

# Cost-based discovery for engineering solutions

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## 1 Introduction

When cost is an impediment to the adoption of new technology, further research must imbed cost as a key performance criterion. The prime example is grid-level storage. The mix of uncommonly high power, long service lifetime, and super-low price point make this an exceptionally difficult technical challenge. The conventional approach to research, namely, cost-ignorant pursuit of the most advanced chemistry with the hope that one can chase down the cost curve in the manufacturing of product has proven to

be inadequate. For example, after over two decades of production of lithium-ion batteries their cost has not fallen low enough for them to enter the stationary storage market, not to mention mainstream electric vehicles. The remedy, in our judgment, is cost-based discovery, i.e., even at the earliest stages of research one must include cost as a determining factor in the choice of chemistry. In other words, the invention of a storage device capable of serving the electricity market rests on the discovery of a chemistry that derives from earth-abundant elements and a design that can be built using simple manufacturing techniques. Inventing to the price point of the electricity market means that parts of the periodic table are axiomatically off limits on grounds of scalability. In this chapter we set forth the methodology of cost-based discovery through the example of grid-level storage.

### ***1.1 The winds of change: integrating intermittent renewables***

On the morning of January 31<sup>st</sup>, 2012 the residents of the west coast seaport of Esbjerg, Denmark woke to the sound of high winds and ripping tree branches. The gusts in the early hours of the morning had been record-setting, with peak recordings at 4:00 AM of 54 mph that maintained strength until noon. With an average annual wind speed of 13.1 mph, Esbjerg is one of the windiest cities in Denmark and would rank in the top five windiest cities were it located in the continental United States<sup>1</sup>. In spite of that morning's anomaly, the city of Esbjerg is not only familiar with such energetic weather, it has come to depend upon it. Since 2010 Esbjerg can lay claim to hosting the largest offshore wind farm in Denmark and the third largest in the world with the complementary Horns Rev 1 and 2 rated together at approximately 369 MW generation capacity.

Denmark is no stranger to wind farms or renewable energy – it is currently the largest producer of wind turbine technology and demonstrates a clear lead in turbine penetration in its own energy sector with nearly 20% of electricity generation coming from renewable wind resources<sup>2</sup>. For this reason, Denmark is a common planning case-study for countries hoping to augment their renewable energy portfolio with intermittent sources like wind and solar and reliably integrate them into the existing network. A common topic of investigation is in the area of balancing grid inflows and outflows – a challenge resulting from the fact that most power grids maintain very little storage and grid operators must therefore maintain in-situ control in order to ensure dispatchable generation can meet demand. Without such minute-to-minute control, oversupply of energy from unexpected generation or undersupply driven by under-predicted demand would equate to economic loss and inefficiency. As a result, integration of intermittent resources like wind power brings with it legitimate concerns regarding increased variability and asynchronicity between production and demand that could render a poorly planned wind farm a resource sink rather than source.

Though unusual for Danish installations, large perturbations like the one experienced in the early hours of the 31<sup>st</sup> do result in substantial impacts upon the market. In fact, Esbjerg wasn't alone in its overproduction, as the entire Danish western grid soon became loaded with greater than 2,600 MWh/h production rates for 14 straight hours, 2.6 standard deviations above the hourly wind production mean for this area<sup>3</sup>. Shortly after the initial generation spikes from the local wind turbines, Nordpool's Elspot energy price for the western Denmark power grid dropped to below €0 for over four hours, indicating the need to distribute excess energy so rapidly that the western Danish grid operators were literally paying to have their excess energy exported to neighboring countries. Events like these, though uncommon, have led some researchers to believe that Denmark's renewable energy business model creates a perverse outcome that disproportionately exports tax-supported renewable energy at depressed spot prices to neighbors<sup>4</sup>. On the opposing side, there are just as many researchers that have shown that intermittent exports do not appear to abnormally correlate with periods of peak wind production and that wind-generated electricity goes disproportionately to satisfying domestic demand while higher merit order sources are exported or recouped<sup>5</sup>. In either case, there is agreement that the ability to store excess energy, regardless of its source, provides not only significant economic gain but also improved efficiency and reliability. The case study of Denmark teaches that moving towards a fully renewable future is fundamentally predicated on our ability to intelligently deploy grid-scale storage options to smooth fluctuations implicit with variable demand and intermittent supply.

## ***1.2 Cost is the determining factor***

Though perhaps the most poignant and popular example, wind installations are just one of many integration points where storage could offer benefits in economy, efficiency, and reliability. Numerous reports<sup>6,7</sup> have identified more than a dozen unique, though not mutually exclusive, functional areas in which tandem storage could improve our ability to supply electricity sustainably in excess of approximately 4,000 TWh<sup>8</sup> to US consumers. Though the United States has made great strides in the research and development of renewable energy technologies, it still lags behind several European peers with approximately 11.5% penetration into the electricity market as of 2011. Of this 470 TWh (134 GW) renewable generation, approximately 117.8 TWh (47.8 GW) comes from intermittent sources like wind and solar<sup>9</sup>.

In spite of the fact that the United States electricity grid is not only significantly more physically expansive but also complicated by multiple layers of federal, regional, and local regulation that do not exist in many smaller European counterparts, a majority of states around the country has continued to set competitive targets via renewable portfolio standards (RPS). Though variable across the nation, some geographic areas

are aggregately targeting greater than 20% renewable penetration by as early as 2020. One such region, under the purview of the Western Electricity Coordinating Council (WECC), has received attention in a recent study by Pacific Northwest National Lab<sup>10</sup> that investigates the balancing requirements implicit in its RPS target as well as cost-effective technology options. The study found that the anticipated renewable expansion via intermittent wind would require a total of 6.32 GW of balancing power with between 0.07 to 0.22 units of new storage capacity per unit of additional wind power. Such an amount is 27% of the total existing storage in the United States<sup>11</sup> and would represent a significant departure from the current storage growth rate.

A more detailed analysis<sup>12</sup> has noted that by taking into account the lifetimes of each technology as well as the full cradle-to-gate energy inputs, most modern electrical energy storage (EES) technologies fall short of being viable candidates for deployment as load-balancing solutions at the global scale. In fact, in spite of the torrent of research into high-technology solutions the most stringent criteria for comprehensive deployment are likely the severe system cost and material availability metrics. Programs like ARPA-E have set aggressive goals for both cost of energy and power delivery for their grid-storage portfolio with <\$100/kWh and <\$1000/kW, respectively. Amortized over the range of proposed lifetimes (10 to 20 years), most cost metrics yield levelized energy costs (LECs) of between \$.025/kWh to \$.15/kWh which is well in league with existing gas and oil peaker technologies and the average retail price felt by residential consumers. Many authors<sup>13,14</sup> have offered similar ranges and placed special emphasis on the global scalability<sup>15</sup> of any candidate technology.

Due to the fact that we are globally trending towards increased representation of renewables in national energy portfolios, because such energy sources are aperiodic and stochastic, and because demand is so large and continually increasing, one may propose that grid-scaled storage is the final bottleneck between our energy landscape today and a renewable and sustainable energy future<sup>16</sup>. Breaking this impasse will take more than scientific and technological ingenuity. The solution requires a process of cost-driven discovery guided by the realities of materials availability and the political economy.

### ***1.3 The path forward***

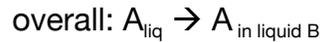
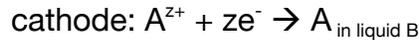
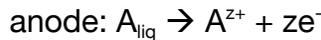
Herein, in the form of a case study, we set forth a method to address the challenge of grid-scale storage and integration of intermittent renewables by the discovery of next-generation Liquid Metal Battery (LMB) chemistry with the view to advance the system's ability to deliver energy at low levelized costs for extended lifetimes. To do so, en route we target a dramatic reduction of system operating temperature through investigation and characterization of novel electrolytes. Discovery of molten salts with liquidity on the interval, 150 - 300°C, will not only reduce total system cost but will also

simultaneously unlock simplifications in system assembly and sealing. Along each phase of the research path, cost and availability are applied as guiding principles in order to provide a framework for making materials and design choices.

## 2 The Liquid Metal Battery as a Grid Storage Solution

### 2.1 Principles of operation

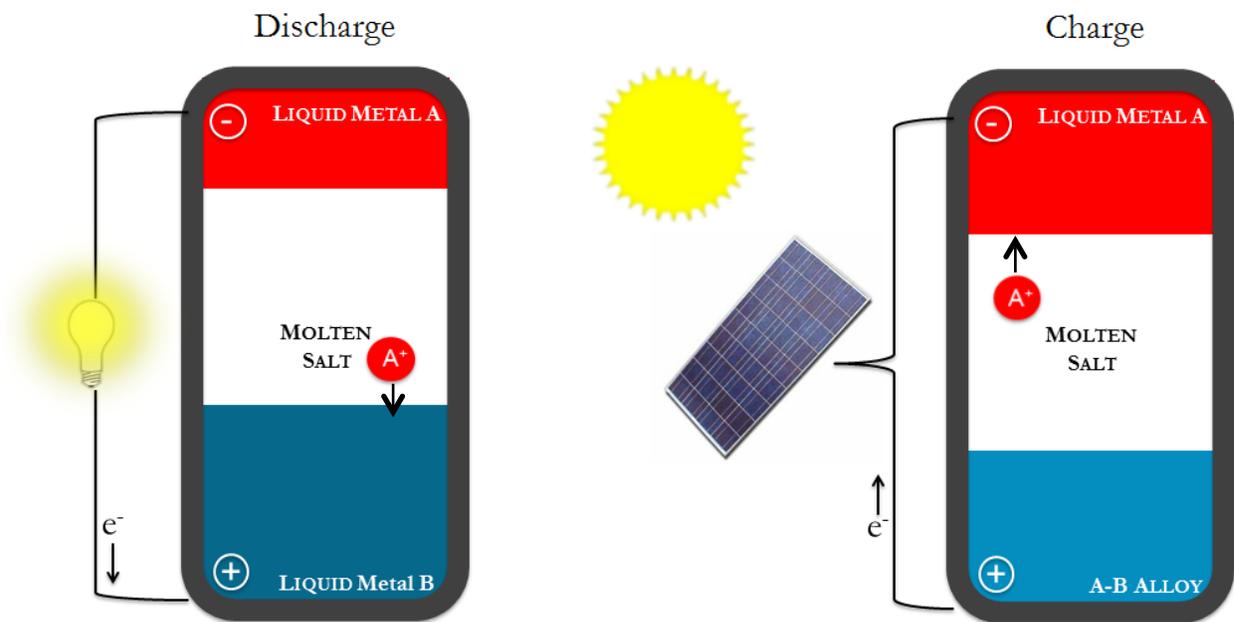
The liquid metal battery (LMB) is composed of a liquid anode, cathode, and electrolyte that self-segregate into three distinct layers due to density differences and immiscibility. The negative and positive electrodes are electrically isolated from each other by a non-aqueous electrolyte and simple cell geometry designed to separately conduct electrons to or from the electrodes through an external circuit. Similar to most other electrochemical energy storage devices, the driving force behind this electrical energy is functional on the free energy difference between the complementary reduction and oxidation reactions on either side of the cell. Unlike many other systems, however, the LMB's reactions do not involve complex displacement or intercalation processes but instead follow the chemical pathway of alloying and de-alloying as the discharging and charging mechanisms, respectively.



where  $\Delta\bar{G}_{\text{cell}} = \bar{G}_{A \text{ in liquid B}} - \bar{G}_{\text{liquid A}}$ .

