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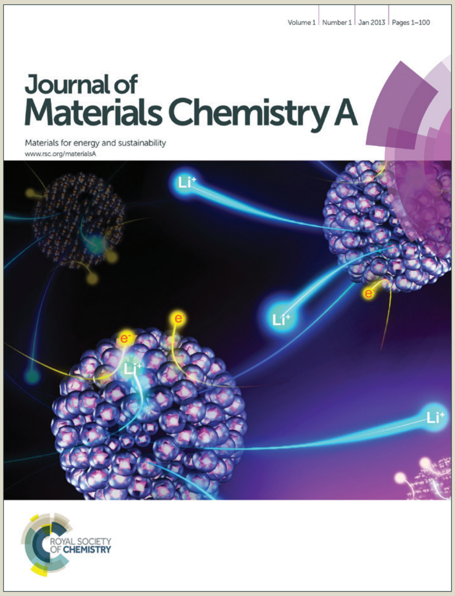

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Critical Advances for the Iron Molten Air Battery: A New Lowest Temperature, Rechargeable, Ternary Electrolyte Domain

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A new rechargeable iron molten air battery is demonstrated for large-scale energy storage. The operational temperature range of the battery is lowered by 230°C using a KCl-LiCl-LiOH eutectic electrolyte with added NaOH. The battery cycled stably at 500 °C for 60 cycles with average discharge potential of ~1.04 V and average charging potential of ~1.21 V. When the active interface area for oxygen reduction reaction on air electrode is improved, 85.2% coulombic efficiency is obtained and 99.1% to a 0.5 V discharge cutoff. The iron molten air battery has advantages of higher capacity, low cost, sustainability, and environmental friendliness compared to existing secondary batteries.

1. Introduction

Due to the growing concerns of the impacts of climate change and the depletion of traditional fossil energy resources, developing renewable energy production has recently become a priority of scientific. This has increased the call for environmentally responsible alternative sources for both the generation and storage of energy. Although wind and solar generated electricity is becoming increasingly popular in several industrialized countries, these sources provide intermittent energy, and can be limited by the energy storage systems required for load-levelling, i.e., storage of energy until needed by the electrical grid.[1] Therefore, the investigation of novel types of green, safer and less-expensive battery systems is needed for storing or supplying electric power. Rechargeable metal–air batteries have attracted considerable attention owing to their high theoretical specific energy density capacities that exceed those of lithium-ion (Li-ion) batteries, and because no oxygen in the air needs to be stored as the active material in the positive electrode. Li–air batteries are the most popular among metal–air batteries, but retain many challenges including dendritic charging of the anode which can facilitate battery malfunction by shorting.[2] Alternatively, iron as an anode has been known since the time of Edison, and tends not to form dendrites during charge–discharge cycling. The iron-air battery has the advantage of large capacity, in addition to iron being low cost, sustainable, and not toxicologically threatening environmental; to date the iron battery developments have focused on improved anode configurations in the aqueous alkaline iron air battery or solid electrolytes for the iron air battery.[3]

The conventional iron–air batteries normally use an aqueous alkaline electrolyte such as KOH, which has a good electrical conductivity and is not too corrosive to the iron electrode. The main problem of the iron air battery is that substantial hydrogen evolution takes place.[4] A variety of compounds, such as Bi_2S_3, Bi_2O_3, FeS, Na_2S and K_2S, were added to the iron electrode to reduce the rate of hydrogen evolution at the electrode surface during charging.[5-10]

Solidification of the electrolyte is one of the effective means to enhance the reliability of the batteries from several drawbacks like the volume change by leakage and freeze of liquids.[11] Tsuneishi and co-workers reported a solid oxide iron–air secondary battery using the KOH–LDH (Mg–Al layered double hydroxide) as a solid electrolyte and Fe_3O_4 particle-supported carbon as an anode material, but only about a stable 30% charge–discharge efficiency is achieved at room temperature.[12]

Xu and co-workers reported a new solid oxide iron–air battery with a combination of solid oxide fuel cell (SOFC) using Y_2O_3 stabilized ZrO_2 electrolyte to the redox of H_2/H_2O-mediated FeO/Fe, as a means of storing electrical–chemical energy in situ via the H_2/H_2O-mediated FeO/Fe reversible electrochemical-chemical looping reactions at 800 °C.[13] Inoishi and co-workers also proposed a Fe–air rechargeable battery using $LaGaO_3$ based oxide ion conductor as an electrolyte at 600 °C.[14] However, the redox cycle stability due to reoxidation and aggregation of the anode is a common issue that needs to be overcome.[15]

