Communication—Molten Amide-Hydroxide-Iodide Electrolyte for a Low-Temperature Sodium-Based Liquid Metal Battery

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The low cost and high abundance of sodium make it an attractive choice for the negative electrode in a liquid metal battery. However, sodium has not found use in this application owing to the high solubility of the metal in its molten halides which results in poor coulombic efficiency and an unacceptably high rate of self discharge. In this work, we investigated the electrochemical behavior of the ternary eutectic of NaNH2, NaOH and NaI (m.p. 127°C) and evaluated its usefulness as an electrolyte for sodium-based liquid metal batteries. Cyclic voltammetry revealed an electrochemical window of 1.3 V at 180°C. The anodic limit is set by the oxidation of amide anions to form hydrazine gas.

Liquid metal batteries consist of two metals of different electronegativity separated by molten salt. During discharge, the battery operates through alloying an electropositive liquid metal (e.g. Mg, Na, Li, or Ca) in an electronegative metal (e.g. Bi, Pb, Sb, or Zn). The all-liquid design allows the battery to operate at high current densities (1 A/cm^2) with low overvoltage due to fast mass transport in the liquid state and high ionic conductivity of molten salts. Moreover, the absence of solid electrodes endows the battery with an extended operating temperature below 200°C which can substantially reduce metal solubility thereby allowing batteries to be built in the absence of solid electrodes endows the battery with an extended operating temperature below 200°C which can substantially reduce metal solubility thereby allowing batteries to be built.

Metal solubility in the electrolyte varies exponentially with operating temperature. High metal solubility in the electrolyte can influence the performance of liquid metal battery through increasing electronic conductivity, which increases the rate of self-discharge leading to lower coulombic efficiency. A low-melting electrolyte (≤200°C) can substantially reduce metal solubility thereby allowing batteries to be built with low-cost negative electrodes (e.g., Na, Ca) that are otherwise inaccessible at higher temperatures (>500°C). Moreover, reducing the operating temperature below 200°C can also reduce the total battery cost through savings associated with cell container, thermal insulation, and wiring.

Early work on low-melting sodium-bearing salts focused on mixtures of NaOH, NaI, and NaBr and was driven by their utility for sodium electrolyte batteries. Spatocco et al. investigated a binary eutectic of NaNH2 and NaI as an electrolyte operable at intermediate temperature (≤280°C). An electrochemical window of 2.4 volts was measured at 180°C (2) A535-A537 (2017) A535/C. The anodic limit is set by the oxidation of sodium amide (NaNH2) to form ammonia and sodium hydroxide according to the reaction:

\[
\text{NaNH}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{NaOH} \quad [1]
\]

It is important to note that NaNH2 can react violently with oxygen to form Na2O according to:

\[
4\text{NaNH}_2 + 7\text{O}_2 \rightarrow 2\text{Na}_2\text{O} + 4\text{NO}_2 + 4\text{H}_2\text{O} \quad [2]
\]

Therefore, all dried salts were stored and tested in an argon atmosphere with O2 levels below 1 ppm. A eutectic mixture comprising 52% NaNH2, 38% NaOH and 10% NaI was prepared in an Al2O3 crucible. The salts were heated to 200°C to promote homogenization before the final working temperature was set at 180°C. All Al2O3 crucibles, tungsten, low carbon steel, and Monel-400 wires were cleaned with acetone and dried under vacuum before use.

Assembled inside an argon glove box the three-electrode setup shown in Figure 1 was used to determine the electrochemical window of the melt with an AutoLab PGSTAT 302N potentiostat/galvanostat. Working electrodes of tungsten, Monel, and low carbon steel wires (Φ = 1 mm) were tested against a reference electrode consisting of liquid Na in β'-Al2O3 (Ionotec Ltd.) and a tungsten counter electrode.

**Results and Discussion**

To test the viability of this electrolyte with low-melting liquid positive electrodes such as those found in a Na|Bi-Pb or Na|Bi-Sn liquid metal battery the temperature of the experiments was set at 180°C. The electrochemical window was determined by multiple voltage sweeps at different scan rates in both the cathodic and anodic directions. Figure 2 shows cyclic voltammograms on a tungsten wire. The electrochemical window of the electrolyte is greater than 1.3 V. The reduction and oxidation peaks around 0 V vs. Na (s) are attributed to sodium deposition and stripping, respectively. Integration of the current during deposition and stripping indicates 30% loss of charge. This indicates that irreversible chemical reactions, such as formation of soluble ionic compounds (e.g., intermetallic compounds, sodium
tungsten oxides) or gas evolution (e.g., hydrogen) occur on tungsten in the negative voltage sweep.

