Economic Assessment of Candidate Materials for Key Components in a Grid-Scale Liquid Metal Battery

by

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Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degree of

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ABSTRACT

In order to satisfy the growing demand for renewable resources as a supply of electricity, much effort is being placed toward the development of battery energy storage systems that can effectively interface these new sources with today's electric grid. To be competitive with the prices dictated by the sources currently in use, namely fossil fuels, these new systems must be able to deliver energy at a cost of about \$100/kWh for the active materials. Several battery systems have been developed and that target has been slowly coming into focus. The liquid metal battery attempts to redefine the typical storage system by maintaining components in a molten state and seeks to do so using cheap, widely available materials.

One of the biggest problems facing the future of the LMB is that of resource scarcity. There are several candidate materials that can satisfy the operating needs of an LMB, but not all are available in large enough quantities to meet the new LMB demand without significant impact to the supply/demand equilibrium and, ultimately, price. A detailed model was built to investigate the use of various metals in this new technology and measure the impact expected as a result of large-scale LMB adoption. The report explains why antimony is the most likely candidate for the positive electrode due to its large, mature market and the relatively high energy output compared to other candidates. Alkali and alkaline earth materials make excellent candidates for the negative electrode and the vast quantities available will be more than enough to support the LMB market many times over.

The analysis has also revealed a substantial concern that is often overlooked in battery development: electrolyte costs. The current use of ultra-pure, anhydrous salts cannot be sustained if the LMB is to be profitable and competitive. Large savings can be anticipated from purchasing tonnage-quantity salts, but the only way to bring these costs down to reasonable levels is through the use of lower-purity materials. This study shows that a reasonable LMB can be built with an active materials cost of less than \$62/kWh and total system cost of around \$1,000/kWh for a 1 MW facility. In the most optimistic case, assuming electrolyte costs on par with those of current battery technologies, the total sytem cost can be reduced to under \$300/kWh, much cheaper than many of the most recent technologies.

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1. Introduction

On August 14, 2003 a massive blackout occurred that spread throughout the Northeast and Midwest of the United States and southeastern Canada. The effects reached 10 million people in Ontario and 45 million people in eight states and it all occurred within a few hours. A similar incident occurred in 1965. Back then, the infrastructure of the grid looked very much like the one we currently utilize, despite the fact that annual consumption of electricity has grown by 80% from about 16,000 TWh in 1965 to 29,000 TWh in 2008 (1). In fact, many wires in the New York City grid are over 50 years old (2). Conditions like this are the reasons why the United States is known as a "superpower with a third-world electricity grid." We are constantly reminded by events like the Northeast Blackout that our country's electricity grid can barely support the demand imposed upon it. And, unless the grid experiences a drastic modernization, we will encounter those events with increasing frequency and severity in the near future.

The most promising method of fixing this problem is bulk energy storage. Currently, the electricity markets operate with an instantaneous dynamic. In other words, "electricity must be produced when it is needed and used once it is produced (3)." Bulk energy storage would fundamentally change this principle and allow producers and, in some cases, consumers to store the energy for later use. This creates numerous benefits for the economy and the environment. Stored energy can be used to satisfy peak demand without putting any extra strain on the generators' resources. In turn, consumers will receive much more reliable electricity and producers will maintain efficiency. In addition, having a backup reserve in storage media will reduce or eliminate the need for facilities such as coal-powered peaker units and, thus, have favorable environmental impacts. Not only will bulk energy storage improve the environment through decreased use of hydrocarbons like coal, but it will also open the way for increased use of renewable energy sources that can reduce our dependence on fossil fuels entirely.

Several technologies currently exist to make use of renewable energy sources like the sun and wind. In fact, the technologies themselves are already pretty reliable but the same cannot be said for the energy sources. Sunlight and wind are notoriously intermittent. Unless you are in a tropical region or at high altitudes, sunlight and wind will come and go with no predictable pattern. Figure 1.1 illustrates the intermittency of solar radiation and wind speed. As the graphs show, the amount of solar radiation that reaches the ground consistently peaks during the day; however, the intensity is not predictable. Since the amount of energy able to be generated from the sun varies directly with intensity, this means that there will not be a reliably consistent source of energy. Similarly for wind generation, speeds vary dramatically throughout the day and week, which makes another unreliable energy source. Bulk storage can solve this problem by storing the energy as it becomes available and distributing it to consumers as it is needed. This will alleviate the adverse effects that arise from a mismatch between the amount of electricity demanded and the amount supplied.

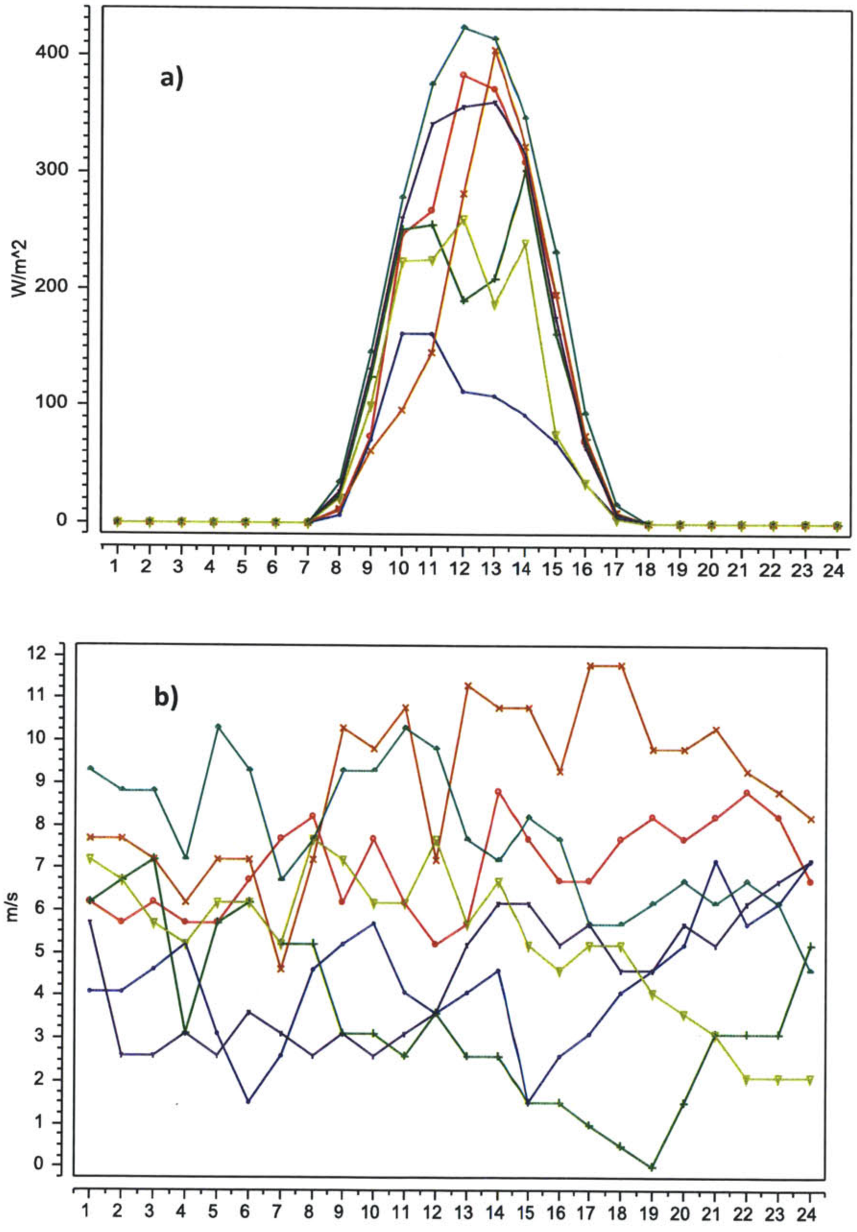


Figure 1.1: a) Solar radiation reaches a peak during the day time but its intensity varies widely. Each color represents a different day of the week.

b) Wind speed is very erratic during the course of a week. Each color represents a different day. Data retrieved from (4)

1.1 Current Technologies

Several forms of bulk energy storage currently exist and more are being developed. Some are in the form of batteries while others are much larger, complex structures. Pumped hydro electric storage (PHES) is the most prevalent technology for large-scale energy storage on power systems today (5). Pumped storage uses the potential energy between two vertically displaced bodies of water to generate electricity. During peak demand, a pumped hydro facility will release water from the top reservoir which will fall and rotate a turbine that generates electricity. Then during off-peak periods (at night for instance) the facility will use the power from the electric grid to pump water from the lower reservoir back to the top. Due to efficiency losses during the pumping of water, a pumped hydro facility is a net user of electricity; however, it generates profit by consuming cheap, off-peak electricity and selling it during peak demand where prices are higher. There have been several advances recently in the areas of turbine and pump design, which have improved efficiencies and response times for these large storage structures. In 2005 there were plants operating in many different countries totaling about 90 GW of available power, where typical plants can generate from 250-2000 MW for discharge times of four or more hours (5).

Another physically large method of storage is the compressed air energy storage system (CAES). Compressed air energy storage actually uses hydrocarbon fuel to generate electricity but the efficiency is greatly increased through the use of compressed air because, rather than recovering the energy directly using an air turbine, the compressed air would be fed into the combustion chamber of a gas turbine. Similar to pumped hydro, CAES uses off-peak electricity to compress the air which it then stores, usually in underground caverns. With CAES, the air is pre-compressed cheaply and then used when electricity is needed. This results in energy consumption on the order of 40% less than conventional gas turbine peaking units with no loss in output (6). There were only two CAES plants in the world as of 2005, including a 2600 MWh plant in Alabama, but plans have been proposed to construct more (5).

Lead-acid (LA) batteries are well-known for their use in automobiles, usually as starting-lighting-ignition (SLI) battery units. As an SLI unit, these batteries are capable of delivering a high current pulse but for a short period of time, ideal for starting a vehicle. The lead-acid technology, however, is versatile and has been adapted to grid storage in many different applications such as peak shaving, load leveling and spinning reserve. Since 1980, several installations have been built worldwide from a 400 kWh plant in Germany to a 40 MWh plant in California. Storage systems like the lead-acid battery are very important because they allow for transmission and distribution facility deferral. In other words, instead of building new transmission lines, distribution lines and transformers power companies can supplement existing networks with easily sited battery components (7).

One of the more recent developments in battery technologies came in the form of high-temperature technologies like the sodium-sulfur (NaS) battery and introduced a markedly different operating principle from traditional batteries. The NaS battery operates at temperatures where the two electrodes (sodium and sulfur) exist in a liquid state. High temperatures (300°C-350°C) and liquid electrodes allow for very fast kinetics within the NaS battery and make them ideal for stationary storage applications where large units can be safely operated. The technology was originally developed by Ford Motor Company in the 1960s for use in electric vehicles but was commercialized for storage purposes by NGK Insulators, Inc in Japan. There are still high costs involved with building the battery for large-scale applications but there are a few large installations around the world (8). The largest NaS battery in the Unites States is a 32 MWh unit in Texas (9).

With the importance and excitement of the NaS battery a lot of research went into making the technology even better. One of the results is the sodium-nickel chloride battery, or ZEBRA battery. The ZEBRA battery is very closely related to the NaS battery. In fact, ZEBRA cells use liquid sodium as the negative electrode as well as a beta-alumina solid electrolyte for separation. Where the ZEBRA battery differs is in the positive electrode, which is made of nickel chloride, and also with the existence of a second, liquid electrolyte (sodium chloroaluminate), which gives it the classification of a molten salt battery. These batteries were initially developed with uses in electric vehicles as the main focus but there have been recent investigations into more stationary applications, like uninterrupted power supply services. The extremely long life cycle of these batteries (3,500 cycles at 100% DOD) can potentially offset the much higher costs of production, especially in hot climates that require frequent cycling (10).

1.2 Viability Metrics

We can see that several different technologies exist to satisfy the need for bulk energy storage ranging from the classical use of mechanics to the use of novel molten electrode batteries. Of course, not all methods are interchangeable and so it is important to examine the metrics by which a particular technology is deemed appropriate for a given application. One of the first limitations to consider, especially with a group of technologies like those listed above is the **geographic footprint**. Basically, the units should be in relatively close proximity to the consumer(s) they are serving. The transmission of electricity is, quite literally, lightning fast so being directly adjacent to the consumer is not necessary; however, transmission losses are inevitable and become more significant the longer it has to travel. Since many of these storage units/facilities will be used for purposes like power quality and peak shaving, it is important to minimize as many disruptive variables as possible, distance being one of them. For example, a town in the desert can benefit from energy storage devices to help satisfy demand during the hottest part of the day. It is unlikely that a pumped hydro storage facility will be a valid solution, simply because it cannot be built since there is no water nearby. Similarly, there could be small town near a water source, surrounded by beautiful scenery. Neither a pumped hydro nor CAES facility is likely to be built because they both require a lot of land and a significant amount of environmental development, which is likely to be met with strong opposition. In both of these scenarios, smaller, more portable battery facilities could provide a more acceptable solution.

Another metric to consider when developing storage facilities is the **life cycle** of the technology being implemented, which can be expressed as number of cycles before replacement or as the number of calendar years before replacement. For a given technology, a longer life span is obviously preferred because it reduces the overall cost of operation. Intuition says that the PHES and CAES facilities would offer the longest lifetime, which is correct. Their usable lives are found to be over 10,000 cycles or more than 25 years for PHES (longer for the actual dam) and over 5,000 cycles or more than 10 years for CAES (11). This is not surprising given the sheer magnitude of the projects and since any significant maintenance would be both time consuming and costly; they are built to last. Batteries, on the other hand, are much more manageable and require much less capital expenditure as far as construction goes. As a result, shorter life spans are acceptable, but there have been many exciting technologies developed such that some batteries have exceedingly long lives. The lead-acid battery has one of the shortest life spans (~1,000 cycles and 7-15 years) but also requires the least amount of investment costs. Due to their ease of maintenance, often involving little more than venting and refilling with water, LA batteries are still a competitive choice but are expected to lose market share as innovations work to lower the costs of better performing batteries (11). The NaS battery is particularly robust unit due to the raw materials it uses and the operating parameters under which it can perform. Drastic cost reductions have been realized as more work goes into scaling up the technology and their cycle life can range from 2,500-4,500 cycles over a span of 15 years. Although ZEBRA batteries have not yet been implemented into a large-scale storage project, units developed for the auto industry show some promising characteristics. Sudworth shows that a 32 Ah cell can complete over 3,000 full cycles with only slight losses in capacity (12) and Dustmann has shown stable capacity performance over a span of 11 years with over 3,500 cycles (10). It is obvious from these statistics that when developing a new battery technology, cycle and calendar lives are very important metrics to optimize.

As usual, whenever considering potential markets for any products the costs associated with operating it are of utmost importance. A useful metric to look at when examining energy storage technologies is the cost of energy storage in dollars per kilowatt-hour (**$/kWh**). In the area of energy storage, $/kWh can be a much better gauge of costs than the often cited $/kW. Batteries can have a very high power rating but only be able to deliver it for a very short amount of time. Basing the cost off of the rated power introduces a lot of ambiguity when trying to compare different technologies; therefore, normalizing by the total amount of energy capable of being stored makes cost advantages much more transparent. Energy costs can vary widely across different storage technologies. Due to their very large size, PHES and CAES both have extremely low unit storage costs at $10/kWh and $1/kWh, respectively (13). The vast amounts of generation source for both facilities means they can provide power for a very long time, thus driving down the unit cost. Of course, this would be slightly offset by the enormous costs associated with building the facilities. Such low costs are likely never to be reached by a battery technology, which puts PHES and CAES in a different category as far as selecting a technology is concerned. For example, when we look at the cost of a lead-acid battery at around $150/kWh (14) it appears to be expensive relative to CAES, but these two will never really be in competition for the same application. Lead-acid batteries are actually among the cheapest battery chemistries. According to the Tokyo Electric Power Company, mass production of NaS batteries should drive the storage costs down to around $250/kWh (15). Although nearly twice the cost of the LA battery, the long lifetime of the NaS battery works to reduce the total cost. It is difficult to get a storage cost for the ZEBRA batteries because none have been deployed for large-scale, grid energy storage. In 1990, the California Air Resources Board set a goal for batteries in electric vehicles to cost less than $150/kWh and, at the time, first production of the batteries came out around $300/kWh (16). While expensive now, both NaS and ZEBRA batteries are expected to benefit from continued innovation and economies of scale such that their prices can decline toward a $100-$150/kWh target.

Costs can also vary widely among different battery chemistries. In general, the prices cited for batteries are relative to the active materials involved in the generation of electricity. Basing costs off of the active materials makes it easier to compare the chemistries, but can also leave out very important information with regards to application. Some battery chemistries and operating conditions are very harsh and will require specialized materials to construct the physical housing. These can add significantly to the total cost and can even turn a promising technology into an economically infeasible one. For the purposes of this work, however, the active materials cost will be studied in depth and a look at the secondary costs will be provided later.

One of the biggest drivers that can determine the cost of storage is the **availability** of the materials being used. If the materials necessary to make the battery chemistry work are difficult to find, the costs will inevitably be higher. Two qualities by which a metal can be judged affordable are its abundance and recyclability. Naturally, an abundant metal will be easily accessible for producers and will ultimately become commoditized as several competitors enter the supply market, which will drive the price down for the battery manufacturers. Recyclability, in this context, refers mostly to the ease with which the metal can be recovered from a spent battery. A metal with high recyclability will have favorable pricing over others that have low rates because recycling creates a whole new source of supply. All of the batteries discussed so far utilize materials that satisfy these conditions. The LA battery uses lead and lead oxide, which constitute one of the largest commodity markets in the world, so there is no shortage of lead. Furthermore, lead can be easily recovered from old batteries, which also means it makes up one of the largest markets for secondary metals. In fact, the lead-acid battery is famous for having over 96% recycling rate, meaning that 96% of the batteries retired each year are recycled (17). According to USGS, most of the lead recovered from this 96% are used to make new batteries. This illustrates perfectly why the LA battery is one of the cheapest alternatives for battery energy storage.

Technology	Cycles	Useful Life (years)	Cost ($/kWh)	Footprint	Reference
PHES	10,000	25+	10	Very large	(13)
CAES	5,000	10+	1	Very large	(13)
LA	1,000	5-7	150	Custom	(14)
NaS	3,000	15	250	Custom	(15)
ZEBRA	3,000+	10+	300	Custom	(16)

Table 1.1: Summary of storage technologies and the storage cost (of active materials)

Obviously, it is important to be judicious in the choice of materials as any new technology is being developed. The problem becomes even more salient when developing new batteries because not all cheap materials will possess the desired electrochemical properties. If the materials do not produce a reasonable open circuit potential, it will not matter how cheaply they can be obtained. Further difficulties arise when having to select an appropriate, cheap electrolyte because not everything will conduct the right ions and not everything can withstand the operating conditions being targeted. Many salt electrolytes used in batteries today have voltage limits, beyond which they begin to break down, rendering the battery useless. The materials selection process is definitely the most complicated optimization problem when designing a new battery.

1.3 The Liquid Metal Battery

1.3.1 Conceptualization

Inspired by an ordinary aluminum smelter, the liquid metal battery (LMB) was conceptualized by reversing the process and turning a smelter from a huge current sink into a current generator. A typical smelter produces aluminum via the Hall-Heroult process and is shown in Figure 1.2 below. A single Hall-Heroult cell consists of a pure carbon anode opposite a metal cathode that is usually carbon coated. In between the electrodes is cryolite (Na_3AlF_6) which dissolves alumina (Al_2O_3) and serves as the electrolyte for the process. A potential of 3-5 volts is then applied between the plates with a current on the order of 100,000 amperes or more. Operating at a temperature well above 1,000 °F, pure liquid aluminum is deposited at the cathode and can be siphoned off for further refining. This is essentially a unidirectional process and the reason can be seen from the overall reaction:

$2Al_2O_3 + 3C \rightarrow 4Al_{(s)} + 3CO_2$

This reaction releases carbon dioxide gas which cannot be recovered and, thus, the process cannot be run in reverse. The inspiration for the LMB came from the idea that if the smelter utilizes so much electricity to produce aluminum, would it be possible to run the reaction in reverse to generate large amounts of electricity? Of course the answer is “no” due to the release of carbon dioxide, but there may be a different chemistry that can prove more effective.

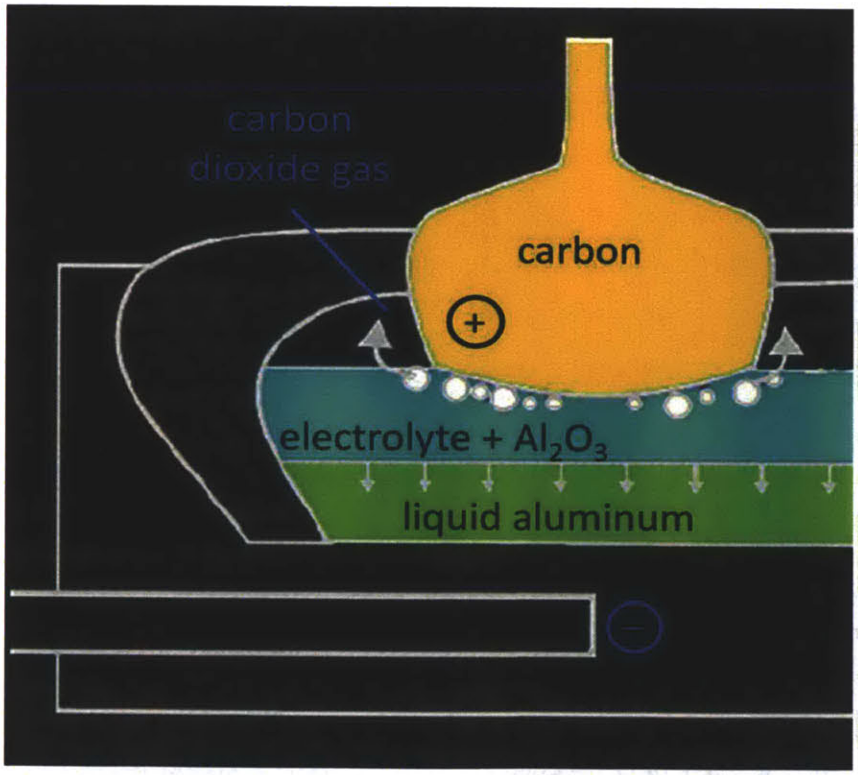


Figure 1.2: Illustration of the aluminum smelting process

The idea was conceived to develop a technology that would eliminate gas as a byproduct by using pure metallic electrodes with a molten salt in between. Staying true to its inspiration, the liquid metal battery looks very similar to an aluminum smelting pot (see Figure 1.3). The major difference is that the battery is operated at a high enough temperature so that all materials inside are kept in a liquid state, including the electrodes. The molten salt electrolyte is chosen such that it has relatively low electronic conductivity but a very high ionic conductivity of A^+. Upon discharge, ions from the negative electrode diffuse through the molten salt layer and form a liquid-phase alloy with the positive electrode. The only thing released would be electrons and reversing the reaction upon charging would bring the battery almost exactly to its original state. With no solid components, there is minimal concern of dendritic growths that often plague battery life spans, even with 100% depth of discharge (DOD). With careful selection of the materials, a battery can be made with a reasonable voltage and very cheap metals. By taking advantage of differences in densities, the battery would be self-assembling and proper insulation would make it self-heating.

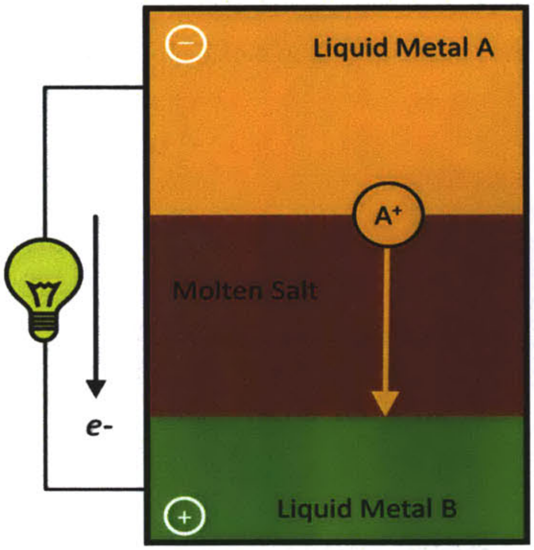


Figure 1.3: Illustration of the LMB process.

1.3.2 Manufacturing Targets

One of the most promising applications for an LMB is in the area of renewable energy and its integration into our nation's electric grid. As discussed previously, the intermittency of renewable energy makes it impossible to integrate effectively without some mode of energy storage. Extracting energy from renewable sources is already an expensive task, so the technology used to store it should be as cheap as possible to make renewables a competitive option. Therefore, special care must be taken to develop a cheap LMB. In this case "cheap" means a cost of around \$100/kWh for the active materials (electrodes).

Several couples exist that can yield a reasonable battery and many may even meet the \$100/kWh target, but for a new technology like the LMB, there are other dynamics to consider. Specifically, it does no good to develop a technology that works perfectly but cannot be scaled up. The eventual storage target for the LMB is 20% of renewable generation. By 2025, solar and wind-generated electricity is estimated to supply over 200 BkWh of America's energy needs (18), which means the LMB will store 40 BkWh. With the average LMB facility size expected to be around 1 MWh, a lot of LMBs will be manufactured and a lot of metal will need to be consumed. When such large quantities of a material are needed there is the possibility of disrupting the supply/demand balance that drives all aspects of our economy. This is especially true for metals that currently have small demand volumes, some of which are LMB candidate materials. As a result, a metal that starts out cheap enough to use in the LMB can become too costly if the new demand just cannot be supported by current supply.

This analysis attempts to investigate these dynamics as they apply to some of the more promising candidate materials. A detailed model was built to estimate the current costs associated with building different permutations of the LMB as well as predicting the economic impact that a large-scale operation would have on the metals chosen. Rather than attempting to predict an exact price for a metal under the influence of LMB, 20 years into the future, this study uses a combination of quantitative methods and qualitative interpretations to determine the feasibility of pursuing a candidate material.