We introduced a new class of rechargeable batteries, the molten (electrolyte) air batteries, which exhibit amongst the highest

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reversible electrical energy storage capabilities of any battery.[16] Originally, we used Li_2CO_3, which melts at 723 °C, as electrolyte, and which facilitates up to 50% dissolution of iron oxide into the electrolyte.[17] The iron molten air batteries at 730 °C exhibit a high rate charging capability and recharge-ability. From the viewpoint of functionality as a battery for energy storage devices, lower operating temperatures would be preferable. Recently, we replaced the Li_2CO_3 with a lower melting carbonate eutectic ($Li_{0.87}Na_{0.63}K_{0.50}CO_3$ eutectic that melts at 393 °C). At 600 °C, the iron molten air battery exhibits reversible cycling at 60% coulombic efficiency to a 0.8 V voltage cut-off with a constant current average charge at 1.3 V and a constant load (200 Ω) average discharge of 1.0 V, and to 92% coulombic efficiency to an 0.5 V voltage cut-off, but exhibits excessive polarization at 500 °C over a 100 Ω load.[18]

In this study to lower the temperature and to decrease the discharge polarization, we investigate iron molten air batteries with a new lower melting eutectic electrolyte. We probed the discharge efficacy and demonstrated a pathway to lower the temperature in a rechargeable iron molten air battery.

2. Experimental

Anhydrous lithium chloride (AR, >95, China), potassium chloride (AR, 99.5wt%, China), and lithium hydroxide (AR, anhydrous, 95 wt%, China) are combined to form a molten electrolyte with low melting points. The pure anhydrous lithium chloride melts at 605°C; potassium chloride at 776°C, lithium hydroxide at 462°C. Whereas, the 11.5 mol% KCl-45 mol% LiCl-43.5 mol% LiOH eutectic (which are marked as KCl-LiCl-LiOH eutectic) electrolyte melts at 283 °C. Sodium hydroxide (AR, >96%, China) and ferric oxide, Fe_2O_3 (AR, 99.5%, China) are used in the iron metal synthesis and battery studies.

1 mm and 2 mm pure Ni wire (99.5 %, China) and pure Ni foil (99.95 %, China), 1.2 mm Fe wire (Annealed, China), steel foil (316 steel, China), pure alumina (99.7%, China) crucible are used to make electrodes and combine to form various cell configurations.

The cell is situated within a 1800 W Band Heater, and insulated by rigid thermal shock resistant ceramic insulation without binder. Temperature is monitored by thermocouple and controlled by a temperature controller (YUDIAN automation technology Co. LTD, YUDIAN 708P). Battery cycling is carried out as previously described.[8]

The thermal decomposition of Fe_2O_3 and NaOH mix was characterized by thermal analysis (PerkinElmer Diamond TG/DTA). XRD analysis of the electrolysis product, pure Fe_2O_3 and mix of Fe_2O_3 and NaOH was confirmed by powder X-ray diffraction with a Cu K_α source (Rigaku D/MAX-2200). Each sample was scanned from 2θ 20 to 80°.

3. Results and discussion

It is seen that this 500 °C iron molten air battery with the KCl-LiCl-LiOH eutectic containing 0.5 m (m = molal, moles per kilogram of electrolyte) Fe_2O_3 exhibits a significant loss in the discharge compared to the charging potential. The discharge voltage of ~ 0.75 V over a 100 Ω load comprises half of the charging potential (Fig. 1). To improve the cell discharge potential of the cell, 3 m of NaOH was added to the system. The iron molten air battery containing NaOH cycles effectively at 500 °C (Fig.2a) and exhibits substantially less voltage loss hysteresis (Fig.2b) compared to the cell without NaOH in Fig. 1. For example, in the 10th cycle, the voltage efficiency of the cell is about 86 % (the average discharge potential of 1.04 V compared to the average charging potential of 1.21 V, and the discharge potential does not decrease rapidly), and the coulombic efficiency is 65.8% (15.8 coulombs discharge/the injected charge of 0.05 A × 480 seconds) to a discharge cut-off voltage of 0.7 V. Shown in the figures are specific battery experiments. It should be noted that experiments are highly reproducible. Triplicate replication of the battery results in a maximum charge voltage which varies by less than 0.04V, and an average columbic efficiency which varies by less 2% for experiments conducted with the same electrolyte, electrode configuration, temperature and discharge load.