Candidate oxidation reactions around 1.3 V are listed in Table I. The estimated voltages of reactions were calculated at 180°C using HSC (version 6). Based on the data in Table I, the limiting oxidation reaction is most likely to be the oxidation of amide ion according to Equation 3,

\[ 2\text{NH}_2^- = \text{N}_2\text{H}_4 (g) + 2e^- \]  

To confirm that the limiting oxidation reaction is due to amide and not hydroxide, we followed the same experimental procedure while replacing the eutectic melt with pure molten NaNH₂. Figure 3 shows anodic sweeps performed on tungsten wire at 250°C and a scan rate of 100 mV s⁻¹. Here, the oxidation of NH₂⁻ follows that observed in Figure 2 with minor differences due to the effect of temperature and activity of NH₂⁻. The production of hydrazine gas (N₂H₄) from the reaction poses a major safety concern. In addition to being highly toxic, hydrazine is also highly unstable and flammable. Although the measured electrochemical window of the ternary electrolyte is narrow (<1.3 V) compared to those of molten halide salts, the voltages at fully charged state of most LMBs are less than 1.25 V²⁷; therefore, it is possible to design a cell that can safely operate without undesirable hydrazine gas evolution. Figure 3 also shows the anodic sweeps on low-carbon steel and Monel wire, which exhibit narrower electrochemical windows ∼1 V which we attribute to possibly a catalytic effect on the oxidation of NH₂⁻.¹¹ The narrow electrochemical window on the low-carbon steel was confirmed around 1 V in ternary electrolyte as expected (Figure 4). Additionally, there are clear peaks of sodium deposition and stripping around 0 V vs. Na(s). Integration of the current during deposition and stripping reveals an overall coulombic efficiency approaching 90% at a scan rate of 100 mV s⁻¹. This indicates low sodium solubility in the ternary melt and vindicates

Table I. Thermodynamic calculations of candidate reactions at T = 180°C.

<table>
<thead>
<tr>
<th>candidate reaction</th>
<th>free energy of reaction, ΔG (kJ mol⁻¹)</th>
<th>reaction potential, E (V) vs. Na(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH ⇒</td>
<td>245</td>
<td>2.54</td>
</tr>
<tr>
<td>Na + 1/2H₂O(g) + 1/4O₂(g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaH₂Na + NaOH ⇒</td>
<td>388</td>
<td>2.01</td>
</tr>
<tr>
<td>2Na + NH₂(g) + 1/2O₂(g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaNH₂ ⇒ Na + 1/2N₂H₄(g)</td>
<td>129</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Figure 3. Anodic sweep on pure NaNH₂ melt at 250°C, scan rate of 100 mV s⁻¹. Na in β''-Al₂O₃ reference electrode. Three different working electrodes: tungsten (blue), low carbon steel (black) and Monel-400 (red).

Figure 4. Cyclic voltammograms of the eutectic melt at 180°C, scan rates of 50 (blue) 100 (green) and 200 (red) mV s⁻¹. Low carbon steel working electrode measured against Na in β''-Al₂O₃ reference electrode. Current from tungsten counter electrode.
the choice of low-carbon steel as the negative current collector in liquid metal batteries. Interestingly, the overall coulombic efficiency was found to increase with decreasing scan rate. Spatocco et al. made similar observation with the binary system of NaOH and NaI. These results further support Spatocco’s hypothesis that deposited sodium is stabilized by a self-inhibiting reaction with NaOH making it more difficult to remove at higher scan rates.

Conclusions

The ternary mixture of 52% NaNH$_2$, 38% NaOH, and 10% NaI qualifies as a molten salt electrolyte for use in liquid metal batteries operating at temperatures below 200°C provided attention is paid to N$_2$H$_4$ mitigation (moisture level, materials of containment, and voltage limits).

Acknowledgments

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References