1.4 Methodolgy

Time-series regression provides the basis for analyses in this study and is widely used in the field of the economics of commodities. This technique can be used to create a very accurate price model for a metal that includes several different layers of dynamics, but even the most advanced models cannot be relied upon to accurately predict the future price of a commodity. Because this study is interested in making an estimate of future manufacturing costs for the LMB, a simple regression was performed more to establish a direction of price movement and a general price level than to predict what an LMB producer will be paying for a metal 20 years into the future.

The first step in performing a regression is to create a list of all possible variables that could be used to explain the movement in the dependent variable (price, in this case). A regression is run with this initial list and the results are examined to determine which variables are statistically significant. This study adopted a 95% confidence for all regressions, meaning variables are only statistically significant if the p-value is less than 0.05. The insignificant variables were then removed and a new regression performed. This was repeated until all remaining variables were statistically significant. One interesting aspect of time-series regression is that a correlation can be found between all sorts of variables, even if they are not related. Therefore, it is important to include variables that can actually be used to form some kind of story about the dependent value.

In the end, an attempt was made to establish models using similar variables that could easily be implemented into a detailed cost model. The cost model was built with the goal of creating a program that would allow the user to choose aspects of a battery and obtain a materials cost breakdown as well as view the impact that the battery would have on the electrodes chosen. Having a standardized model is another reason that a simple regression model was sufficient.

2. LMB Electrodes

Two characteristics for ideal electrodes have been discussed already: low cost and dissimilar densities. A third quality, low melting temperature, is implied since the electrodes must be liquid at reasonable operating temperatures. Unfortunately, satisfying these three qualities does not make a functioning battery. This introduces another criterion for the selection of materials, which is the degree of alloying between the mobile species and the positive electrode. The selection of proper metals is highly dependent on the phase diagram that exists between two candidate materials. In general, a large two-phase region indicates a larger, theoretical capacity for that couple and the presence of an intermetallic marks the limit for the battery's depth of discharge. For a given temperature, once the intermetallic phase is reached, the electrode will become a solid and no more charge can be stored. Figure 2.1 shows an example of a phase diagram for two candidate materials bismuth (positive electrode) and calcium (negative electrode).

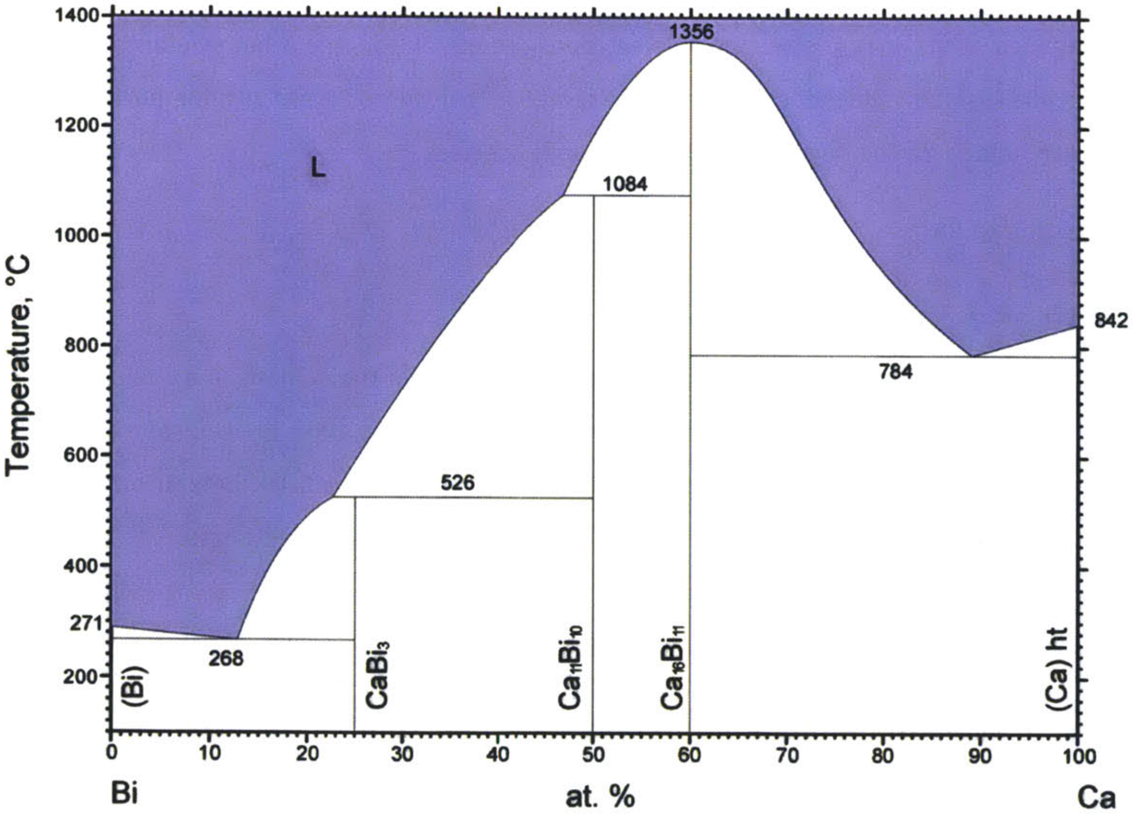


Figure 2.1: Binary phase diagram for calcium and bismuth **(19)**

At 60% calcium in bismuth there is a prominent intermetallic phase that is stable up to 1,356 °C and if we ignore the actual metals, that large peak could shift anywhere on the graph for some arbitrary couple. As the peak shifts left and right, at a given temperature below the intermetallic, a battery with these metals will lose and gain capacity since the total amount of electrons transferred will change as well. Therefore, when choosing a couple, the LMB manufacturer will not want the large peak to be too close to the positive electrode metal because that will greatly limit the battery's capacity. The calcium-bismuth diagram also exhibits a favorable feature to the left of the peak where there is a rather large liquid regime, even for fairly low temperatures, which would give the LMB more freedom in the optimization of operating parameters. A look at the binary phase diagram for any potential couple is the first step in designing an LMB cell.

As it turns out, the metals that satisfy these criteria as a positive electrode are the semimetals that occur near the steps of the periodic table between the metals and nonmetals. Based on preliminary findings, bismuth and antimony provide the most promising options. The elements in this region happen to be fairly electronegative, which means selecting an electropositive metal from the other side of the periodic table could result in a decent cell voltage. That means that the alkali and alkaline-earth metals are very good candidates for the negative electrode (mobile species).

2.1 Bismuth as a Positive Electrode

Several characteristics must be considered when selecting a material for the cathode in a liquid metal battery and a balance must ultimately be reached between them. Besides price, of utmost importance is that the metal have a high density relative to the other components and that the metal have a sufficiently lo w melting point. Although higher temperatures can lead to enhanced battery performance due to faster kinetics, limits must be set if the technology is to provide storage with reasonable operating parameters. One metal that easily satisfies these two qualities with a molecular weight of 209 g/mol and melting point just slightly higher than 270 °C is bismuth. In addition, when paired with several different cations, a bismuth cathode can produce an average open circuit voltage of around 0.6-0.7 V (20). Together, these numbers seem to make bismuth an ideal candidate for the liquid metal battery. Ultimately, of course, there is one remaining variable that can make or break a material that is otherwise perfect and that is price. For the month of September (2010), the average price for bismuth according to metalprices.com was about $20/kg. Preliminary analysis of the battery chemistry has shown that this price level is too high, leading to an energy cost which, at over $280/kWh, is more than twice our target of $100/kWh for active materials.

Based on the direct cost analysis, it makes sense to examine alternative cathode materials; however, a more comprehensive study is not without merit. A quick look at the historical price of bismuth reveals an interesting trend (Figure 2.2). Besides having a couple of periods of drastic price appreciation, after the most recent crash in the late 1970's the price of bismuth seems to have found a floor at around $10/kg. In fact, when looking at the price action over the past two decades, it appears that the $20/kg price is actually on the high side and could soon reach a more attractive level. The fact that this question may be raised indicates that a more extensive model of bismuth price is warranted. Specifically, great insight can be gained from examining the effects of supply and demand on the metal.

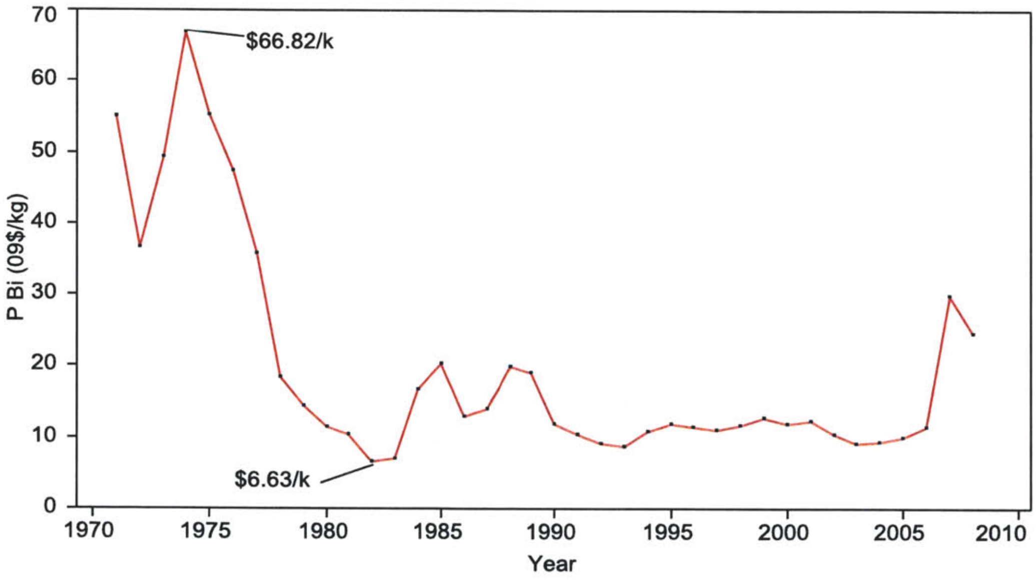


Figure 2.2: Historical price of bismuth (in constant, 2009 dollars) **(21)**

The liquid metal battery technology, ideally, will have a huge impact on the demand for the metals being used. A large increase in demand will create a shortage of supply, and economic forces will consequently drive the price higher. From here, price action will proceed along one of two paths. In the first path, a new equilibrium between supply and demand will be reached at the higher price and the technology will need to be reevaluated for profitability. In traditional economics, this opens the door for newer and cheaper substitutes that can ultimately drive the price back to more appealing levels. A different material can certainly be evaluated in the case of the LMB, but there is no guarantee that the optimized operating conditions will be regained. In the mining industry, another dynamic exists that can lead prices down a second path. Once prices rise to a certain level, more competition will enter the market looking to capitalize on the rich premiums. As time goes on, these new competitors may discover more efficient modes of extraction that can then lead to cheaper prices. Although prices may fall beneath their original threshold, the new entrants can actually remain if they were able to successfully implement the new efficiencies that did not exist upon market entry.

The question of which of these two paths the metal will take is one that a more in-depth analysis aims to answer. In particular, a time-series regression analysis can be conducted to determine certain variables that effectively model the price of bismuth going forward and how it will react to a disruptive technology, such as the liquid metal battery.

2.1.1 Bismuth Regression Analysis

As mentioned, a list of possible explanatory variables was first constructed. A clear choice is bismuth production which, in this analysis, refers to the amount of primary bismuth concentrate that is removed from the world's mines. Basic economics says that price and supply are tightly correlated. To ensure completeness, it is important to understand a little about the production of bismuth.

According to USGS, bismuth is primarily obtained as a byproduct of lead ore processing, except in China where it is also mined with tungsten. This implies that production numbers for lead and tungsten should also be considered. One might expect the supply of bismuth to increase when the production of lead and tungsten increases. Along the same lines, important information could be gleaned from including variables for lead and tungsten prices. Theoretically, if lead prices were to rise, miners would have incentive to produce more, which would lead to increased production of bismuth. Will bismuth prices rise as well, or will they fall due to a flood of the market?

Furthermore, it is known that bismuth is a reliable, non-toxic substitute for lead in various applications. Since lead is an industrial metal, its primary production is strongly correlated to the GDP of developing countries. For example (Figure 2.3) shows a plot of lead production over time along with the real GDP (2009 U.S. dollars) of the U.S. and China. The graph shows that primary lead production and U.S. GDP are inversely correlated and there is little to no correlation with that of China prior to 1993. However, when China's economy began its rapid expansion in the mid 1990's (double digit growth in 1994), lead production seemed to turn around and mimic the movement in China's GDP. This suggests that including variables for GDP might be useful. The reason to only include the GDP of the United States and China is that, together, they account for over 60% of the world's supply of lead. Australia is a major player as well but it tracks so closely with the United States in terms of production that, for simplicity, we will just look at the U.S.

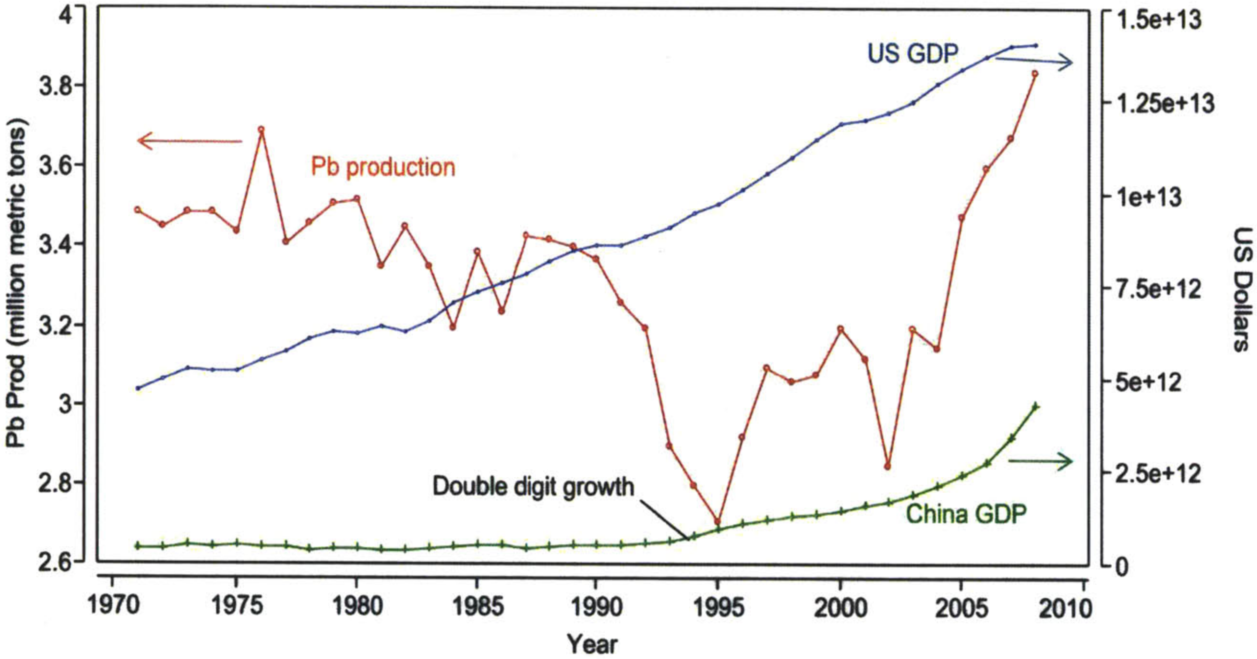
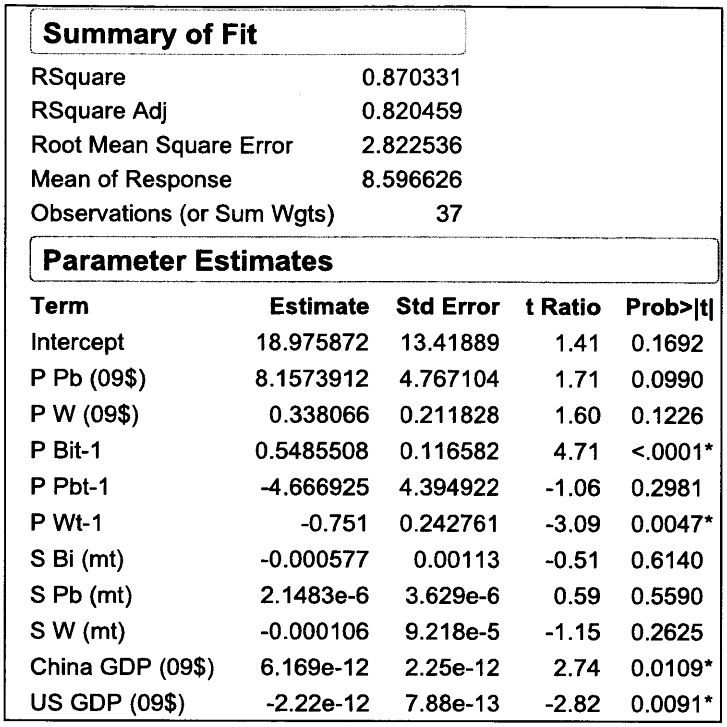


Figure 2.3: Lead production versus GDP of China and U.S. **(22)**

A few more variables can be included: the prices of tungsten and lead, and the "lag prices" of bismuth, tungsten and lead. Including lag price is an effective way to determine the magnitude of the effect that a variable's history has on its current value. The lag prices of tungsten and lead are included because they are so important to bismuth supply. For simplicity during analysis, the prices will only be lagged by one period (one year).

We now have a bank consisting of 10 possible independent variables for the regression: lag prices for the three metals (P_{Bit-1}, P_{Pbt-1}, P_{Wt-1}), prices for lead and tungsten (P_{Pb}, P_W), production numbers in metric tons for the three metals (S_{Bi}, S_{Pb}, S_W) and the real GDP numbers for China and the U.S. (GDP_{China}, GDP_{US}). Using this list, we can run a regression to get an idea of how effective these variables are in explaining the fluctuations in the price of Bismuth. Figure 2.4 shows the results of this first regression.



Summary of Fit

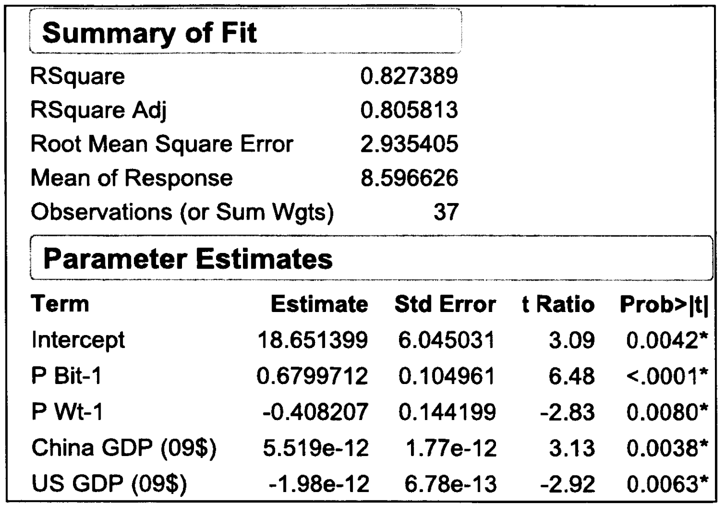
RSquare	0.870331
RSquare Adj	0.820459
Root Mean Square Error	2.822536
Mean of Response	8.596626
Observations (or Sum Wgts)	37

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	18.975872	13.41889	1.41	0.1692
P Pb (09$)	8.1573912	4.767104	1.71	0.0990
P W (09$)	0.338066	0.211828	1.60	0.1226
P Bit-1	0.5485508	0.116582	4.71	<.0001*
P Pbt-1	-4.666925	4.394922	-1.06	0.2981
P Wt-1	-0.751	0.242761	-3.09	0.0047*
S Bi (mt)	-0.000577	0.00113	-0.51	0.6140
S Pb (mt)	2.1483e-6	3.629e-6	0.59	0.5590
S W (mt)	-0.000106	9.218e-5	-1.15	0.2625
China GDP (09$)	6.169e-12	2.25e-12	2.74	0.0109*
US GDP (09$)	-2.22e-12	7.88e-13	-2.82	0.0091*

Figure 2.4: Response of bismuth price versus selected variables (1st iteration)

With an R-squared value of 0.82, it appears that this set of variables accounts for a significant portion of the variance in bismuth price. However, some of the variables are statistically indistinguishable from zero and will be removed for the next iteration. In Figure 2.5 we see that the removal of six insignificant variables has little effect on the overall correlation (R-squared changes by just .02) and the remaining variables are all statistically significant. Technically, this is where a regression analysis could be stopped. We have several significant variables that account for over 80% of the movement in the price of bismuth. An equation could be formulated and used to calculate future bismuth prices with relatively high confidence. However, rather than blindly accepting the equation, it is important to evaluate the result and determine how effective its use would be.



Summary of Fit

RSquare	0.827389
RSquare Adj	0.805813
Root Mean Square Error	2.935405
Mean of Response	8.596626
Observations (or Sum Wgts)	37

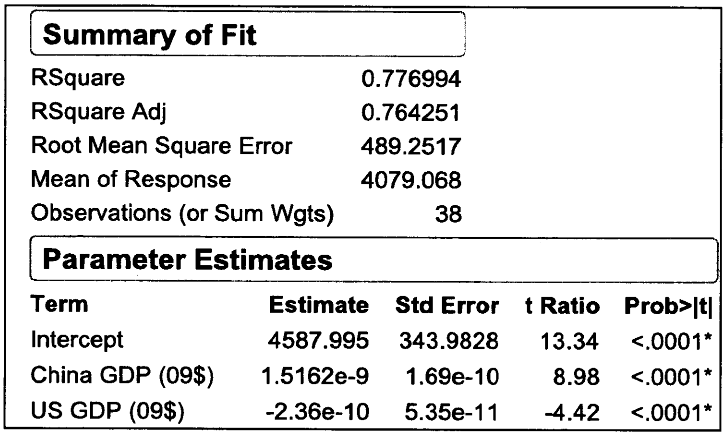
Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	18.651399	6.045031	3.09	0.0042*
P Bit-1	0.6799712	0.104961	6.48	<.0001*
P Wt-1	-0.408207	0.144199	-2.83	0.0080*
China GDP (09$)	5.519e-12	1.77e-12	3.13	0.0038*
US GDP (09$)	-1.98e-12	6.78e-13	-2.92	0.0063*

Figure 2.5: Response of bismuth price versus selected variables (2nd iteration)

The hypothetical equation is a function of the prices of bismuth and tungsten as well as the GDP of China and the U.S. Being tied to China is no surprise given that the country accounts for over 60% of the world's bismuth production. The United States is a big driving force for much of the materials demand in the world, so a dependency on its GDP is also expected. Even a correlation with tungsten could be predicted considering the fact that China, the biggest producer of bismuth, retrieves the metal from tungsten as well as lead ore (21). It seems as if these proposed variables could all provide a valid explanation for the variance in bismuth price, but there are underlying issues that suggest they may not be so useful. Perhaps the most troubling concern is the strong dependence on lagged bismuth price. This indicates a strong autocorrelation and implies that we can predict the future price from past prices. If the lagged price were a small part of the correlation, there might not be a concern. However, a single-variable regression using only lagged price results in an R-squared value of 0.76, meaning that 76% of the movement in bismuth price in the current year is dictated by its price in the previous year. A model including the lagged price would essentially be unsustainable because we would need to know the future price of bismuth, which is exactly why we made the model in the first place. If we were to remove the lagged price, the new model would have an R-squared value of about 0.60, which is respectable; however, another problem persists. The ultimate goal of this study is to produce a model that can be used to predict the price of bismuth after a large surge in demand from the liquid metal battery. Nowhere in this model is there a variable describing bismuth demand – it was deemed insignificant during the first iteration. Therefore, even if our current model predicted 99% of the price movement in bismuth, it would not be useful for our target analysis. The model would only help if we believed the introduction of LMB would have a significant and measurable effect on the world's GDP which, while exciting, is not a reasonable expectation.

One way to get around the lack of demand integration is to build a different model that does incorporate it. Consequently, this analysis yielded an outcome that showed the supply variables for nearly all of the metals included in this study have a strong correlation with the three following variables: US GDP, China GDP, US Consumption. This fact makes it much easier to build a standardized model that can be used to predict the impact that a large-scale LMB operation would have on any metal chosen for the electrodes. The results of such a regression are shown in Figure 2.6 below for bismuth.



Summary of Fit

RSquare	0.776994
RSquare Adj	0.764251
Root Mean Square Error	489.2517
Mean of Response	4079.068
Observations (or Sum Wgts)	38

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	4587.995	343.9828	13.34	<.0001*
China GDP (09$)	1.5162e-9	1.69e-10	8.98	<.0001*
US GDP (09$)	-2.36e-10	5.35e-11	-4.42	<.0001*

Figure 2.6: Regression results for bismuth production (final iteration)

Incidentally, bismuth production does not depend greatly on US consumption, which is a result of China's dominance over the metal as well as a very low demand market. Having this model allows an easier analysis of how the LMB demand will impact the metal's market. Due to the models' simplicity, it would do little good to predict LMB demand and add it into the regression, since it would just increase linearly with demand. On the other hand, the model can be used to get an idea of the level of metal production in the future (assuming no major disruptions). This can then be compared with the projection for LMB demand obtained based on the projected storage targets. This kind of comparison will be performed in chapter 5.

2.1.2 Bismuth Qualitative Analysis

Having eliminated the variables that were indistinguishable from zero in the regression and ending up with an uninspiring model, it seems that the analysis will need to take a more qualitative route. This means we can use the data to establish a probable price range for bismuth and then determine where the range of profitability for the LMB lies. We will then make a reasonable estimate for the size of LMB demand based on target projections of the amount of energy stored. Finally, we can compare the demand estimate with a projection of bismuth supply and look at the potential effects on price.

