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### **A Preliminary Examination of Safer Novel Stabilization Methods for Room Temperature Sodium Sulfur Batteries**

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#### **ABSTRACT**

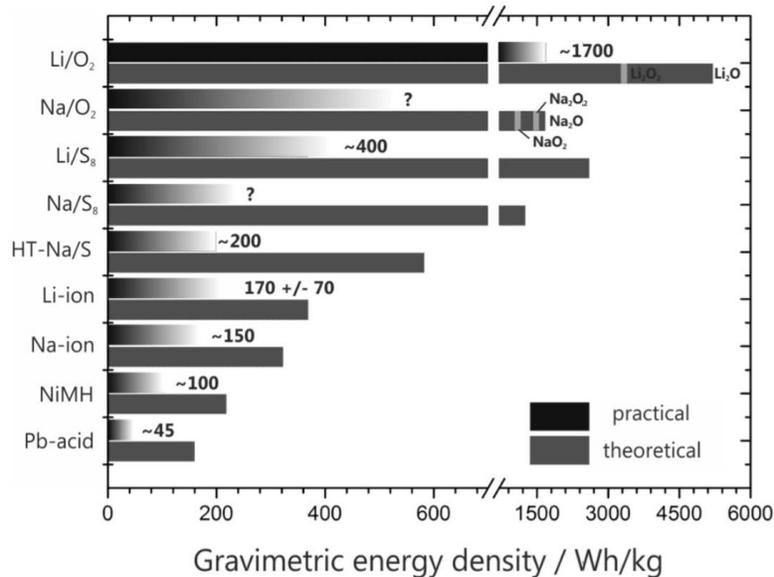
A description of sodium sulfur batteries (SSBs) and their shortcomings is presented, as well as an introduction to the emerging field of room temperature SSBs (RTSSBs). A case is made for the use of RTSSBs in the storage of energy at the grid scale. Research objectives for creating a stable, low-cost, low-toxicity RTSSB are given. Criteria for both battery testing and RTSSB testing are established and discussed.

#### **Key words:**

Sodium sulfur battery, room temperature sodium sulfur battery, grid scale energy, kinetics.

## I. INTRODUCTION

Current industrial standard battery arrays for energy storage at the grid scale typically employ lithium ion (Li ion) chemistries [1,2] to meet capacity and cycle rate requirements [3-5]. However, concerns exist about the performance and practicality of Li ion at larger scales, including their high cost per kWh [6,7], their intolerance for extreme temperatures and exposure [8], and the potential for thermal runaway when assembled into large arrays [7,9]. Alkali-sulfur batteries (Li-S, Na-S) have been proposed as stable, cost-effective, high energy density alternative [10-13] readily suited for expansion into larger systems



*Fig. 1: Gravimetric energy density comparison of Li ion and Na-S battery chemistries. [Adelhelm et al.]*

due to the use of scalable liquid electrodes [12]; however, Li-S systems suffer from many of the same resource availability and cost concerns as Li ion. As a result, sodium sulfur batteries (SSBs) have drawn attention as a potentially competitive, sustainable alternative to lithium ion systems for energy storage at the grid scale [11-14]. SSBs overcome many shortcomings faced by industry-standard lithium ion technology at larger scales, including component cost and scarcity, thermal runaway in arrays, and climatic vulnerability [12,13,15]. However, most SSBs at present are only able to operate at temperatures of approximately 300°C (molten sulfur regime) [12], and existing room temperature SSBs (RTSSBs) rely on environmentally hazardous additives to maintain the phase of liquid components [14,15]. This work seeks to explore alternative solutions for creating RTSSBs without the use of hazardous stabilizers, while maintaining substantial room temperature functionality.