Upon discharge, the more electropositive metal A (negative electrode) undergoes an oxidation reaction at the electrode-electrolyte interface to produce ionized  $A^+$  and an electron that is conducted back through electrode A and then collected to be sent around an external circuit. Because only the ionized species is significantly soluble in the electrolyte,  $A^+$  travels across the electrolyte under chemical concentration and electrical potential gradients until it reaches the positive electrode composed of metal B. Once reaching the interface,  $A^+$  reduces back to form an alloy with metal B, and then diffuses away from the interface under a concentration-driven diffusion mechanism. Charging reverses this process and results in an oxidative de-alloying of metal AB and deposition of pure A back at the negative electrode (Figure 1).

Because the operation of the battery demands that both electrodes and the electrolyte remain liquid, the temperature of an LMB must remain elevated throughout charge and discharge. Rather than needing to constantly supply this energy in the form of heat from external sources, simulations have shown that given a certain electrolyte resistivity, one can tailor the electrolyte thickness and current density to produce enough IR-based joule heating to keep the cell at operating temperature, which is generally 25°C above the melting point of the highest melting component. As will be discussed, because ionic bonding in salts tends to be stronger than metallic bonding in the conjugate metals, the electrolyte frequently plays the role of setting the operating temperature of the device.



**Figure 1: Operation of the liquid metal battery during discharging and charging**

## 2.2 Strengths and weaknesses

### 2.2.1 Scientific

Although the discharge voltage is capped at a theoretical thermodynamic limit, all batteries incur operational losses that are manifested as voltage reductions. These inefficiencies, known as overpotentials, are the result of passing charge and generally increase with increasing current density. The most common overpotential losses batteries face are:

$$V_{operational} = V_{theoretical} - \eta_{ct} - \eta_{ohm} - \eta_{mt}$$

- charge transfer overpotential,  $\eta_{ct}$  – also generally referred to as the activation overpotential, this inefficiency arises out of the activation barrier required to facilitate the heterogeneous electron-transfer reaction at the electrode interfaces.
- ohmic overpotential,  $\eta_{ohm}$  - also generally referred to as the resistance overpotential, this inefficiency arises from the linear resistance components implicit with both electronic and ionic currents. Contributions come from junction potentials, electrical resistivity of electrodes/current collectors/wires, and resistive losses from the passage of ions through the electrolyte.
- mass transport overpotential,  $\eta_{mt}$  – also generally referred to as the concentration overpotential, this inefficiency arises from the development of a gradient in the concentration of one or more species participating in the reaction at the electrode-electrolyte interface, e.g., depletion or exclusion (as in the case of bubble generation) of a reactant or accumulation of a product.

Though LMBs incur penalties from the above overpotential inefficiencies, one of their major strengths is in significantly suppressing the effects of each due to its unique all-liquid design and materials properties. The liquid-liquid interface between the electrolyte and electrode facilitates rapid charge transfer by lowering the potential energy barrier and increasing attempt frequency; the high conductivities of molten salt at elevated temperatures give rise to low resistances in the  $m\Omega \cdot cm$  regime, resulting in minimal resistive loss across the electrolyte and thus high conductivities; and the use of an all-liquid system improves electrode diffusion and obviates traditional solid-state fade/failure mechanisms characteristic of incumbent technologies and can therefore result in a battery lifetime that is theoretically limited only by corrosion of the container.

LMBs do suffer from distinct disadvantages when compared to existing battery systems. The liquid-architecture that endows the system with rapid charge transfer kinetics also makes it sensitive to motion and therefore unqualified as a candidate in portable power applications.

### **2.2.2 Scale-up to product**

Unlike many other storage technologies that were developed as a result of some fundamental or ground-breaking discovery, LMBs are instead a story of a technology that has been resurrected and advanced at a time much different than the economic and political climate originally encountered<sup>17</sup>. As a result, the development of LMB systems takes as their origin a rather basic design and cost-conscious materials selection. Unlike many other modern systems that rely upon non-equilibrium or finely-tuned microstructures, LMBs can be produced by simply pouring in the active components, weld-sealing the container closed, and heating up to temperature. For this reason, mass production and scaling of LMBs should not only be more

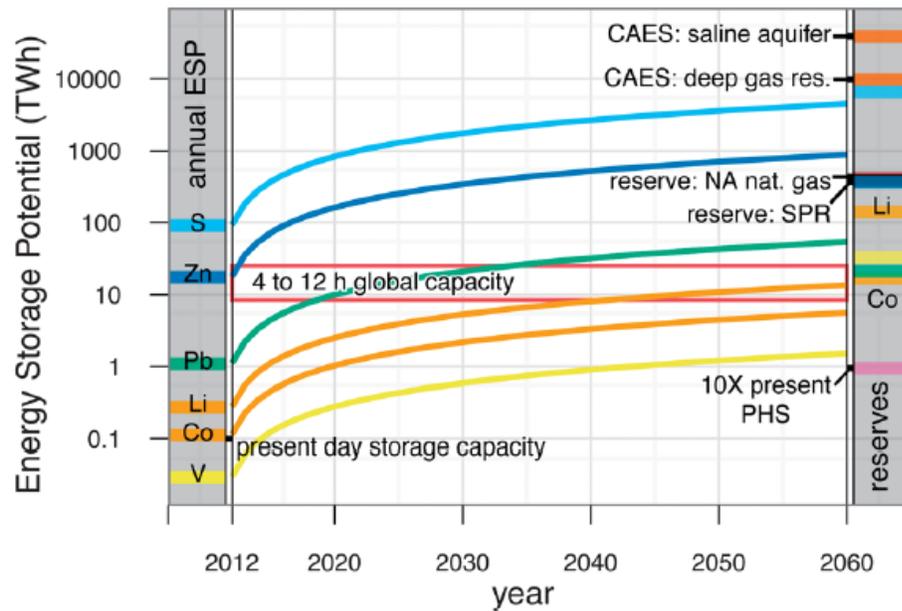
straightforward than competitor technologies but also begin at a cost competitive price point before economies-of-scale or movement along the production experience curve is factored in. Finally, because of the simpler construction, little specialized equipment or labor should be required, and as a result LMBs may potentially move outside the capital-intensive cleanroom-type facility paradigm and empower more capital-constrained regions to domestically produce solutions to their own energy problems.

Although LMBs do not exhibit the same thermal failure or runaway as do lithium-ion systems<sup>18</sup>, uncontrolled temperature swings can reduce output or exacerbate corrosion and reduce service lifetime. In addition, because LMBs operate in the molten state, a compromise in the sealing or packaging materials could result in catastrophic failure if the entire system does not maintain some secondary containment. For these reasons, LMB scale-up necessitates additional system-level considerations to ensure safe operation.

### **2.2.3 Market considerations**

Because of their relative simplicity in design and operation, active components can be interchanged with far fewer complications than with other intercalation- and displacement-type batteries. In other words, LMB researchers can more easily test and design for various chemistries of active components than would be possible in the case of proposing a new intercalant ion (e.g. sodium) to move away from lithium. This is because the most important information about new chemistries can be determined from phase diagram investigations and basic thermodynamic EMF measurements. The reason this adapts LMBs to diverse markets well has to do with the desire to maintain the flexibility in material down-selection based on cost, energy intensiveness, local availability, and regional security. Depending on whether a country or company wants to provide energy storage at a local minima functional on domestically processed, available, and secured materials or at a global minima functional more closely linked to global resource and transport prices, the choice of active components may vary.

For the global scenario, depending on the penetration of renewables into the electricity market and evolution of micro-grid modular infrastructures the demand for grid storage may significantly tax not only resource production but also the energy inputs required to manufacture such storage devices. Barnhart et al.<sup>12</sup> project that for a conservative penetration scenario (4 to 12 hours of world average power demand) one could expect a grid capacity demand to range from 8.4 to 25.3 TWh. Such demands, were they to be met by existing storage technologies, could significantly perturb existing resource production to the point of needing to expand into further reserve sites in some cases (Figure 2<sup>12</sup>).



**Figure 2: The energy storage potential (ESP) for storage technologies based on material resources and appropriate geologic formations. The chart is divided into three sections: (left) ESP based on global production, (center) linear growth in ESP as a function of time, (right) ESP based on economically viable reserves and estimates for CAES and PHS appropriate geologies.**

Figure 2 shows that even if all of the vanadium currently produced in the world were directed into providing storage via Vanadium Redox Batteries (VRB), the devices built would fall short of the 4 hour global capacity mark by over two orders of magnitude. In addition, in order to produce this much vanadium-based storage, Barnhart et al. estimate that one would require a 3% increase in global primary energy production annually for the next 30 years. The lesson is that solving global problems like grid storage necessitates a system that is materials-constraint conscious, sensitive to embodied energy inputs, and flexible to changes in supply and pricing of various lithospheric resources.

### **2.3 Review of competitive technologies**

It is important to note that not all storage technologies can easily be compared solely on the basis of energy or power storage metrics as their fitness is highly functional on the application space in which they are to be deployed. For example, though a technology may have a lower energy density or cost, it may have particularly rapid response times and ramp rates and therefore be the best choice in an application that prioritizes this metric above storage cost or density. Choosing the right technology therefore requires first an intimate knowledge of the application space, the potential

economic incentives for deployment, and the cost of integrating such a solution into the existing infrastructure. Table 1 reports on the most prominent grid-scale EES technologies. Such an analysis not only provides policy makers with a general framework for comparing technologies according to well-understood metrics but also doubles as a strategic tool for technologists in identifying fruitful research directions to address unmet needs.