In order to establish a price range for bismuth, we refer back to Figure 2.2, which charts the average, annual price of bismuth (in 2009 USD/kg) since 1971. Although it has experienced some dramatic fluctuations, bismuth price never falls much below $9/kg over the entire range of the chart. A lead refinery is going to produce pure bismuth as it refines the lead but has no practical use for it other than to make whatever money they can from selling it. Consequently, it appears that in the absence of strong demand, refiners are willing to sell bismuth at $9/kg.

We now have a potential floor, below which the bismuth price is not likely to fall, but what about the upper end of the range? This is actually where a very interesting trend appears. It has been mentioned several times throughout that bismuth is produced primarily as a byproduct of lead or tungsten processing. This is not true in the case of one Bolivian mine. According to the USGS, "[t]he world's only significant potential source where bismuth could be the principal product is the Tasna Mine in Bolivia." Unfortunately, the Tasna mine shut down in 1985 due to a sustained decline in bismuth price. Referring to Figure 2.7 we see that this corresponds to the period of time when the price dropped from an average of about $60/kg to around $20/kg representing a precipitous 67% decline. At these low levels, primary bismuth production was no longer profitable and the mine was forced to close. A fully operational Tasna mine would undoubtedly be very useful to this analysis, however, there are conclusions that can be drawn from the historical data available. Figure 2.7 shows a fascinating relation between bismuth price and Bolivian production.

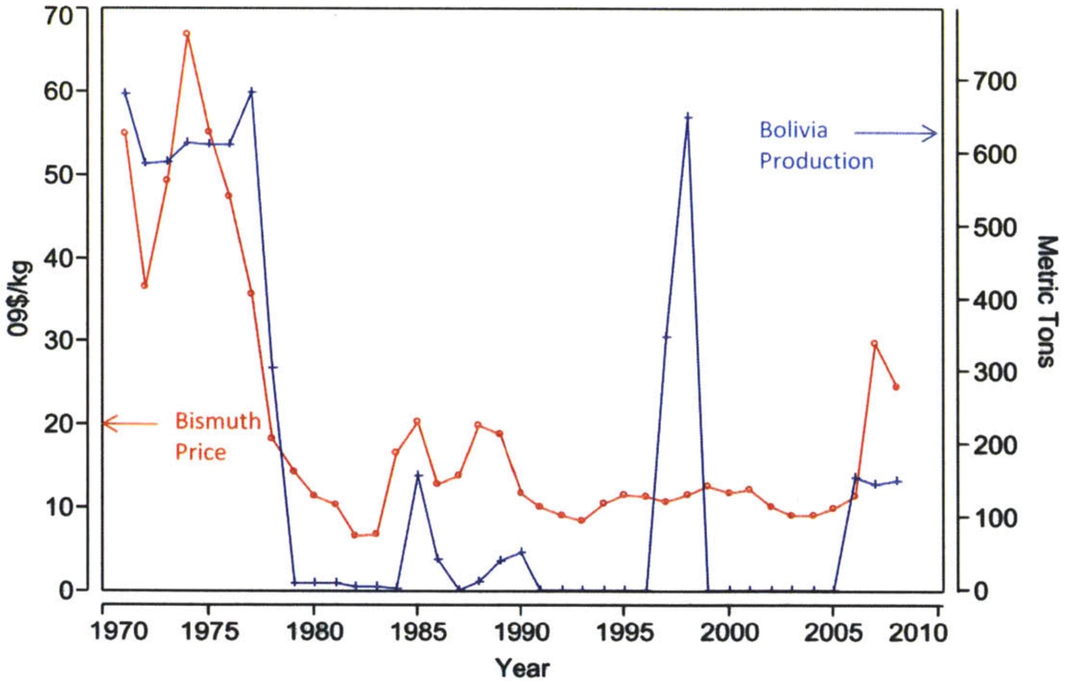


Figure 2.7: Plot showing relation between bismuth price and production in Bolivia **(21)**

There is no reason to assume that Bolivian bismuth only comes from the Tasna mine, but with a nationwide capacity of over 500 metric tons before 1985 and much less than 100 metric tons after 1985, it's safe to conclude that Tasna was a significant source of the metal for Bolivia. Therefore, this analysis will use Bolivian production as a proxy for the Tasna capacity in Figure 2.7. This graph shows at what price a dedicated bismuth mine would be able to operate profitably and, consequently, it appears that the cutoff is around $21/kg; below that, bismuth production is essentially zero. The mine was reported to have closed in 1985, which is at the same time as the price spiked to the $21 level, whereas the few years before saw lower prices and production levels barely above zero. Apparently, this price was not good enough for the mine which saw zero production in all years afterward until another price surge above $21/kg around 2006. In several reports, the USGS stated that the Tasna mine was on stand-by "awaiting a sufficient and substantial rise in the metal price" and in the 2010 Mineral Commodity Summary "there were reports that it had reopened" in late 2008. This corresponds to a unit price of between $20 and $25.

Figure 2.8 is a replot of Figure 2.7 except it shows the cutoff price at $20.38/kg. It indicates several instances where the Tasna mine came back online once the price of bismuth reached a certain (presumably profitable) threshold. Whenever the price (red line) remains below the cutoff, production (blue line) is minimal. Ultimately, we can use this fact to ascertain the level at which mines specializing in bismuth production would begin to appear, but how can this information be applied to the current analysis? Although a study of bismuth production in Bolivia seems rather arcane, its conclusions are actually quite relevant. If a bismuth-based LMB is built for large-scale energy storage, there will be a sudden demand for the metal to cover the uses of this new technology, but this demand will meet with a rather sparse market. In all likelihood, supply will not be able to sustain demand and the price will be driven upward. This will persist until that magic threshold is crossed whereby mines dedicated to bismuth production can begin to operate profitably. In an ideal world, that price will be high enough to encourage sufficient supply to meet LMB needs, but will be low enough that an LMB manufacturer will be able to use the metal and still make a profit.

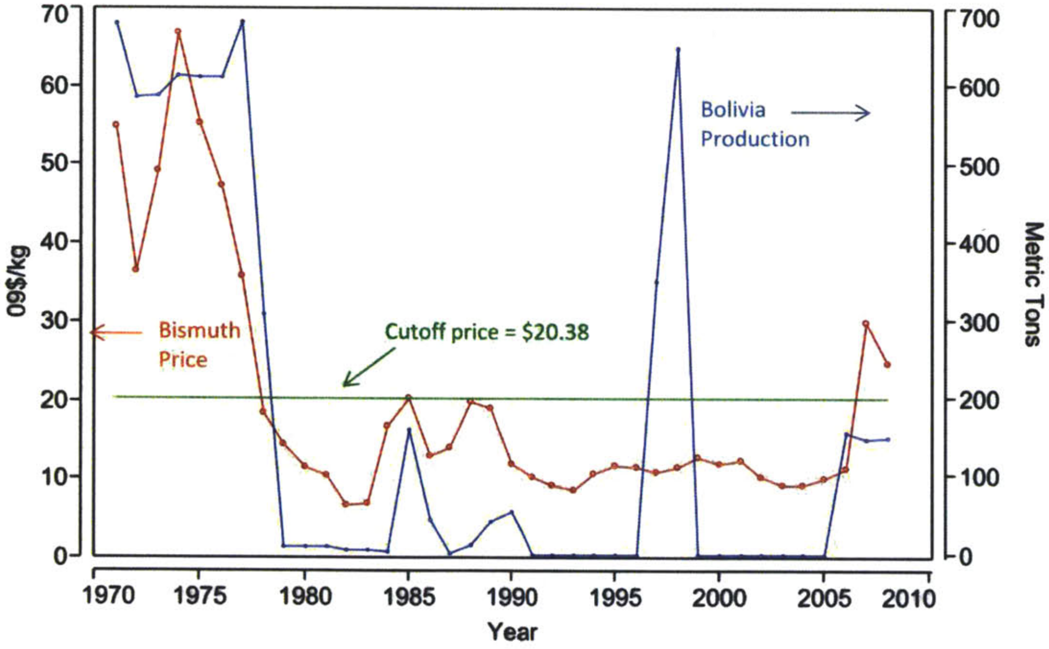


Figure 2.8: Bolivian bismuth plot showing little to no production beneath cutoff price **(21)**

Because the LMB technology is still very nascent, the profit that can be made is not yet important. Of more significance is whether the batteries can be produced at a cost that is at least on par with current technologies in the market. The predicted use of the LMB is storage for intermittent renewable energy sources, thus the estimated costs of LMB production should not exceed the cost for current, comparable technologies such as lead-acid batteries, sodium-sulfur batteries and flow batteries. As a first-round estimate, the aim of the LMB team is to keep production costs limited to $100/kWh for the active materials, which is in line with current technologies that exhibit energy storage costs of $100-$150/kWh

(23). Active materials, here, refer to the positive and negative electrodes. Often, the mobile species cannot be placed in the battery by itself and, in such cases, an additional host metal will be included in the costs. The beauty of the LMB is that its technology allows for the use of cheap materials that, for the most part, are widely available. In fact, the positive electrode uses the less common metals (i.e. bismuth, antimony), which means that this is where the majority of the cost will result. At the time of this analysis, the price of bismuth is reported to be about $21/kg. Based on a cost model built for the project, this translates into an energy cost of over $140/kWh. Depending on the chemistry, the cost can approach $300/kWh. In reality, the price of bismuth would need to fall to about $7/kg before this particular battery chemistry can be produced economically. This price is essentially the all-time low reached by the metal ($6.63 in real dollars) back in 1982.

2.1.3 Bismuth Results

The ultimate goal of the LMB project is to store at least 20% of solar and wind energy produced in the United States (see Appendix B). Assuming base case operating conditions, an initial rollout capable of storing 1% of renewables and a ramp rate of about 1.25% per year (additional energy stored), the LMB demand for bismuth averages to about twice the annual production predicted to be supplied through 2025. This should not come as big surprise considering the current market conditions for the metal. With very few applications, one would not expect a lot of production; however, the LMB is a new, disruptive technology that will essentially create a whole new market for bismuth. Regardless of the expected outcome, the fact remains that in order to simply satisfy the LMB demand, annual bismuth production will need to ramp up 100% above what is predicted based on current consumption. This is great news for bismuth investors and bismuth producers, but probably not for the LMB project. As stated above, the current price for bismuth is $21/kg and it is considered too expensive for the project. Let us assume the LMB technology is announced and production will begin immediately. How will the price of bismuth react? It would be safe to assume that the only way for bismuth production to meet LMB needs is for dedicated bismuth mines to come online, including the Tasna mine in Bolivia. We have established that the current trading price for the metal is right at the profitability limit for the Tasna and, presumably, any other bismuth mines. Unfortunately it is also over three times more expensive than needed by the LMB. Most likely, more mines will not be initiated until the price rises even further which, with demand exceeding supply by 100%, is inevitable. Ultimately, the bismuth price will diverge even further from the level desired by the LMB, meaning that the $100/kWh target will never be met unless a revolutionary process for mining bismuth is discovered that can drop the key price for profitability to under $7/kg.

So, bismuth investors should not rejoice just yet. Using current market conditions to assess the influence exerted by the liquid metal battery, it will not be feasible to use bismuth in the technology. While the heavy metal provides great operating conditions for the battery, it is, and will continue to be, too expensive for use as the positive electrode and the project will need to look at other metals to bring production costs down to the $100/kWh target.

2.2 Antimony as a Positive Electrode

The next metal of interest to use as the LMB cathode is antimony. Antimony is cheaper than bismuth, but also allows for more favorable operating conditions within the battery, particularly a higher voltage (20). Last year, primary production of antimony was 187,000 metric tons with reserves just over 2 million tons. Compared with bismuth, which had annual production and reserves of 7,000 and 300,000 tons, repectively, antimony is also much more widely available. As we discovered in the analysis of bismuth, capacity and future availability are extremely important when discussing the feasibility of using certain materials for large scale production. In fact, a cheap metal can become very expensive very quickly if enough demand is brought forth. As with the case of bismuth, it would be prudent to take a look at the future prospects of antimony and get an idea of how the LMB may affect its market.

Antimony is a relatively low melting metal with a variety of uses in both metal (solder, ammunition, cable covering, bearings) and nonmetal (ceramics, plastics, fireworks) applications. The two most prominent uses for the material, however, are in flame retardants (as antimony oxide) and automotive batteries (as antimonial lead). Part a of Figure 2.9 shows the trend of US consumption over time. US consumption peaked in the early 1970s, when applications for metals and nonmetals accounted for the vast majority of consumption. However, an interesting trend emerges after 1975: consumption of antimony for use in metals and nonmetals began to fall dramatically while usage in flame retardants grew steadily. Part b of Figure 2.9 shows the resultant shift in proportions between the three categories, which indicates that flame retardants now account for nearly 50% of US consumption compared to around 20% each for metals and nonmetals.

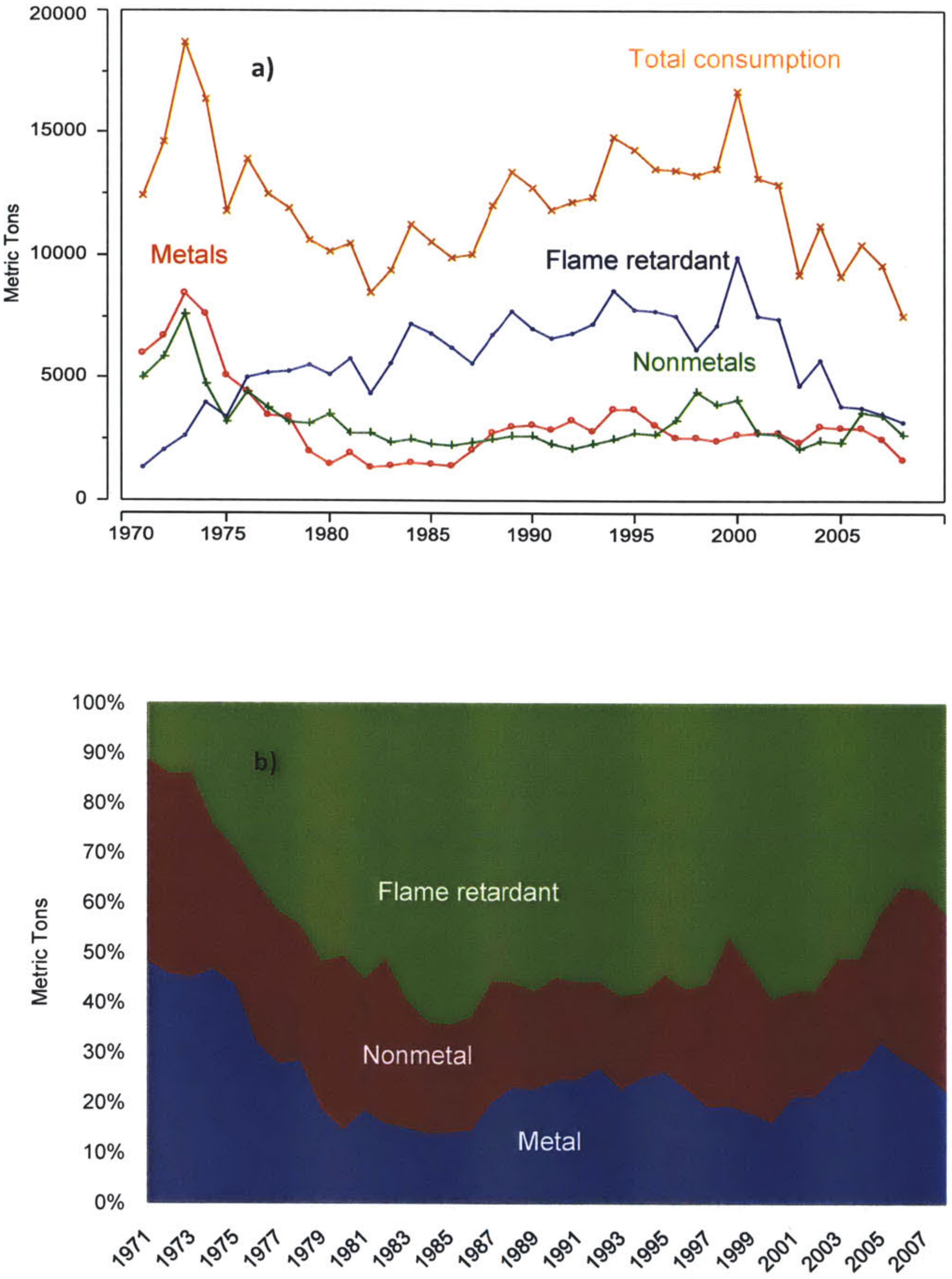


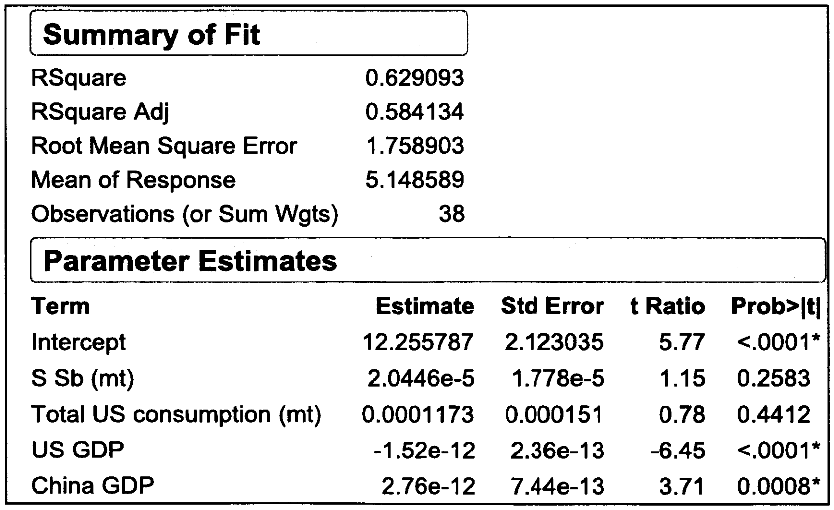
Figure 2.9: a) U.S. antimony consumption by end use. b) End use category as percentage of total consumption **(24)**

The initial drop can be attributed to the economic conditions around that time, coinciding with the Vietnam War, high oil prices and general stagflation in the economy. Something else occurred around 1975 that, arguably, had a bigger impact on antimony consumption and that was the advent of the maintenance-free battery. The push for a maintenance-free battery was a natural progression in order to ease the lives of battery consumers, but these new batteries tended to be manufactured with a calcium alloy that needed very little antimony to be molded easily. As these batteries continued to become the norm, it was obvious that less and less antimony would be going into them. This particular use of antimony falls under the "metals" category for usage, which is why we see such a pronounced drop in that category even after the recession. The decline in nonmetals consumption can also be attributed to new substitute materials. For the present analysis, the situation created by the new battery technologies will prove to be very useful and, as such, we will return to it later.

2.2.1 Antimony Regression Analysis

Ultimately, as before, we would like to know how the price of antimony will react when supply is met with increased demand from LMB manufacturing. To start, we can run through a similar analysis to that of bismuth, looking for potential explanatory variables to describe the price movement over the years.

The same logic for choosing variables in the bismuth case applies to antimony as well, which means the first iteration will include antimony supply, US consumption and China and US GDP. One marked difference from the bismuth regression is the absence of the prices of any other metals. Antimony is obtained predominantly from the ore stibnite, which can be mined as a primary product. While stibnite can be co-mined with other minerals, none are a driving force for the recovery of antimony as lead was for bismuth. This makes the regression analysis much simpler and the results of the first iteration are shown below in Figure 2.10.



Summary of Fit

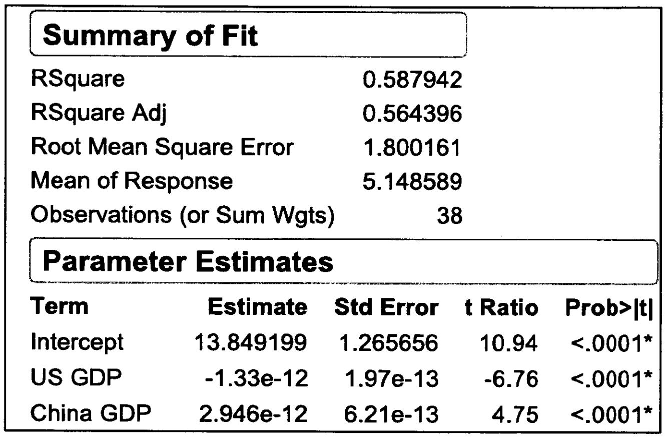
RSquare	0.629093
RSquare Adj	0.584134
Root Mean Square Error	1.758903
Mean of Response	5.148589
Observations (or Sum Wgts)	38

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	12.255787	2.123035	5.77	<.0001*
S Sb (mt)	2.0446e-5	1.778e-5	1.15	0.2583
Total US consumption (mt)	0.0001173	0.000151	0.78	0.4412
US GDP	-1.52e-12	2.36e-13	-6.45	<.0001*
China GDP	2.76e-12	7.44e-13	3.71	0.0008*

Figure 2.10: Regression results for antimony price (1st iteration)

As with bismuth, it seems that antimony production does not have a large bearing on its price, which is surprising given that antimony is a widely used metal with a mature market. US consumption is also deemed insignificant, which must be due, in part, to the fact that antimony is no longer used in car batteries, which used to see large production within the US. Removing these variables, the model is left with US and China GDP and the results are shown in Figure 2.11.



Summary of Fit

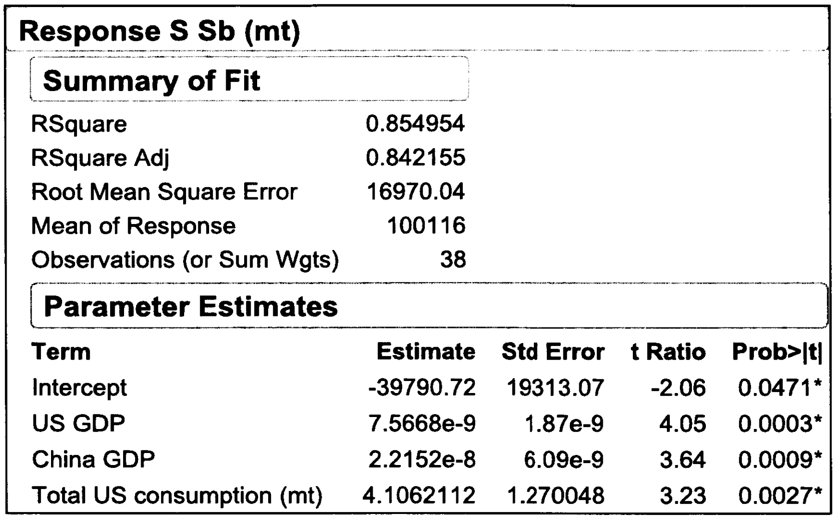
RSquare	0.587942
RSquare Adj	0.564396
Root Mean Square Error	1.800161
Mean of Response	5.148589
Observations (or Sum Wgts)	38

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	13.849199	1.265656	10.94	<.0001*
US GDP	-1.33e-12	1.97e-13	-6.76	<.0001*
China GDP	2.946e-12	6.21e-13	4.75	<.0001*

Figure 2.11: Regression results for antimony price (final iteration)

Because the United States is the world's largest economy, it is no surprise that its GDP would affect the markets of many materials. China's economy was also predicted to have a large influence given that it currently controls over 90% of antimony supply. While this leaves a reasonably effective model, like that of bismuth it offers no correlation between the demand and price of the metal. Turning to a supply model gives the following result (Figure 2.12).



Response S Sb (mt)

Summary of Fit

RSquare	0.854954
RSquare Adj	0.842155
Root Mean Square Error	16970.04
Mean of Response	100116
Observations (or Sum Wgts)	38

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	-39790.72	19313.07	-2.06	0.0471*
US GDP	7.5668e-9	1.87e-9	4.05	0.0003*
China GDP	2.2152e-8	6.09e-9	3.64	0.0009*
Total US consumption (mt)	4.1062112	1.270048	3.23	0.0027*

Figure 2.12: Regression results for antimony production (final iteration)

2.2.2 Antimony Qualitative Analysis

The first thing to note is that future demand of antimony will be met solely by supply from China, which is responsible for 90% of all the antimony mined in the world. The effects of China's growth and the introduction of maintenance-free batteries on antimony production in the United States can be seen in Figure 2.13. The United States was never a large producer of primary (mined) antimony, but it did contribute significantly to secondary supply as well as primary antimony refined in smelters. Both of these operations show drastic declines over the last three decades.

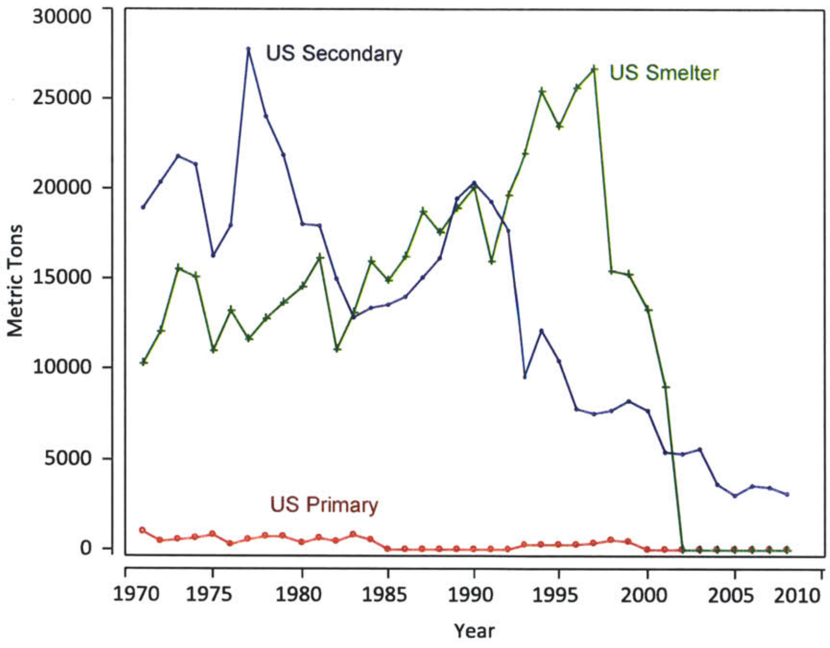


Figure 2.13: Antimony production in the United States has fallen dramatically **(24)**

The drop in smelter refining is best explained by the rise of Chinese production. As more supply began coming from Asia with cheaper costs, fewer refineries were needed for operation in the United States and capacity quickly fell as smelters began to shut down. The closing of operations is seen clearly from the progression of reports from USGS. Up until the early 1990s, production was growing and surveys were being answered by several manufacturers. In recent years, so many refineries have shut down that USGS can no longer report production numbers because they essentially would be divulging proprietary information as so few still exist (zero production in Figure 2.13 represents numbers that were "withheld for proprietary reasons"). This development doesn't necessarily affect the absolute supply of antimony, but does lend credence to the fact that negotiations with Chinese manufacturers will be imperative for the LMB. Recent developments in the rare-earth markets are testament to the implications of relying on metals dominated by a single country. In the past few months, China has announced tighter restrictions on the exports of rare-earth metals and as a result the prices for those materials have risen substantially.