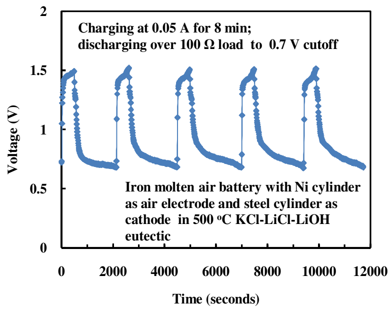

Fig. 1 Cycling characteristics of an iron molten air battery exhibiting large hysteresis. The molten KCl-LiCl-LiOH electrolyte contains 0.5 m Fe_2O_3 without NaOH. Insert photo: cell configuration with nickel foil air electrode (15 cm^2) outside the iron foil counter electrode (4 cm^2), prior to addition of the electrolyte to alumina crucible.

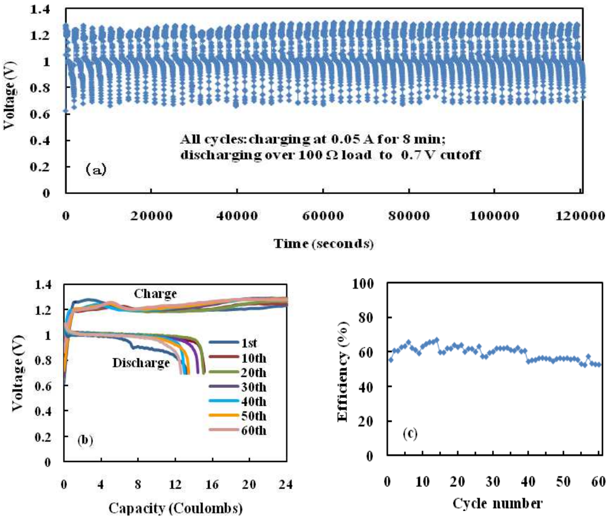

Fig. 2 Cycled charge-discharge behavior of the KCl-LiCl-LiOH iron molten air battery with 0.5 m Fe_2O_3 and 3 m NaOH at 500 °C. **(a)** Cycling characteristics of an iron molten air battery exhibiting small hysteresis. Cycle charges at 0.05 A and discharges over a 100 Ω load

to 0.7V cutoff. **(b)** Voltage profiles for 1st, 10th, 20th, 30th, 40th, 50th and 60th cycles. **(c)** Cycle performance.

The iron molten air battery exhibits stable cycling behavior (60 cycles) and the highest coulombic efficiency reaches 66.7% in the 14th cycle (Fig.2c). The coulombic efficiency decreases slowly with battery cycling, but remains over 55.1% in the 60th cycle. Compared to the battery with $Li_{0.87}Na_{0.63}K_{0.50}CO_3$ eutectic,[18] the operational temperature of the rechargeable molten air battery with KCl-LiCl-LiOH eutectic is decreased from 600 °C to 500 °C, and compared to the iron molten air battery with the Li_2CO_3 electrolyte,[16] the operational temperature is decreased by 230°C.

KCl-LiCl melt is considered as a significant supporting electrolyte in a range of molten salts processes due to its low melting point and a wide electrochemical window.[19] Fig.3 compares the measured battery potentials of similar iron molten air batteries, either only with 50 mol% KCl-50 mol% LiCl electrolyte that melts at 459 °C, or the previous 11.5 mol% KCl-45 mol% LiCl-43.5 mol% LiOH eutectic electrolyte that melts at 283 °C. We observe that the LiOH-free electrolyte is more viscous and becomes heterogeneous with the addition of 0.5 m Fe_2O_3 and 3 m NaOH, requiring an increase of operation temperature to 530°C (in which case the electrolyte is homogeneous). As shown in Fig.3, the binary KCl-LiCl eutectic electrolyte battery exhibits excessive polarization at 530 °C, and during discharge only a small shoulder potential is observed at 0.9 V when discharged over the constant 100 Ω load. Compared with the binary system, the 500 °C ternary (two chlorides and a hydroxide) eutectic battery exhibits an extended duration plateau and a higher discharge voltage above 1.0 V. We extracted the air electrodes after charge-discharge from either electrolyte, and washed them with water to remove the electrolyte. Compared to the fresh air electrode (the left photo of Fig.3), after ten-cycles of charge-discharge, the ternary KCl-LiCl-LiOH electrolyte cell has developed a black coating of NiO on the air electrode (the right photo of Fig.3), which is not evident after cycling in the binary electrolyte system (the middle photo of Fig.3). NiO has been considered to be a good catalyst for reduction of O_2 to oxygen ion on the air electrode of molten carbonate fuel cells (MCFCs).[20]