**Table 1: Comparison of competitive technologies for use in grid applications**

Type	Energy Efficiency (cycles)	Power Cost (\$/kW)	Energy Cost (\$/kW.h)	Maturity	Embodied Energy (MJ/kg)†	ESOI †
Li-ion	90 – 94 (4,500) <b>94 – 99 (4,000)</b> 85 (4,000) 85 – 95 (6,000)	1800 – 4100	900 – 1700 600	demo	454	10
Sodium Sulfur	75 (4,500) <b>75 – 90 (4,000)</b> 75 (3,000) 75 – 83 (4,700)	3200 – 4000	445 – 555 350	commercial	488	6
Vanadium Redox	65 – 70 (>10,000) <b>65 – 80 (5,000)</b> 65 (5,000)	3000-3310	750 – 830 600	demo	694	3
Zinc Bromide	60 – 65 (>10,000) 70 (3,000)	1670 – 2015	340 – 1350 400	demo	504	3
Lead Acid	75-90 (4,500) <b>50 – 75 (1,000)</b> 75 (20,000)	2000-4600	625 – 1150 330	demo	321	2
LMB (Li Pb-Sb)	<b>65 – 70 (5,000 – 10,000)</b>	<b>283‡</b>	<b>84‡</b>	<b>R&amp;D</b>	<b>500 - 700</b>	<b>5 -14</b>

Blue data from 2010 EPRI Report<sup>6</sup>, Red data from 2010 Yang Report<sup>14</sup>, Green data from various literature compiled in 2011 Sandia Report<sup>19</sup>, Orange data from 2010 Argonne Report<sup>20</sup>, Black bolded data from GroupSadoway experiments and calculations

† Embodied Energy and Energy Stored on Investment (ESOI) data from Barnhart Work<sup>12</sup>

‡ Indicates calculation with only active component costs

## 2.4 Down-selection

Though there is a wide variety of potential LMB chemistries, determining optimal electrolyte chemistries for every couple is far beyond the scope of a purely experimental research program. Herein, we offer a systematic down-selection methodology to assist in identifying the most promising chemistries for LMB development. Candidates are screened on the basis of cell couple costs, operating temperature, and scalability to assist in narrowing the scope of the laboratory work.

### 2.4.1 Cost

Because LMBs are relatively simple devices, their cell materials input costs are fairly well understood prior to scale-up and can therefore be optimized during the research stages. Typically, the active materials cost comprises between 30-40% of the cost of the entire unit. As a result, it is possible to de-risk the process of scale-up by first targeting cost savings through intelligent selection of electrode materials. Table 2 below is a chart demonstrating the cost of various couples based on tonnage materials costs from various world market exchanges<sup>21</sup>, voltages of the various couples as distilled from previous thermodynamic literature<sup>17</sup>, and approximate compositional utilization for each of the couples based on intermetallic presence in their phase diagram data<sup>22</sup>.

**Table 2: Theoretical prices (\$/kWh) for various battery chemistries.**

	<b>A</b> (T <sup>MP</sup> /°C)	<b>Li</b> (181)	<b>Na</b> (98)	<b>K</b> (64)	<b>Mg</b> (650)	<b>Ca</b> (842)	<b>Ba</b> (727)
<b>B</b> (T <sup>MP</sup> /°C)	<b>\$/mol</b> <b>e</b>	\$0.444	\$0.064	\$5.080	\$0.069	\$0.140	\$0.822
<b>Al (660)</b>	\$0.056	\$62	N/A	N/A	\$24	\$10	\$51
<b>Si (1414)</b>	\$0.067	\$32	N/A	N/A	\$17	\$11	N/A
<b>Zn (419)</b>	\$0.127	\$103	N/A	N/A	\$22	\$23	N/A
<b>Ga (30)</b>	\$30.875	\$2,014	\$10,994	N/A	\$5,766	N/A	N/A
<b>Ge (938)</b>	\$101.372	\$6,606	N/A	N/A	\$11,128	N/A	N/A
<b>Cd (321)</b>	\$0.269	\$57	\$103	N/A	\$73	N/A	N/A
<b>In (157)</b>	\$66.390	\$4,749	\$13,774	\$20,512	\$14,162	\$4,959	N/A
<b>Sn (232)</b>	\$2.496	\$172	\$285	N/A	\$343	\$147	\$117
<b>Sb (631)</b>	\$1.648	\$84	\$86	\$323	\$139	\$64	\$60
<b>Hg (-39)</b>	\$0.422	N/A	\$45	\$519	N/A	\$38	N/A
<b>Pb (327)</b>	\$0.420	\$58	\$53	\$621	\$96	\$30	\$36
<b>Bi (271)</b>	\$4.974	\$248	\$310	\$555	\$575	\$222	\$176
<b>Te (450)</b>	\$27.886	\$611	\$653	\$689	\$2,193	\$2,195	\$2,222

Each estimated couple price, C<sup>est</sup> is calculated via the following relationship

$$C^{est} = \frac{\sum_i x_i \hat{P}_i}{x_{A,d} z F \hat{E}_{cell}}$$

where  $x_i$  is the mole or mass fraction of component  $i$  in the cell,  $\hat{P}_i$  is the average monthly bulk metal market price per mole of component  $i$ ,  $x_{A,d}$  represents the estimated positive electrode full-discharge composition,  $z$  is the valence change of the ion in the redox reaction,  $F$  is Faraday's constant, and  $\hat{E}_{cell}$  is the linearized average equilibrium cell voltage over the discharge range.

From these data one is quickly able to eliminate various couple chemistries on the basis of cost per mole. Provided that the active materials cost makes up approximately a third to half of the total cell cost one can project that couples with active costs over \$300 would likely result in a final cell design that places behind many of the aforementioned competitive technologies as well as moving out of range of being able to address grid storage's stringent price points. For this reason, one can eliminate couple chemistries based on K, Ga, Ge, In, and Te. These couples are highlighted in light red (Table 3) to signify they have been removed from consideration due to cost.

## 2.4.2 Temperature

As noted earlier, the electrolyte tends to set the operational temperature of the device due to the higher melting temperatures of molten salts in comparison to the electrodes. In addition to having relatively high intrinsic costs due to the need for higher purity materials, the electrolyte also plays a substantive role in impacting the final cost of the device through a number of indirect, temperature-related cost contributions. For two of these cost reductions, sealing and corrosion, one is able to preliminarily estimate the savings accrued from lower temperatures.

### 2.4.2.1 Sealing

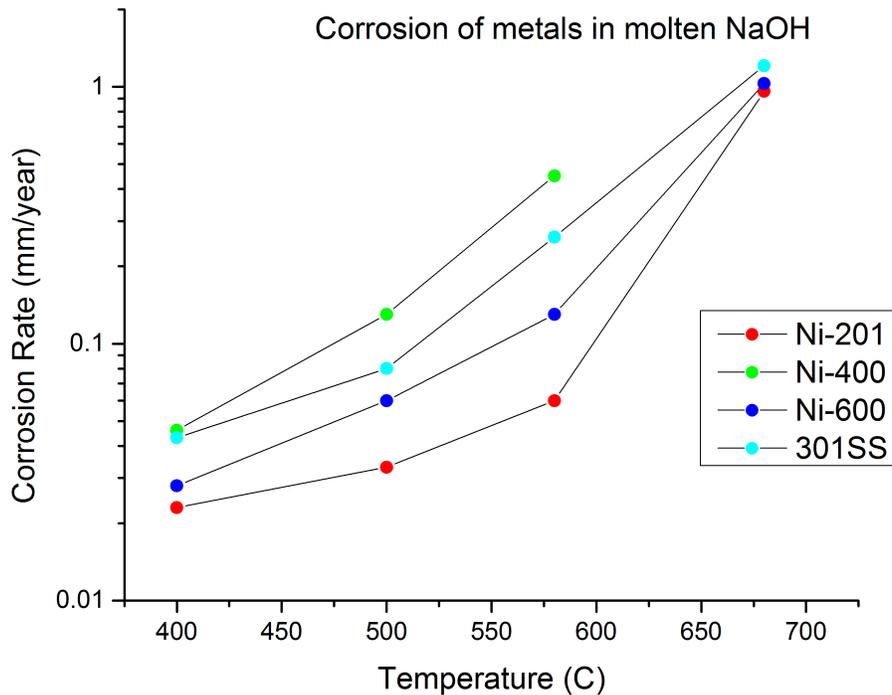
Sealing of high-temperature electrochemical devices like LMBs requires not only hermetic protection from the environment for keeping atmospheric contaminants like  $O_2$  and  $H_2O$  out but electrical isolation of the positive and negative leads. In selecting a seal for LMBs, there are two general categories to choose from: compressive and adhesive seals. Compressive seals are commonly found between metal parts in the form of metal fittings or compressed elastomeric gaskets and O-rings. Unfortunately, the need for electrical insulation rules out the use of metal-based seals. Similarly, the high temperatures of operation of modern LMBs renders elastomeric materials unsuitable. As a result, most high temperature electrochemical devices, like the NaS and ZEBRA battery, use adhesive-type seals like glass seals or ceramic-metal diffusion bonding.

A major challenge with both of these adhesive seal options is their cost and energy intensiveness. A study<sup>23</sup> on the cost breakdowns of 100 Ah NaS batteries used by the British Rail found that diffusion bond seals are the second most expensive part and compose approximately 17% of the total manufacturing cost of the device. In this case the cost of sealing came out optimistically at \$21.60/kWh. For a similar 100 Ah LMB cell with a 6" diameter, the ability to seal with a simpler Teflon O-ring would cost \$14.34 before bulk savings. This would represent at least a 33% savings in sealing though closer to 50% could be expected from scale-up. Such savings are only possible if the device's operating temperature were dropped to below 300°C.

#### **2.4.2.2 Corrosion**

Corrosion of metals by molten salts is a well-studied and reviewed phenomenon<sup>24</sup> that occurs via both dissolution and metal oxidation reactions. Both reactions are dependent on temperature, oftentimes exhibiting Arrhenius-type behavior. These corrosive reactions result in self-discharge currents, parasitic capacity losses, or degradation of the cell container. Reducing the temperature can drastically suppress the aforementioned corrosion pathways and increase service lifetime.

Though every salt-metal combination is different, one can look to similar systems to get a sense of the orders of magnitude decrease in corrosivity resulting from temperature decrease. For halide degradation of steel, Colom et al.<sup>25</sup> found that for a KCl-LiCl eutectic, a decrease from 500°C to 400°C resulted in a 73% decline in corrosion (0.3 to 0.08 mg cm<sup>-2</sup>h<sup>-1</sup>). For nitrate systems<sup>26</sup> (KNO<sub>3</sub>-NaNO<sub>3</sub>) a decrease from 630°C to 600°C depresses corrosion from 0.1 mm year<sup>-1</sup> to 0.01 mm year<sup>-1</sup>. Finally, for a molten sodium hydroxide system<sup>26</sup> corrosion can be reduced by up to two orders of magnitude with a 300°C decrease (Figure 3). Thus, a minor depression in operation temperature can multiply the service lifetime of the device by 2× to 10×. This increased lifetime feeds directly back into the \$/kWh metric by growing the amortizing period and linearly dropping the cost of energy.



**Figure 3: Examples of corrosion rate vs. temperature for common structural materials.**

#### 2.4.2.3 Thermal management

LMBs require ancillary heating units to raise them to temperature from the solid state. In addition, temperature management systems are required to protect against temperature fluctuations and failure. Lowering the temperature of the device may not only bring it in range to harvest waste heat from other commercial equipment such as boilers/heaters but also reduces the capacity demands on active cooling and heating units.

Though there have been no rigorous quantitative modeling approaches to understanding the functional impact of temperature on cost in LMBs or any other high-temperature storage device (e.g. Na-S) the impact of temperature on the total cost (\$/kWh) of the cell would be directed principally to the remaining 60-70% cost contribution of cell packing materials, assembly, ancillary systems, as well as the amortizable life. Whereas intelligent selection of active materials directly linearly impacts the \$/kWh metric through raw material input prices,

decreasing temperature has the potential to simultaneously suppress costs from a number of downstream reductions.

