

Low-Temperature Molten Salt Electrolytes for Membrane-Free Sodium Metal Batteries

Brian L. Spatocco,^a Takanari Ouchi,^{a,*} Guillaume Lambotte,^a Paul J. Burke,^b and Donald R. Sadoway^{a,*,z}

^aDepartment of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA ^bNew Valence Robotics Corp., Boston, Massachusetts 02210, USA

The liquid metal battery (LMB) is attractive due to its simple construction, its circumvention of solid-state failure mechanisms and resultantly long lifetimes, and its particularly low levelized cost of energy. Here, we provide a study of a unique binary electrolyte, NaOH-NaI, in order to pursue a low-cost and low-temperature sodium-based liquid metal battery (LMB) for grid-scale electricity storage. Thermodynamic studies have confirmed a low eutectic melting temperature (220° C) as well as provided data to complete the phase diagram of this system. X-ray diffraction has further supported the existence of a recently discovered compound, Na₇(OH)₅I₂, as well as offered initial evidence toward a NaI-rich compound displaying Pm-3m symmetry. These phase equilibrium data have then been used to optimize parameters from a two-sublattice thermodynamic solution model to provide a starting point for study of higher order systems. Further, a detailed electrochemical study has identified the voltage window and related oxidation/reduction reactions and found greatly improved stability of the pure sodium electrole against the electrolyte. Finally, an Na|NaOH-NaI|Pb-Bi proof-of-concept cell was assembled. This cell achieved over 100 cycles and displayed leakage currents below 0.40 mA/cm². These results highlight an exciting class of low-melting molten salt electrolytes that may enable low cost grid-scale storage.

Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0441514jes] All rights reserved.

Manuscript submitted July 14, 2015; revised manuscript received September 8, 2015. Published October 20, 2015.

The pressing need for highly scalable and economically viable battery systems for grid-storage has prompted many researchers to pursue entirely new electrochemical approaches. One such technology that has recently grown from the university lab bench to the commercial production floor is the liquid metal battery $(LMB)^{1,2} - a$ system that takes advantage of a three liquid-layer design to store and deliver large quantities of energy at particularly low levelized costs.

The LMB is designed with an electropositive liquid metal anode, A, separated from an electronegative liquid metal cathode, B, by a molten salt electrolyte. Upon discharge, the anode, A, oxidizes, transports across the A-itinerant electrolyte, and reduces at the cathode interface to form an A-B alloy. The reaction is driven by the partial free energy difference of A in the high activity negative electrode environment versus that of the alloyed metal A (in B) in the positive electrode.

anode:
$$A_{liq} \rightarrow A^{z+} + ze^{-}$$
 [1]

cathode:
$$A^{z+} + ze^- \rightarrow A(in B)_{liq}$$
 [2]

overall:
$$A_{liq} \rightarrow A(in B)_{liq}$$
 [3]

$$E_{cell,eq} = -\frac{\Delta \bar{G}_{cell}}{zF} = -\frac{RT}{zF} lna_{A(in\ B)liq}$$
[4]

Because all three active battery components are liquid phase, the system is able to operate at high current densities with minimal overpotential losses. In addition, because the cell is restored to its virgin liquid state upon each recharge, the device is immune to solid-state failure mechanisms common in lithium-ion batteries³ and, as a result, is expected to provide exceptionally long amortizable service lifetimes.

In spite of the benefits of the LMB system, the high temperatures required to achieve a fully molten state present challenges when scaling the battery to production. Higher temperatures drive costs due to issues associated with device sealing, expensive wiring and busing equipment, and required safety margins. As a result, there is great interest in lowering the operating temperature of the device through careful selection of the three active components. Because there are a variety of earth-abundant and low-temperature anode^{2,4} and cathode metals¹ and alloys the component that most frequently sets the operating temperature of the device is the molten salt electrolyte. Such dependencies motivate the search for newer and lower-melting electrolytes to unlock both lower temperature battery designs as well as cheaper device operating costs on a \$/kWh-cycle basis.

Sodium-based systems are particularly attractive as they simultaneously fulfill the requirements of low-cost, high-abundance, low melting temperature, and high alloying voltage. The most relevant work on low-temperature, non-aqueous molten electrolytes can be found in the sodium electrodeposition work produced by Okada and Yoshizawa.⁵⁻¹⁰ Unlike early sodium-based batteries¹¹⁻¹³ that required operation at high temperatures to harvest waste heat but subsequently incurred losses due to metallic sodium solubility in the electrolyte,¹⁴ sodium production has principally focused on the depression of operating temperature so as to reduce cost, mitigate metallic sodium solubility, and enable amalgamation-type processes that would otherwise suffer from mercury contamination at high temperatures.¹⁵ The relevant low-temperature (<300°C) melts featured hydroxides, cyanides, and amides as key additions.^{15,16} In spite of their promise, these mixtures were never adopted for use as the value of sodium produced was deemed too low to justify the marginal cost of the improved electrolyte.