With antimony supply currently around 135,000 metric tons (coming out of a deep economic recession), it is not expected that LMB demand will have a great impact on the total market. In fact, it could be posited that the LMB will simply fill the void caused by maintenance-free batteries. A look into the history of antimony use in battery production can provide a rough idea of how big that void may be. Table 2.1 uses data from USGS reports to follow the trend of primary antimony used in car batteries from 1971 to 1977. It is not hard to pick out the year in which maintenance-free batteries were introduced. In 1974, there was approximately 0.118 kg of primary antimony in car batteries, while in 1975 there was only 0.088 kg per battery.

Year	Primary Sb (kg/unit)
1972	.100
1973	.127
1974	.118
1975	.088
1976	.056
1977	.038

Table 2.1: Trend of antimony content in SLI batteries

Getting an estimate for the void left by the new batteries means projecting the amount of primary antimony that would go into car batteries today, if the maintenance-free batteries had never been introduced. In this case, the assumption is that each car battery today contains 0.100 kg of primary antimony – the average amount in batteries prior to 1975. In 2007, USGS estimated that nearly 118 million SLI units were produced that year. If each battery contained 0.100 kg of primary antimony, the total consumption for antimony by car batteries would be approximately 11,000 metric tons. Making the big assumption that the market dynamics for antimony are the same today as they were prior to 1975, then it may be said that the current market could sustain an extra 11,000 metric tons. Though this is a bold assumption, it is not outrageous considering that there has not been a major, new application for antimony to disrupt an otherwise calm economy. In other words, LMB demand of up to 11,000 metric tons might not be hard to sustain.

2.2.3 Antimony Results

As in the bismuth analysis earlier, the best approach is to look at the price effects on antimony from an indirect route using forecasted supply using the model obtained earlier. Forecast data for GDP is widely available (25) and all that remains is to obtain a reasonable estimate for consumption (without LMB).

Historically, the US has consumed an average of 12,135 metric tons of antimony annually, with less than 10% variation on either end. Based on that result, a prediction of the average consumption through 2025 yields the range 10,747 to 13,524 metric tons with 95% confidence. Consequently, it is assumed that the annual consumption of antimony through 2025 will be 12,135 metric tons. Plugging this value into the regression equation yields the expected supply of antimony out to 2025.

Comparing the projected supply to expected LMB demand will help to gain an understanding of how the antimony market will actually respond. Across a range of battery chemistries, the LMB is not expected to require more than an average of 28,000 metric tons annually, compared with expected production of over 300,000 metric tons. This ratio is much easier to stomach than that of the bismuth model, which suggested that, across many chemistries, the smallest impact LMB could have is a demand equal to 100% of total, expected annual production. Actually, in many cases the LMB is expected to consume less antimony than the size of the cushion that can hypothetically be supported (11,000 tons).

Once the LMB comes online the antimony price will inevitably spike due to an imbalance being created. Ultimately, the LMB would represent only a small fraction of the overall market. The presence of such a large market means that current mining technologies will be sufficient to satisfy LMB needs. In the case of bismuth, a drastic change in the way the metal was mined would need to occur in order to keep up with the new battery because the market is so thin. Furthermore, the battery industry is famous for the high participation rate of recycling. The liquid metal battery is no exception and, in fact, the technology was built on the premise of using simple materials that were widely available and easy to recycle. This means that after the first LMB life cycle, there will be a new flood of antimony supply coming from the recycled batteries. As a result, the long-term price should not be greatly impacted.

2.3 Negative Electrodes

The discussion on negative electrode materials is much less in-depth than that of the positive electrodes. This is because the negative electrode materials are expected to comprise a very small fraction of the total LMB cost as shown in Figure 2.14.

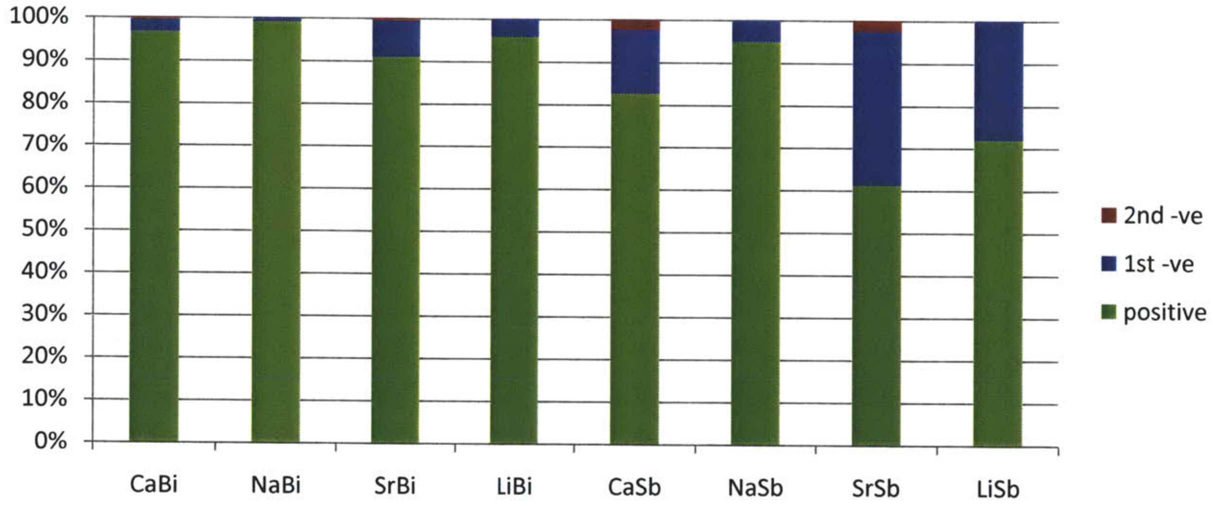


Figure 2.14: Relative costs of LMB active components

Only in the case of a Li-Sb or Sr-Sb battery does the negative electrode make up a significant portion of the cost. This is due to the high energy density of that particular chemistry, which means less metal is needed for the positive electrode. In all other cases, the negative electrode makes up less than 10% of total costs. This indicates that the big driver for LMB costs will come from the positive electrode.

Four important metals being considered for the negative electrode are calcium, lithium, sodium and strontium. These four elements are sufficiently electropositive to create a reasonable potential difference when paired with the candidate positive electrodes. Further analysis into calcium and sodium is unnecessary due to the enormous abundance within the earth, namely as lime and table salt, respectively. In fact, for both metals the USGS does not even quantify their reserves. The liquid metal battery industry would simply be a drop in the bucket for these markets, even in the most optimistic scenarios (wide prevalence of LMB). The only concern with calcium and sodium is in the form of electricity prices because the pure metals of these elements are obtained electrolytically, which is very energy intensive. While lithium and strontium also have large reserves, an analysis is still enlightening. Strontium is not as much of a household name as the others, which could imply, at first glance, a small market. Due to the recent explosion in portable, consumer electronics and electric vehicles, everyone knows about lithium and that is exactly why a closer look is worthwhile. Lithium is not nearly as abundant as calcium and sodium, yet there is a huge demand for the metal which is growing larger each year. Throughout the last decade, lithium consumption grew at an annual rate of 6% (26) and this is before a pervasive presence of electric vehicles. This means that the use of lithium by LMBs could meet with strong competition for the resource, which could lead to a scarcity problem and inflated prices.

2.3.1 Strontium

According to USGS (27), strontium can be found in two minerals – celestite (strontium sulfate) and strontianite (strontium carbonate) – of sufficient ore grade to extract the metal. Although strontium is not a well-recognized element, it has uses in very commonplace markets such as pyrotechnics and magnets used in electronic equipment. Its biggest area of consumption has been in television screens for sets that use a cathode-ray tube (CRT). For all its uses, strontium has seen annual production rise steadily throughout the years. Very little of that growth is being fueled by U.S. consumption though. Figure 2.15 shows a graph of world production and U.S. consumption, the salient feature being the precipitous decline in U.S. consumption beginning around 2000. The large decline can be attributed, almost exclusively, to the emergence of flat-screen televisions, which emerged around the turn of the century. The new displays eliminated the need for CRTs, which meant that strontium was no longer needed to shield the x-rays. Flat-screens and plasmas were still very expensive in 2000 so their effect was minimal. Today, however, the technology is everywhere and U.S. consumption has declined from a peak of about 45,000 metric tons in 1992 to its current value around 10,000 metric tons. As a result of the technology shift, strontium mines are no longer operated in the United States. Obviously world production was not affected and that is due to developing economies, like those in Asia and Mexico. These countries still produce and consume CRT televisions and as the economies continue to grow at a fast pace, world production will keep up. In its most recent report, the USGS mentions that even Asia and Mexico have begun to see declines in strontium consumption as flat-screens make their way into consumer homes (27). This explains the apparent plateau in production over the last five years.

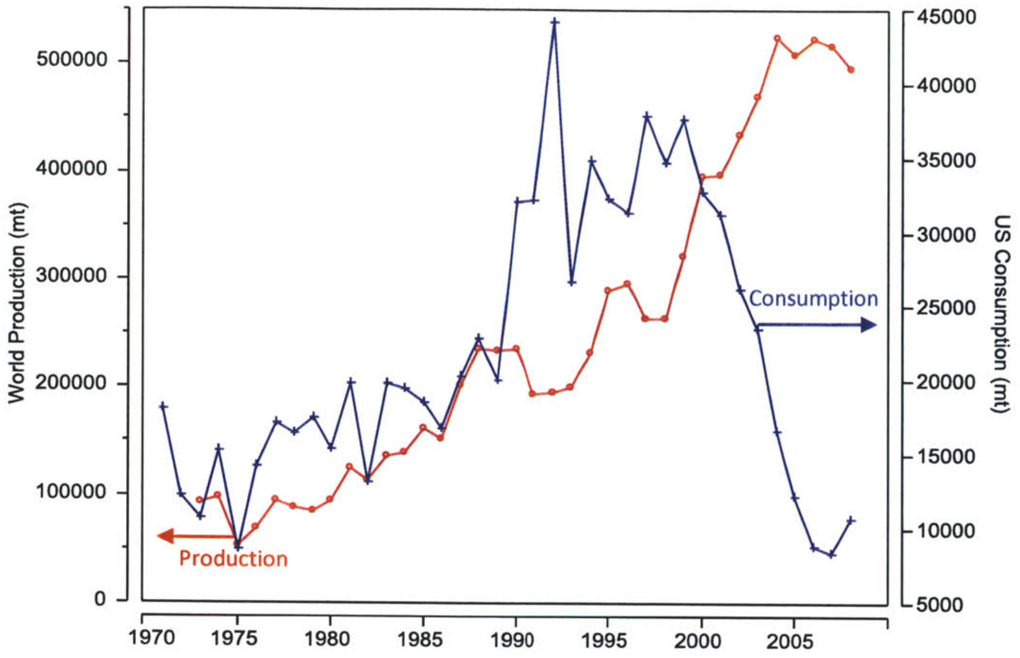


Figure 2.15: Graph comparing world production of strontium to U.S. consumption of strontium **(28)**

With global demand beginning to follow in the steps of U.S. consumption and reserves nearing 7 million metric tons, there is no concern of a shortage in the future. The cost model built for this work projects LMB consumption of strontium at around 7,000 metric tons per year, much less than projected world production of more than 700,000 metric tons. Although the model does not account for a drop in demand as CRTs are phased out, even a large drop in production should more than support the LMB market. A 75% decrease results in production of 175,000 metric tons. In addition, there are still large strontium reserves in the United States than can be drawn upon in the unlikely event world production cannot keep up (28). As expected, using strontium for the mobile species in the LMB would be sustainable for decades to come.

Another favorable quality for strontium that is absent from metals like bismuth and antimony is the geographical diversity of its production. China controls nearly the entire supply of both bismuth and antimony, which opens the door for vulnerability to geopolitical uncertainty. As Figure 2.16 shows, however, strontium is produced in a few countries. Although China has been increasing its share, Spain and Mexico still account for over 40% of world production, which means prices for strontium should remain competitive in the foreseeable future.

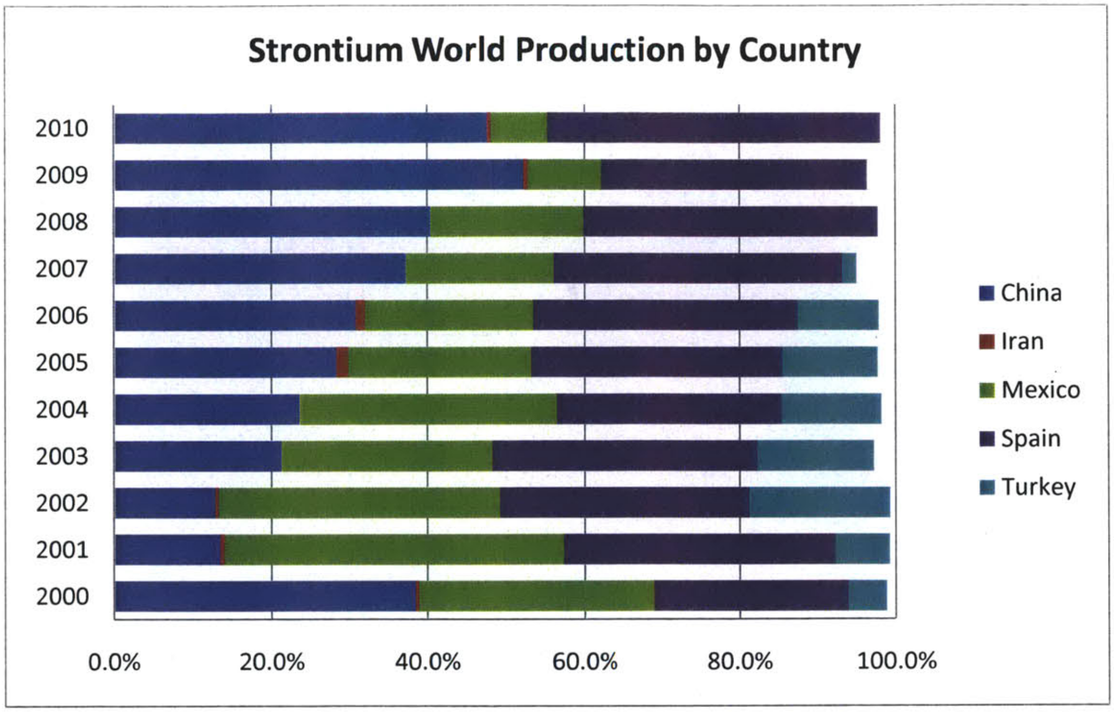


Figure 2.16: Geographical diversity of strontium production over the past decade **(28)**

2.3.2 Lithium

The project's cost model predicts that LMB demand for lithium will be less than 1,000 metric tons annually. The most recent estimate, according to USGS, provides global production and reserves of 25,000 and 13,000,000 metric tons, respectively (29). Again, LMB will have little to no impact on the state of the lithium market as overall demand will continue to grow. In its 2009 lithium report, Roskill Information Services Ltd states that consumption of lithium has grown at an average of 6% per year since 2000. Even more impressive is the growth in lithium consumption by the battery industry which logged a compound annual growth rate of 22.1% between 2000 and 2008 (26). With all the excitement growing over lithium the only concern for the LMB, given its relatively insignificant demand, would be lithium demand from other industries outstripping supply, resulting in a large price spike. Even though the aggregate LMB demand would be small, lithium makes up one-third of the battery cost for the relevant chemistries. A large enough price spike could pose a threat to the economics of the technology. Unfortunately, this kind of move is not unprecedented in the metal's history. Figure 2.17 shows the price of lithium carbonate, which is the predominant form of lithium recovered from mines.

The price of lithium carbonate will be used in this analysis as a proxy due to a lack of historical data on the price of the pure metal. As a reference, at the time of this writing the most recent price for the carbonate was around \$4/kg (30)while the quoted price for lithium metal was around \$62/kg (31). The vast difference in prices accounts for the fact that pure lithium metal must be extracted electrolytically in a very controlled environment. For the cost models used herein, the \$62 unit price was the input but for the purposes of analyzing trends, the carbonate proxy will suffice as any increase in the raw material should result in a consummate rise in the metal's price, assuming no appreciable rise in the cost of energy.

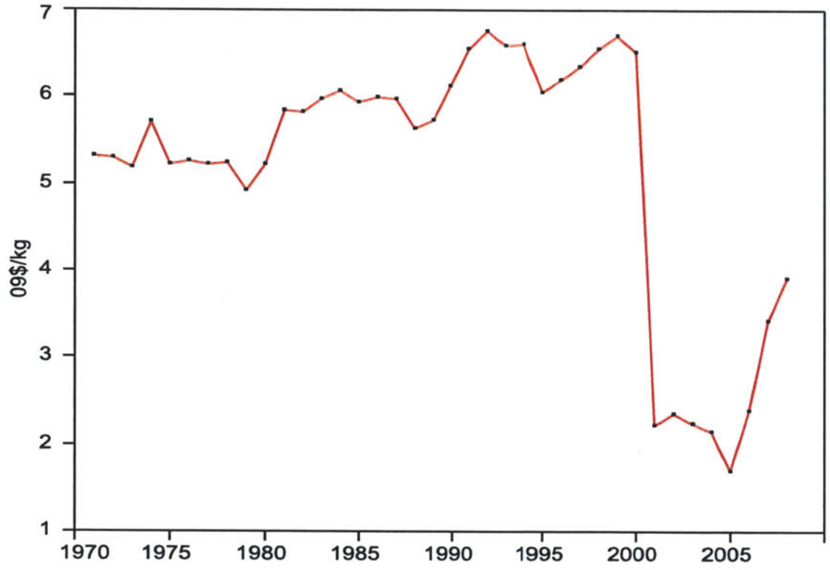
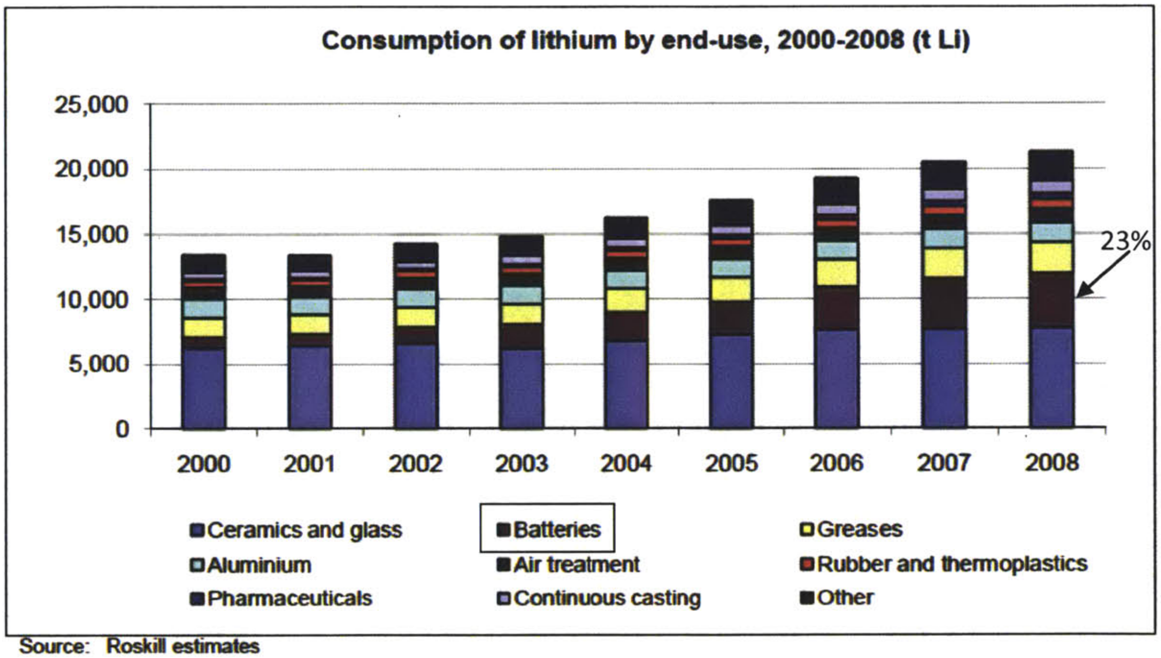


Figure 2.17: Real price of lithium carbonate in 2009 dollars **(30)**

Figure 2.17 shows lithium carbonate hitting a generational low in 2005 at \$1.70/kg. The most recent data lists the price at \$3.90/kg, which is an increase of 130% in three years. Luckily, the cost model was run using recent data, meaning the LMB cost target is met even after the 130% run-up. This rise, however, means that subsequent spikes are not out of the picture; especially when considering the cause. Further investigation into the meaning behind the price movements actually reveals very important information for the interplay between new technologies and resource scarcity.

The case of lithium is the perfect example of how a new technology can impact the markets of a particular commodity. Using lithium in batteries is not a brand new idea: primary batteries using lithium were commercialized in the 1980s. Secondary batteries, on the other hand, were first commercialized in 1992. Once consumer electronics, namely personal computers, became more portable it was clear that lithium would be extremely important. In fact, the revolution in portable devices and, hence, the wide adoption of lithium-ion batteries could be seen as a disruptive event in the lithium markets. According to the 1994 Minerals Yearbook for lithium put out by the USGS, batteries accounted for only 7% of lithium consumption in the United States. Fast-forward to the trends illustrated in Figure 2.18 taken from the 2009 report by Roskill Services.



Source: Roskill estimates

Figure 2.18: Roskill graph showing the consumption of lithium by end-use for the past decade **(26)**

According to Roskill, the battery industry consumed 23% of the lithium produced in 2008 and it has been the fastest growing end-use by far, as evidenced by the 22% CAGR. This growth could be compounded in the future if electric vehicles become prevalent. Roskill estimates that lithium consumption for batteries in portable devices will grow through 2013 at a CAGR of 7% while batteries in EVs are projected to grow at 56% per year. In other words, there is real demand for lithium. Now it is fruitful to look at the effect of this demand on carbonate prices. Figure 2.19 shows the same graph as Figure 2.17 with an overlay of world production. On the graph, point A marks 1992, the first year of commercialization of secondary lithium batteries (lithium-ion), and point B denotes the year that a new supplier entered the lithium market (SQM, 1996).

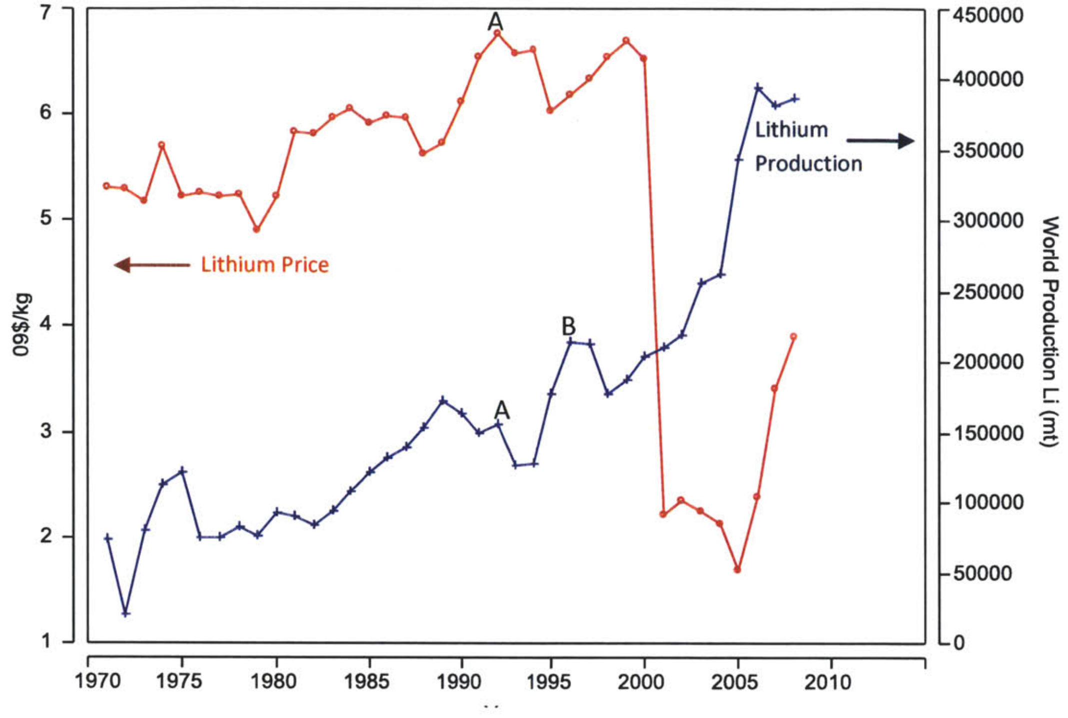


Figure 2.19: Lithium price and production over time illustrating the effect of real demand on prices **(30)**

There were only two major producers of carbonate until 1996 when Sociedad Quimica y Minera de Chile entered with an "aggressive pricing strategy" (32). Presumably, the presence of strong demand from the new secondary batteries encouraged new players to enter the lithium supply business as would be expected for any potentially profitable market. A few years after the entrance of SQM and its aggressive pricing, the price of lithium plummeted from \$6.52/kg to \$2.22/kg as competitors had to respond to the newest player. The fact that production continued to rise, while the price fell so dramatically, underscores the true strength of the lithium demand, driven predominantly by the new batteries. This is the first important dynamic exemplified by the lithium case. Prior to a disruptive technology, price and production will usually rise steadily with stable growth in demand. However, once a brand new demand is introduced (i.e. secondary lithium batteries) the landscape changes. Even before prices show any signs of disturbance, suppliers begin entering the market in hopes of cashing in on the imminent demand spike. These new players help fuel production growth while introducing competitive pressures in the form of better efficiencies or smaller operating margins. Soon, other suppliers must respond and prices drop. The subsequent spike in prices over the last few years is no mystery either. Fueled by "increased global demand, especially for lithium batteries," (33) prices had to rise along with production in order to prevent a supply shortfall.