Based on this criterion all negative electrode materials with temperatures far above 300°C are discounted. Though there are several positive electrode materials with temperatures exceeding 300°C, there is a pathway for alloying such metals to form low temperature eutectics with minimal penalty to the voltage of the system. Hence, removing elements from the positive electrode column would be premature. The negative electrode materials, on the other hand, are significantly more complicated to suppress in melting temperature through alloying as doing so both decreases itinerant species activity as well as introduces another electropositive species that may co-oxidize and deposit during cycling. Couples ruled out due to negative electrode temperature are shown below in Table 3 as light orange.

**Table 3: Symbolic representation of Table 2 in which red indicates couples ruled out due to price, orange due to temperature, and gray due to lack of thermodynamic data or phase separation.**

(T <sup>MP</sup> /°C)	Li (181)	Na (98)	K (64)	Mg (650)	Ca (842)	Ba (727)
Al (660)						
Si (1414)						
Zn (419)						
Ga (30)						
Ge (938)						
Cd (321)						
In (157)						
Sn (232)						
Sb (631)						
Hg (-39)						
Pb (327)						
Bi (271)						
Te (450)						

### 2.4.3 Scalability

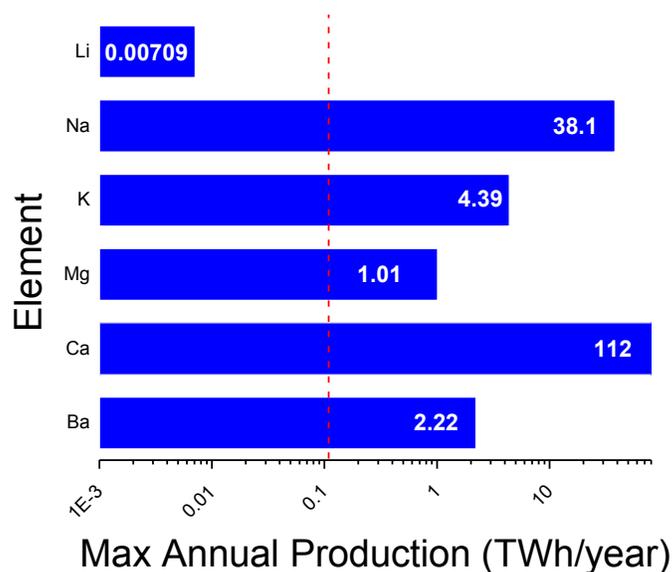
Due to the sheer scale of the grid-storage problem space, candidate solutions may potentially infringe upon both the annual production and natural abundance of resources as well as constraints stemming from the need to spend large sums of energy up-front in order to manufacture a large volume of batteries. Although one

cannot yet use the latter energy-investment analysis (ESOI) to discriminate on a metal-by-metal basis, Wadia's work<sup>15</sup> on the impact of resource constraints does provide an initial screening tool for determining which couple chemistries stand to create the greatest impact for grid storage.

By using the 2012 annual production of raw negative electrode materials<sup>27</sup>, an efficiency of 95%, and a voltage value averaged over all known candidate positive electrode materials<sup>17</sup>, one is able to develop rough estimates for how much total energy storage could be built each year if the entire production were diverted towards making LMB batteries. This upper boundary defines the absolute maximum amount of storage available for a given negative electrode chemistry deployed in a LMB battery.

**Table 4: Energy storage production estimates based on annual production of elements.**

Element	Ore Source	Element Mass (g)	Theoretical Capacity (Ah/g)	Annual Production (g/year)	Couple Voltage (vs. Sb)	Energy Storage Potential (TWh)
<b>Li</b>	LiCO <sub>3</sub>	6.941	0.208	3.70E+10	0.92	0.0071
<b>Na</b>	NaCl	22.99	0.185	2.80E+14	0.74	38.11
<b>K</b>	potash	39.09	0.167	3.40E+13	0.78	4.39
<b>Mg</b>	brine, hydroxide, carbonate	24.30	0.367	6.10E+12	0.45	1.01
<b>Ca</b>	lime	40.06	0.331	3.40E+14	0.99	111.50
<b>Ba</b>	barite	137.327	0.207	8.40E+12	1.28	2.2



**Figure 2: Energy storage production estimates shown vs. 1% of the daily US electricity consumption**

Figure 2 finds that even in the impossible scenario that all global metal production is dedicated to LMB production, not all metals meet the short-term goal of 1% of the United States' 2009 daily electricity usage (109 MWh). This amount serves as an annual production rate target that should simultaneously allow the US to pursue its RPS goals in the short term (10-15 years) without incurring significant penalties from concurrent penetration of intermittency<sup>15</sup>. Using this metric one is able to identify a clear difference between sodium- and lithium-based chemistries. There is also an opportunity to drastically expand magnesium production via seawater desalination though such ramp-up would likely need to occur during the same time period as renewable ramp-up is expected to take place.

Following this down-selection methodology one arrives at the conclusion that the most promising negative electrode chemistries to pursue, and therefore the best systems for investigating candidate electrolyte systems, are sodium-based. This result is somewhat unsurprising given sodium's low cost (\$0.06/mole), low melting temperature (97.8 °C), lithospheric abundance (1,150× more abundant than lithium), and strongly electropositive properties.

### 3 Historical odyssey

In addition to the more generalized molten salt investigations of the early 20<sup>th</sup> century, historical work specifically targeting sodium-based non-aqueous electrolytes can be

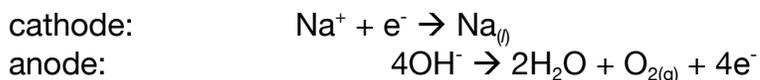
grouped into three rough categories: sodium metal electrodeposition, nuclear energy heat transfer media development, and electrochemical regenerative battery research. Each of these applications coveted different characteristics of sodium-based fused salts. It is interesting to understand why research in each of the three aforementioned areas came to a close and why activity was confined to a limited suite of sodium-based molten salt systems.

### **3.1 Molten salts in sodium electrodeposition**

Since its discovery in 1807 by Sir Humphrey Davy<sup>28</sup>, sodium has grown in importance and usefulness as chemists and engineers have found its unique physical, thermal, and electrochemical properties of utility. Though initially a curiosity, following the discovery (1825) by Hans-Christian Oersted that sodium metal could be used to reduce aluminum chloride to pure aluminum, interest in the metal rapidly grew. Initial production methods utilized a thermochemical deposition similar to the initial technique deployed by Davy. Such approaches most commonly involved the reaction of a fused sodium salt with a variety of heated reducing agents including materials like carbon<sup>29-32</sup>, calcium carbide<sup>31-34</sup>, iron carbide<sup>35</sup>, iron<sup>36</sup>, and magnesium<sup>32</sup>. The sodium salts most commonly reduced were sodium carbonate<sup>32</sup>, sodium hydroxide<sup>37</sup>, and sodium chloride<sup>38</sup>.

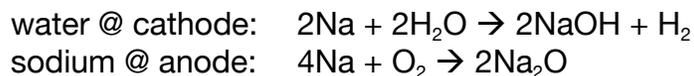
Though bulk thermochemical reductive processes like the Deville process<sup>39</sup> (1854) rapidly grew the supply of sodium to support early aluminum production and dropped the latter's price from \$1200/kg in 1852 to \$40/kg in 1859, the process's inefficiencies and impurities drove Charles Martin Hall and Paul Héroult to simultaneously develop an electrochemical method for production of aluminum. This leap in aluminum production coupled with the yield inefficiencies and product impurities implicit in thermochemical pathways reduced demand for metallic sodium and motivated researchers to devise a similarly efficient and cheap electrochemical manner of producing sodium. In 1888, the Castner process<sup>40</sup> was born.

The electrochemical Castner process involves the electrolysis of sodium hydroxide (NaOH) to form pure sodium on the cathode while oxygen and water are generated on the anode. The primary reactions are shown below:



Due to the hygroscopicity of NaOH and the solubility of metallic sodium at high temperatures, the Castner process also experiences a number of detrimental side

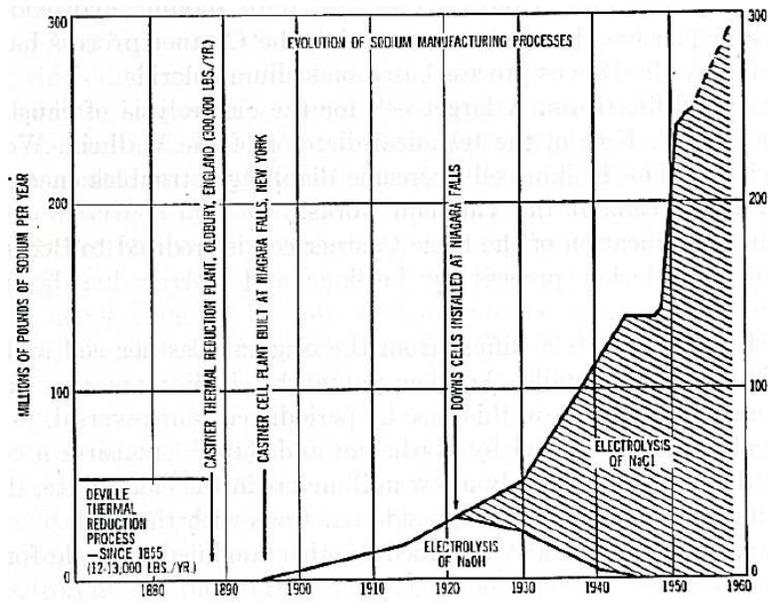
reactions that act to reduce the efficiency of the process and lower the yield. Two such parasitic reactions are shown below:



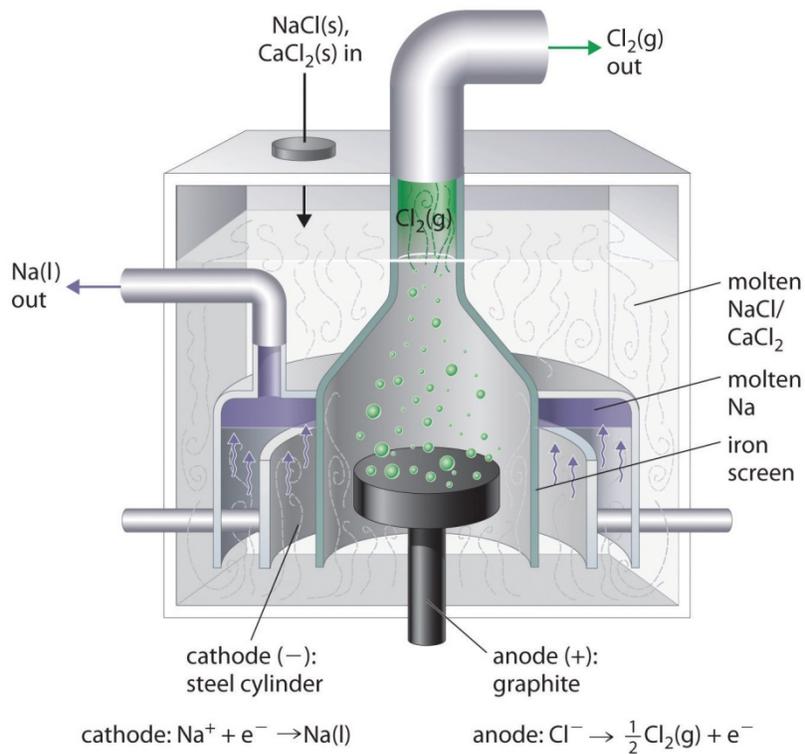
In the first reaction sodium metal produced at the cathode is lost back to its ionic state through a reaction with dissolved water. In the second reaction sodium metal that has dissolved in the melt reacts with oxygen to form a relatively insoluble sodium oxide product. These two inefficiencies resulted in an electrochemical processing route that rarely attained greater than 50% current efficiency or 18% energy efficiency. Though seemingly unique to the NaOH system, these two loss mechanisms, the solubility of sodium in its molten salt electrolytes and the challenges imposed by contaminant water, are in fact principal challenges of modern sodium-based molten salts.