In order to lower salt melting temperatures for Castner- and Downstype electrolysis cells, researchers often explored multi-component systems where one or more polyatomic anion salts such as NaOH or NaCN were added to simple halide salts like NaI or NaBr.¹⁵ Unlike lithium analogues in which LiOH is vigorously attacked by Li metal, Na systems present a pathway toward improved stability against hydroxide-based molten salt electrolytes.¹⁷ Specifically, metallic sodium (Nam) in contact with pure molten NaOH demonstrates a very slightly negative change in Gibbs free energy for the reaction (ΔG_{rxn}) at normal molten temperatures (>320°C) and is nearly 100 kJ/mole (~1 V) less reactive than Li in the presence of its hydroxide. By reducing the activity of NaOH through dissolution in NaI and by lowering the melting temperature via deep eutectics, it is postulated that the reactivity and therefore detrimental solubility of Na_m in a NaOH-based electrolyte should be sufficiently suppressed to allow operation of a rechargeable long-lifetime battery. In addition, earlier studies^{8,18} report binary melt conductivities between 0.45 and 0.55 S/cm at temperatures around 250°C. This is approximately an order of magnitude greater than traditional ceramic sodium-ion

^{*}Electrochemical Society Active Member.

^zE-mail: dsadoway@mit.edu

conductors¹⁹ and minimizes overpotential loss incurred during the high current density operation of an LMB.

Although NaOH-based binary melts offer unprecedented potential to provide an intermediate temperature, low-cost, and high conductivity LMB electrolyte, no prior work has explored such systems for purposes other than electrowinning. In addition, of the limited work conducted, there are discrepancies and vacancies in the literature regarding phase diagram construction, binary compound stoichiometry, and the electrochemical stability of the melt. The aim of this work is to demonstrate the utility of NaOH-NaI eutectic salt as an electrolyte for sodium metal batteries. The operating window of the electrolyte in terms of temperature, composition, and voltage is explored by electrochemical, thermodynamic, and crystallographic measurements and paired with thermodynamic modeling. Additionally, early cycling data and leakage current results are provided to highlight the promise of the hydroxide-iodide eutectic system for a sodium-metal battery.

Experimental

Materials preparation and containment.- NaI was supplied from Alfa Aesar (99.99% purity, ultradry) and NaOH from American Elements (99.9% purity, anhydrous). The NaOH granules were dried at 550°C in Ni-201 crucibles under vacuum according to a schedule described by Yurkinskii²⁰ in order to minimize formation of putative Na₂O or Na₂O₂ by-product in the melt. Omission of this drying process resulted in strong water reduction signals during voltammetric studies. The dried salts were then combined to form various compositions inside of an argon-filled glove box. These compositions (Supplementary Table I) were melted under argon in Ni-201 crucibles to promote homogenization. Due to the high volatility of NaI near its melting temperature, NaOH salt was placed on top of the NaI powder and allowed to melt and solubilize the NaI salt slowly over time. This method (Supplementary Table II) allowed binary salt preparation at temperatures between the melting points of NaOH (318°C) and NaI (661°C).

All salt-containing Ni-201 parts were cleaned with acetone, deionized water, pickled briefly,²¹ and dried under vacuum at 150°C prior to use. Nickel crucibles showed minimal or no corrosion throughout the experiment. Though corrosion of Al_2O_3 has been reported,⁷ minimal corrosion was observable when this containment material was used as a standard Differential Scanning Calorimetry (DSC) crucible. Further, β'' -Al₂O₃ has been found to resist corrosive attack in hydroxide environments for time periods much greater than the length of conducted experiments.²² Various salt compositions were exposed for over 300 hours in both static and dynamic conditions to a number of different container materials, and upon cooling the salts were pulverized, homogenized, and tested for impurities via direct current plasma emission spectroscopy (Luvak Inc. following ASTM E 1097-12). High purity Ag, Pt, and Ni and Al₂O₃ demonstrated satisfactory resistance, and the salt withstood hydration throughout the duration of the experiments (Supplementary Table III).

Thermal analysis and phase studies.— All thermal measurements were carried out on a Netzsch STA 409 CD in differential scanning calorimetry mode. Crucibles were composed of Al_2O_3 and were not sealed to allow for constant pressure measurements in the argon environment. Because of this, salt samples were briefly (<10 s) exposed to dry atmospheric conditions. The instrument was calibrated at a heating and cooling rate of 5°C/min using calibration materials of 99.99% purity or greater over a temperature range corresponding to the range of predicted liquidus temperatures for the various NaOH-NaI compositions.

Each experiment began with a full-temperature scan at 20°C/min to initially identify transitions followed by at least three temperature cycles through each targeted phase transition. At the end of each temperature cycling, the sample was left to anneal at sub-transition temperatures to minimize the presence of non-equilibrium transitions involving metastable phases. For transitions that were separated by temperature intervals exceeding 100°C, each individual signal was characterized by a discrete set of temperature cycles. Each sample was tested on two different occasions over a month-long period and in randomized order to ensure reproducibility. In addition, each composition was resynthesized six months after the first round of tests, and selected experiments were rerun to attest reproducibility of sample preparation and to eliminate potential equipment drift. Only phase signals that appeared in all temperature cycles in both samples have been considered for the modeling and are reported here.

