000 to 3,300, to 1,000 to 333 coulombs. In this latter case the 100% coulombic efficiency is (by voltage) attributed $\sim 80\%$ to iron oxidation (in the 1V domain) & 20% to the iron/graphite oxidation transition towards 0.5V. This is a sufficiently small storage capacity that the cell may be discharged in a reasonably short time period ($<$ one day).

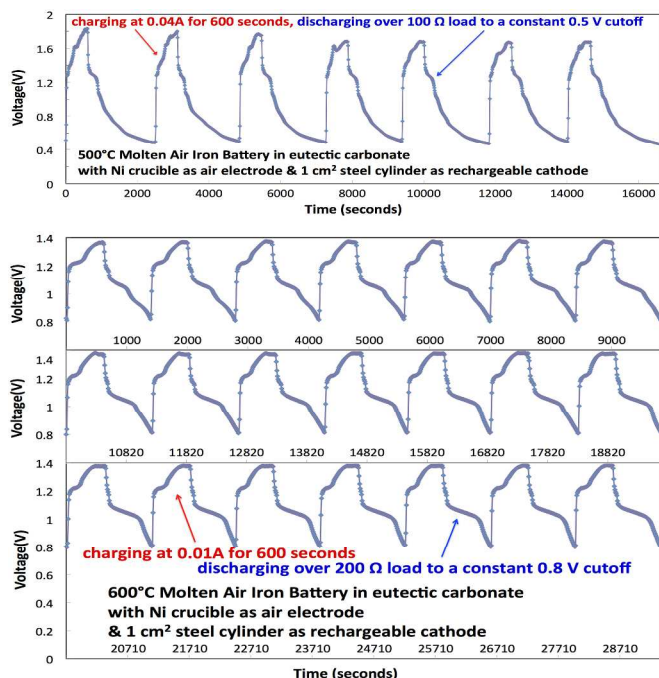


Fig. 4 Cycled charge /discharge behaviour of the $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ Iron Molten Air Battery with $3m$ Li_2O and $0.05m$ Fe_2O_3 at $500^\circ C$ (top row) or $600^\circ C$ (bottom 3 rows). $500^\circ C$ cycling is at $0.04A$ charge and 100Ω discharge, and $600^\circ C$ battery cycling is at $0.01A$ charge and 200Ω discharge.

Fig. 3 establishes that a high coulombic efficiency, Fe(III) limited Iron Molten Air battery can be prepared with $0.05m$ Fe_2O_3 and $3m$ Li_2O in a $730^\circ C$ Li_2CO_3 . An analogous, but lower temperature battery was prepared with a lower melting $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ eutectic. At $395^\circ C$ polarization is high, a $0.04A$ cm^{-2} constant charge voltage is excessive at $2.8(\pm 0.1)V$, and precludes cycling. The $0.04A$ charge voltage decreases to $1.6(\pm 0.2)V$ at $500^\circ C$, or $600^\circ C$ to only $1.5(\pm 0.1)V$.

As seen in Fig. 4, the eutectic Iron Molten Air battery cycles effectively at $600^\circ C$ (lower three rows) but exhibits excessive polarization at $500^\circ C$ (top row showing 7 cycles). The $500^\circ C$ 100Ω discharge exhibits a small shoulder at $0.8V$. At $600^\circ C$ this shoulder potential increases to $\sim 1V$, and increases further to $\sim 1.1V$ over a 200Ω load. At heavier load

the polarization is larger. Over a 10Ω constant load the discharge voltage is respectively $0.1V$, $0.2V$ or $0.5V$ at $395^\circ C$, $500^\circ C$ or $600^\circ C$. At $600^\circ C$ and a lower constant current of $0.01A$, the charging voltage further decreases to $1.3(\pm 0.1)V$.

In Fig. 4 the lower 3 rows present 21 cycles of the $600^\circ C$ Iron Molten $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ Air Battery. The $\sim 1.1V$ discharge plateau is high compared to the $1.3(\pm 0.1)V$ voltage at $0.01A$ charge. The cell is discharged reproducibly to $0.8V$ cut-off yielding 60% coulombic efficiency of the injected charge. A separate $600^\circ C$ battery cycled to a $0.5V$ discharge cut-off (not shown) discharges to 92% of injected charges and includes a low voltage plateau. Variation of other rates during discharge will be presented in a future study. Overpotential increase with load is highlighted by the decrease in voltage in Fig. 2; discharge under pure O_2 marginally improves voltage.¹ The variation of molten salt resistance with carbonate cation and temperature has been highlighted in our previous studies.^{6,12} At $600^\circ C$ reversible cycling of the Iron Molten Air Battery performance is shown with constant current average charge at $1.3V$ and constant load average discharge at $1.0V$ to 60% coulombic efficiency, and to 92% coulombic efficiency when the battery is discharged to a lower ($0.5V$) cut-off voltage.

Conclusions

Temperature, current density, electrolyte composition and cell configuration optimization lead to rechargeable behaviour approaching 100% coulombic efficiency for the Iron Molten Air Battery. The rechargeable Molten Air Battery operational temperature has been decreased from $700-800^\circ C$ to $600^\circ C$ or less with a low melting point $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ eutectic. High voltage efficiency and cycling is observed at $600^\circ C$, but polarization is excessive at $395^\circ C$. In contrast to the low temperature advantage the eutectic electrolyte has two challenges. Li_2CO_3 is more conductive than electrolytes containing Na_2CO_3 or K_2CO_3 ,^{8,9} and Li_2O is more stabilizing than Na_2O or K_2O in carbonates,¹⁰ or chlorides.¹¹ We hope to explore if a new $BaCO_3$ additive¹² can offset the disadvantages.

Acknowledgements

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Notes and references

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