The price movements in lithium carbonate introduce another dynamic within the commodities industry. In the long-run, prices should be correlated to the resource scarcity. That is, as the resource becomes scarcer, through increased demand and production, prices will necessarily rise to reflect the increasing difficulty of extracting the commodity. This, however, is really only true when the resource is near extinction. In reality the dynamic plays out as shown in Figure 2.20.

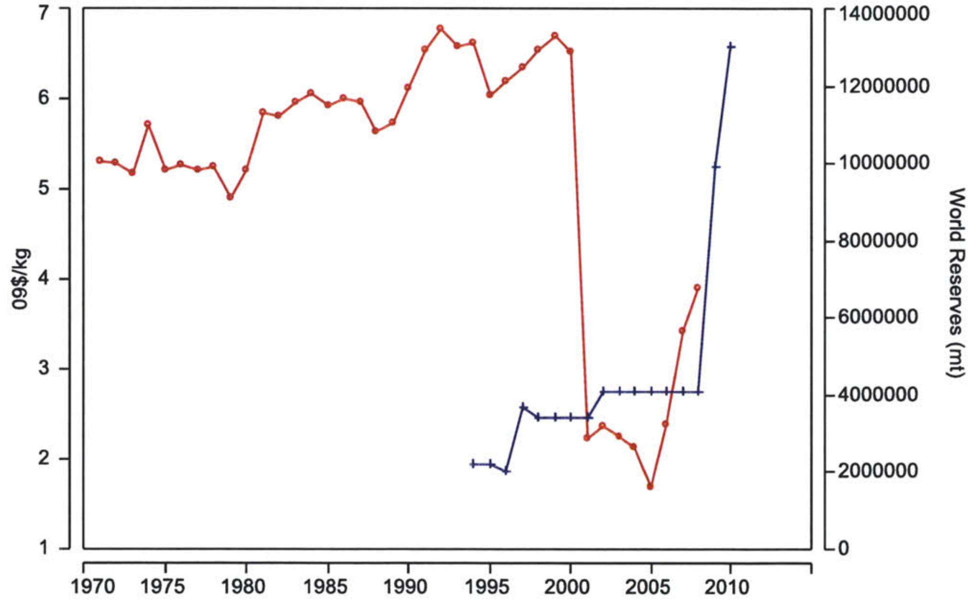


Figure 2.20: Lithium price and world reserves **(30)**

One metric used to measure the amount of a material available is the commodity's reserve. This is defined as the amount of material that is available to be extracted in an economically viable manner given the resource's current price. As a result, price and reserves should be directly correlated since a higher price will cause more material to be available "economically." Put another way, higher prices provide an incentive for exploration and future extraction. This trend is shown nicely in the graph above, especially in the latter part of the decade: as the price makes the 130% jump, reserves go from 4 million to 13 million metric tons. Reserves can increase due to price increases from natural growth in demand but they can also increase with the introduction of new extraction techniques. If a method is discovered to remove a resource more efficiently than existing techniques, then the amount that is economically feasible can increase even as prices fall due to the new efficiencies. This may be what happened in the first part of the 2000s when reserves stepped up with the drastic fall in price. Around this time Chile became the world's largest producer and most of the operations in the country extract lithium carbonate from ocean brine, a much more cost efficient method than pure mining. Although plausible, it is not clear that this was definitely the cause. Reserve numbers from USGS have a large uncertainty, especially for international suppliers. The numbers are received based on surveys sent out to producers, who are not obligated to complete them. As a result, many numbers must be simply estimated by the USGS specialists (34). Another potential explanation is that when a company explores a new mine, they may choose to withhold some information about its potential until operations are underway, which could be a few years after the initial discovery (35).

So far this discussion has been about the scarcity of lithium with no immediate relevance to the LMB given that it would use such a relatively small amount compared to the element's abundance. However, looking at the way lithium batteries affected supply and demand for the metal provides unique insight into the way disruptive technologies can impact a commodity's market. An argument can be made that says a similar scenario will play out should the LMB move toward using bismuth, where the new demand will surely cause a disturbance in the market equilibrium. Even for antimony, the cost model predicts LMB demand could equal nearly 10% of projected supply, which could have a material impact considering batteries only consumed 7% of lithium supply when that technology first was commercialized. On the other hand, the LMB only seems insignificant in the scheme of lithium carbonate. If the liquid metal battery were to use lithium, it would use the pure metal, which is actually a small market at 1% of lithium consumption (26). An LMB manufacturer could choose to produce its own pure metal electrolytically from the carbonate, but if it were to purchase the metal there could be a disturbance in the markets. It is, of course, naïve to say that the same thing would happen to bismuth and antimony that occurred with lithium because the methods of extraction are very different. Bismuth is mainly produced as a byproduct of lead refinement, which clouds the ability to predict what could happen with new demand. Antimony is mined by itself in the form of stibnite, but as a resource it has a more definite life expectancy than the nearly limitless brine supply of lithium carbonate, which means scarcity would play a much bigger role in its market dynamics. Nevertheless, an analogy can be drawn between the portable battery's effect on lithium and the liquid metal battery's effect on its relevant metals.

2.3.3 Negative Electrode Results

All of the candidate materials for the negative electrode of the LMB have vast reserves and are not expected to meet with a scarcity problem any time soon, meaning there should be no surprises as far as prices are concerned. With the mobile species making up less than 10% of total costs for most of the LMB chemistries, even substantial price increases would not have a large impact on overall cost as illustrated in the sensitivity analysis at the end of this report. Consequently, from a price standpoint, no metal emerges as a clear choice for the negative electrode.

Even though the analysis did not point to a winning pick, looking at the history of lithium and how it reacted to the emergence of lithium batteries can provide a unique insight into how the LMB may affect the markets of some of the metals it is targeting.

3. Molten Salt Electrolyte

After discussing the repercussions of selecting appropriate metals for the electrodes, it may seem that a look at the electrolytes is superfluous. This is not completely unreasonable considering the most important specifications of a battery – voltage and capacity – rely solely upon characteristics of the two electrodes. When examining the costs of a battery, it is often expected that the electrolyte will contribute little to the total and discussion of energy costs often only include the cost of the "active" materials, namely the positive and negative electrodes. Consequently, the cost of the electrolyte will be added in with the manufacturing and balance of system costs to arrive at the total cost of the battery. This makes sense when discussing batteries that use cheap salts, like the lead acid battery used in automobiles. Sulfuric acid is very cheap - \$0.10/kg according to USGS (36) - and is used as an aqueous solution within a flooded-cell battery. More advanced batteries, however, usually require more exotic salts which can actually contribute a significant amount to the total costs. For example, the common lithium-ion battery (18650 cell) uses an electrolyte of lithium hexafluorophosphate ($LiPF_6$). According to a report by Argonne National Lab, LiPF6 had a cost of \$50/kg, two-orders of magnitude larger than sulfuric acid (37). Even with the huge performance improvements offered by a Li-ion cell, it is obvious that the cost of its electrolyte cannot be ignored.

3.1 Electrolyte Salts

A similar situation holds true for the liquid metal battery. Unlike the previous batteries, the LMB is designed to run at high temperatures (~700 °C or less), which means electrolytes must be selected such that the salt will be molten at the appropriate operating temperature. In fact, developing a satisfactory electrolyte has proven to be very complicated. Ionic conductivity is probably the most important aspect of an electrolyte salt. In the LMB labs, this is accomplished by using alkaline salts that have the same cation as the mobile species between electrodes. For example, NaCl will be used in a Na-Bi cell, where Na^+ is the mobile species. Unfortunately, a salt made entirely of NaCl would not work because the melting point of pure NaCl is 801 °C, well above the operating temperature of the battery. An easy way to lower the melting point is by mixing in another salt. Figure 3.1 shows the calculated phase diagram if NaI is mixed with NaCl and we see that a 50/50 mixture of the two can result in a molten salt at 700 °C. While helping solve the melting point issue, adding a second and third compound increases the mixing possibilities exponentially and makes it slightly more difficult to optimize, especially if a salt of a different cation is added. Adding in a different cation can be beneficial by reducing the amount of solvation that can occur at the electrode interface if a salt were made entirely of the mobile ion species. On the other hand, this introduces the problem of premature deposition of a foreign species on the electrode. To clarify, the cathodic potential at which K^+ deposits on bismuth is less negative than Na^+, which means as the potential is swept cathodically, it is more likely that the potassium ions will deposit onto the bismuth electrode before the sodium ion. This can be very detrimental to the capacity of the battery. Therefore, even though adding a foreign cation into the electrolyte melt can benefit in one respect, an eye must be kept on another issue entirely. All of this discussion goes to show that choosing an electrolyte (or rather electrolyte mix) is no simple task and it is not possible to just choose the cheapest salt with the appropriate cation.

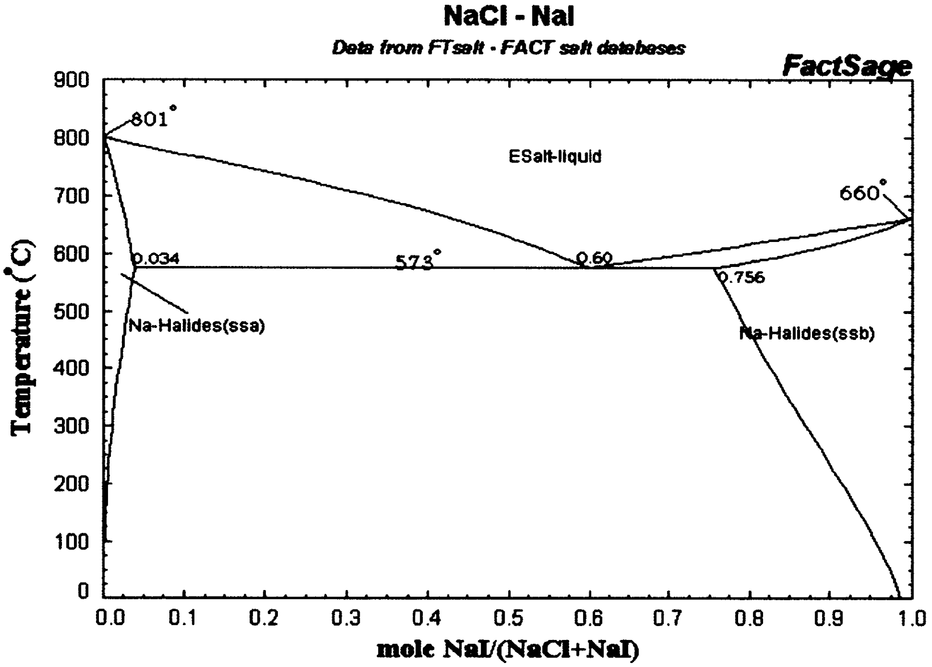


Figure 3.1: Phase diagram for NaI in NaCl **(38)**

As if there were not enough complications already, recent tests of the LMB have found that impurities within the salts can be very harmful to the battery, as well. At such high temperatures, with everything in a liquid state, kinetics within the battery are extremely fast, which makes it almost impossible to control or predict what an impurity might do. Thus, it has been prudent to use high-purity, ultra-dry salts in the preliminary cells of the LMB. The discussion to follow will show that use of these salts is not sustainable if the LMB is to be scaled-up for grid storage.

3.2 Low-Purity versus High-Purity

Based on the chemistries that have been studied to date, the common electrolytes being investigated contain cations of sodium, potassium, calcium and lithium in various forms of halide salts. A study was performed to analyze the costs incurred by using these high-purity salts and compare them to the expected costs of bulk quality salts at scale, ultimately deciding whether electrolyte costs pose a threat to the target cost. As mentioned previously, the $/kWh units used throughout this analysis have been with respect to the electrode-active materials. In other words, the $100/kWh target does not factor in electrolyte costs. The discussion above, however, proved that electrolyte costs in advanced batteries cannot necessarily be ignored until production starts. It is possible that the electrode costs come in under target, but if the electrolytes come in at $500/kWh, before any packaging and manufacturing costs, the final product will not be competitive with current technologies. A quick comparison of the salts being considered along with the energy costs associated with their high-purity and low-purity forms is shown below in Figure 3.2 and Figure 3.3.

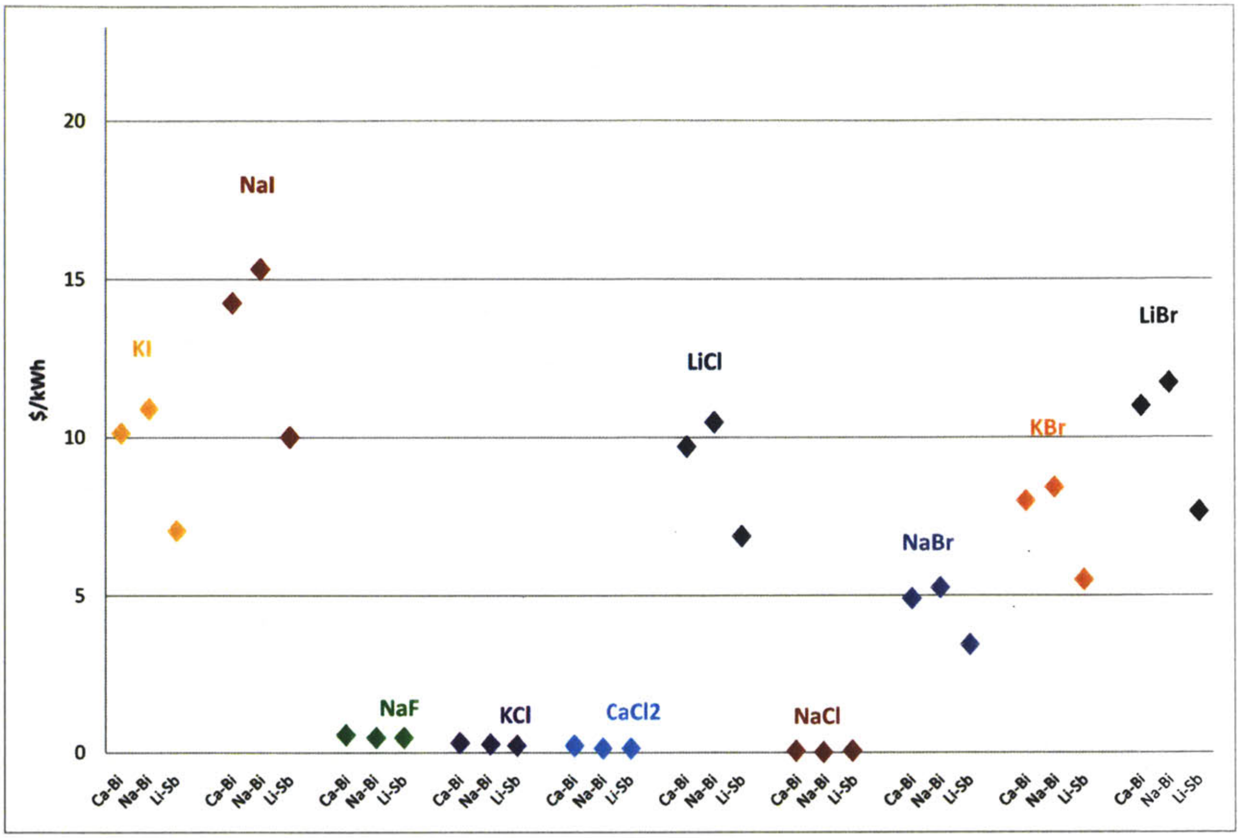


Figure 3.2: Energy costs for low-purity electrolyte salts based on specific battery chemistries. Prices based on quotes from bulk-scale suppliers

Three battery chemistries were chosen to illustrate the energy costs: Ca-Bi, Na-Bi and Li-Sb. Across all salts (both high and low-purity), the Li-Sb battery offers the cheapest energy cost due to its high energy density. In general, the low-purity lithium salts are more expensive, as are the salts containing the bromine and iodine anion. This should not come as a surprise because these salts do not exist in nature in raw form. Unlike the fluoride and chloride salts (excluding LiCl), the production of these salts involves at least a little bit of processing like reacting lithium carbonate and hydrogen bromide to get LiBr.

The trend among high-purity salts is very similar except for one key difference. According to Figure 3.3, the price of high-purity, anhydrous calcium chloride is much higher relative to the other salts than it was in the low-purity comparison. This is an interesting aspect that helps explain the influence of processing costs on the final price. Calcium chloride is known to be very hygroscopic and salts that bond so strongly to water molecules are very difficult to dehydrate. The process of removing water must be done under carefully controlled conditions and the final product must be stored accordingly. As a result, salts like calcium chloride can be expensive to purify and dry which is why their prices are much higher.

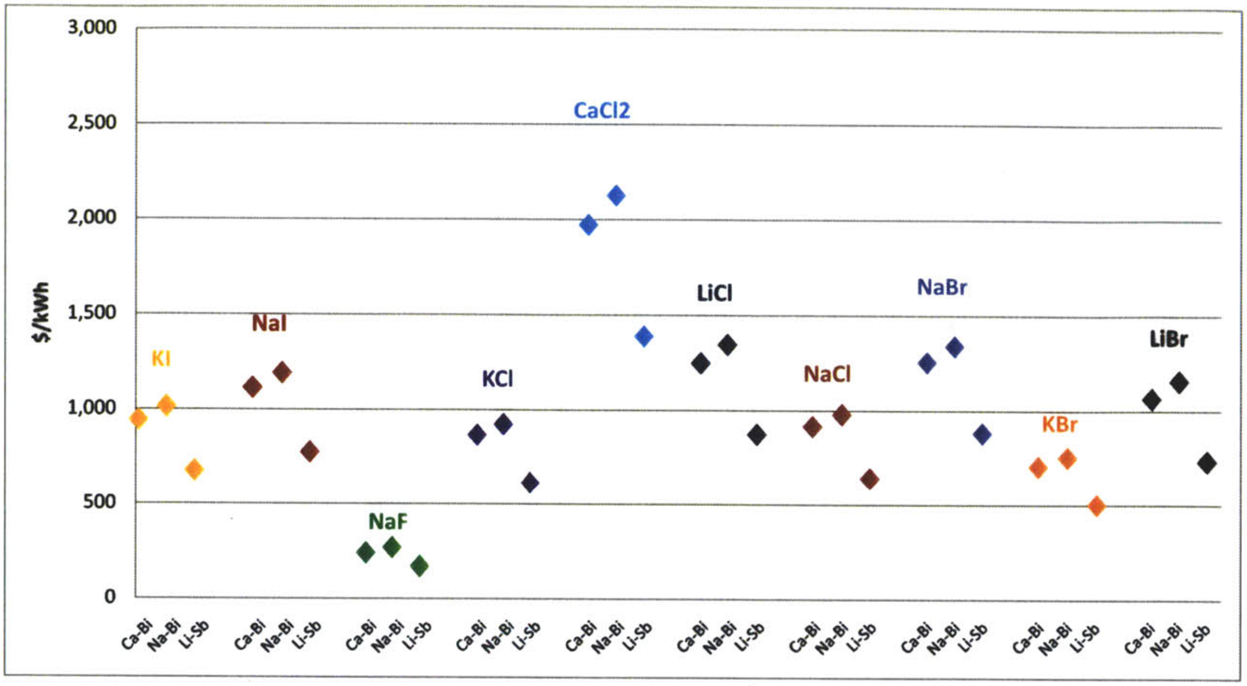


Figure 3.3: Energy costs for high-purity electrolyte salts based on specific battery chemistries. Salt prices based on 1 kg-quotes from lab suppliers.

In order to fully understand the impact of the salt costs, it is important to realize that in the lab large quantities of material is seldom necessary. Instead, it is common practice to purchase small quantities from suppliers such as Alfa-Aesar and Sigma-Aldrich. Unfortunately, this often skews a cost analysis because these suppliers are, naturally, businesses that must make a profit from the products they sell. Incidentally, it is quite inefficient for them to sell small (less than a few kilograms) amounts of material so they make up for it by imposing a very high mark-up, often more than 1000%, over the cost that could be obtained directly from a mass producer. In addition, part of the mark-ups for the LMB salts come from the fact that the suppliers must refine the salts to the high purity needed. Astronomic mark-ups will render any technology economically infeasible.

In order to estimate the extent of these markups, the author obtained several price quotes from a laboratory supplier covering various quantities of all the commonly used, LMB salts. Afterward, price quotes were obtained from larger, industrial suppliers of the same salts to get an idea of what to expect from a, more or less, at-cost price. The quotes obtained from the lab supplier were for the highest purity, ultra-dry salt in packages of no more than 1 kg and those from the manufacturers were for bulk amounts in excess of 100 kg. The term "bulk" here implies a low-purity product, i.e. what is essentially mined from the ground and shipped directly to the buyer. Ultimately, two sets of data were gathered: a list of quotes for high-purity salts of varying amounts and a list of quotes for low-purity salts in a very large amount. By getting several quotes from a the lab-scale, the strategy is to build a commoditized curve, that is obtaining a graph to show the progression from high unit costs to low unit costs as more of the material is purchased at one time. Due to the inefficiencies of shipping small amounts of these salts, one would expect the unit costs ($/g) to be very high when purchasing just a few grams of material and then decrease with increasing purchase amounts. Theoretically, such a curve would asymptote toward an amount that represents the cost of refining the salts, plus an additional amount for profit. At this point, one would expect the shipping costs to be negligible on a unit basis. Finally, overlaying this plot with the bulk quotes obtained from manufacturers should give an idea of the costs involved to mine the salts and refine them to an ultra-high purity once profit margins and overhead costs are removed. An example of a typical plot obtained is shown in Figure 3.4 for lithium bromide (LiBr).

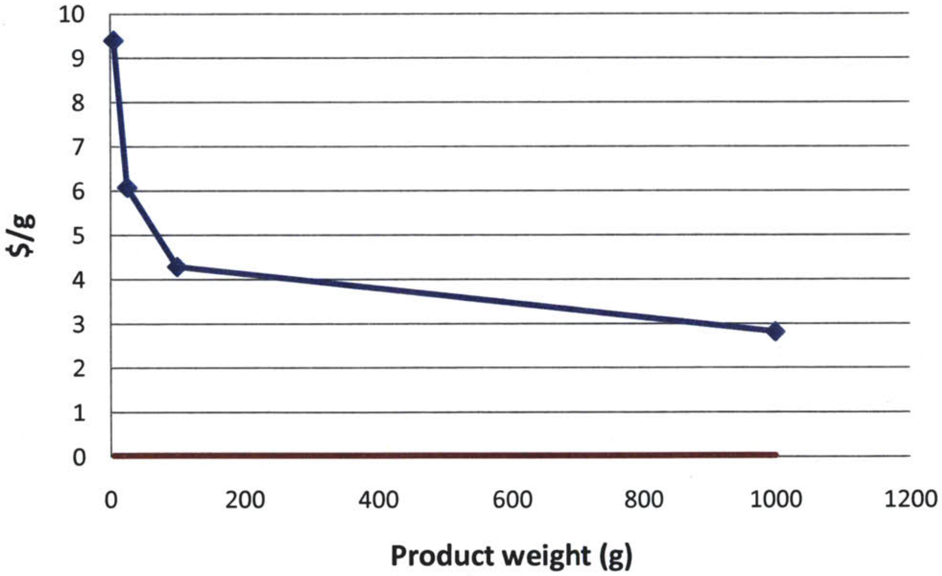


Figure 3.4: Commoditized plot for LiBr reflecting the cost of refining

For ease of reading, the units are in $/g. The fact that the bulk price ($0.03/g) is indistinguishable from zero implies a very high cost of refining to get a high-purity material. This plot also clearly shows the relationship between amount purchased and unit price.

The implications of salt purity on overall costs are illustrated in Table 3.1 below. This table compares the electrolyte cost of the LMB to that of the lead-acid and lithium-ion batteries. The two different LMB entries account for the use of high-purity salts (LMB-hp) and low-purity salts (LMB-lp).

Battery	Capacity (Ah)	Discharge Potential (V)	Electrolyte mass (/cell)	Electrolyte cost (/cell)	Storage cost (/kWh)
LA	60	2.1	5.5 kg[a]	\$0.55[b]	\$4.37
Li-ion	2.4	3.7	—	\$0.13[c]	\$14.64
LMB-hp	1	1	2.7 g	\$1.52[d]	\$817
LMB-lp	1	1	2.7 g	\$0.08[d]	\$43

Table 3.1: Comparison of electrolyte costs across three battery chemistries.
a) Electrolyte mass calculated based on 20 kg battery
b) Prices for sulfuric acid from USGS Sulfur Commodity Yearbook 2008
c) Lithium-ion bill of materials (39)
d) Calculations made for the LMB entries assume a pure LiBr electrolyte in a LiSb cell at 0.5 A/cm^2

The peril of using such high-purity salts is immediately apparent. At a cost of over \$800/kWh, a high-purity electrolyte is an order of magnitude more expensive than the electrolyte in a lithium-ion battery, and the idea of cheap energy storage that inspired the LMB is nullified. On the other hand, a low-purity salt puts the electrolyte cost on a more reasonable comparison. The use of a salt of such a low-purity is not necessarily feasible for the LMB given the possibility of detrimental side reactions, but this enforces the argument against using high-purity materials, at least those purchased from a distributor.