In concert with thermal analysis from the previous section, X-Ray Diffraction (XRD) was employed to elucidate or confirm the presence of compound phases and locate their stoichiometric positions. XRD was performed on a PANalytical X'Pert Pro Multipurpose Diffractometer with a rotating sample stage (1 Hz) and Bragg-Brentano divergent beam optics for 12 hours per scan at 1,000 s/step scan rate. Due to the hygroscopicity of salt samples, a special air-sensitive sample holder was prepared in an argon-filled glove box to prevent atmospheric contamination. The polymer dome creates known low-angle scattering that can be accounted for during data processing. Analysis took place using PANalytical HighScore Plus software that allowed for amorphous polymer dome scatter fitting as well as crystallographic indexing methods.

Prior to XRD, samples were synthesized slightly off compound stoichiometry to ensure that each compound was in two phase equilibrium with its respective unary end component, annealed for one week at sub-eutectic temperatures to promote solid state equilibrium, and then pulverized to promote homogeneity.

Thermodynamic modeling.— The computational thermodynamic modeling performed to obtain parameters to reproduce the phase diagram data for the binary system NaI-NaOH has been carried out according to the CALPHAD method²³ within the FACTSage Thermochemical Software. An assessment of the experimental data has been conducted to determine their reliability and weigh them appropriately during the modeling process. The method consists of modeling the thermodynamic properties of a system by first considering the unary end-members, i.e., NaOH and NaI, for which the thermodynamic properties are available in thermodynamic compilations²⁴ as well as in databases used by thermodynamic calculations software. For the present work, data for NaOH and NaI have been taken from the Pure Substances database (FactPS) of FactSage 6.3.²⁵

The thermodynamic properties of the binary system are then fit to solution models to describe the liquid phase and, if necessary, solid solutions. A two-sublattice polynomial solution model with Redlich-Kister parameters has been used for the binary NaI-NaOH melt. Cation, Na⁺, and anions, I⁻ and OH⁻, are confined to their respective, separate model sublattices. Values of the model parameters were optimized with the Optisage module of FactSage leveraging the NOMADS algorithm.²⁶ Binary intermediate compounds without solubility range are modeled in a similar fashion as the endmembers by adjusting their enthalpy of formation, absolute entropy, and temperature-dependent functions for the heat capacity obtained via Kopp-Neumann law approximations.

Electrochemical measurements.— All electrochemical measurements were performed using an AutoLab PGSTAT 302N potentiostat/ galvanostat. Experiments were conducted within a sealed, argonfilled, stainless steel chamber that was placed inside of a PIDcontrolled Thermo Scientific furnace. The stainless steel chamber is designed (Supplementary Figure 1) with ultra-torr ports to allow multiple air-tight and insulated electrodes and thermocouples access to the electrochemical system. The eutectic salt was held in a Ni-201 crucible surrounded by an Al_2O_3 crucible to shield the melt crucible from electrical contact to the stainless steel chamber.

A three-electrode setup was used for cyclic voltammetry of the eutectic NaOH-NaI melt (Supplementary Figure 2). Working and counter electrodes utilized Ø 1 mm platinum and nickel wires (99.95% Sigma Aldrich and 99.98% Goodfellow, respectively) depending on



Figure 1. Proof-of-concept Na|NaOH-NaI|Pb-Bi cell. The sodium metal is immersed in nickel-plated steel foam to improve contact while the Pb/Bi alloy is connected via an immersed wire that is shielded from the rest of the system by an Al_2O_3 tube.

the direction of the polarization sweep. Platinum working electrodes were used for anodic sweeps and nickel working electrodes were used for cathodic sweeps in order to obviate oxidation or alloying, respectively. Uncompensated resistance was measured and removed. The reference electrode was comprised of a tantalum (99.95% Ø 1 mm, Alfa Aesar) wire immersed in pure sodium metal (99.98%) contained within a β'' -Al₂O₃ tube (6.5 mm Ø, Ionotec). To confirm the stability of the Ta/Na/ β'' -Al₂O₃ (TaNaB) reference electrode a second identical electrode was placed in the melt, and the potential difference between the two was monitored throughout the duration of the experiment. Measurements demonstrated excellent electrode stability with a voltage shift only 5 μ V over a seven-day period (Supplementary Figure 3).

An electrochemical cell consisting of a $Na_{(m)}$ negative electrode, a eutectic Pb-Bi alloy (44–56 mol%) positive electrode, and the eutectic NaOH-NaI salt was assembled. An Fe-Ni foam served as the negative current collector (NCC) to increase contact area, a Ni wire as the positive current collector (PCC), and an Al_2O_3 crucible as the cell

Table I. DSC transition measurement result	ts.
--	-----

	Transition 1		Transition 1 Transition 2		Transition 3	
NaOH %	T (°C)	Error (°C)	T (°C)	Error (°C)	$T(^{\circ}C)$	Error (°C)
100	285.3	0.9	292.1	0.6	314.1	0.1
90	219.4	0.3				
80	220.4	0.2				
70	219.8	1.0	230.1	0.7		
60	218.3	0.1	229.6	0.3		
50	219.1	0.6	229.2	1.1	285.7	0.7
40	228.8	0.8	287.9	1.1		
30	229.5	0.5	286.8	0.3		
10	287.1	0.3				
0	660.7	1.8				

container (Figure 1). The cell cycling tests were performed with a Maccor (Model 4300) battery tester.