## I.ii. Sodium Sulfur Batteries

Before proceeding, a brief description of sodium sulfur cells will likely be necessary. Standard contemporary sodium sulfur cells operate using a molten sulfur cathode and a

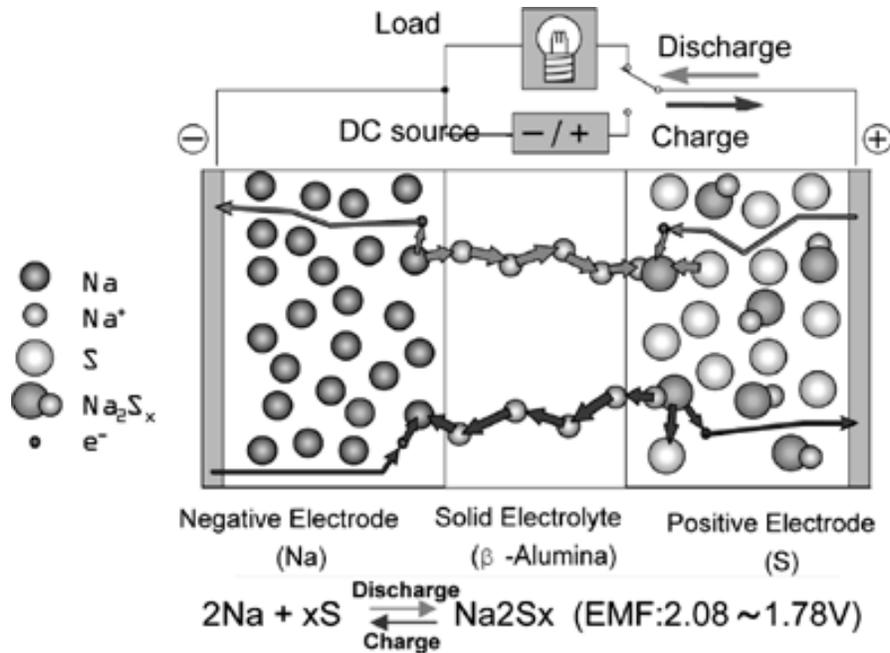


Fig. 2: A sodium sulfur battery. [Oshima et al.]

molten sodium anode, with a solid beta-alumina container acting as the electrolyte [12].

SSBs' attractive high capacity stems from the two-electron redox reaction carried out during cycling, effectively lending twice the capacity achievable by comparably dense systems, while maintaining cost-effective and abundant components [15]. Operating at a temperature that maintains liquid electrodes ensures smooth charge transfer and favorable kinetics between each electrode and the electrolyte, allowing for faster cycling [12]. The central focus of this research will be to maintain liquid electrodes for the reasons listed above, while reducing the operating temperature substantially to allow room temperature operation without the use of potent additives that may be harmful to users.

## II. METHODS

A few analysis criteria and methods to be used during testing will now be discussed. Firstly, a centrally important task at the beginning of any piece of research is to outline what experimental criteria will be tracked, so as to maintain a consistent benchmark for performance throughout. In the case of this research, a few traditional markers of battery performance will be used:

- Open circuit voltage

Open circuit voltage catalogues the voltage baseline against which we calibrate the actual battery voltage for each electrode during cycling. It is a necessary value to collect before any battery testing can begin in earnest.

- Maximum theoretical and practical voltage

Maximum theoretical voltage is a value calculated solely from the standard reduction potentials of materials, rather than any testing whatsoever. It provides a value against which practical voltage can be compared to derive the efficiency or inefficiency of a battery: the closer one is able to come to their maximum theoretical voltage, the more efficient and less kinetically hindered their test cell is. Practical voltage is simply the difference between the maximum and minimum voltages measured during cell cycling, i.e. is the experimental counterpart to theoretical voltage.