From 1891 until around 1920, Castner's process was responsible for a vast majority of the sodium metal produced in the United States and Europe<sup>41</sup>. It operated at around 4.5 to 5.0 volts, a current density of 1.5-2 A cm<sup>-2</sup>, and resulted in approximately 15,000 tonnes/year (~10 kg/day per cell) for nearly 30 years. In addition to the noted inefficiencies, sodium hydroxide was still a relatively energy intensive component to produce as chloralkali Hooker diaphragm cells had not yet been invented<sup>42</sup>. As a result, the Castner process fell out of favor (Figure 6)<sup>41</sup> when compared to a newer process that utilized plentiful NaCl as cell feedstock. This new device, the Downs Cell<sup>43</sup>, is still in use today with only minor modifications and remains the industry standard for sodium production.

It would be incorrect to say that the Downs cell was the first to use NaCl as a feed electrolyte. Rather, various configurations, including the Acker cell<sup>44</sup>, the Ashcroft cell<sup>45</sup>, the McNitt cell<sup>46</sup>, the Seward Cell<sup>47</sup>, and the Ciba cell<sup>48</sup> were developed based on adaptations or permutations from earlier Castner concepts. Compared to this prior art, the Downs cell leveraged two distinct advantages in its design as well as its chemistry. First, it deploys a cylindrically symmetric carbon anode and steel cathode separated by an iron screen to prevent cross-contamination of electrolysis products (Figure 7)<sup>49</sup>.



**Figure 3: Historical Trends in Sodium Manufacturing**



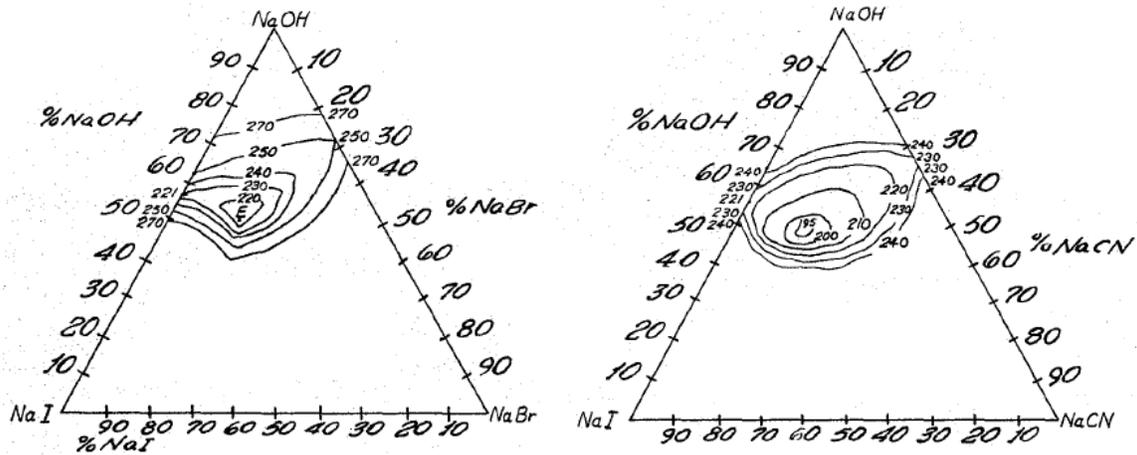
**Figure 4: Schematic representation of a Down's Cell for producing sodium metal and chlorine gas**

Secondly, it obviates the traditional challenge of high NaCl melting temperatures (MP = 801°C) by using a second CaCl<sub>2</sub> (58% by weight) component to lower the overall

operating temperature of the melt. Such a reduction in temperature not only reduces chlorine-based corrosion but also retards metallic sodium vaporization as well as sodium solubility in the electrolyte. In addition to producing higher purity sodium (>98%) the Downs cell also provides an additional benefit of generating pure chlorine gas on the anode. With these enhancements, the device operates between 590-610°C, at approximately 7 V, with current densities ranging between 0.6 to 0.9 A/cm<sup>2</sup><sup>50</sup>. The overall current efficiency of the cell is around 80-90% with the losses coming mostly from solubility of sodium metal in the melt and its passage through the iron screen to recombine with anodic Cl<sub>2</sub> product<sup>50</sup>.

Though the NaCl-CaCl<sub>2</sub> baths were used to great effect in the first half of the 20<sup>th</sup> century, as applications requiring sodium metal became more advanced, their tolerances for calcium contamination in the product as well as purchasing cost became more stringent and drove researchers to investigate new sodium-based electrolyte chemistries. In 1958, Wilson Cathcart investigated and patented<sup>51</sup> the replacement of calcium-based chlorides with strontium and barium chlorides to reduce sodium metal impurities from 1% to 25 ppm. He also experimented with further additives like sodium fluoride to increase the conductivity of the melt and improve the energy efficiency. Four years later, William Loftus, also working for du Pont, patented<sup>52</sup> work on a process utilizing barium-heavy salts that operated at 610°C with an efficiency of 89%.

In addition to the development of the Down's process, electrometallurgists occasionally resurrected older technologies with new approaches in hopes of finding a pathway towards cheaper and lower temperature sodium production. A 1939 patent by Gilbert<sup>53</sup> that improved the one-pot sodium hydroxide Castner cell by decoupling the reaction into two vessels in order to enable the usage of aqueous electrolytes rather than molten salts set the stage for two major patented works by Yoshizawa<sup>54</sup> in 1966 and Heredy<sup>55</sup> in 1969. Yoshizawa conducted electrolysis with several novel ternary systems employing NaCN, NaBr, and NaI. Such electrolytes (Fig 8<sup>54</sup>), previously unattainable in the dehydrated state, expanded the number of sodium salt permutations available for electrolytes to work with. Similarly, Heredy's work introduced NaNH<sub>2</sub> as a polyanionic chemistry with the ability to substantially reduce molten salt melting points.



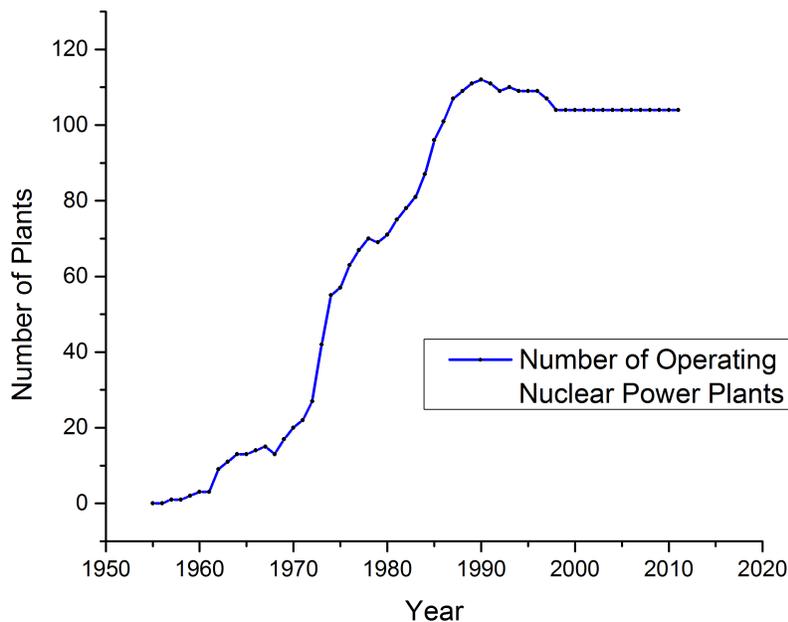
**Figure 5: Experimental phase diagrams of NaI-NaOH-NaBr and NaI-NaOH-NaCN ternary phase diagrams**

The development of cheaper and lower temperature sodium production resulted in significant growth over the next several decades. The two principal research paths that benefitted from the ample supply of sodium and advanced our understanding of sodium-based salts were the post-war nuclear power industry beginning in the 1950s and the early molten-salt based energy storage devices that were developed in the 1960s to harvest waste heat from the rapidly growing portfolio of nuclear power plants. These two research paths produced vast physical, thermal, chemical, and electrochemical knowledge that aid our understanding today.

### **3.2 Molten salts in nuclear reactor development**

#### **3.2.1 Properties**

Though it had long been recognized that sodium had many suitable properties to serve as a heat transfer medium, it wasn't until the growth and subsequent demand of the nuclear age with its molten salt and molten metal breeder reactors (Figure 9<sup>56</sup>) that production and research into sodium and sodium salts achieved international preeminence and support.



**Figure 6: Number of operable nuclear power plants in the United States since 1950**

Whereas much of the earlier sodium electrolysis research was conducted by private companies like DuPont and patented to secure intellectual property rights, the results of molten salt and sodium research of the 50s and 60s can be found more prominently in the peer-reviewed literature. Various government agencies and labs, including the Atomic Energy Commission, National Bureau of Standards, Argonne National Laboratory, and Oak Ridge National Laboratory collaborated closely with private companies such as General Electric, Atomics International, and North American Rockwell to produce a sizable body of literature covering thermophysical properties, kinetic models, and corrosion measurements. Simultaneously, and driven by cold war competition, Soviet scientists developed a sizable tome of molten salt research.