Results and Discussion

Thermal analysis and phase studies.— Table I presents the results from the DSC tests of various compositions of the binary system NaOH-NaI. Since the liquidus has been reported previously in the literature,^{5,10,27} focus here is placed on accurately characterizing other solid-solid and solid-liquid transitions.

The data demonstrated high reproducibility within each experiment and when the results from multiple sets of experiments were compared. Of note is that samples richer in NaI exhibited higher vapor pressures and therefore presented experimental challenges as mass loss was often significant; this, in turn affected the strength of signal and changed the composition of the sample.

Figure 2 plots the transition points alongside existing liquidus values from the literature. A eutectic signal corresponding to approximately 220°C is clearly identifiable on the NaOH-rich side. There are similarly two additional thermal arrests, at 229°C and 287°C, repeated at various compositions that likely derive from peritectic transitions resulting from incongruently melting compounds. In addition to the current and previously reported DSC data points, the calculated phase diagram resulting from the thermodynamic modeling is overlaid in Figure 2. The experimental and calculated phase transition values are provided in Table II alongside values reported in the literature.^{5,10,27,28}

Though the phase diagram in Figure 2 represents our final conclusions following XRD analysis, different stoichiometries were tested during phase diagram construction and modeling. The $Na_5(OH)I_4$



Figure 2. DSC data (red circle) with historic literature values (blue, green orange) overlaid on the predicted NaI-NaOH binary system phase diagram. The binary eutectic is predicted to exist at 80% NaOH though the model fits the diagram at 81.2%.

Table II.	Phase	Transformation	Data.

 Source	Eutectic	Peritectic #1	Peritectic #2
Scarpa ²⁷	220	N/A	300
Okada ⁵	225	N/A	N/A
Yoshizawa ¹⁰	225	234	290
Sangster ²⁸	231	N/A	312
This Work - Exp.	219.9 +/- 0.4	228.9 +/- 1.4	286.4 +/- 0.7
This Work - Model	222.8	229.2	286.9

compound has been proposed¹⁰ and is again corroborated in this study by the disappearance of the 287° C peritectic signal in the 10/90 NaOH-NaI salt. No previous confirmation of stoichiometry or crystallographic study of this compound has been conducted prior to this work. Of equal interest is the identification and crystal structure of the second stoichiometric compound that incongruently melts at 229°C. On the basis of Differential Thermal Analysis (DTA) Yoshizawa¹⁰ has proposed the presence of a Na₃(OH)I₂ compound. More recent studies,²⁹ however, have experimentally demonstrated a Na₇(OH)₅I₂ phase to exist and have proposed a matching crystal structure that corroborates the stoichiometry of this compound. The results from XRD testing of Na₅(OH)I₄ and Na₇(OH)₅I₂ are shown in Figure 3.

The spectrum in Figure 3a reveals a strong match for the new Na₇(OH)₅I₂ compound and its coexistence with trace α-NaOH. Figure 3a also presents five unmatched peaks as well as several others whose intensities cannot be explained solely by the Na7(OH)5I2 or α -NaOH spectra. For example, the α -NaOH peak at 38.17° is out of proportion from other peaks in its pattern in a manner that cannot be accounted for by preferred orientation artifacts. These anomalies can be best explained by looking to the spectrum in Figure 3b which clearly identifies highly crystalline NaI as well as 11 peaks that are not explainable by any known phases composed of elements present in the experiment. Rather, this unknown phase shows direct correspondence with the five unmatched peaks in Figure 3a as well as the peaks that show intensities disproportionate with the binary $Na_7(OH)_5I_2$ /NaOH system. As a result, it is proposed that these unmatched peaks (Table III) are representative of an as-yet unidentified compound of NaOH and NaI.

Though a precise stoichiometry is not available, the symmetry of the indexed pattern shows a very strong match to Pm-3m (space group 221) type systems. The minor presence of this unknown NaI-rich phase in the Na₇(OH)₅I₂ sample is consistent with two-phase formation between 229°C and 287°C and metastable existence below 229°C due to slow solid state diffusion kinetics. Though the Na₇(OH)₅I₂ appears

Table III. Peak List of unknown NaI-rich phase.

Peak #	2θ (degree)	Intensity (%)	Comments
1	18.8479	47%	High background error
2	26.7453	100%	
3	32.921	32%	
4	38.1703	29%	
5	42.8764	22%	
6	47.1846	25%	
7	55.0378	13%	
8	58.689	5%	
9	62.2	9%	
10	65.608	9%	
11	68.92	1%	twinned peak with #12
12	68.99	2%	twinned peak with #11
13	72.15	1%	*
14	75.335	4%	

to be the most likely candidate for the incongruent melting thermal arrest at 229°C, this does not address the fact that eutectic signals were detected compositionally as far out as 50-50 amongst the various samples tested with DSC. Such an anomaly, also seen by Yoshizawa et al.¹⁰ and used as justification for an Na₃(OH)I₂ compound, is here explained as the result of a Scheil-Gulliver solidification model in which the composition of the liquid-phase follows closely the liquidus upon cooling. In this scenario, as a salt system with bulk composition to the left of the Na7(OH)5I2 cools, the rejected liquid phase material is enriched in NaOH beyond the 2:5 stoichiometry. This process continues down toward the eutectic composition until the enriched liquid phase reaches the eutectic at approximately 220°C and freezes, creating a thermal signal in spite of the compound's overall composition indicating a different positioning on the phase diagram. This eutectic phase is then re-melted upon heating due to the slow solid-state diffusion between the metastable solid phases.