Technology	Nominal DC Voltage (V)	Reference
Li-ion	860	Vendor specifications <sup>(a)</sup>
Li-ion	1,221	Samsung (2018)
Sodium metal halide	640	Same value assumed as Sodium Sulfur
Sodium sulfur	640 (5 modules, each module 64 V or 128 V)	Kishinevsky (2005)
Zinc-hybrid cathode	768	EoS (2018a) <sup>(b)</sup>
Lead acid	756 <sup>(c)</sup>	May et al. (2018)

*Table 1: System voltages of typical Li ion and Na-S battery arrays. [Mongird et al.]*

- Maximum theoretical and practical specific capacity

Maximum theoretical specific capacity, similarly to voltage, is a value derived from calculation intended to provide a benchmark for a material's expressed specific capacity to be compared against. Specific capacity refers to the amount of energy a material is able to store per either unit mass, unit volume, or some other similar scaling metric. Maximum practical specific capacity is simply the measured capacity achieved while the battery is charged to its maximum voltage and held at that potential until capacity is seen to appreciably plateau during testing. This is an especially important metric for grid scale systems, as only materials with dense capacities per unit volume should be considered for use at large scales.

- Electrode crystallization temperature

While not a typical metric by which batteries are judged, an integral component of this work will be assuring that both electrodes of our designed RTSSB remain liquid at both standard room temperature and at any temperature of operation that could feasibly be encountered in any global climate or anticipated specialized application.

- Cycling rate

Cycling rate refers to the time taken to cycle the cell during testing and, more loosely, refers to its performance under varying cycle rates. Some cells, for example, are prone to deterioration or loss of structural integrity when cycled many times consecutively at high rates. Typical cycle duration, regardless of cell capacity, is one hour; this is also referred to cycling a cell at a rate of '1-C.' Cycling over half an hour, i.e. twice the rate of 1-C, is referred to as utilizing a rate of 2-C, and so

on. Therefore, the performance of any cell over a one-hour test cycle is a critical metric. Usually, these tests are carried out in groups of anywhere from 50 to 1,000 consecutive cycles.

- Cycle life

Cycle life refers to a cell's retained percentage of original maximum capacity after some number of cycles; that is to say, it is a measurement of durability over usage. Cycle life is typically measured after 50-100 cycles or more, so as to provide a genuine idea of a cell's capacity retention.

As well as a few important markers not directly related to battery performance:

- Material costs

Material cost simply refers to the price to either produce or acquire some component of a cell. Cost is a central factor for competing against current lithium technologies, both due to the price of lithium and lithium salts themselves and to the price of cobalt, which is frequently employed as a component or dopant in lithium ion cell cathodes. Abundant or

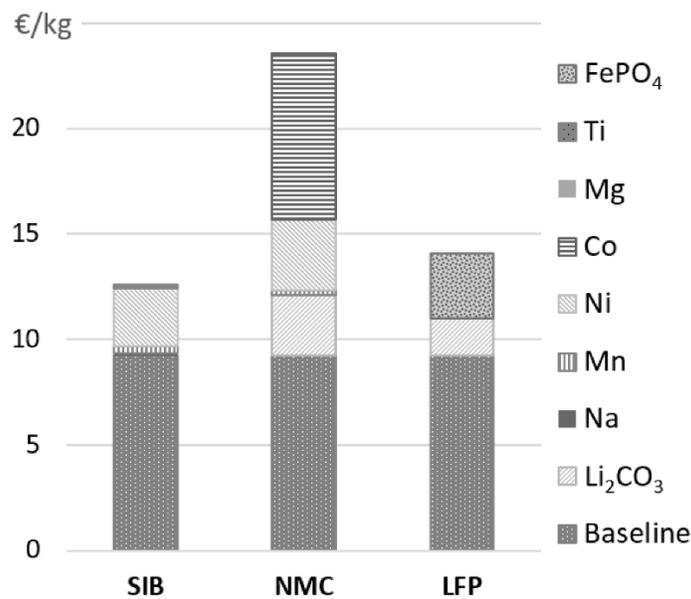


Fig. 3: Cost comparison of sodium cathode material (SIB) and lithium cathode material (NMC). [Peters et al.]