A thorough treatment of this period’s molten salt work is beyond the scope of this review and the reader is directed to a number of excellent works on general molten salt properties<sup>50,57</sup>, the structure and modeling of molten salts<sup>58,59</sup>, corrosion in molten salt systems<sup>60,61</sup>, and transport properties<sup>62</sup>. Of interest here are those works that present either physical property data for sodium-based systems or address solubility/corrosion phenomena with sodium salts. Fortunately, beginning in 1968 the U.S. National Bureau of Standards, under the Secretary of Commerce, contracted an aggregation of all known molten salt work up to that point. Much of what is presented below<sup>63</sup> (Table 6,

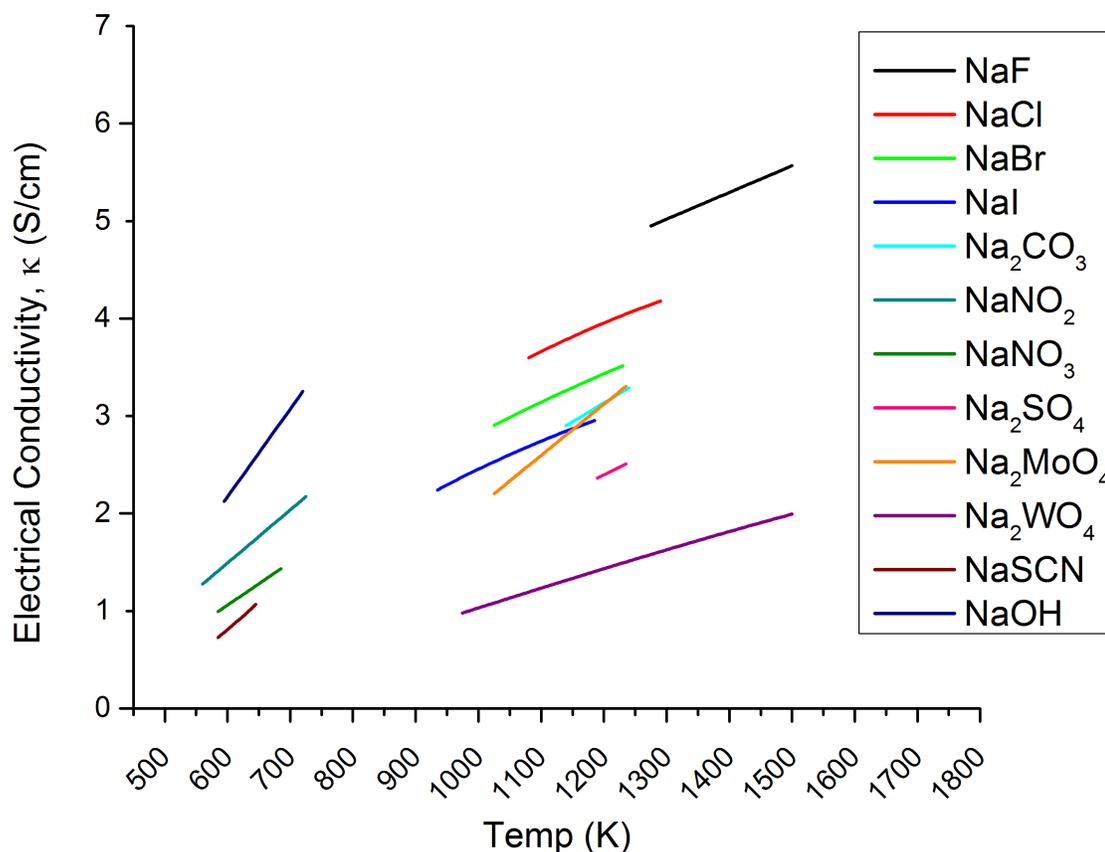
Figure 10) has been aggregated by Janz et. al in their comprehensive publications (Table 5) with only minor supplements from work scattered throughout the subsequent years.

**Table 5: Listing of all U.S. Bureau of Standards Molten Salt Studies conducted by Janz et. al.**

Volume (Part)	Year	Description
1	1968	Single Salts - conductivity, viscosity, density
2	1969	Single Salts - surface tension
3	1972	Binary Mixtures - nitrates and nitrites
4 (1)	1974	Binary Mixtures - fluorides
4 (2)	1976	Binary Mixtures - Chlorides
4 (3)	1977	Binary Mixtures - bromides and iodides
4 (4)	1979	Binary Mixtures - mixed halides
5 (1)	1980	Binary mixtures - mixed anions other than nitrates, nitrites, and halides
5 (2)	1983	Additional Systems

**Table 6: Melting Temperatures, Conductivities, and Viscosities of common sodium-based salts.**

Salt <sup>ref</sup>	T <sup>MP</sup> (K)	Conductivity, k	Density	Viscosity
NaF <sup>64,65</sup>	1253	$1.46 + 2.73 \times 10^{-3} T$	$2.65 - .54 \times 10^{-3} T$	
NaCl <sup>66,67</sup>	1073	$-2.49 + (8.04 \times 10^{-3} T - 2.22 \times 10^{-6} T^2)$	$2.13 - .54 \times 10^{-3} T$	$81.90 - .18 T + 1.42 \times 10^{-3} T^2$
NaBr <sup>68,69</sup>	1023	$9.09 e^{-2324/RT} - 2.89 + 7.58 \times 10^{-3} T$	$3.17 - .81 \times 10^{-3} T$	$64.32 - .15 T + 1.23 \times 10^{-4} T^2$
NaI <sup>69,70</sup>	935	$- 2.23 \times 10^{-3} T^2$	$3.62 - .94 \times 10^{-3} T$	$7.17 \times 10^{-2} e^{5673/RT}$
Na <sub>2</sub> CO <sub>3</sub> <sup>71,72</sup>	1127	$13.75 e^{-1327/RT}$	$2.47 - .44 \times 10^{-3} T$	$3.8 \times 10^{-5} e^{26260/RT}$
NaNO <sub>2</sub> <sup>73,74</sup>	558	$13.2 e^{-2600/RT}$	$2.22 - .74 \times 10^{-3} T$	$187.11 - .87 T + 1.41 \times 10^{-3} T^2$
NaNO <sub>3</sub> <sup>73,75,76</sup>	583	$-1.57 + 4.38 \times 10^{-3} T$	$2.32 - .71 \times 10^{-3} T$	$10.41 \times 10^{-2} e^{3886/RT}$
Na <sub>2</sub> SO <sub>4</sub> <sup>77,78</sup>	1157	$11.89 e^{-3819.9/RT}$	$2.62 - 4.83 \times 10^{-3} T$	
Na <sub>2</sub> MoO <sub>4</sub> <sup>79</sup>	960	$-3.17 + 5.24 \times 10^{-3} T$	$3.40 - .62 \times 10^{-3} T$	
Na <sub>2</sub> WO <sub>4</sub> <sup>79</sup>	971	$7.45 e^{-3931/RT}$	$4.62 - .79 \times 10^{-3} T$	
NaSCN <sup>80</sup>	583	$43 e^{-4740/RT}$	$526.39 - 2.49 T + 3.96 \times 10^{-3} T$	
NaOH <sup>81</sup>	591	$-3.23 + 9 \times 10^{-3} T$	$2.06 - .47 \times 10^{-3} T$	$164.77 - .61 T$



**Figure 7: Plot of conductivity vs. temperature for various pure molten salts**

Considering the ten basic sodium salts (excluding  $\text{Na}_2\text{MoO}_4$  and  $\text{Na}_2\text{WO}_4$  due to rarity), there are 45 possible binary combinations and 120 possible ternary combinations. Although with each combination there is a continuous range in compositional variation, there will generally be one, or a continuous range centered on one, composition that corresponds to the eutectic, which offers optimal performance for a battery electrolyte. In addition to sodium salts, sodium itinerant batteries may also be able to use lithium-based salts as lithium is sufficiently electropositive relative to sodium to avoid unintended co-deposition during charge and discharge cycles<sup>1</sup>. With this addition of ten simple salts we are left with 190 binary combinations and 1140 ternary combinations. Although sodium binary systems have been moderately studied, the ternary systems have been nearly untouched. This is in contrast to lithium binary and

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<sup>1</sup> Calcium has been shown repeatedly to co-deposit with sodium as in the Down's Cell.

ternary systems that have been exhaustively researched<sup>82</sup> due to their potential application in metal sulfide “thermal” batteries<sup>83</sup> to be discussed later.

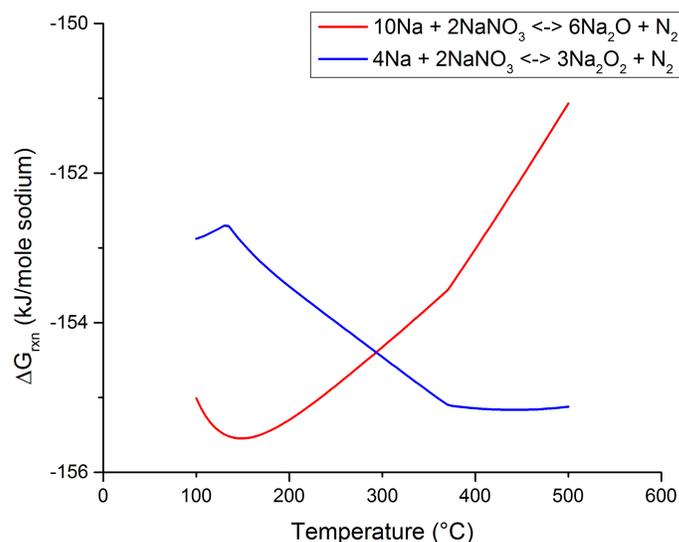
### 3.2.2 Corrosion

The use of molten salts at elevated temperatures as a heat transfer medium instigated work in sodium and sodium-salt based corrosion processes<sup>84</sup>. In the context of liquid metal batteries the following processes are worth considering when mitigating the effects of corrosion:

- I. corrosion of the metal container by the liquid molten salt via chemical reaction
- II. corrosion of the metal container by the liquid metal anode or cathode via solubility
- III. corrosion of the positive or negative electrode by the liquid molten salt via chemical reaction
- IV. corrosion of the positive or negative electrode by the liquid molten salt via solubility

Processes I and II have been variously explored in the literature as they most closely mirror those issues faced by nuclear breeder reactors and thus were the topic inquiry for many years<sup>85</sup>. Process I is generally subdivided by the anionic component and purity of the molten salt as this most often drives the chemical oxidation of the metal species. Process II is typically driven by solubility of one metal in another and can be understood via the location of the solidus line in a phase diagram. Though the selection of appropriate container materials for a given system is by no means a trivial task, the exploration and identification of such materials should be considered following an initial investigation into sodium-based chemistries. In addition, several common candidate container materials like aluminum and stainless steel have shown preliminary signs of compatibility with liquid sodium<sup>86,87</sup> and molten sodium salts<sup>88</sup>.

In contrast to corrosion of the structural components in processes I and II, processes III and IV are less studied and have more to do with the selection of active components in the battery. Process III can be subdivided into corrosion of the positive and negative electrodes, with the negative (sodium) electrode frequently being trivial as the simplest molten salts provide no potential chemical pathways for corrosion outside of those afforded by impurities such as water. Some of the salts with larger anionic species do have the tendency to react with pure or high activity alkali metals such as the sodium nitrate in contact with sodium metal (Figure 11<sup>89</sup>).