Thermodynamic modeling.— The binary salt liquid solution was modeled within the framework of the Compound Energy Formalism (CEF) as a two-sublattice solution.^{30,31} The Gibbs free energy is given by:

$$G = \sum_{i} \sum_{j} \left(y_i^{cation} y_j^{anion} G_{ij}^0 \right) - TS + G^{excess}$$
[5]

Where y_i^{cation} and y_j^{anion} are site fractions of constituent i and j on the cationic and anionic sublattices, respectively, and G_{ij} corresponds to end member standard Gibbs free energy. The second term accounts for



Figure 3. XRD spectra of two proposed binary compounds with a) 71.4/28.6 and b) 80/20 NaI and NaOH mole percent, respectively. Setup used 1.8 kW sealed X-ray tube with Cu source, nickel filter, and programmable fixed slit of $\frac{1}{4}$.

Compound	$\Delta H_0^{298.15 \text{ K}} \text{ (kJ.mol}^{-1}\text{)}$	S ₀ ^{298.15 K} (J.mole ⁻¹ K ⁻¹)	$\Delta C_p (J.mol^{-1}K^{-1})$
Na ₅ (OH)I ₄	-1,634	355.690	298.15 → 570.15 K: 333.98126T + 2.56E ⁻⁴ T ² 570.15 → 593.15 K: 345.43
Na7(OH)5I2	-2,758	422.513	$298.15 \rightarrow 570.15 \text{ K}: 68.346 + 1.586\text{T}0013\text{T}^2$ $570.15 \rightarrow 593.15 \text{ K}: 559.819$
NaOH-NaI	Solution	$egin{array}{c} L^0 \ L^1 \ L^2 \end{array}$	Interaction Parameter (J) -6189.489–8.028T -585.075–4.825T -15989.2–20.717T

Table IV. Optimized properties of binary compounds and 2-sublattice solution.

the ideal entropy of mixing (Temkin-like³²). The excess term, G_{excess} captures the non-idealities of the solution via interaction parameters, L^k , expanded as Redlich-Kister polynomials. In the case of a single cation, this excess term reduces to

$$G^{excess} = Y_{OH}Y_I \sum_{k} L^k (Y_{OH} - Y_I)^k$$
[6]

The model parameters have been optimized primarily with liquidus data in which the solution is in equilibrium with one of the binary end members. Further refinements of the parameters for the liquid have been conducted simultaneously with the optimization of the thermodynamic properties of the intermediate compounds in order to reproduce the thermal arrests for the eutectic and the peritectics. The best compromise corresponds to the phase diagram presented in Figure 2, and experimental data are reproduced within the experimental errors. The optimized two-sublattice solution interaction parameters as well as the enthalpy of formation, absolute entropy at 298.15 K, and heat capacity functions for the two intermediate compounds are provided in Table IV. Additional data including the end-member thermodynamic values can be found in supplementary Table IV.

Cyclic voltammetry – cathodic study.— Cyclic Voltammetry (CV) was conducted on the eutectic salt (80/20) in order to determine the electrochemical window and limiting cathodic and anodic reactions of the melt. Nickel was found to be preferable for cathodic deposition sweeps due to its minimal solubility with sodium³³ and its lack of known low temperature intermetallics as occur with silver and platinum. Scans were conducted at various rates though the cathodic limit of interest appeared independent of scan rate due to the very fast kinetics of sodium ion diffusion and charge transfer involved in liquid

sodium deposition. Figure 4 shows the electrochemical behavior as a function of temperature at the cathodic limit.

The 0 V cathodic limit corresponds to the deposition of sodium metal whereas the anodic process driven on the counter electrode is likely due to oxidation of the hydroxide species, similar to the 2.3 V reaction carried out in pure molten hydroxide on the anode during the Castner electrodeposition process.³⁴

cathode:
$$2Na^+ + 2e^- \rightarrow 2Na_{(liq)}$$
 [7]

anode:
$$2OH^- \rightarrow \frac{1}{2}O_{2(g)} + H_2O + 2e^-$$
 [8]

overall:
$$2NaOH \rightarrow 2Na_{(liq)} + \frac{1}{2}O_{2(g)} + H_2O$$
 [9]

The lack of a water reduction signal between 0.9 V and 1.0 V indicates a highly oxo-basic sample that has little water initially present in bulk. Continued cycling and reduction of sodium at the working electrode are predicted to create water by-product at the counter electrode. As a result, a minor cathodic signal at around 900 mV vs sodium and similar to those found in NaOH-KOH studies³⁵ occasionally appeared after several days of investigation. Another remarkable feature relates to the unusual presence of a sodium stripping peak upon voltage sweep reversal when at lower temperatures ($< 300^{\circ}$ C). Prior work³⁵ investigating sodium electrodeposition from hydroxide melts finds that deposited sodium rapidly reacts with or dissolves into the caustic melt, resulting in little anodic return signal following deposition. In the NaOH-NaI eutectic binary system, however, it is believed that lower temperatures coupled with the reduced activity of NaOH suppress these dissolution reaction pathways. CV data were integrated above and below the 0 V deposition potential to quantify deposition to stripping efficiency. Figure 5 demonstrates a sharp decrease in efficiency between 280°C



Figure 4. Cyclic voltammagrams at increasing temperatures. A TaNaB reference electrode here is measured against a nickel working electrode while utilizing a platinum counter electrode.