waste materials such as biomass [18,19] have been investigated as battery materials due to the critical importance of this consideration; in addition, battery material recovery techniques for end of product life have seen attention for the purposes of both cost reduction and environmental protection [20,21]. While the cost per unit of SSBs as an emerging technology spans a much larger price range than their well-established and extensively optimized LIB counterparts, the two technologies' lowest reported per-kWh prices are comparable at \$319 and \$357, respectively [16]; furthermore, a material cost comparison suggests that SSBs possess far greater potential for further cost reduction due to the relative inexpensiveness of sodium and sulfur compared with lithium and cobalt.

- Material availability

Material availability refers not only to the natural abundance of elements and minable minerals containing elements, but also to the accessibility of resources with regard paid to such factors as country of origin and its potential implications of tariffs and embargos, number and diversity of suppliers in a market, and security of supply chains. These considerations, while often overlooked, can critically impact cost and supply of vital engineering materials, and an unstably narrow industry, i.e. one supplied by a single manufacturer operating a single factory, holds the potential to completely halt an entire global supply chain in the event of a closure. For example, if a natural disaster in central Africa disrupted the majority of the supply of cobalt to battery manufacturers in Japan and America, lithium ion battery production would all but cease overnight.

Rank	Atomic Number	Element Name	Crustal Abundance (%)	Annual Production, 2016 (metric tons)
1	8	Oxygen	46.60	--
2	14	Silicon	27.72	7,200,000
3	13	Aluminum	8.13	57,600,000
4	26	Iron	5.00	1,150,000,000
5	20	Calcium	4.15	--
6	11	Sodium	2.36	255,000,000
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33	3	Lithium	0.002	35,000

*Table 2: Abundances of elements in the Earth’s crust, including lithium and sodium. [Tanaka et al.]*

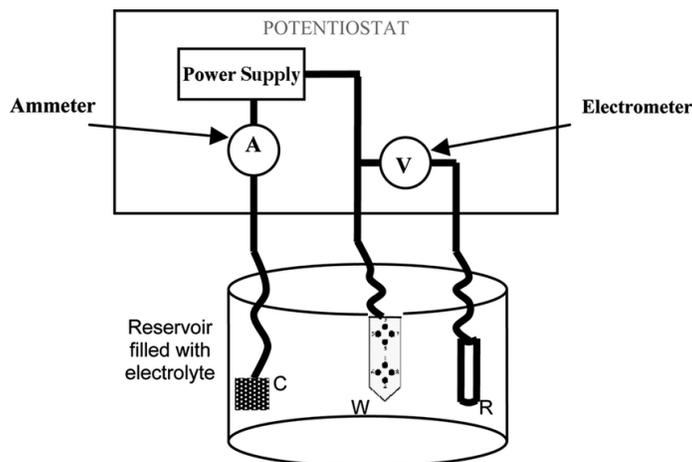
- Material safety hazards

Safety is also a critical discussion surrounding the topic of lithium ion replacement. One of the greatest concerns for lithium ion energy storage at the grid scale is the threat of thermal runaway across an entire battery array; that is to say, that conflagratory failure of one cell in an array will incite a chain reaction, leading to destruction of the entire array. At grid scale, this could mean damages in excess of \$10M (for a 20 MWh array) [16], loss of all energy stored at the time of failure, and catastrophic short- and long-term health concerns for both station workers and any surrounding population. Typically, ignition of lithium cells in such situations begins with the overheating of flammable liquid organic electrolyte employed as a standard component of these technologies. In comparison, an especially attractive aspect of sodium sulfur systems is their use

of an extremely non-volatile electrolyte: solid  $\beta$ -alumina. However, safety concerns do still exist regarding the operating temperature of sodium sulfur, which is indeed the precise issue this project seeks to remedy. Fortunately, sodium is universally known to be less reactive than lithium, and as such bears no comparative concerns about material safety *per se*. While sulfur is known for its toxicity, lithium ion cathodes prominently employ hydrated transition metal salt solutions in their synthesis that cannot in any way be praised for their material safety or low toxicity, comparatively or otherwise.