3.3 In-House Refinement

Given the exorbitant costs of purchasing ultra-pure materials from a distributor and the deleterious effects of using low quality salts, a decision has to be made on how best to obtain the required electrolytes. One obvious route is to produce the salts in-house, meaning the manufacturer of the LMB will also buy bulk quantities of salt from producers and refine them itself up to the required specifications. The reason this can be a viable solution is because when purchasing refined product from distributors the consumer is not paying only for the material, they are paying to keep the distributor's facilities running, their employees paid and their coffers filled. In other words, there are several hidden costs tucked beneath the quoted price that add a significant amount on top of what it actually costs to refine the salts.

3.3.1 Cost of Goods Sold

In order to determine the feasibility of in-house refining, it is necessary to estimate how much it will cost to do so and whether or not it will allow adequate savings that will trickle down to a cheaper LMB. Absent a detailed schematic of the refinement process for the salts, refining costs will need to be estimated from an existing distributor's financial records. Using a 2009 annual report for a well-known distributor, the relative fractions of expense categories were calculated. The results are shown in Figure 3.5.

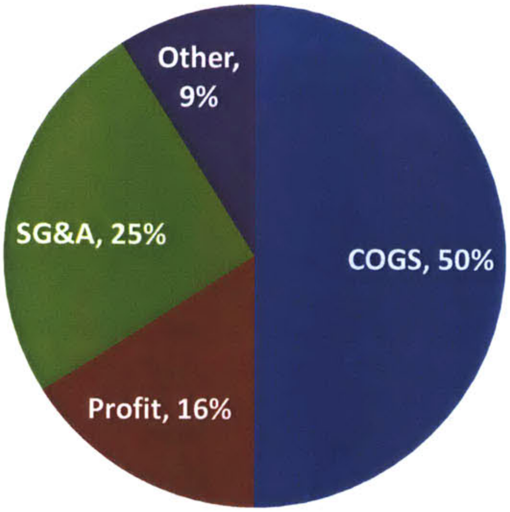


Figure 3.5: Relative fractions of costs incurred by a lab supplier, which are covered by the sales price

Here, SG&A represents "sales, general and administrative" and often encompasses salaries, corporate overhead and advertising. Cost of goods sold (COGS) covers all costs associated with obtaining and processing materials to be sold and will often include the cost to buy raw materials, labor costs to refine the final product and manufacturing overhead.

3.3.2 Processing Costs

Cost of goods sold can be assumed to consist of two main components: the cost to purchase raw materials and the cost of processing. All of the overhead costs associated with running a refinery can be wrapped up into the processing costs since anybody planning to refine salts can expect a similar cost structure. Naturally, it is the processing cost that is of interest to the LMB project.

In order to estimate the processing costs, it would be useful to gain an idea of how much the raw materials would cost for a refiner/lab supplier. To accomplish this, graphs similar to Figure 3.4 were made for each of the 11 salts studied in this report. Although these were made by obtaining bulk quotes from suppliers, the "bulk" sizes were only one kilogram. Considering a refiner would be purchasing quantities by the ton, estimating prices from these curves via visual estimates of the asymptotes would be very crude. Instead, an attempt was made to fit a regression to the curves in the form of a power law and an interesting trend emerged as summarized in Table 3.2.

Salt	Coefficient	Exponent
NaF	18.5	-0.51
NaI	16.1	-0.28
NaCl	13.5	-0.25
NaBr	17.8	-0.24
KCl	6.0	-0.15
KI	9.8	-0.23
LiCl	12.0	-0.20
LiI	19.4	-0.27
LiBr	12.95	-0.23
CaCl2	18.4	-0.20
KBr	6.4	-0.20

Table 3.2: Summary of regression results for electrolyte salts

The regressions were all performed on charts of price in \$/g versus quantity in grams and the resulting equations were of the form $y = Ax^c$ where y is the price in \$/g, A is the coefficient, x is the quantity purchased in grams and c is the exponent. It is immediately noticeable that the vast majority of regressions follow a power law with a -0.2 exponent. In fact, with the exception of NaF, all of the exponents can be found within a range of -0.15 and -0.28. The average of all exponents is -0.25. Excluding NaF does not change it that much (-0.22) so it will be left in for completeness. The average coefficient is 13.7 but is insignificant once large quantities are considered. Therefore, using the equation $y = 13.7x^{-0.25}$ should provide a reasonable estimate for the retail price per gram of pure salt for quantities in the tons. Incidentally, a one-ton supply of high-purity salt will sell, on average, for \$433/kg. That is the amount expected to be charged by a lab supplier. This value was used to represent the selling price for a general salt when attempting to break down the components of COGS.

Using the same group of salts, prices for large quantities of the raw materials were estimated by either contacting bulk suppliers directly or referring to USGS reports. The average raw materials price for these salts was found to be \$31/kg. See Appendix C for the list of salts investigated.

As shown earlier, when a salt is purchased from a lab supplier it can be assumed that 50% of that purchase price covers the COGS associated with producing that salt. In the case of some generic salt, with a price of \$433/kg, COGS will be about \$217/kg. Assuming a raw materials cost of \$31/kg, that implies that it costs \$186/kg to refine the salt to a high-purity, anhydrous product. A more detailed cost breakdown can be seen in Figure 3.6. Ultimately, processing costs account for about 43% of the price paid for high-purity salts.

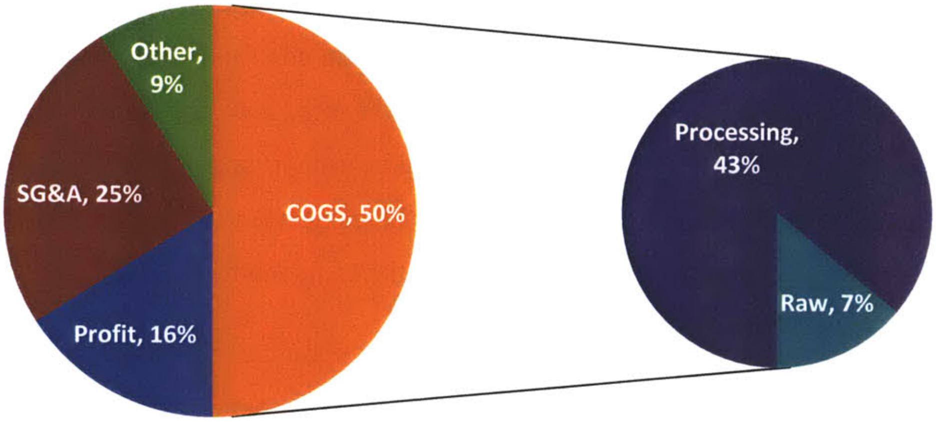


Figure 3.6: Detailed breakdown of costs covered by the retail price of a generic electrolyte salt

3.3.3 Processing Costs for LiBr

To make the analysis more concrete, the above steps can be used to examine the costs for one particular salt, namely lithium bromide (LiBr). As a distributor, there are two ways to produce high-purity, ultra-dry LiBr salt: a simple reaction of Li_2CO_3 with HBr followed by refinement; purchasing bulk LiBr from a supplier and refining. For simplicity, we assume the second alternative is accepted. This is reasonable because the cost of purchasing bulk quantities of Li_2CO_3 comes to around \$4.44/kg (33). Add to that the costs of HBr, operating the reactors, shipping and storage and the costs associated with obtaining low-purity LiBr will not be much less than purchasing it directly from a supplier at \$30/kg (40). Remembering that the \$433/kg price was only used to establish the cost breakdown for a generic salt, the power law regression specific to LiBr can be used to estimate the expected unit price for one ton of salt purchased, which comes to be \$563/kg. Following the expense breakdown, the cost of refining LiBr and bringing it up to specifications will be around \$253/kg. The complete breakdown is shown in Figure 3.7.

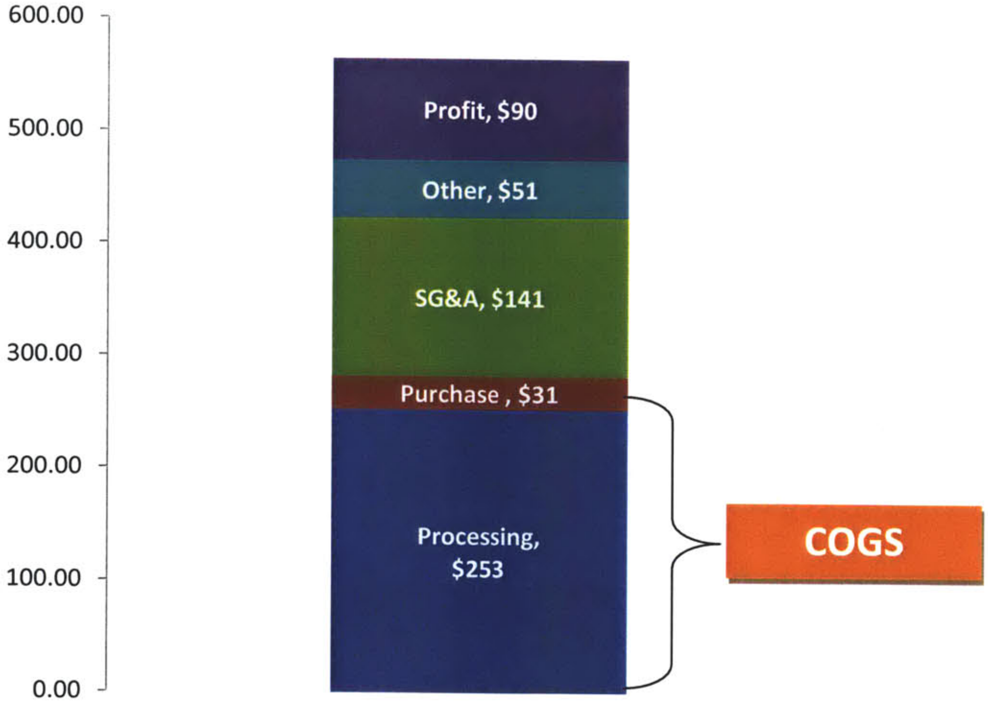


Figure 3.7: Cost breakdown for high-purity LiBr. Values are per kilogram of salt.

Therefore, if an LMB manufacturer decided to purchase bulk LiBr and refine in-house, they could expect to pay $253/kg in processing costs in addition to the raw material cost of $31/kg. As shown in Table 3.3, this translates into $408/kWh. While this is still significantly greater than existing technologies, it is a marked improvement over buying high-purity from a distributor, exhibiting a savings of nearly 50% (due to the cost structure broken out above). This kind of savings is consistent across all the other salts. In reality, the processing costs will be larger due to inefficiencies in the unit operations. Assuming a product yield of 93%, the processing costs for LiBr are $390/kg and the energy cost becomes $436/kWh. Fortunately, most of the electrolyte mixes used in the LMB are made of expensive salts like LiBr and cheap salts like NaCl. Thus, not only does mixing salts help lower the melting point of the electrolyte but it can also help to cut the cost.

Battery	Capacity (Ah)	Discharge Potential (V)	Electrolyte mass (/cell)	Electrolyte cost (/cell)	Storage cost (/kWh)
LA	60	2.1	5.5 kg	$0.55	$4.37
Li-ion	2.4	3.7	___	$0.13	$14.64
LMB-hp	1	1	2.7 g	$1.52	$817
LMB-lp	1	1	2.7 g	$0.08	$43
LMB-ih	1	1	2.7 g	$2.05	$408[a]

Table 3.3: Comparison of costs of electrolytes made in-house versus being purchased from distributors. The battery simulated assumes a current density of 0.5 A/cm^2 and a LiSb couple.

a) Assumes 100% processing yield

3.4 Electrolyte Results

There is no easy decision to make when selecting an electrolyte. It is obvious that using low-purity salts provides an enormous cost advantage over the high-purity materials, but the exact effects of doing have not been tested and substitution may not even be feasible. Outside of salt quality, cost cannot be a big driver for electrolyte selection because other aspects are much more important, like ionic conductivity and the eutectic temperature. These are criteria that may not be properly satisfied by simply choosing the cheapest salts. In general, however, it was shown that chlorides are the cheapest alternative unless purchasing ultra-pure calcium chloride, which is the most expensive salt.

Beyond the fact that high-purity, ultra-dry salts are very expensive when purchased from distributors, this analysis has shown that an LMB manufacturer can actually save quite a bit of money by purchasing the raw materials from a supplier and refining the salts in-house. Of course, this was a very rough analysis that makes several generalizations that might not hold true across all candidate materials. For example, the discussion has assumed that processing takes up the same fraction of costs for all the salts. Some salts, like calcium chloride, are very hygroscopic and thus involve a lot more effort to make anhydrous. This could include extra processing steps or special, ambient processing conditions which could make refining much more expensive. Extra costs like these would obviously be reflected in the sales price but operating leverage would actually change the distribution of costs. In other words, just because it costs more to process does not mean SG&A expenses will increase proportionally; therefore COGS as a percent of sales will actually be higher than the 50% calculated above. Similarly, the calculations for processing were carried out by subtracting the bulk price from COGS, which may skew the costs for salts with extremely cheap bulk prices. This analysis was intended to be generic and standardized, however, so the use of averages will suffice. Finally, this analysis has ignored any capital expenditures associated with buying the necessary equipment, which will add to the expenses as the costs are depreciated throughout their useful lives. It is often the case, however, that one unit can be used to process different materials meaning that if the LMB manufacturer needs to refine three different salts, they will not necessarily need three different sets of refining equipment. Finally, in-house processing will expose the manufacturer to rising and potentially volatile energy costs, which were also not taken into account. A more exact and detailed analysis could be envisioned by investigating the different steps needed in refining the salts and modeling a plant to carry out the processes in order to arrive at a unit cost, but this is outside the scope of this work, which was to simply gauge the feasibility of in-house refining.

To get an idea of the lower electrolyte cost limit for which an LMB manufacturer should aim, the magnesium industry provides a reasonable look. The most prevalent method used to produce magnesium metal is the electrolysis of magnesium chloride. Magnesium chloride is available from sea water and so is nearly infinitely abundant, but it is also very hygroscopic. For the electrolysis to run efficiently, the feed salt must be anhydrous and pure, much like the salts investigated herein. Consequently, a large portion of the production cost of magnesium metal comes from the preparation of the salt feed. Despite such importance, the cost of attaining the right quality salt comes in around \$0.13/kg (41). This is significantly cheaper than any of the salts examined in this analysis, but may not be out of reach for some of them. Many of the chloride salts of interest like calcium chloride and strontium chloride (not included in this analysis) have properties similar to the magnesium salt. As a result, it is expected that those salts can be dried and purified in a manner similar to magnesium chloride. While not found in sea water, they are also very abundant. These qualities imply the possibility of obtaining large amounts of some of the electrolyte salts very cheaply, as done in the magnesium industry. Other salts, like lithium chloride, bromides and iodides are not nearly as simple to obtain. Therefore, these are likely to remain more expensive, but in the most optimistic case these costs may be lowered to that of some of the more expensive electrolytes currently used (around \$15/kWh as in Table 3.3). There is a lot of research to be done if the costs of the salts in this study are to drop from a few hundred dollars to a few dollars per kilowatt-hour, but thinking this way allows a more fair comparison of total system costs based solely on technology fundamentals, as will be shown in chapter 5.

4. System Costs

The focus up to this point has been on the materials pertinent to the batteries' chemistries: positive and negative electrodes and electrolytes. Of course there is more to a battery than the energy-generating materials. In fact, when developing a battery for the purpose of grid-scale energy storage there are many more elements that factor into the final cost. The storage medium (electrodes, electrolyte) must be contained in a vessel, which often constitutes the current collectors. Insulation will also play an important role in a self-heating system such as the LMB. The unit consisting of the storage medium, current collectors and insulation is referred to as the battery cell.

Lithium-ion cells are capable of generating a potential of a little over three volts. Most other battery chemistries fall well short of this value, in the range of one volt or less. Therefore, in order to handle the voltages needed by the electric grid, which can be in the kV range depending on the application, several of these cells must be connected in series. A MW-rated NAS battery system will require nearly 900 cells (42). This is an extreme number due to the size limitations of the solid electrolyte used in the NAS battery, which constrains cell capacity, but even a scalable technology like the LMB could require a network of hundreds of cells. All of these cells must be stored in a facility and must be interfaced with the grid. The costs associated with the buildings, support structures, transformers and wiring make up the balance of plant (BOP) and, consequently, a large part of the final cost for a complete storage system. The final and most important level of costs for an energy storage technology is the power conversion system (PCS), which mainly consists of an AC-DC converter and a DC-AC inverter. An efficient PCS is of utmost importance because the grid uses alternating current to deliver electricity to consumers but batteries use direct current to convert electrical energy to chemical energy and vice versa. Therefore, dedicated power electronics are necessary to allow the electrical energy to be transferred back and forth. Most of the costs of the storage medium have been discussed and a look at the BOP and PCS will round out the analysis for the expected cost of a grid-scale energy storage system based on the liquid metal battery.

4.1 Storage Medium

4.1.1 Negative Current Collector

As mentioned, the electrode and electrolyte costs have already been addressed. For cost estimates, the storage medium plus void space for expansion is assumed to be 7.4 cm thick. The negative current collector is an inactive component that allows electrons to flow from an external source into the top (negative) electrode. The negative electrode in the LMB is a liquid alkali/alkaline earth metal such as lithium, calcium or strontium. To maximize efficiency, a current collector must have good electronic conductivity and must be impervious to attack by the liquid metal with which it is in contact. Luckily, simple steel will suffice as the negative current collector for the LMB as evidenced by the two binary phase diagrams in Figure 4.1 and Figure 4.2 below. Figure 4.1 shows the phase diagram for iron and lithium while Figure 4.2 shows that of iron and calcium. Although they are diagrams of specific couples, each figure is representative of the interactions between iron and the alkali metals and alkaline earth metals, respectively.

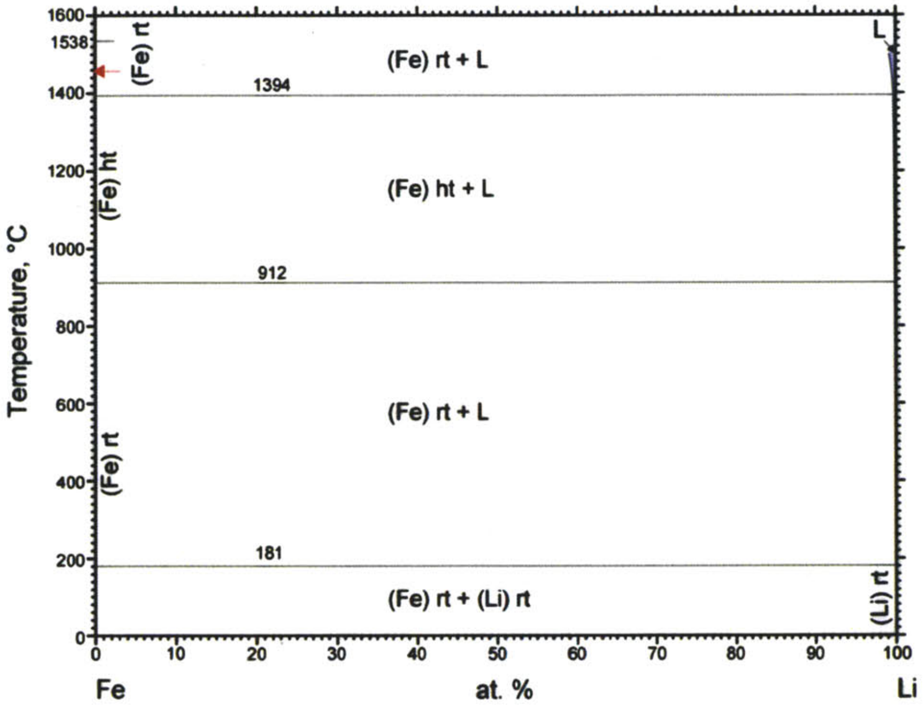


Figure 4.1: Binary phase diagram of iron and lithium is representative of the other alkali metals **(43)**

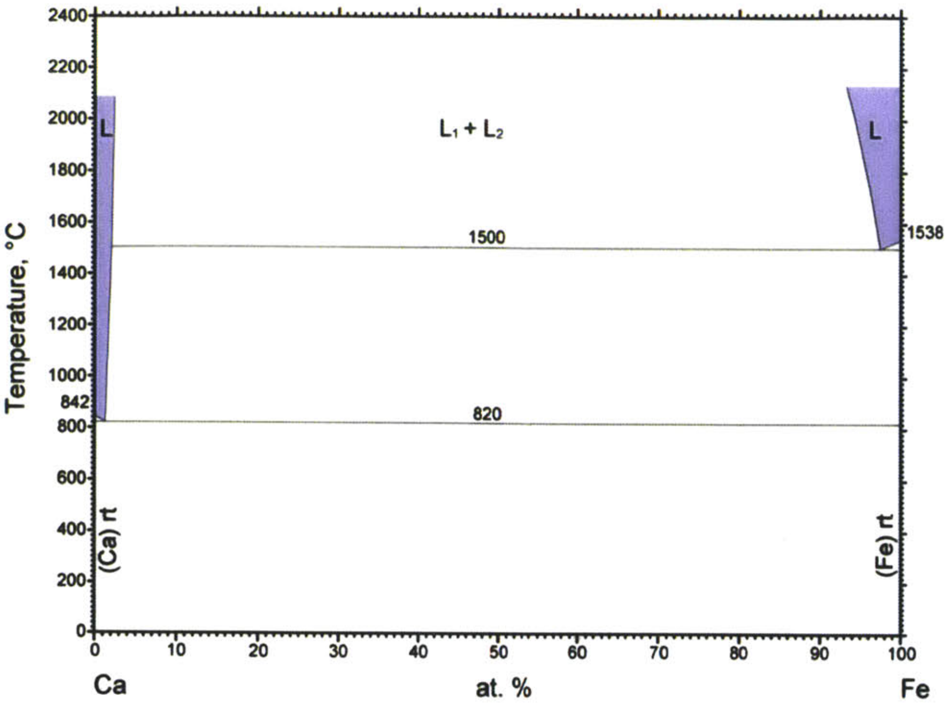


Figure 4.2: Binary phase diagram of iron and calcium is representative of the other alkaline earth metals **(44)**

Both diagrams show that iron and the cation candidate materials do not alloy, meaning a current collector made of steel truly will be inactive and, most importantly, cheap. Several variations of the current collector have been tested in small cells in the laboratory, but the shape is not expected to be complex, which means manufacturing costs will remain at a reasonable level. For relatively simple processes, raw materials costs should make up a significant portion of the total manufacturing cost. When making hot rolled coil steel, raw materials make up about 30% of the total processing costs (45). Assuming that the current collectors do not involve any complex processing, which would decrease the fraction of raw costs relative to processing costs, a factor of 30% can be used to estimate their manufacturing costs as well. Steel prices depend on the type of steel purchased, but steel billet is quoted on the LME at about \$0.55/kg (46). Assuming this price makes up 30% of the total cost to manufacture the current collectors, the unit price of these steel components comes to about \$1.80/kg. To estimate the total cost of producing each cell, the negative current collector is assumed to be 1 cm thick.

4.1.2 Positive Current Collector

Manufacturing the positive (bottom) current collector is not as straightforward as its counterpart and a look at Figure 4.3 shows the reason.

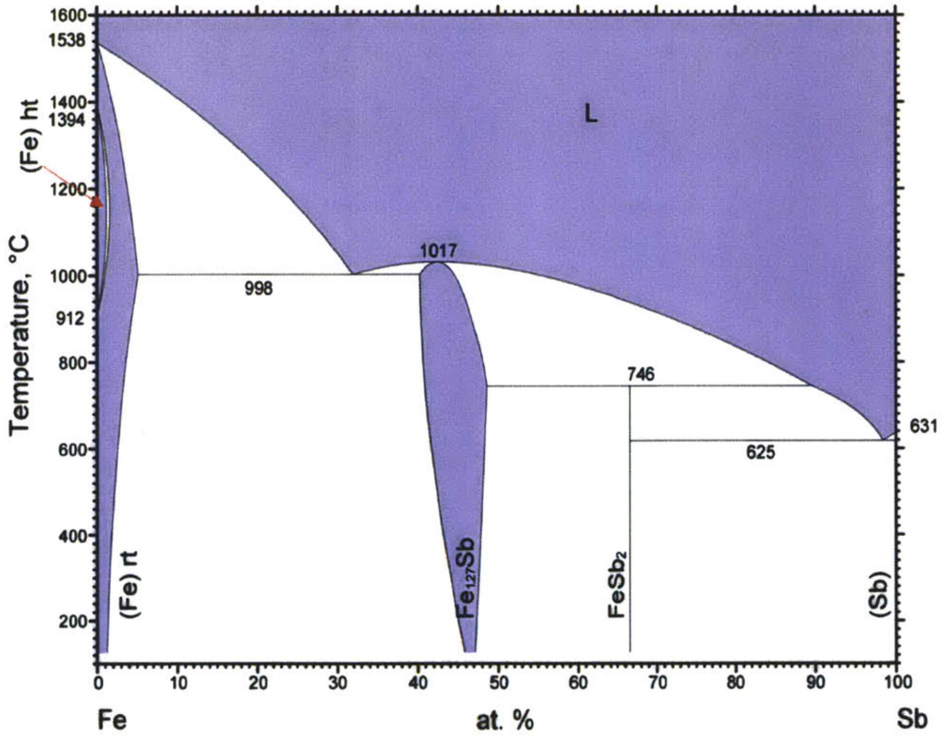


Figure 4.3: Binary phase diagram for iron and antimony showing the possibility of alloying **(47)**

Looking at the most promising candidate material for the positive electrode, antimony, Figure 4.3 shows that an alloy can form between it and a steel current collector. Even though an alloy can be electronically conductive, the process of alloying means a reduced coulombic efficiency as well as degradation in cell capacity as the electrode is consumed. Therefore, it is important to try and minimize any possibility of alloying. This is a difficult issue to overcome because antimony alloys with nearly everything. Table 4.1 shows the results of several experiments carried out by the LMB team to test several different materials against an antimony electrode. Among all of the metals tested, tungsten proved to be the only one that could withstand antimony attack, even if its activity were reduced by alloying with lithium (as in the second column).