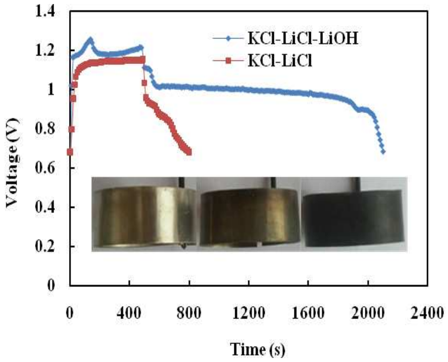

Fig. 3 Discharge–charge voltage profiles of iron molten air batteries. The battery with KCl-LiCl-LiOH electrolyte at 500 °C, while the battery with KCl-LiCl electrolyte at 530 °C, charges and discharges at 0.05 A for 480 seconds over a 100 Ω load. Insert photo: left: fresh air electrode; middle: the air electrode used in cell with KCl-LiCl electrolyte; right: the air electrode used in cell with KCl-LiCl-LiOH electrolyte. The height of each of the air electrodes is 1.5 cm. The molten electrolyte covers the iron foil counter electrode. The immersed depth of the air electrode in the molten salt is 1 cm.

Three configurations of the air electrode, either 1, 1.5 or 2 cm in height, and comprising a surface area of 10, 15, and 20 cm^2 respectively (Fig.4). The immersed depth of the air electrode in the molten salt is 1 cm. The exposed portions of air electrodes above the molten electrolyte are 0, 0.5 or 1 cm, respectively. These air electrodes are formed from nickel and are divided into two areas with bi-functionality separated by the air/molten electrolyte interface. The portion below the air-electrolyte interface is flooded facilitating the oxygen evolution reaction (OER) during battery charging. We also observed that the molten electrolyte acts to wet and spread over the air-exposed to cover the surface of the electrode. The portion above the molten electrolyte provides an active interfacial area to enhance the rate of gas diffusion to the electrode surface to facilitate the efficacy of the oxygen reduction reaction (ORR). As shown in Fig. 4, as expected, the discharge voltage falls sharply for the battery with the fully submerged air electrode configuration (the 1 cm height air electrode) due to the difficulty of air/oxygen access to the air electrode. For the battery with a 1.5 cm height air electrode (including 0.5 cm exposed above the air-electrolyte interface), the coulombic efficiency is 66.7%, and improves to 85.2% (from 16.0 to 20.45 coulombs discharged) for the battery with a 2 cm height air electrode (situated equally above and below the air-electrolyte interface), again attributed to the improvement in the active interface area for the ORR, and further improves to 99.1% when the battery discharged to a 0.5 V, rather than 0.7 V cutoff.

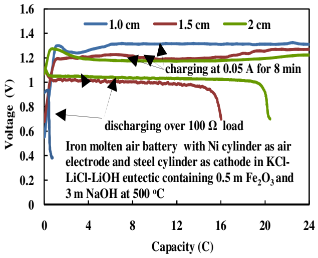

Fig. 4 Charge/discharge voltage profiles of iron molten air batteries with 1, 1.5, and 2 cm height air electrodes. KCl-LiCl-LiOH electrolyte contains 0.5 m Fe_2O_3 and 3 m NaOH. Molten electrolyte is sufficient to cover the iron foil counter electrode. The immersed depth of the air electrodes in the molten salt is 1 cm. Cycle charges at 0.05 A and discharges over a 100 Ω load to 0.7 V cutoff at 500 °C.

Iron metal synthesis in this molten KCl-LiCl-LiOH electrolyte is conducted via constant current electrolyses at a high rate of charging. Post electrolysis, iron deposited on an extracted cathode is shown with an overlay of electrolyte, and after water wash this pure iron powder is attracted to a magnetic stirrer (Fig. 5a). The electrolysis product is analyzed by quantitative analysis,[21] and contains electrolyte, 4.4 wt % zero-valent iron, and no divalent iron.

The XRD analysis of our post-electrolysis cathode product exhibits 2-theta peaks at 44.7 and 65.0°(no 2-theta peaks appear at 44.7 and 65.0° in XRD analysis for mix of electrolyte, NaOH and Fe_2O_3), matching the library XRD of pure iron (MDI Jade 5.0, PDF 06-0696) (Fig. 5b).