Figure 5. Coulombic integration of the deposition and stripping of sodium metal at different temperatures. The dotted line occurs at 280°C, Yoshizawa's reactivity point.

Downloaded on 2016-03-10 to IP 18.115.5.3 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).



Figure 6. Cyclic voltammagrams with lowest cathodic voltage programmed to post- and pre-deposition potentials. A TaNaB reference electrode is here measured against a nickel working electrode while utilizing a platinum counter electrode.

and 306°C. This behavior was similarly observed by Yoshizawa via an H_2 production measurement.⁹

Two other features, a reductive signal above 0 V and an oxidative signal beginning around 325 mV vs. Na are noteworthy at higher temperatures. By restricting the CV cathodic sweep to pre-deposition voltages (Figure 6) we find a relationship between the reductive and oxidative signal. This indicates that the reaction occurs in the absence of metallic sodium and that the processes may be linked by a species that reversibly oxidizes and reduces on the surface of the nickel electrode.

Furthermore, the coulombic efficiency of the CV measurements increases as scan rate is decreased. The contrary is expected to be true for solubilization and subsequent sodium fog production as has been alternatively proposed in other sodium halide systems.³⁶ This may also indicate that the products formed and re-oxidized are stable and perhaps self-inhibiting as they are more efficiently removed at slower rates. Though these findings do not fully clarify the mechanism, the most likely candidates are postulated to be reversible and inhibiting H₂/Na₂O production or the reduction and oxidation of an unidentified exotic subvalent species such as Na₂ or Na⁻ as has been identified in analogous Na-NaBr systems.³⁷

Cyclic voltammetry – *anodic study.*— Eutectic (80/20) anodic studies employed a platinum working electrode (0.78 mm^2) to facilitate gas evolution and obviate metallic iodide or hydroxide production as occurs on silver (2.2 V) and nickel (1.5 V), respectively. Figure 7 shows a CV conducted at the anodic limit of the melt at different temperatures. The electrochemical window of the melt is found to range from approximately 2.4 V to 2.5 V between the eutectic melting temperature and the upper limit of battery operation, which was determined herein to be 280° C.

Though the major oxygen evolution event, IV, occurs at voltages above 2.4 V oxidation steps are present at less anodic potentials: in particular, signals corresponding to oxidation events at 1.45 V (I), 1.9 V (II), and 2.1 V (III). The first electrochemical process, I, likely derives from the oxidation of trace Na₂O impurities to the peroxide Na₂O₂ (~1.5V).

The latter two oxidation processes, II and III, are proposed to come from complete oxidation of remnant Na_2O (1.80 V) and Na_2O_2 (2.07 V), respectively. These values are predicted assuming pure substances at 250°C using FACTSage 6.3 and the relevant NIST-JANAF Thermodynamic Tables. These compounds have been variously con-



Figure 7. Anodic study of the impact of temperature on oxidation potential. A TaNaB reference electrode is here measured against a platinum working electrode while utilizing a nickel counter electrode.

firmed in hydroxide melts and may form via reactions between solubilized sodium metal and oxygen or during extensive drying processes. Though these impurity reactions restrict the upper anodic boundary for operation to 1.8 V, alloying type cells rarely operate with voltages above 1.0 V^1 , and therefore this electrolyte window is suitable for all known LMB systems.

The experimental electrochemical window as a function of temperature can be extracted by using a Tafel plot to identify the unique regimes between earlier Na_xO_y reactions and those corresponding to the final oxidation, peak IV. This region is then linearly extrapolated back to the zero current position to determine the anodic limit and therefore the electrochemical window (ECW) after uncompensated resistance removal. This experimental value can then be compared to that predicted from the thermodynamic model for the binary solution at the eutectic (20–80) composition. The theoretical voltage of the proposed oxidation reaction can be modeled as

$$\Delta V_{ECW} = -\frac{1}{nF} \left(\Delta G^0 + RT ln \left(\frac{(a_{Na})^2 (p_{O_2})^{1/2} (p_{H_2O})}{(a_{NaOH})^2} \right) \right)$$
[10]

where the activity of pure sodium is set to unity, the activity of NaOH is predicted by the thermodynamic model, and the partial pressures of O_2 and H_2O are approximated as the stoichiometric production values of 1/3 and 2/3, respectively. Figure 8 provides a comparison between the experimental and theoretical OCV values.

Of greatest note is that the experimental and theoretical data show strong agreement in their trend as a function of temperature. The slopes, related to the entropy of the reaction, are found to be within approximately 16% of each other. Because the activity values for NaOH would need to be an order of magnitude lower to match the experimental findings, we speculate that the differences in the absolute voltages of the reaction are related to the oxygen production overpotential and its functionality on temperature. In spite of this, the thermodynamic modeling of the liquid solution is here confirmed to produce results that are realized experimentally.