	Sb, 700 °C		Li30-Sb70, 700 °C	
Material	Corrosion /mm yr^{-1}	Result	Corrosion /mm yr^{-1}	Result
Mild Steel	117	Severe attack	67	Severe attack
304SS	20	Severe attack	47	Severe attack
316SS	21	Severe attack	38	Severe attack
321SS	22	Severe attack	20	Severe attack
430SS	35	Severe attack	24	Severe attack
Molybdenum	35	Severe attack	45	Severe attack
Tantalum	3	Moderate attack	9	Moderate attack
Titanium	∞	Complete dissolution	67	Complete dissolution
Nickel	∞	Complete dissolution	∞	Complete dissolution
Niobium	6	Moderate attack	2	Moderate attack
Tungsten	0	No attack	0	No attack

Table 4.1: Results of corrosion experiments showing that tungsten is the only metal not attacked by antimony **(20)**

The positive current collector also acts as the cell casing and, as such, tungsten is prohibitively expensive when compared to a more reasonable material like steel. In addition, tungsten is difficult to machine which means processing costs will also be high. One way to get around machining is to coat a steel collector by depositing tungsten onto the surface. This is a viable option since it would fix the problem of alloying with antimony and would also significantly reduce the required amount of such an expensive metal. One drawback is, of course, the deposition costs which can be quite expensive in the long run. All hope is not lost though. Graphite is known to be inert with many materials, including antimony. While a current collector made completely of graphite is not practical, it could be used as a passivating layer between the positive electrode and the current collector. Since graphite is also a good electronic conductor, there will be a negligible loss in passing current through it. Based on numbers from USGS, a high-end estimate for graphite prices is around $1.50/kg (48). Like the negative collector, the positive current collector is assumed to be 1 cm thick on all sides.

4.2 Cell Enclosure and Construction

Ultimately, the goal is to get an idea of the total energy cost of a grid-scale LMB system. To simplify calculations going forward, a cell geometry similar to that in (49) will be used. Similar secondary materials will be adopted as well: perlite for insulation, copper for wiring and alumina for the sheath.

These are auxiliary components whose purposes remain the same regardless of battery chemistry and geometry. The amounts of each material used will differ based on geometry but the exact effect is beyond the scope of this analysis and will be neglected, so no other geometries are considered. Figure 4.4 shows a simple illustration of a typical cell, which is not drawn to scale but does represent a reasonable aspect ratio. The spacers between the current collectors are small and their costs were neglected. The dark layer underneath the negative electrode represents graphite, whose use was explained earlier. Using the dimensions discussed above, the combined storage costs for both current collectors is under $10/kWh.

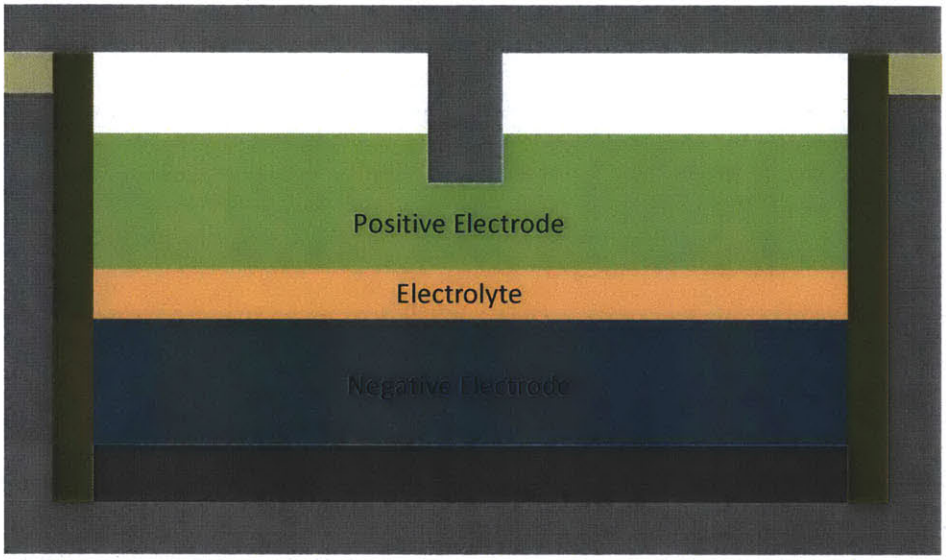


Figure 4.4: Simple illustration of an LMB cell

4.2.1 Insulation

Perlite is an interesting mineral in that it can expand to up to twenty times its original volume when heated and becomes very porous, perfect for insulation (50). There is huge supply and demand for the volcanic glass with the United States being one of the largest producers. At $50/ton it is also very cheap. To calculate how much will be needed, it is assumed that the perlite will be wrapped around each cell and have thickness of 3 cm and this results in storage costs less than $0.50/kWh.

4.2.2 Wiring

Copper is one of the most important industrial metals and is used in all manner of construction, but being such an important metal is really a double-edged sword for copper consumers. Several emerging economies (China, India, Brazil) have been experiencing rapid growth over the past few years. With such expansion comes the need to grow manufacturing and construction to maintain sustainability and copper is being consumed at a very high rate. Organic growth in demand alone is enough to increase prices but with that comes an increase in speculation by commodity traders. Prices for front-month, copper futures at the time of this writing value the metal at $9.74/kg – a 95% increase from 2009 prices (51). Luckily the copper wiring is not expected to account for a large portion of the LMB, so price changes should be insignificant to overall cost. Regardless of its immediate impact, manufacturers cannot completely ignore volatility in prices for auxiliary materials as they can quickly eat into gross margins. There are other metals, like aluminum and steel, that can be substituted for copper if prices appreciate too much; however, these are also closely tied to economic expansion and could run into similar problems. In the event of substitutions, aluminum has an electrical resistivity that is very close to that of copper. Steel has a resistivity one order of magnitude larger than copper but should offer similar results. Over all, costs associated with the wiring are relatively small and come to less than $2/kWh.

4.2.3 Insulating Sheath

Alumina is another widely used material and it will serve as the sheath in the LMB. The purpose of the sheath is to protect the walls of the current collector as well as ensuring there is no direct, electrical connection between the positive and negative electrodes. A cost analysis for the alumina will be highly dependent on the geometry used because machining costs will be different depending on whether the sheath is rectangular, circular or otherwise. For the present work, unit prices will be based off of simple, cylindrical alumina tubes. Unlike the electrolytes, this work will assume that the sheaths are purchased from a vendor because it is not clear that a large enough savings can be gained from in-house production. Calculations from prices at (52) show that industrial, cylindrical, alumina tubes (both ends open) cost around $150/kg. The website states that discounts are given for orders of even 10 tubes, so large savings can be expected if ordering on a very large scale. As such, a bulk discount of 30% will be used, putting the price at $105/kg. These savings are based on the idea that negotiations can be made for a continuous supply of very large quantities of tubes. This kind of guaranteed business is favored by suppliers and usually results in significant savings off of retail price. For this model, the sheath was assumed to have a thickness of 0.5 cm, resulting in storage costs of less than $32/kWh. Ultimately, these prices result in the sheath being the most expensive part of the cell construction. This is not surprising due to the fact that alumina products are often very expensive. It would be useful to obtain more accurate quotes for these components to allow a better estimate of the cost it brings to the cell.

4.2.4 Cell Construction

The next level of costs involves the actual construction of the cells. This mainly includes labor costs of the manufacturing employees, but it will also encompass less significant components like screws, bolts and fasteners. As a preliminary estimate, these costs will be assumed to add 10% to the cost of the solid state materials (i.e. those excluding the storage medium). The complete storage cost for a cell will vary based on the battery output, but the range for the chemistries considered is between \$35 - \$50/kWh.

4.3 Battery Enclosure

The costs of battery enclosures are very difficult to generalize across different storage technologies since most facilities are custom built to fit one particular application, yet they often make up a significant portion of the final cost. As is customary when estimating costs, a conservative approach will be taken to set an upper limit by designing the structure around the chemistry with the least energy output – NaBi.

At 0.66 V, many more NaBi cells will be needed to provide the appropriate voltage than with something like LiSb. For a system with a maximum of 600 V, there will need to be 909 cells connected in series. These cells will be stacked into towers, which will be set in an array of five rows. Assuming 15 cells per tower, there will be about 60 towers arranged in 5 rows of 12. Based on the assumptions made earlier, each cell will have dimensions of 3 x 1 x 0.29 m which means each tower will be 4.3 m high. Leaving a space of 20 cm between all sides of the towers results in a footprint of 179 m^2.

An EPRI study that investigated the costs associated with several battery projects included a lead-acid system rated at 1 MW and 1.4 MWh (Metlakatla BESS) that was housed within a 40 x 70 ft structure at a cost of \$683,566 (1997 USD). This consisted of the building and engineering of the general structure (53). Using this cost, adjusted for inflation, the footprint cost of an LMB enclosure can be estimated at \$5,000/m^2, which results in a total cost of \$895,000, across all chemistries. It should be noted again that this is for one particular arrangement of cells and the cost will vary based on how they are arrayed.

4.4 Power Conversion System

Finally, one of the most important costs associated with building an energy storage facility is that of the PCS. The PCS acts as a rectifier (converting AC into DC) while the storage subsystem charges and it acts as an inverter (converting DC into AC) when the subsystem is discharged. Units are usually rated based on the power they are built to handle and prices, for comparison purposes, are often cited in \$/kW. Similar to many other commercial products, including a few in this analysis, PCS units also benefit from economies of scale relative to their power ratings. In other words, their unit cost in \$/kW decreases as their power rating increases. Figure 4.5 shows this relation using the facilities studied in the Sandia report.

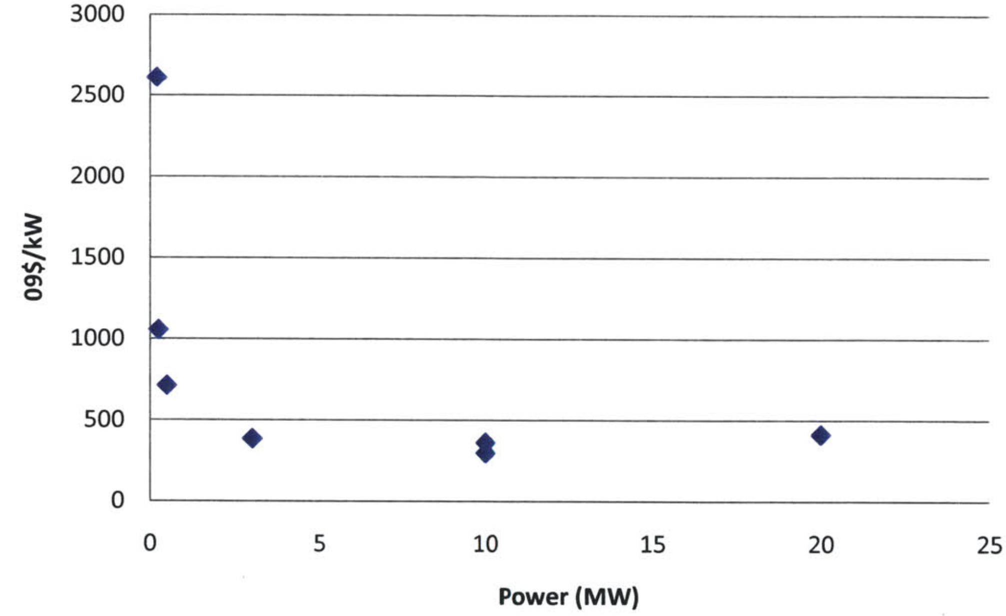


Figure 4.5: Economies of scale for power conversion systems using results from **(54)**.

It is apparent from the graph that high power installations enjoy cheaper unit costs for their PCS. Unfortunately, battery chemistry dictates what the cell voltage will be. These cells are then linked by networks of series and parallel connections to form modules. The modules can then be connected and a battery system is made with a nominal voltage based on how the sub-units were linked. This can pose a problem for technologies, like the LMB, with low voltages who may want to take advantage of the PCS economics. It would be inefficient, of course, to purchase the largest power-rated converter if there would be unused capacity. If an LMB system wanted to maximize the power of a PCS, there are two obvious ways to do so: increase the voltage across the system or increase the current through it.

Technically, performing either of these would successfully decrease the per-kilowatt cost of the PCS, but the necessary changes would trickle into other costs.

Power converters are current limited and their rating is dictated by the unit's ability to dissipate the heat generated by the system current (54). Since a system's power goes as the square of the current passing through it ($P = I^2R$) a slight increase in current can result in a large power gain and, consequently, larger amounts of heat being generated. This has implications for other system costs, especially the balance of plant. This additional amount of heat will require increased cooling efforts which could range from simply increasing the size of the PCS storage structure to implementing more advanced cooling methods. In addition, the increased current could require more durable wiring. Not to mention charging and discharging a battery at higher rates can severely limit its storage capacity.

The other method of increasing power – raising voltage – can only be accomplished by adding more storage subsystems. As mentioned, a cell's voltage is determined by its chemistry and the only way to increase the potential is by connecting more cells in series (voltage is additive in series) and the incremental costs here are obvious. More cells will need to be built, more structures will be needed to house the additional cells, more wiring will be required to connect them, etc. This is a particular problem in the design of an LMB facility because even the most promising chemistries have potentials of little over one volt. For a given power rating, lower voltages need higher current which increases losses due to inefficiencies in the conductive medium. Increased resistive heating also requires larger BOP costs (55). Ultimately, PCS designs must be made where the cheapest available unit for that application may not be the most optimal since costs will increase elsewhere.

As expected, prices vary widely for power converters depending on the exact application and while they are a small part of the total system, physically, the PCS actually contributes a significant amount to the overall cost as shown in the summary data in Table 4.2 from the Sandia plants.

Power (MW)	Cost* (/kW)
0.25	$1,056
0.2	$2,613
0.5	$713
3	$387
20	$414
10	$299
10	$366

Table 4.2: Summary of PCS costs in the Sandia study (54). *Costs are in 2009 dollars

Unlike most technologies, the prices for power converters are not expected to decrease significantly. Currently, the price of power semiconductor devices is falling at a rate of about 2-5% annually (56). The Sandia report, published in 1995, expects prices for PCSs used in energy storage to fall by only 10%, with the majority of price reduction coming from increased production volumes once the applications become more prevalent. The Sandia study found prices to be around $300/kW (in 1995). In a 2002 EPRI report, the average price for a PCS in a grid-interactive system was found to be $280/kW (42). The book "Energy Storage: A Nontechnical Guide" was published in 2006 and says prices range from $100-$200/kW for storage applications (57), which is a much larger drop than the Sandia report had anticipated. Many of the applications addressed in these studies, however, were characterized by fairly high power ratings, which means their prices fell on the low part of the pricing curve. The LMB is expected to have a power rating of between 300 kW and 1 MW, meaning it will not realize the full benefit of the PCS pricing curve.

In order to obtain a reasonable estimate for the lower power LMB system, a regression analysis similar to that performed on the electrolyte salts can be used. Using the same data from Figure 4.5, it appears that again a power law regression should provide a decent fit, and it does as shown in Figure 4.6.

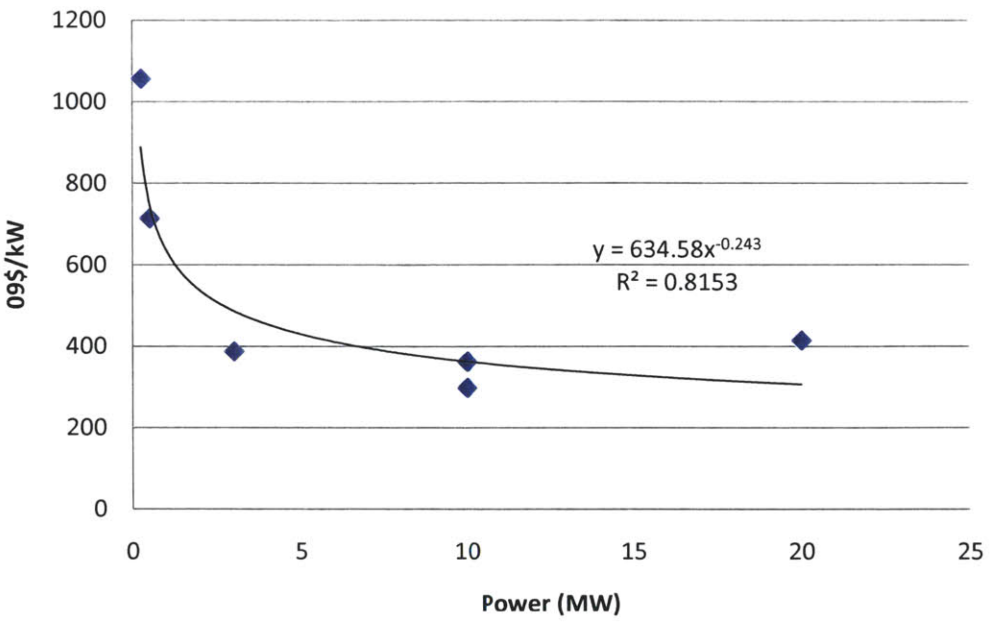


Figure 4.6: Power law regression on PCS data from Sandia report (54)

The first data point from the original graph was excluded because of the extreme price difference from the other units. The Sandia report notes that this particular system was "over engineered in many respects," which explains why the cost is so high. Consequently, that point was not considered realistic for the purposes of this analysis. Interestingly, the regression shows an exponent of -0.24, very similar to those obtained in the electrolyte analysis. One potential issue with using this data is the fact that they are quite old, some even from the 1980s, and so they may not accurately represent today's prices. With that in mind, communication was made with a team at Raytheon who provided the following prices: \$500-\$750/kW for power ratings between 300 kw and 500 kW. If these new prices were included in the previous graph, they would actually fall well in line with the old data as seen by the red prisms in Figure 4.7.

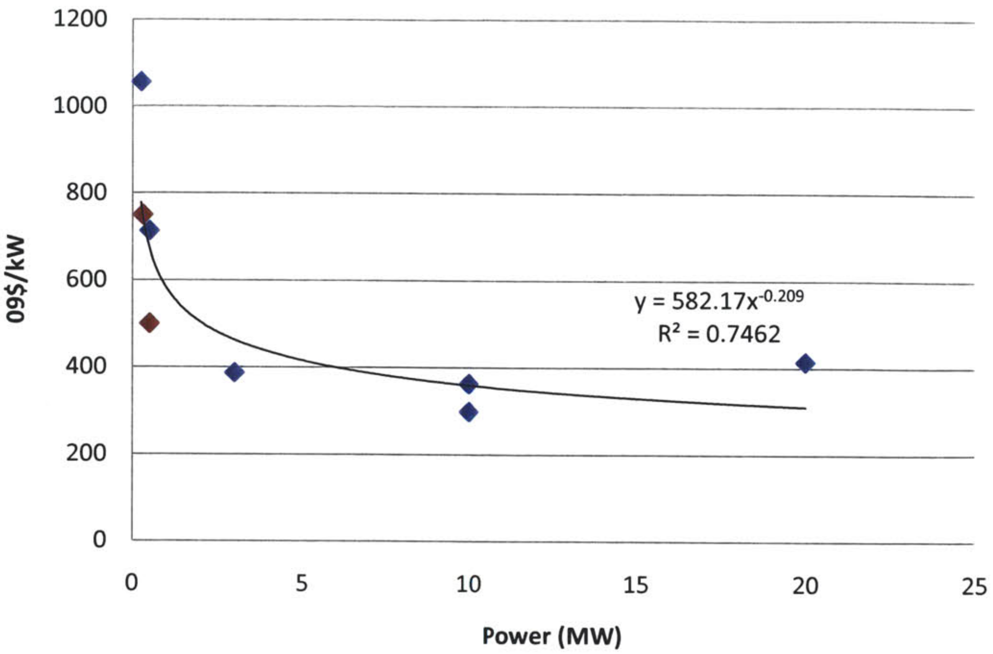


Figure 4.7: Power law regression performed with new PCS prices from Raytheon (55)

Not only do the new data fit well with the old prices, but they also yield a power law regression with an exponent consistent with those found previously (equal to -0.21). These results, from the salts and PCS, are very interesting and almost imply an inherent law in pricing for economies of scale, but that analysis is best left to an economist.

Taking an optimistic view for an LMB system, a power rating of 1 MW will be assumed. According to the first regression, this results in a unit price of about $635/kW. The new regression implies a price of $582/kW. Splitting the difference, the PCS unit for the LMB will be set at $600/kW, or $75/kWh for an 8-hour discharge.

One potential saving grace for PCS costs may come in the form of modularization. Modular PCSs would consist of several smaller units networked in parallel and programmed to handle the same power rating as one larger unit. This would have two sizable benefits for storage facilities. First, small, modular units are ideal for mass production, which would drastically reduce their production costs and their prices. The second benefit is redundancy, which is a term used to describe the presence of multiple components performing the same task. Having redundancy among a PCS acts as a fail-safe for the entire system because if one unit happens to give out, there are always others to keep the system online, though at a reduced voltage. Whether these kinds of savings can be realized remains to be seen. In the realm of battery energy storage, no two technologies are alike and they all require different system designs, which is antithetic to the idea of mass production.

5. LMB Manufacturing

After including elements from the previous chapter, a cost model can now be used to project the total storage costs of a liquid metal battery facility. A detailed cost model will help compare associated expenses for various battery chemistries by allowing customization of battery size, electrode metals and electrolytes. Although the model may not provide an exact picture of the costs that will be incurred when actually building a facility, it will be useful in determining which chemistries are viable and which should be avoided all together.

In this example, the LMB will be used for renewable energy storage and will be rated for an 8-hour discharge. The model is very flexible, allowing the user to change many different parameters, but for the purposes of this study a few assumptions will be made in addition to the cost assumptions laid out in the previous chapter. Since this analysis is only concerned with the storage costs ($/kWh), the size of the cell does not matter but will mimic the expected size, which will have an active area of 22,400 cm^2 (280 cm x 80 cm)and a height of 7 cm. The cell enclosure will have a thickness of 10 cm on all sides. The current density will be set to 0.5 A/cm^2 to more accurately represent the LMB applications. The thickness of the electrolyte will be set at 1 cm. In general, a thinner electrolyte allows for faster kinetics but making it too thin can increase the possibility of shorting the cell. Current tests in the LMB lab use a 1-cm thick molten salt layer in 1 A-h cells but little work has been done to ascertain the appropriate thickness of a large cell.

The last assumption applies to the electrolyte. The model is built to accommodate all possible permutations of electrolyte mix (limited to the eleven salts discussed) which makes it nearly impossible to form a consistent comparison. As a result, the electrolyte for all batteries will be 100% LiBr. The costs associated with this particular salt are representative of the average for all the salts in the study. It is important to note that LiBr may not work in all batteries and there is also no condition under which an actual electrolyte would consist of only one salt.

5.1 Battery Comparisons

The first study that can be performed is simply comparing the storage costs across various battery chemistries. Using the assumptions put forth, Table 5.1 shows the results from the cost model. The first column shows the energy stored by a single cell. The column labeled "Total Cost" represents the storage cost that can be expected from a complete LMB system. The operating parameters used are as follows: each cell has a cross-sectional area of 22,400 cm^2; the system has a current density of 0.50 A/cm^2; 8-hour discharge.

Battery	**Energy Stored (kWh/cell)**	**Electrode Cost ($/kWh)**	**Total Cost ($/kWh)**
Ca-Bi	38.1	231	1,264
Na-Bi	29.6	372	1,682
Sr-Bi	44.8	146	1,035
Li-Bi	36.4	486	1,563
Ca-Sb	45.2	37	919
Na-Sb	33.6	58	1,219
Sr-Sb	44.8	34	923
Li-Sb	41.7	62	1,013

Table 5.1: Cost comparison for various LMB systems

The column labeled "Electrode Cost" can also be considered the cost of the active materials. Based on the $100/kWh target, it is clear that none of the bismuth chemistries will satisfy this metric. This was to be expected considering the high cost of bismuth. It also informs the fact that the LMBs impact on the bismuth market may cause prices to rise even further, making bismuth an even more terrible option. Compared to the other bismuth batteries, the Sr-Bi couple is surprisingly cheap. This is due to the fact that a lot of strontium can transfer into the bismuth electrode because of their alloying properties. In other words, there is a lot of available capacity.

In stark contrast to the bismuth couples, antimony electrodes result in cheap batteries that even satisfy the $100/kWh target. From this analysis it is apparent that antimony electrodes provide cheaper batteries where the Sr-Sb couple is the cheapest alternative of all the couples examined.

Adding this new cost information to the costs available with current technologies, the LMB, even with the most expensive chemistries, falls well within an affordable range as shown in Table 5.2. Considering that the LMB costs include the cost of the expensive electrolyte, the system has the potential to become much cheaper than competing technologies once the salt costs are brought down. If the electrolyte costs are brought down to a level comparable to those of current technologies (i.e. from $800/kWh to $20/kWh), the benefits of an LMB become even more apparent.

Technology	**Total system cost ($/kWh)**	**Reference**
LA	750-1000	(11)
NaS	750-1500	(11)
ZEBRA	571	(58)
Li-ion	1500-3500	(11)
LMB-LiSb	1000	This work
LMB-LiSb[a]	215	This work

Table 5.2: System cost comparison of LMB with current battery technologies.

a) Assuming a "cheap" electrolyte of $20/kWh

5.2 LMB Impact

The impact that LMB manufacturing would have on the markets for the electrode metals was another important consideration addressed in this study. It was already established that no impact would be made on the cation metals because the LMB would use so little compared to projected world production. The following table quantifies the impact that LMB manufacturing may have on the markets for bismuth and antimony. In this case, "impact" is defined as LMB annual demand as a percent of annual world production.