## II.ii. Testing

Testing methods for each of the performance metrics listed above will now be discussed. Open circuit voltage, maximum practical voltage, cycling rate, and cycle life can all be tested on a standard potentiostat. A potentiostat is a device used to perform and record data in most of the electrochemical experiments generally conducted during the standard performance testing of a battery. This includes two- or three-electrode tests performed



*Fig. 4: Diagrammatic illustration of a potentiostat displaying counterelectrode (C), reference electrode (R), and working electrode (W, material being tested). [Karp et al.]*

to record half-cell voltage and cycling rate on each electrode of a cell, open circuit voltage (i.e. passive or uncharged voltage) tests of an entire cell, and charge-discharge experiments, such as cyclic voltammetry, used to ascertain both cell performance at different rates and retention of maximum cell capacity (cycle life) over some number of cycles. Maximum theoretical voltage can be calculated using standard reduction potentials of electrode materials, though it should be noted that these values may themselves require calculation when experimenting with new materials or materials not widely used as electrodes. Maximum theoretical specific capacity can be calculated using various materials properties, such as the specific surface area of complex or porous materials, interpore or interlayer spacing, and density of adsorption sites. In addition to these tests, characterization of materials after each synthesis will be performed. Characterization can be conducted on a range of instruments, including X-ray diffractometers, Fourier transform infrared (FTIR) spectrometers, nuclear magnetic resonance (NMR) spectrometers, and optical and scanning electron microscopes, as well as auxiliary devices such as thermal gravimetric analyzers, etc.

### III. DATA

As no experiments have as of yet been conducted, no data exist to list or interpret. This section will therefore be dedicated to discussion of necessary tests to perform during the course of this investigation, as well as expectations for what would constitute a successful trial of each test.

- Component characterization following synthesis

Component characterization is a necessary step to perform before using any synthesized material whatsoever in further experimentation. Characterization is used to confirm material identity and provide quantitative information about material purity, as well as the presence and makeup of any impurities. Satisfactory characterization data would indicate a low quantity of impurities, as well as no 'red flag' materials: the presence of any totally unexpected elements, or appreciable quantities of materials that can be identified as products of reactions in competition with the intended synthesis, should be investigated further and not considered indicative of an acceptable synthesis.

- Electrode freezing tests

Integral to this research will be a test to identify the freezing point of our electrode materials with additives included. This can also be carried out over a series of pressures and humidities to simulate varied operating environments. Appropriate testing windows will likely range from 0-100% humidity, 0-10 atm pressure (for possible space or sub-aquatic/subterranean applications, and simply to ascertain a freezing temperature across a wide range of pressures for the sake of a complete analysis), and across a wide temperature range from at least -10-120°C or higher, so as to establish an understanding of electrode high-temperature behavior. Simply placing a beaker containing the electrode materials into the appropriate simulated environment for some length of time, likely at least one hour in duration, and noting its phase and consistency afterward will be sufficient for our purposes. Optimal freeze test results will show a liquid phase window at neutral pressures of between  $<<25^{\circ}\text{C}$  and  $>>50^{\circ}\text{C}$  to ensure safe and effective operation across the full range of reasonable environmental temperatures. However, it should be noted that facility temperatures can be controlled if energy is stored indoors; in these instances, maintenance of liquid phase at  $\sim 25^{\circ}\text{C}$  will be sufficient. A successful electrode freezing test would demonstrate an ability for both electrode materials to stably remain in the liquid phase over the target pressure, temperature, and humidity range.