Cell cycling study.— A proof-of-concept cell was constructed using the NaOH-NaI eutectic as the Na⁺ itinerant electrolyte and Na||Pb-Bi as the electrode couple. The Pb-Bi alloy was created at 44/56 mole percent Pb/Bi to take advantage of its low eutectic melting temperature (125°C). The cell was successfully charged and discharged at 270°C with a notably low leakage current of 0.34 mA/cm² (Figure 9). This is two orders of magnitude less than those found in early Na-Bi cells³⁸ and half that demonstrated for promising Li-based LMB chemistries.²



Figure 8. Comparison of the experimentally measured oxygen production voltage with that predicted from the thermodynamic model. Slopes provided next to curves.

The cell was cycled over 100 times and was ultimately limited by the evaporative loss of sodium metal into the much larger testing crucible environment. This failure mechanism likely accounts for a vast majority of the 1%/cycle capacity fade rate experienced as the experiment progressed. Throughout the lifetime of the device, coulombic efficiencies of around 92% and energy efficiencies around 41% were measured (Figure 10).

The fact that coulombic inefficiencies match those seen in the CV efficiency study (Figure 5) indicates that most of the loss must be occurring at the negative electrode and is likely the result of reforming a passivating Na₂O film that suppresses sodium solubility. The low energy efficiency was found to derive principally from suboptimal cell design, the possible existence of a thin dielectric Na₂O film on the anode, and the positive electrode reaction, specifically the overpotential associated with the formation of a solid Na-Bi phase in the positive electrode. These results present the first known LMB-type rechargeable storage device that can operate below 300°C. Future optimization of the NaOH-NaI based systems may consider additions of ternary salt components, improvements in electrochemical cell design, and the selection of different positive electrode materials.



Figure 9. Magnification of scans 9–11. Na||Pb-Bi cycling charged up to a cutoff of 1.2 V, followed by a 1 hour potentiostatic leakage current measurement, and ended with a discharge down to 50 mV.



Figure 10. Cycling data for 112 cycles of the Na|NaI-NaOH|Pb-Bi cell. The cell cycled for over two weeks and maintained self-discharge currents of less than 0.4 mA/cm² for the entirety of the experiment.

Conclusions

The development of suitable molten salt electrolytes for sodiumbased systems at temperatures below 300°C has been a significant historical challenge and driven research toward ion-selective solid membrane technologies in order to mitigate the reactivity and solubility of pure metallic sodium. This work has shown that the high conductivity binary NaOH-NaI molten system exhibits a significantly suppressed eutectic temperature (220°C) at compositions near 80/20 mole percent NaOH/NaI, a suitable voltage window for LMB-type batteries that is theoretically limited by an oxidation reaction occurring at 2.5 volts (at 232°C), and a remarkable reduction of reactivity with elemental sodium. This last point is repeatedly seen in high efficiency stripping during cyclic voltammetry as well as extremely low leakage currents during Na||Pb-Bi battery cycling. These properties identify NaOH-NaI and potential ternary extensions as particularly promising electrolytes for energy storage as well as electrowinning processes. These lower temperatures further enable the use of simple polymeric sealing materials rather than complex metalloceramic or glass seals, reducing the overall capital cost of such electrochemical devices. In addition, the creation of a simple solution model that captures much of the functionality of the thermodynamic properties of the melt empowers intelligent selection of ternary or quaternary components to adjust melt properties as desired. Considering these favorable properties and new thermodynamic understanding, LMBsystems are now better positioned to provide cheap, long-life, and low-temperature energy storage for grid-scaled systems.

Acknowledgments

The authors thank Dr. Charlie Settens for assistance with XRD setup and analysis and Kimberly Aziz for experimental assistance. The financial support of the US Department of Energy, Advanced Research Projects Agency-Energy (Award No. DE-AR0000047), TOTAL, S.A., and the MIT Tata Center for Technology and Design are gratefully acknowledged. D.R.S. is a co-founder of Ambri, a company established to commercialize the liquid metal battery. D.R.S.'s role with the company is advisory; he is formally the Chief Scientific Advisor and is a member of the Board of Directors.

References

 H. Kim, D. A. Boysen, J. M. Newhouse, B. L. Spatocco, B. Chung, P. J. Burke, D. J. Bradwell, K. Jiang, A. A. Tomaszowska, K. Wang, W. Wei, L. A. Ortiz, S. A. Barriga, S. M. Poizeau, and D. R. Sadoway, *Chem. Rev.*, **113**(3), 2075, (2013).

Downloaded on 2016-03-10 to IP 18.115.5.3 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).