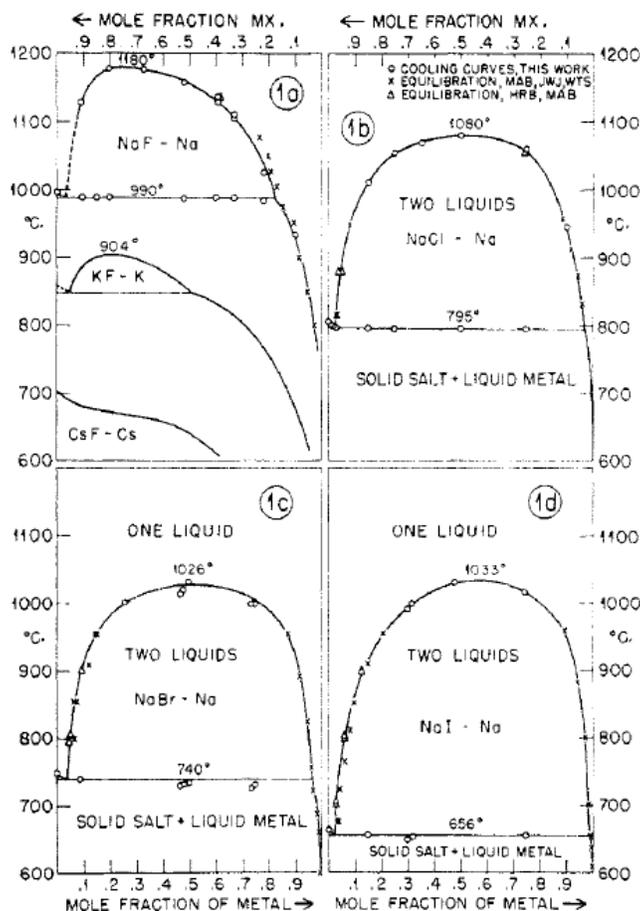


**Figure 8: Theoretical thermodynamic free energies of reaction for two potential nitrate reaction pathways vs. temperature**

As a result, developing a molten salt that is chemically stable with sodium metal requires purification and drying processes for simpler salts and thermodynamic calculations coupled with experimental data for more complex salts. On the other side of the battery, the reaction of sodium-based molten salts with the positive electrode is, with a few notable exceptions including NaCl, NaNO<sub>3</sub>, and NaOH, underexplored. The development of suitable sodium molten salts therefore impacts the range of possible cathode materials (or vice versa).

Corrosion process IV, the solubility of molten metallic species into molten salts, is of principal concern, particularly for sodium-based chemistries. Though it is uncommon for a metal to dissolve in its metallic state into a melt of differing cationic species, it has been numerous documented that sodium is highly soluble in sodium-based melts, particularly at higher temperatures in halide solutions. Bredig first observed and measured<sup>90</sup> this phenomenon through careful mixing, separation, and titration of sodium-sodium halide melts and found that the halide salt and metal species were mutually soluble in each other and demonstrated increased solubility at higher temperatures. Bredig and his associates later went on to use a thermal analysis technique<sup>91</sup>, similar to modern DSC, to detect minor inflections in heat absorption/emission resulting from phase separation at the edge of the miscibility gap. This technique was able to make measurements at higher temperatures with greater

accuracy and was applied<sup>92</sup> to sodium-based melts to determine a compositionally complete phase diagram (Fig 12<sup>92</sup>) for sodium and its various halide salts.

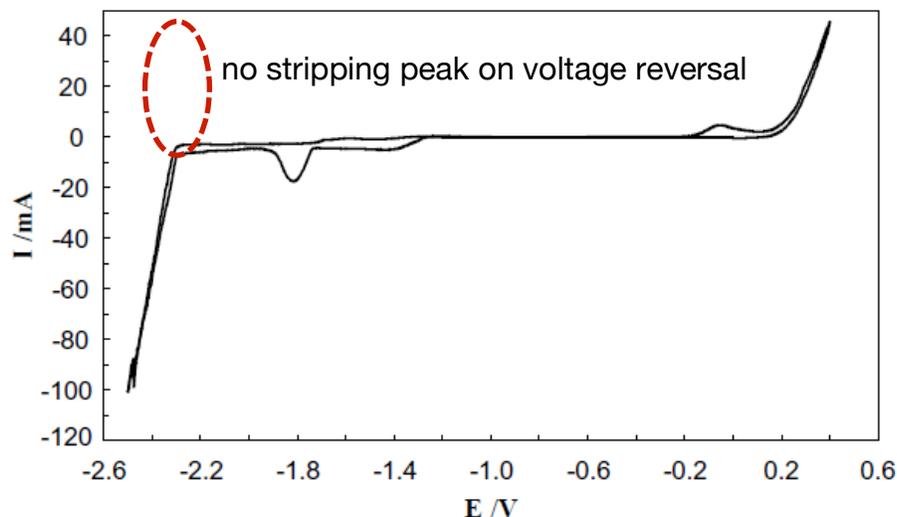


**Figure 9: Sodium metal solubility in NaF, NaCl, NaBr, and NaI, clockwise from top left, as demonstrated with liquid coexistence curves.**

Far from being a scientific curiosity, metal solubilization in its molten salt results in a variety drawbacks for electrochemical processes. Early electrochemical winning of sodium using NaCl was principally held back by the efficiency losses resulting from the sodium “fogs” that indicated product loss and parasitic back-reactions. Similarly, in LMB setups the dissolution of sodium metal not only causes capacity fade due to loss of the negative electrode but it also results in reduced round-trip efficiency as the solubilized sodium can transport to the anode and oxidize. In addition, sodium solubility also worsens fade rate as the solubilized sodium increases the electronic component of conductivity<sup>93</sup> and promotes discharge at non-faradaic voltages.

Although most work on sodium solubility in molten salts has been conducted on halide systems, literature investigating the deposition of sodium metal from non-halide melts

often shows signs of sodium solubility. In a 2003 work investigating hydroxide melts as electrolytes<sup>94</sup>, sodium deposition peaks are repeatedly shown without corresponding stripping peaks in a voltammetric scan (Fig 13<sup>94</sup>).



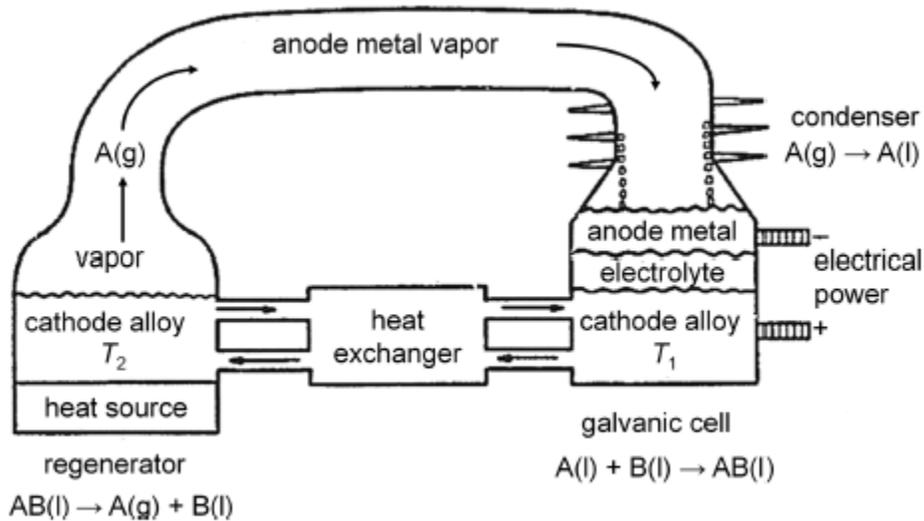
**Figure 10: Voltammetric study at 100 mV/s with a platinum electrode in molten LiOH-NaOH at 270°C**

Nevertheless, explicit studies of sodium solubility in non-halide sodium salts or binary halide melts have not yet been conducted. New investigations of alternative sodium itinerant electrolytes must not only be aware of this detrimental tendency but will also need to quantify the solubility of sodium metal via techniques similar to Bredig's and electronic conductivity contributions via polarization methods as developed by Wagner<sup>95</sup> and employed by Haarberg<sup>96,97</sup>. Current miscibility mitigation strategies<sup>98</sup> include (i) the use of mixtures of molten salts to decrease solubility, (ii) the operation of the device at lower temperatures; and (iii) further separation of the anode and cathode compartments to reduce the rate of back reaction. Determining the effect of polyanionic salt components as well as the suppression of temperatures below 300°C on solubility would be a novel contribution to the literature.

### **3.3 Molten salts in energy storage devices**

Following the rapid growth of nuclear power and concurrent advances in the synthesis and characterization of molten salts, researchers began to turn their acquired skills towards a new problem; namely, power plants and reactors generated significant quantities of waste heat and there existed opportunity to harvest this thermal energy for useful purposes. In 1958 Yeager<sup>99</sup> proposed the concept of a "thermally regenerative closed cycle battery" that would convert waste heat into chemically

stored energy by selectively separating a binary alloy, AB, into its two constituent metals by exploiting large differentials in vapor pressure between liquid A and B. Through this process it would vaporize metal A to recharge a three layer galvanic cell (Fig. 14<sup>100</sup>)



**Figure 11: Diagram of a thermally-regenerative battery.**

Though this device acts similarly to the LMB upon discharge, it is important to note that it is ultimately limited by the Carnot efficiency and that its temperature is set by the harvesting of waste heat from reactors at predetermined operating temperatures. Despite these constraints, research into thermal-type batteries exploded in the 60s and 70s and branched into a number of different directions.

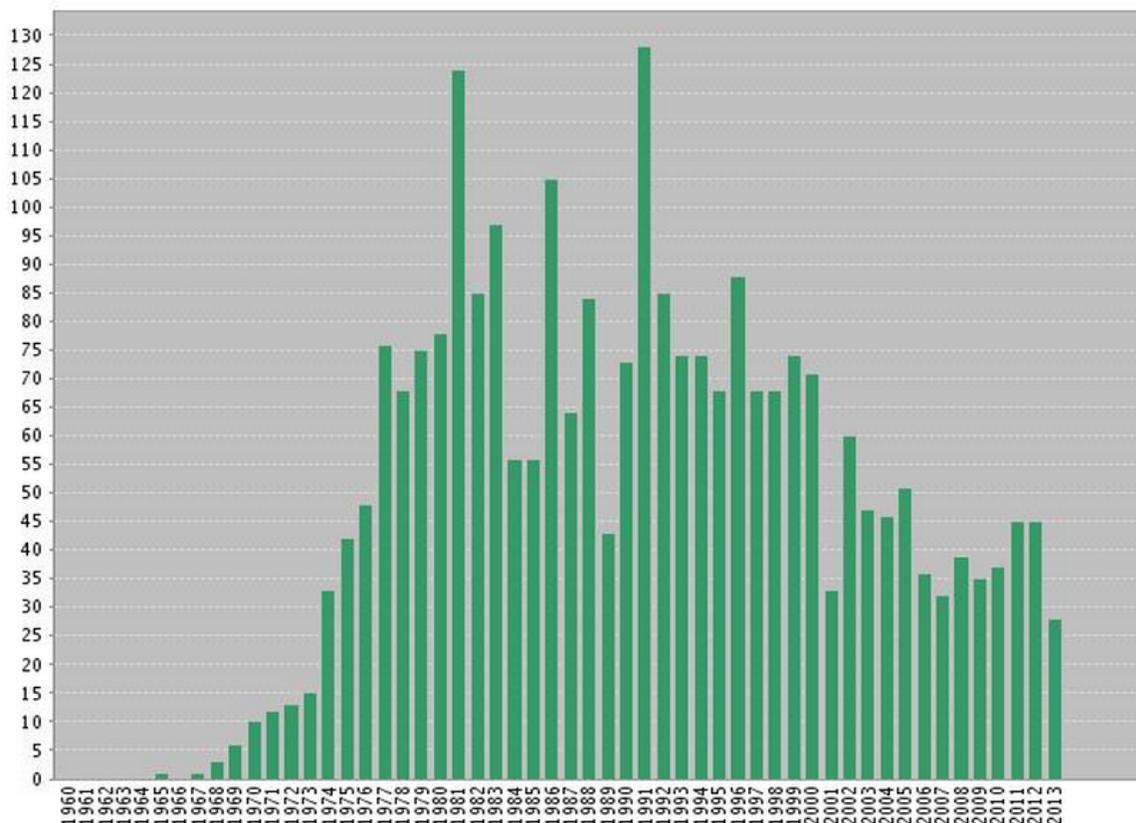
In 1960, Agruss filed for the first patent on thermally regenerative cells<sup>101</sup> and shortly thereafter began publishing work<sup>100</sup> on Na-Sn systems that operated around 700°C with NaCl-NaI electrolytes. Work on similar systems (Table 7 and 8<sup>102</sup>) grew under Atomics International, General Motors, and Argonne National Laboratory until such a point as systems that were fully electrically rechargeable were developed. These secondary bimetallic cells operated similarly to modern LMBs with minor geometric exceptions. At the time, emphasis was placed on increasing the voltage and increasing current density in order to maximize performance of the cells for vehicular applications. Over the next decade, secondary bimetallic battery work split into two major thrusts. The Li-Te<sup>103</sup> cell marked a shift in the research direction of secondary bimetallic cells towards high voltage and rate capability liquid metal cells for vehicular applications. Though tellurium showed promise, its cost drove researchers towards more abundant selenium<sup>104</sup>.