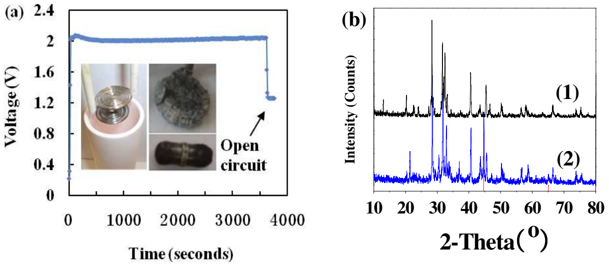

Fig. 5 (a) The electrolysis potential during high rate charging of the iron molten air battery. Insert photos: cell configuration with nickel coil electrode above the iron coil counter electrode, prior to addition of the electrolyte. Right top: the thick iron product formed on the cathode subsequent to a 1 hour constant current charge of 1 A using coiled wire 5 cm^2 nickel electrode & 5 cm^2 steel cathode in 500 ^oC molten KCl-LiCl-LiOH electrolyte. Right bottom: iron powders separated with a magnetic stirrer after washing with water to remove the electrolyte. **(b)** XRD analysis of the products formed on the steel cathode. Red vertical lines: XRD library pure iron spectra, PDF:06-0696. (1) XRD for mix of electrolyte, NaOH and Fe_2O_3 (heated at 500 °C for two hours) before charging. (2) XRD for products after charging.

Fig.S1† presents a characterization of Fe_2O_3 and NaOH mix by TG/DTA. The TG increases slightly and a DTA endothermic event is detected in initial A-B stage because Fe_2O_3 and NaOH mix absorbs water from the air at lower temperature. Then the TG decreases rapidly with increase of temperature due to loss of free water (B-C stage). TG of C-D stage remains stable when free water volatiles completely. However, a larger exothermic event initiates at 296 °C (near the NaOH melting point, 318 °C) due to melting of NaOH. TG of D-E stage decreases markedly again with increase of temperature. This is attributed to the reaction of Fe_2O_3 with molten NaOH to form H_2O and $NaFeO_2$:

$$Fe_2O_3 + 2NaOH \rightleftharpoons 2NaFeO_2 + H_2O \qquad (1)$$

Both pure Fe_2O_3 and the mixture of Fe_2O_3 and NaOH are heated at 500 °C for two hours before XRD analysis (Fig.S2†). As shown, the XRD of the mixture of Fe_2O_3 and NaOH does not match the pure Fe_2O_3 spectrum, but matches the library XRD of the $NaFeO_2$, verifying again formation of $NaFeO_2$ in equation (1). Cox and Fray reported that $NaFeO_2$ spontaneously forms when Fe_2O_3 is added to molten NaOH and can become the starting material for electrolysis of Fe_2O_3.[22] We suggest that the reactions involved in iron molten air battery are during charging, that $NaFeO_2$ is converted to iron metal and Na_2O via a three-electron reduction, and that O_2 is released to the air, while during discharging, iron metal is converted back to $NaFeO_2$.

$$\text{Cycling: } NaFeO_2 \rightleftharpoons Fe + 1/2Na_2O + 3/4O_2 \qquad (2)$$

$1/2Na_2O$ liberated during the electrolysis in equation (2), is then available to continue to form $NaFeO_2$ from Fe_2O_3 as:

$$1/2Na_2O + 1/2Fe_2O_3 \rightleftharpoons NaFeO_2 \qquad (3)$$

Formation of $NaFeO_2$ permits continued electrolysis via equation (2). Overall the charge/discharge reaction occurs as the combination of equation (2) and (3).

$$\text{Overall: } 1/2Fe_2O_3 \rightleftharpoons Fe + 3/4O_2 \qquad (4)$$

4. Conclusions

The iron molten air batteries utilizing KCl-LiCl-LiOH eutectic exhibit a high rate charging capability and rechargeability at 500 °C, but low voltage efficiency. A high voltage efficiency was achieved by the addition of NaOH to electrolyte, which can form $NaFeO_2$ to facilitate charging and discharging. Enhancement of the air electrode area above the surface of molten electrolyte is able to improve coulombic efficiency of the cell. A 85.2% coulombic efficiency is achieved in the iron molten air battery with an air electrode configured at the molten/air interface (1 cm above and below the molten electrolyte surface), using a 4 cm^2 steel iron electrode when charged at a constant current of 0.05 A and discharged over a constant 100 Ω load to 0.7 V cutoff at 500 °C.

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Graphical abstract

The iron molten air battery cycled stably at 500 °C for 60 cycles using cost effective nickel and steel electrodes and KCl-LiCl-LiOH eutectic electrolyte with added NaOH.