- K. Wang, K. Jiang, B. Chung, T. Ouchi, P. J. Burke, D. A. Boysen, D. J. Bradwell, H. Kim, U. Muecke, and D. R. Sadoway, *Nature*, 514(7522), 348 (2014).
- 3. J. M. Tarascon and M. Armand, Nature, 414(6861), 359 (2001).
- X. Lu, G. Li, J. Y. Kim, D. Mei, J. P. Lemmon, V. L. Sprenkle, and J. Liu, *Nat Commun*, 5 (2014).
- S. Okada, S. Yoshizawa, and N. Watanabe, *Kogyo Kagaku Zasshi*, 56(2), 79 (1953).
- 6. S. Okada, S. Yoshizawa, and N. Watanabe, Kogyo Kagaku Zasshi, 60, 377 (1957).
- 7. S. Okada, S. Yoshizawa, and N. Watanabe, Kogyo Kagaku Zasshi, 60, 675 (1957).
- S. Okada, S. Yoshizawa, N. Watanabe, and Y. Omote, *Kogyo Kagaku Zasshi*, 60 670 (1957).
- S. Yoshizawa and N. Watanabe, in "Technical reports of the Engineering Research Institute", Vol. 10. Kyoto University, 1960.
- 10. S. Yoshizawa, N. Watanabe, and Y. Ohara, Denki Kagaku, 32, 162 (1964).
- L. Heredy, M. Iverson, G. Ulrich, and H. Recht, in *Regenerative emf Cells*, C. Crouthamel and H. L. Recht, eds., Vol. 64, p. 30, American Chemical Society, Washington DC, (1967).
- I. J. Groce and R. D. Oldenkamp, in *Regenerative emf Cells*, Vol. 64, p. 43, American Chemical Society, (1967).
- R. Oldenkamp and H. Recht, in *Regenerative emf Cells*, C. Crouthamel and H. L. Recht, eds., Vol. 64, p. 53, American Chemical Society, Washington DC, (1967).
- M. A. Bredig and H. R. Bronstein, *The Journal of Physical Chemistry*, 64(1), 64 (1960).
- S. Yoshizawa, N. Watanabe, T. Morimoto, M. Miura, and Y. Yamada, U.S. Pat. 3,265,490 (1966).
- 16. L. A. Heredy, U.S. Pat. 3,472,745 (1969).
- 17. Y. Sato and O. Takeda, in *Molten Salts Chemistry: From Lab to Applications*, F. Lantelme and H. Groult, eds., Elsevier, (2013).
- A. I. Demidov, A. G. Morachevskii, and N. N. Mit'kina, *Zhurnal Prikladnoi Khimii*, 52(5), 1193 (1979).
- 19. A. Hayashi, K. Noi, A. Sakuda, and M. Tatsumisago, Nat Commun, 3, 856 (2012).
- V. P. Yurkinskii, E. G. Firsova, and S. A. Proskura, *Russ J Appl Chem*, 78(3), 360 (2005).

- 21. J. R. David, Nickel, Cobalt, and Their Alloys, ASM International (2000).
- 22. G. Gunnarsson and B. Johannesson, J. Am. Ceram. Soc., 94(4), 988 (2011).
- R. Schmid-Fetzer, D. Andersson, P. Y. Chevalier, L. Eleno, O. Fabrichnaya, U. R. Kattner, B. Sundman, C. Wang, A. Watson, L. Zabdyr, and M. Zinkevich, *CALPHAD*, 31(1), 38 (2007).
- M. W. Chase, NIST-JANAF Thermochemical Tables, 5th ed., American Chemical Society; American Institute of Physics for the National Institute of Standards and Technology (1998).
- C. W. Bale, E. Bélisle, P. Chartrand, S. A. Decterov, G. Eriksson, K. Hack, I. H. Jung, Y. B. Kang, J. Melançon, A. D. Pelton, C. Robelin, and S. Petersen, *CALPHAD*, 33(2), 295 (2009).
- A. E. Gheribi, C. Robelin, S. L. Digabel, C. Audet, and A. D. Pelton, *The Journal of Chemical Thermodynamics*, 43(9), 1323 (2011).
- G. Scarpa, Atti della Accademia Nazionale dei Lincei, Classe di Scienze Fisiche, Matematiche e Naturali, Rendiconti, 24 (I), 955 (1915).
- 28. J. Sangster, *J. Phase Equilib.*, **21**(3), 241 (2000).
- H. Barlage and H. Jacobs, Zeitschrift f
 ür Anorganische und Allgemeine Chemie, 621(7), 1189 (1995).
- M. Hillert, B. Jansson, S. Jonsson, B. Sundman, and J. R. Taylor, *Journal of Phase Equilibria*, 13(5), 459 (1992).
- M. Hillert, B. Jansson, B. Sundman, and J. Ågren, *Metallurgical Transactions A*, 16(2), 261 (1985).
- 32. M. Temkin, Acta Physicochim. URSS, 20(4), 411 (1945).
- B. Predel, in Li-Mg Nd-Zr, O. Madelung, ed., Vol. 5H, p. 1, Springer Berlin Heidelberg, (1997).
- 34. H. Y. Castner, U.S. Pat. 452,030 (1891).
- 35. M. H. Miles, Journal of Applied Electrochemistry, 33(11), 1011 (2003).
- K. Yasuda, S. Kobayashi, T. Nohira, and R. Hagiwara, *Electrochimica Acta*, 106, 293 (2013).
- L. F. Xu, A. Selloni, and M. Parrinello, *Journal of Non-Crystalline Solids*, 117–118, Part 2, 926 (1990).
- E. J. Cairns, C. E. Crouthamel, A. K. Fischer, M. S. Foster, J. C. Hesson, C. E. Johnson, H. Shimotake, and A. D. Tevebaugh. U. S. At. Energy Comm., ANL-7316, 1967.