**Table 7 and 8: Experimental results from various thermal battery studies during the 1960s and 1970s for thermally regenerative as well as secondary bimetallic devices.**

		THERMALLY REGENERATIVE			
	Unit s	Na-Sn <sup>105</sup>	K-Hg <sup>105</sup>	Na-Hg <sup>106-108</sup>	Na-Pb <sup>109</sup>
Temperature	C	625-650	325	490	575
Electrolyte		NaCl-NaI	KOH-KBr-KI	Na Halides	NaF-NaCl-NaI
Open Circuit Voltage	V	.33-.43	.70-.84	.30-.80	.30-.50
Current Density	A/cm <sub>2</sub>	N/A	N/A	N/A	.11
Duration	hrs	.3	430	1200	45
		SECONDARY BIMETALLIC			
	Unit s	Na-Sn <sup>105</sup>	K-Hg <sup>105</sup>	Na-Bi <sup>109</sup>	Li-Te <sup>109,110</sup>
Temperature	C	700	325	580	480
Electrolyte		NaCl-NaI	KOH-KBr-KI	NaF-NaCl-NaI	LiF-LiCl-LiI
Open Circuit Voltage	V	.33-.43	.70-.84	.55-.75	1.7-1.8
Current Density	A/cm <sub>2</sub>	N/A	.087	.667	2
Duration	hrs	744	N/A	12240	> 300

After difficulty was encountered with selenium's solubility and conductivity, work continued up the chalcogenide family until research landed on Li-S systems<sup>111</sup>. These systems eventually evolved into the Li-Al|Fe<sub>x</sub>S systems that eventually found commercial production.

On the other end of the development spectrum, although the longevity of the Na-Bi secondary bimetallic cells was impressive, liquid cells were ill-suited for vehicular applications. This need inspired further work and development of new solid electrolytes, nearly simultaneously at Ford Motor Company ( $\beta''$ -Al<sub>2</sub>O<sub>3</sub>) and at Dow Chemical Company (glass electrolyte). Both of these advancements removed the challenge of working with molten salts and necessitated that the devices operate above 300°C. By the 1980s  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> work came to dominate the field of Na-based batteries (Fig 15<sup>112</sup>).



**Figure 12: Research papers published that focused on application of  $\beta''$ - alumina electrolytes for energy uses.**

Both of the above research thrusts did produce some relevant molten salt work. Prior to the wide-spread focus on  $\beta''$ - $\text{Al}_2\text{O}_3$ , researchers working on the Na-Hg and Na-Bi system patented a couple of promising low-temperature binary/ternary chemistries including NaF-NaI-NaCN<sup>113</sup> and NaI-NaOH-NaNH<sub>2</sub><sup>114</sup>. Only relatively recently has work refocused on the use of molten salts as electrolytes. This is due to the recognition that the closed-one-end tube format of  $\beta''$ - $\text{Al}_2\text{O}_3$  solid electrolytes has proven difficult to scale economically<sup>115,116</sup>. As a result, Na|S and ZEBRA researchers have begun exploring “intermediate-temperature” electrolytes by using ionic liquids<sup>117</sup> and low-temperature molten salts mixed with aluminum chlorides<sup>118</sup> to achieve safety improvements without performance compromise. Large companies have also moved towards lower temperature research following NGK’s NAS battery explosion in 2011<sup>119</sup>. Sumitomo, in partnership with Kyoto University, has announced the development of a proprietary sodium-itinerant molten salt with a melting temperature of 57°C. In spite of these recent advances, these devices all retain the  $\beta''$ - $\text{Al}_2\text{O}_3$  separator, which imposes severe limitations on scalability and manufacturability.

On the Li-based chalcogenide side, work has remained focused on molten-salt based systems. A variety of review papers<sup>82,83</sup> and recent investigations into iodide-based Li salts<sup>120,121</sup> can be found in the literature. Companies have also been active in developing or claiming a variety of chemistries and mixtures of molten salts. One recent patent by Panasonic<sup>122</sup> targets Li-based molten salts with melting points between 350°C and 430°C with conductivities of 2.2 S cm<sup>-1</sup> and provides 155 quaternary mixtures as claims. Though more strategic than inventive, the approach and state of Li-based molten salt research can be used to guide work in the relatively untapped sphere of sodium molten salts.

### **3.4 *The window of opportunity***

Before embarking on a research program targeting low-temperature sodium-based liquid metal batteries it is important to address two important questions whose answers could indicate a null solution set to the search.

1. If low-temperature sodium-based salts exist and were researched by sodium producers, why haven't they been deployed over the higher temperature NaCl-CaCl<sub>2</sub> salts?
2. If LMB-like batteries have been known since the 60s and sodium has been investigated as a negative electrode material, why hasn't there already been an exhaustive search of sodium-based electrolytes?

Regarding the first question, the reaction at the anode is of great interest to sodium-producers. Aside from producing valuable chlorine by-product it is also the place where undesirable reactions with larger anionic compounds could take place. Since the lowest melting temperature salts often use more than a halide-based solution, this oxidation reaction not only produces undesirable by-product but may also be highly corrosive to the device. The second line of reasoning, and likely more influential answer to the question has to do with cost. Although the energy storage market is highly constrained by cost, the costs of the components of an electrochemical battery can be amortized over many cycles and thus the sum of each input only needs to be less than the value of energy saved over the lifetime of the device. In sodium production the feedstock is the reactant and as a result is consumed on a 1-to-1 basis with the product, sodium. In this scenario, the cost of the electrolyte must come in below that of product on a per unit basis. Because of this, salts more complex than NaOH and NaCl, although researched in the patent literature, are likely not economically realistic solutions for sodium production.

On the second question, during the period of molten salt battery development in the 60s the main down-selection criteria for materials selection were vapor pressure

differentials, voltage performance, and stability at high temperatures. In all of these categories, sodium is outdone by lithium due to the latter's lower vapor pressure, lower electronegativity, and lower solubility in its salts. It wasn't until solid electrolytes like sodium itinerant glass and  $\beta''\text{-Al}_2\text{O}_3$  were developed to support research into vehicular battery technologies that sodium was reengaged as a potential battery component. Following these innovations, sodium-based battery research has been nearly entirely devoted to Na-S and ZEBRA cells that utilize solid electrolytes and/or membranes and as a result have not devoted much attention to fully molten electrolytes.

The window of opportunity that now exists is driven by the fact that the explorations of sodium electrolytes have occurred in the context of sodium production and are limited by cost and anionic species while studies of molten salt batteries have not investigated sodium molten salts due to the historic desire to produce vehicular batteries and the subsequent attractiveness of Na-S and ZEBRA systems. Future work would harness the knowledge accumulated but not put into practice from sodium production with the increasing demands for cheap grid-scale energy storage by identifying exciting candidates and systematically characterizing them for use in LMB-type batteries.

#### 4 Project description

Based on the previous analysis a credible research program would comprise identification and characterization of promising low-temperature sodium-based molten salt electrolytes for liquid metal battery applications. Historic Down's cell studies and analogous research paths in Li-based molten salt electrolytes would supply early candidates to be initially screened through a process of thermodynamic calculations, basic phase diagram modeling, and electrochemical characterization, e.g., voltammetry and impedance spectroscopy. These tests would identify candidates on the basis of their thermodynamic stability with sodium, predicted melting temperatures and liquidity range, and electrochemical stability window.

Following down-selection, a number of physical and electrochemical tests would be performed on the selected salt(s) to characterize their phase transitions, densities, conductivities, and sodium solubilities as a function of composition and temperature. These data will not only allow for the construction of experimentally confirmed binary/ternary phase diagrams but also insight into the conduction mechanisms and stability of the electrolyte(s) in question. With this baseline, electrolyte modifications such as insoluble additives and binders can be attempted.

## 5 Conclusion

It has been systematically shown that growing demand upon energy resources coupled with the renewable targets set by nations drives one to conclude that an important enabler for a sustainable energy future is the ability to store vast quantities of energy for grid back-up and intermittent enabling. Because of the low price of natural gas and coal and the high cost of most battery technologies, current electrochemical energy storage solutions have only made very modest entry into the grid-storage market. For this reason, the development of a truly low-cost grid-scaled battery systems would fundamentally evolve our grid from a wasteful generation-on-predicted-demand system to one that responds more accurately to actual usage.

Liquid metal batteries, due to their simple construction, are both low-cost and predictably scalable at the sizes required to solve storage needs on the grid. Temperature has been identified as a variable that can be adjusted to provide “cascading” depressions on final assembly cost and to bring the device below the threshold for ubiquitous deployment.

A number of lower-temperature sodium electrolytes has been shown to exist, yet very little work has been done on molten sodium electrolyte systems due to the restrictions posed by Down’s cell anodic contamination and Na-S/ZEBRA’s attention to  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> solid electrolytes. The methodology set forth herein offers a path forward to bridge the gap in knowledge that exists between sodium-based electrolyte chemistries and Li-based systems like Li-Al/Fe<sub>2</sub>S by scanning a handful of candidate systems and conducting a rigorous electrolyte study on those flagged most promising. By adopting a cost-based discovery model we believe that successful completion of the work would make a difference in the marketplace.

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