- Open circuit voltage test

The open circuit voltage test is a standard preliminary step preceding any electrode cycling, i.e. charge-discharge, tests. Prior to the execution of battery cycling tests, target maximum and minimum voltages must be established, which, once reached, will trigger the reversal of current; determination of an open circuit voltage, or 'neutral' voltage, provides a value for these thresholds to be calibrated around. In the specific case of the experiment being performed in this work, an open circuit voltage test will also provide confirmation that our electrodes are conducting ions, i.e. that they have remained liquid after assembly into a cell. In an experiment heavily reliant on addition of strong, novel dopants to battery components, this fact is not assured. If no open circuit voltage can be measured, then either one or more electrodes has solidified or our electrolyte is no longer compatible with our heavily doped electrodes (the result of the last test should indicate which of the two is the case). In the event that our electrolyte is now incompatible, new options

will need to be explored. In these ways, the presence of a non-zero open circuit voltage acts as an indicator that the cell is assembled correctly and operating normally, prior to the performance of any electrochemical testing.

- Potentiostat testing

Maximum practical voltage, rate cycling, and cycle life testing can all be carried out on a potentiostat. These tests are simply used to collect all relevant information being sought about the performance of the cell; in other words, potentiostat tests are the core of battery testing. In the case of these tests, no specific criteria exist for what constitutes a successful or unsuccessful test (besides undisturbed execution of the tests); rather, data is simply collected and compared against literature and industry standard values. While voltages can vary substantially between chemistries and do not impact viability in most normal circumstances, cycle life tests should ideally indicate a maximum capacity retention in excess of 90-95% after 500 or more cycles to establish commercial viability. By contrast, a ‘successful’ test of rate cycling simply refers to any series of varied-rate cycling stress tests in which an ability to cycle without system failure or substantial performance dropoff is demonstrated.

- Maximum theoretical specific capacity

While a less essential metric than cell voltage or cycle life, specific capacity of electrodes also establishes a useful parameter when building a body of information about a new energy storage technology. In the case of liquid-electrode systems such as sodium sulfur, specific capacity of anode and cathode materials also directly indicates total capacity: the greater mobility of liquid solutions negates many kinetic hindrances generally present in porous solid electrodes (which was the motivation behind the creation of a liquid-electrolyte system to begin with, along with the increased ease of ion transfer at the electrode-electrolyte interfaces), meaning that concentration of ions in each solution is essentially the sole determiner of energy density and total capacity, assuming the total volume of each solution is known. Tests for specific capacity in liquid materials differ substantially from those used for solids, in which surface adsorption of N<sub>2</sub> gas is measured, as a simple calculation of ion donor density is the only necessary step in making an initial determination of a theoretical maximum. However, practical corroboration of this calculation is required by measurement of the charge produced by a known volume of liquid. Agreement of these two calculations constitutes a successful specific capacity test.

#### **IV. CONCLUSIONS**

As no experiment has yet been conducted, this section will be dedicated to a brief description of what satisfactory completion of this research would include.

A few essential objectives exist for this work. Firstly, the integrity of our objective must be proven. This is to say that the existence of dopants that allow a sodium sulfur battery to operate at room temperature must be proven. Fortunately, literature already exists claiming to have achieved this end [14,15,24-26], indicating that this will likely be the most straightforward of our critical objectives.

Secondly, solutions that successfully meet our criteria as novel, cost-effective, safer sodium sulfur battery electrode materials that predictably remain liquid at room temperature in most terrestrial

humidity and pressure conditions must be identified. This comprises the bulk of research and development efforts in this study, and will likely be the largest and most involved section.

Thirdly, the viability of the technology as a battery must be established. This is a critical component that, while perhaps easy to overlook for the sake of the second objective, remains the core of any electrochemical research. Demonstrating competitive performance in both battery stability and longevity at a variety of cycling rates is necessary, and unavoidable, regardless of whatever other research criteria were fulfilled satisfactorily. As such, any cell created will need to perform comparably against other RTSSBs, and ideally would also stand viably against other SSBs of any kind. Once these criteria are fulfilled, successful completion of the research will, in premise, have been achieved.

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