Year	Bi Impact	Sb Impact
2015	123%	3.6%
2016	190%	5.6%
2017	251%	7.4%
2018	307%	9.2%
2019	360%	10.8%
2020	405%	12.3%
2021	702%	21.4%
2022	781%	35.5%
2023	1140%	39.2%

Table 5.3: LMB impact as a percent of annual world production for a SrBi cell and LiSb cell. See Appendix B.

As the table shows, the LMB demand will put an enormous strain on projected bismuth supply but will fit in nicely with that of antimony. This is another argument for the use of antimony as the positive electrode.

While still much smaller than that of bismuth, the antimony impact is increasing and actually starts to become significant by 2022 at over 30%. This seems to warrant caution at first, but looking back to the analysis of lithium, it may actually be a good sign. Table 5.4 shows how the impacts of lithium (real data) and antimony (projections) progress over a 9-year period. The lithium impact is calculated as the amount of lithium used in batteries as a percentage of total consumption. This is technically different from the definition used in this report where impact is found as a percent of world production. However, assuming a stable market, it is reasonable to use world production as a proxy for world consumption.

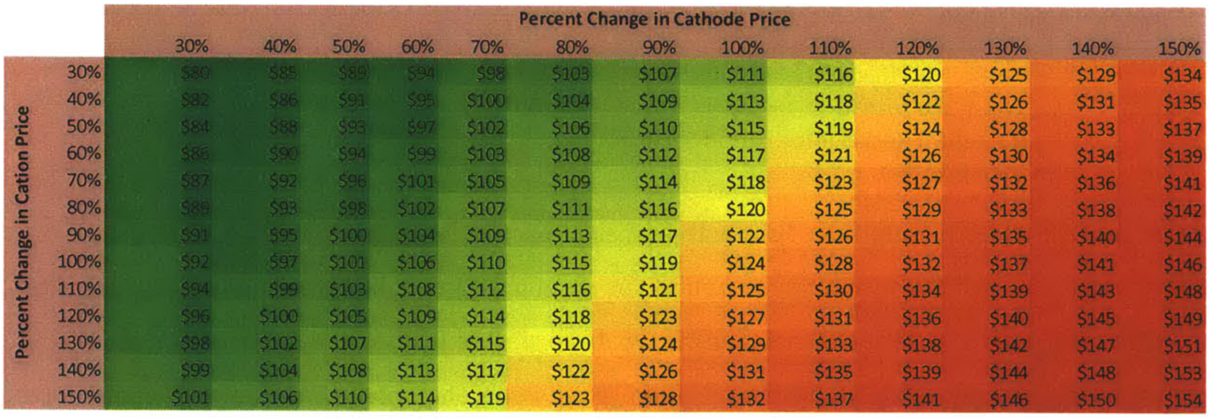
	Lithium Impact [1]	Antimony Impact [2]
Year 0	6%	4%
Year 8	20%	36%

Table 5.4: Comparison of lithium and antimony impacts. Year 0 represents 2000 for lithium and 2015 for antimony
[1] Data from Roskill Information Services (26)
[2] Data from this work

This table shows that both metals start out with a small impact but then grow to quite a large significance at the end of the selected time period. As mentioned in the lithium analysis, the dynamics of lithium in response to batteries is analogous to what is expected from the LMB, particularly in the case of antimony, and this table supports that vision. In addition, this should provide more confidence in the use of antimony as an electrode material because even thought lithium's impact grew during that period, the price of lithium carbonate decreased.

6. Conclusions

Following the analysis in this report, it is clear that in order to ensure an economically feasible product the LMB should be made with an antimony positive electrode. Furthermore, based on the cost of active materials as well as the overall storage cost, pairing the antimony electrode with a strontium negative electrode results in the cheapest battery of all the couples considered in this study. Although, the other negative electrode candidates also result in reasonable active material costs when used with antimony (i.e. less than $100/kWh). The one caveat with the Li-Sb battery is the effect that other battery industries may have on the lithium price, specifically the introduction of electric vehicles using lithium-ion battery packs. Due to the high energy density of the Li-Sb and Sr-Sb couples, much less antimony is needed relative to lithium than in other chemistries. This means that the battery becomes more susceptible to changes in the price of lithium than it would be with other mobile species like sodium and calcium. An important aspect to consider then is how sensitive the battery cost will be to changes in the prices of both metals. Figure 6.1 lends some insight to those effects.



	Percent Change in Cathode Price												
Percent Change in Cation Price	30%	40%	50%	60%	70%	80%	90%	100%	110%	120%	130%	140%	150%
30%	$80	$85	$89	$94	$98	$103	$107	$111	$116	$120	$125	$129	$134
40%	$82	$86	$91	$95	$100	$104	$109	$113	$118	$122	$126	$131	$135
50%	$84	$88	$93	$97	$102	$106	$110	$115	$119	$124	$128	$133	$137
60%	$86	$90	$94	$99	$103	$108	$112	$117	$121	$126	$130	$134	$139
70%	$87	$92	$96	$101	$105	$109	$114	$118	$123	$127	$132	$136	$141
80%	$89	$93	$98	$102	$107	$111	$116	$120	$125	$129	$133	$138	$142
90%	$91	$95	$100	$104	$109	$113	$117	$122	$126	$131	$135	$140	$144
100%	$92	$97	$101	$106	$110	$115	$119	$124	$128	$132	$137	$141	$146
110%	$94	$99	$103	$108	$112	$116	$121	$125	$130	$134	$139	$143	$148
120%	$96	$100	$105	$109	$114	$118	$123	$127	$131	$136	$140	$145	$149
130%	$98	$102	$107	$111	$115	$120	$124	$129	$133	$138	$142	$147	$151
140%	$99	$104	$108	$113	$117	$122	$126	$131	$135	$139	$144	$148	$153
150%	$101	$106	$110	$114	$119	$123	$128	$132	$137	$141	$146	$150	$154

Figure 6.1: Sensitivity table showing effects of price changes for both electrode metals on LMB active cost (Li-Sb couple)

This figure shows the resulting storage cost of the active materials for several possible price increases in cathode (antimony) and cation (lithium). According to the chart, if both antimony and lithium experience a 100% increase in price, for example, the active cost of an LMB system based on that couple will be around $120/kWh, assuming all other costs stay the same, which is still cheaper than some of the current battery technologies shown in Table 1.1. Ultimately, this sensitivity chart shows that the Li-Sb battery can sustain very large price increases in the metals before becoming prohibitively expensive. All of the percentage changes illustrated are large, much larger than would be expected based on the LMB impact that has been discussed. This analysis has shown that the Li-Sb couple not only provides good storage capabilities but also that it can be very cost-effective. The active materials come in well under the target of $100/kWh ($62/kWh) and total system costs put it on par with competing technologies. Furthermore, the Li-Sb couple represents the most expensive antimony chemistry, which means the other materials have even more reasonable costs.

Unfortunately, the cheap cost of the Li-Sb electrodes is necessary to cover the high cost of the ultra-pure, anhydrous electrolyte. Cost savings are possible by refining the salts in-house rather than purchasing from a supplier (even at bulk discounts) but the energy costs are still significant – on the order of $100/kWh. The best hope for alleviating this effect is to investigate the use of lower purity salts for the electrolyte. One example of how lower-purity salts may not be extremely detrimental to the cells is the deposition potentials for the different metals. Lithium deposits at a much more cathodic potential than does sodium or potassium, for instance. This means that for sodium or potassium-based batteries, the electrolytes can contain lithium impurities because at the potentials used by the cell, the lithium ions will not deposit onto the electrodes and will simply remain as ions in the melt. Of course this study has shown that a sodium battery is not feasible, the principle remains: low-purity electrolytes can be designed based on the relative deposition potential of the impurities and electrode materials.

The LMB also satisfies many of the viability metrics discussed in chapter 1 (not enough cells have been tested to determine a reliable lifetime). If the electrolyte cost problem can be solved, the LMB can offer a wonderfully cheap and environmentally benign solution for the storage of renewable, intermittent energy sources.

Works Cited

1. **U.S. Energy Information Administration.** *Annual Energy Review 2009.* 2009.

2. **Little, A.** Our electric grid is no match for our new green energy plans. *Grist.* [Online] October 2009. http://www.grist.org/article/benefits-of-large-scale-energy-storage.

3. **Makansi, Jason and Kristina.** A shock absorber for the grid to enhance efficiency, reliability, and security. *Grist.* [Online] July 2007. http://www.grist.org/article/2009-10-13-our-old-electric-grid-is-no-match-for-our-new-green-energy-plans.

4. **National Renewable Energy Laboratory.** Boston Radiation Data. [Online] www.nrel.gov.

5. *Electrical energy storage - a review of technology options.* **Price, A.** s.l. : Institution of Civil Engineers, 2005. pp. 52-58.

6. **Electricity Storage Association.** CAES - Compressed Air Energy Storage. *ESA.* [Online] electricitystorage.org/tech/technologies.htm.

7. *Lead-acid battery energy-storage systems for electricity supply networks.* **Parker, C.** 1-2, s.l. : Elsevier, 2001, Journal of Power Sources, Vol. 100, pp. 18-28.

8. **NGK Insulators, LTD.** Reference Installations. *NGK Insulators, LTD.* [Online] www.ngk.co.pj/english/products/power/nas/installations/index.html.

9. **Wertheimer, L.** In Texas, One Really Big Battery. *www.npr.org.* [Online] April 2010.

10. *Advances in ZEBRA batteries.* **Dustmann, C.H.** 1-2, s.l. : Elsevier, 2004, Journal of Power Sources, Vol. 127, pp. 85-92.

11. *Utility Scale Applications of Energy Storage.* **Oudalov, A., Buehler, T. and Chartouni, D.** Atlanta : IEEE, 2008.

12. *The sodium/nickel chloride (ZEBRA) battery.* **Sudworth, J.L.** 1-2, s.l. : Elsevier, 2001, Journal of Power Sources, Vol. 100, pp. 149-163.

13. *Energy Storage Technologies for Utility Scale Intermittent Renewable Energy Systems.* **Cavallo, A.J.** s.l. : American Society of Mechanical Engineers, 2001, Journal of Solar Energy Engineering, Vol. 123, pp. 387-389.

14. **Buiel, E.R.** *Advances in Battery Development for Vehicles (Advanced Lead Acid and Li-ion), Near Term Electrification of Transportation System, Feasibility of Near Term Retrofitting of Inefficient Vehicles to EV's.* s.l. : Axionx Power International, Inc., 2008.

15. **Kamibayashi, M.** *Advanced Sodium-Sulfu (NAS) Battery System.* s.l. : Tokyo Electric Power Company, Japan.

16. *ZEBRA battery meets USABC goals.* **Dustmann, C.H.** 1, s.l. : Elsevier, 1998, Journal of Power Sources, Vol. 72, pp. 27-31.

17. *Batteries, 1972 to 2002.* **Brodd, R.J. et al.** 3, s.l. : Electrochemical Society, 2004, Journal of the Electrochemical Society, Vol. 151, pp. K1-K11.

18. **U.S. Energy Information Association.** *Annual Energy Outlook 2010.* 2010.

19. **Notin, M.** Bismuth-Calcium Binary Phase Diagram. *Alloy Phase Diagrams Center.* [Online] 1995. www1.asminternational.org.

20. **GroupSadoway.** Preliminary results.

21. **U.S. Geological Survey.** Bismuth. *Minerals Yearbook.* 1971-2008.

22. —. Lead. *Minerals Yearbook.* 1971-2008.

23. **Schoenung, S.M. and Hassenzahl, W.V.** *Long-vs. Short-Term Energy Storage Technologies Analysis.* s.l. : Sandia National Labs, 2003. SAND2003-2783.

24. **U.S. Geological Survey.** Antimony. *Minerals Yearbook.* 1971-2008.

25. **The World Bank.** GDP growth (annual %). *The World Bank.* [Online] data.worldbank.org/indicator/NY.GDP.MKTP.KD.ZG.

26. **Roskill Information Services, LTD.** *The Economics of Lithium.* s.l. : Roskill Information Services, LTD., 2009.

27. **U.S. Geological Survey.** Strontium. *Minerals Yearbook.* 2009.

28. —. Strontium. *Minerals Yearbook.* 1971-2008.

29. —. Lithium. *Mineral Commodity Summaries.* 2011.

30. —. Lithium. *Minerals Yearbook.* 1971-2008.

31. Lithium. *www.metalprices.com.* [Online]

32. **U.S. Geological Survey.** Lithium. *Minerals Yearbook.* 1998.

33. —. Lithium. *Minerals Yearbook.* 2006.

34. **Carlin, J.** USGS Specialist. *Personal communication.* March 2011.

35. **Alonso, E.** MIT ESD Researcher. *Personal communication.* March 2011.

36. **U.S. Geological Survey.** Sulfur. *Minerals Yearbook.* 2008.

37. **Henriksen, G. et al.** *Materials Cost Evaluation Report for High-Power Li-ion HEV Batteries.* s.l. : Argonne National Labs, 2003. ANL-03/5.

38. **FactSage.** NaCl-NaI. *FTsalt - FACT Salt Phase Diagrams.* [Online] www.crct.polymtl.ca/fact/documentation/FTsalt/FTSalt_Figs.htm.

39. *Drug Discovery Approach to Breakthroughs in Batteries.* **Werbos, P., Sadoway, D.R. and Delgass, W.N.** 2008.

40. **Elements, American.** *Personal communication.* November 2010.

41. *Magnesium for Automotive Applications: Primary Production Cost Assessment.* **Das, S.** November 2003, Journal of Materials, pp. 22-26.

42. **Eckroad, S.** *Handbook of Energy Storage for Transmission or Distribution Applications.* s.l. : Electric Power Research Institute, 2002. 1007189.

43. **Effenberg, G.** Iron-Lithium Binary Diagram. *Alloy Phase Diagrams Center.* [Online] 1990. www1.asminternational.org.

44. **Schurmann, E.** Calcium-Iron Binary Diagram. *Alloy Phase Diagrams Center.* [Online] 1987. www1.asminternational.org.

45. **Ireland, L.** Steelmakers show industrial Germany is weathering downturn. *Reuters Online.* [Online] http://blogs.reuters.com/globalinvesting/tag/steelmaking/.

46. *Metalprices.* [Online] www.metalprices.com.

47. **Pei, B.** Iron-Antimony Binary Diagram. *Alloy Phase Diagrams Center.* [Online] 1995. www1.asminternational.org.

48. **U.S. Geological Survey.** Graphite, Natural. *Minerals Yearbook.* 2009.

49. **Bradwell, D.** *Technical and Economic Feasibility of a High-Temperature Self-Assembling Battery.* Department of Materials Science and Engineering, Massachusetts Institute of Technology. 2006. M.Eng. Thesis.

50. **Mineral Information Institute.** Mineral Photos - Perlite. *Mineral Information Institute.* [Online] http://www.mii.org/Minerals/photoperlite.hmtl.

51. **Wall Street Journal.** HG Copper Apr 1. *MarketWatch.* [Online] www.marketwatch.com.

52. **GraphiteStore.** Alumina Tubes - Open Both Ends. *GraphiteStore.* [Online] http://www.graphitestore.com/items_list.asp/action/prod/prd_id/348/cat_id/48.

53. **EPRI.** Energy Storage Project Activities. [Online] disgen.epri.com/downloads/Storage_Projects_Demos_v092710.xls.

54. **Akhil, A. et al.** *Cost Analysis of Energy Storage Systems for Electric Utility Applications.* s.l. : Sandia National Labs, 1997. SAND97-0443.

55. **Bergeron, B.** Raytheon Engineer. *Personal communication.*

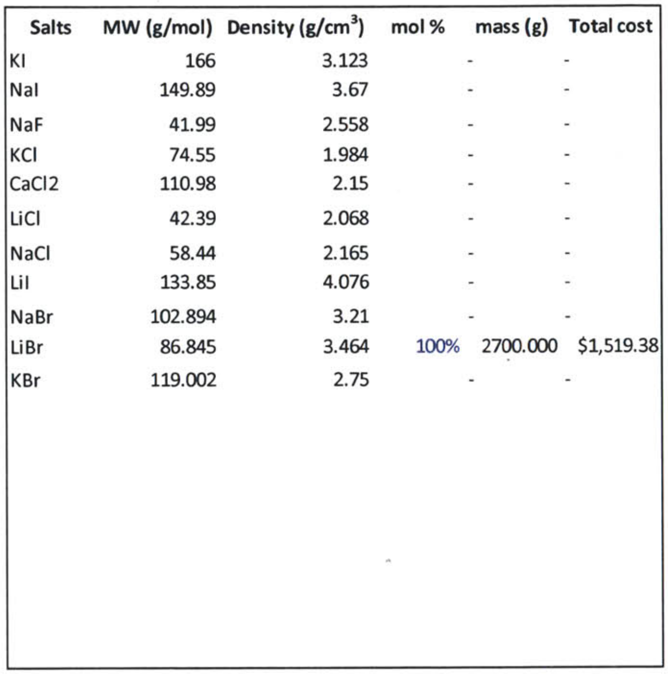
56. **Blaabjerg, F. and Chen, Z.** *Power Electronics for Modern Wind Turbines.* s.l. : Morgan & Claypool Publishers, 2006.

57. **Baxter, R.** *Energy Storage: A non-technical guide.* s.l. : Penwell Corporation, 2006.

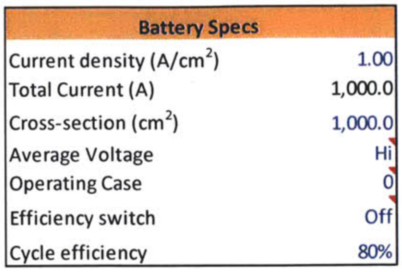
58. **Supplier.** *Personal Communication.* March 2011.

59. *Electric Vehicle Using a Combination of Ultracapacitors and ZEBRA Battery.* **Dixon, J. et al.** 3, s.l. : IEEE, 2010, IEEE Transactions on Industrial Electronics, Vol. 57, pp. 943-949.

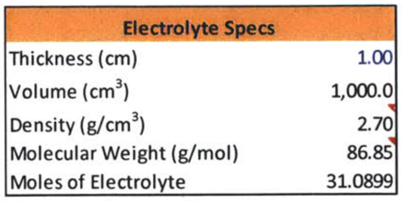
Appendix A: Battery Cost Model



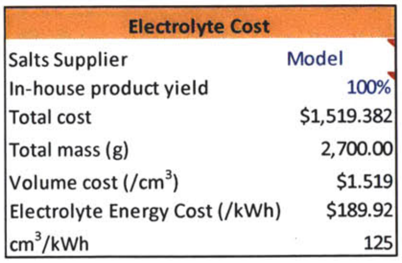
Salts	MW (g/mol)	Density (g/cm^3)	mol %	mass (g)	Total cost
KI	166	3.123		-	-
NaI	149.89	3.67		-	-
NaF	41.99	2.558		-	-
KCl	74.55	1.984		-	-
CaCl2	110.98	2.15		-	-
LiCl	42.39	2.068		-	-
NaCl	58.44	2.165		-	-
LiI	133.85	4.076		-	-
NaBr	102.894	3.21		-	-
LiBr	86.845	3.464	100%	2700.000	$1,519.38
KBr	119.002	2.75		-	-



Battery Specs	
Current density (A/cm^2)	1.00
Total Current (A)	1,000.0
Cross-section (cm^2)	1,000.0
Average Voltage	Hi
Operating Case	0
Efficiency switch	Off
Cycle efficiency	80%



Electrolyte Specs	
Thickness (cm)	1.00
Volume (cm^3)	1,000.0
Density (g/cm^3)	2.70
Molecular Weight (g/mol)	86.85
Moles of Electrolyte	31.0899

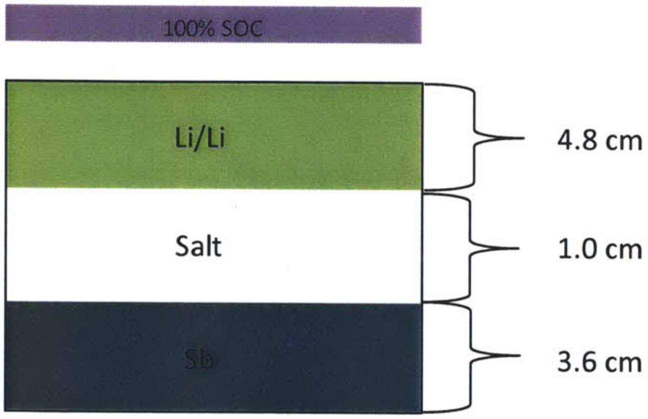


Electrolyte Cost	
Salts Supplier	Model
In-house product yield	100%
Total cost	$1,519.382
Total mass (g)	2,700.00
Volume cost (/cm^3)	$1.519
Electrolyte Energy Cost (/kWh)	$189.92
cm^3/kWh	125

This model was developed using Microsoft Excel. Any values in blue font can be changed by the user and allow the examination of infinite permutations of battery chemistries and operating parameters. The target output is a breakdown of system storage costs in \$/kWh and is shown in the next page. The metal prices that were used are shown in the following table. Prices for names with one asterisk were taken from www.metalprices.com and those with two were estimated based on their similarities to magnesium metal (ore and extraction methods)

Li*	62.207
Na**	2.5
Mg*	5.00
Ca**	5.00
Sr**	5.00
Pb*	2.23
Sb*	9.09
Bi*	20.83

Electrodes		
Cation	Li	
Cation mass (g)		2,076.7
Cation cost		$129.187
Cathode	Sb	
Cathode mass (g)		24,237.5
Cathode volume (cm^3)		3,619.2
Cathode cost		$220.416
Anode	Li	
Anode mass (g)		519.2
Anode volume (cm^3)		4,807.2
Anode cost		$32.297
Battery Name	*LiSbH5*	
Average Voltage (V)		1
Power (W)		1,000
Energy stored (Wh)		8,000
Energy density (Wh/kg)		298
Total Electrode Volume (cm^3)		8,426.4
Total Electrode Mass (g)		26,833.5
Total Electrode Cost		$381.900
Electrode Energy Cost (/kWh)		$48



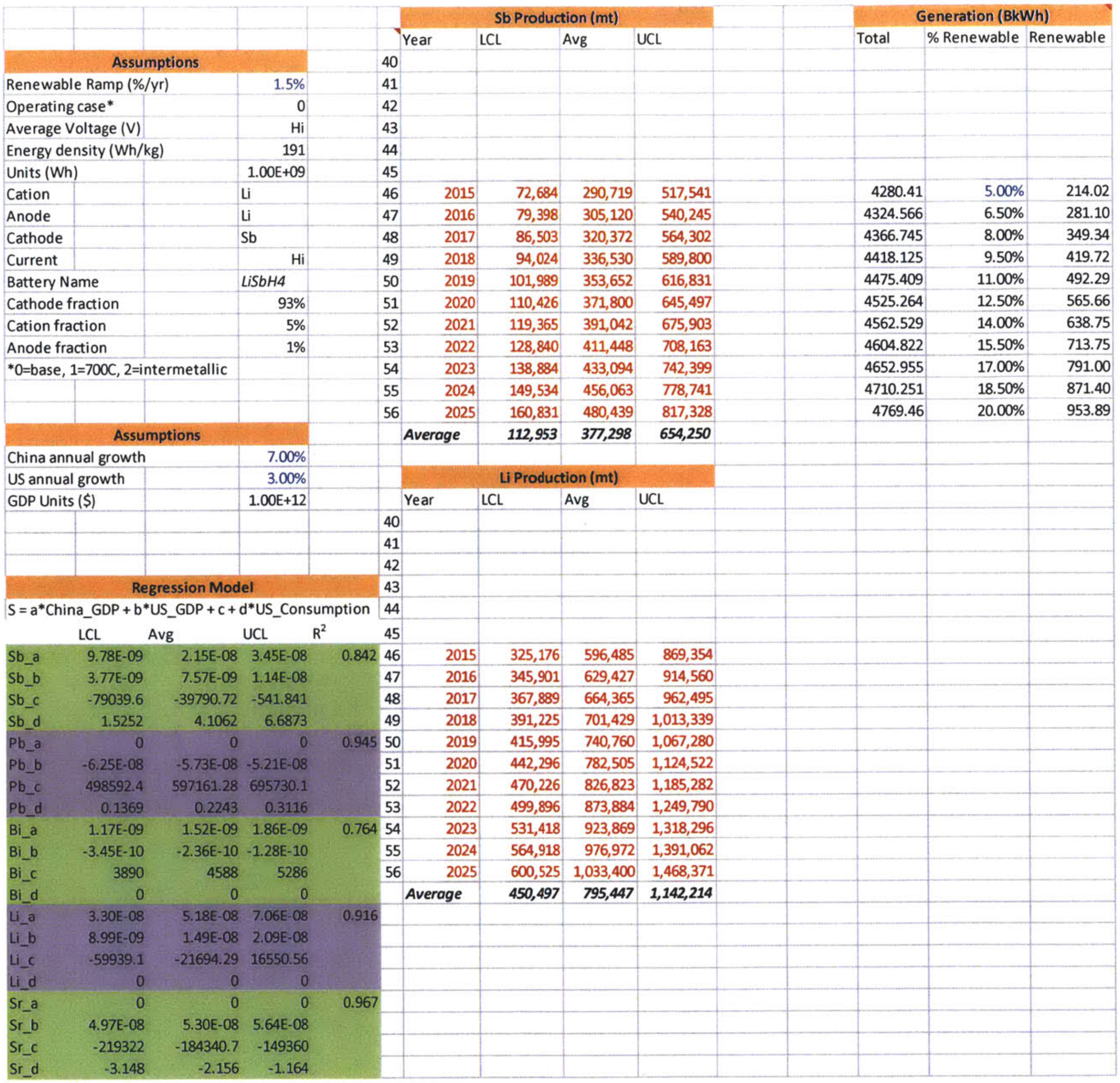
Active materials (including electrolyte)

Total cost	$1,901.28
Energy cost (/kWh)	$238
Total volume (cm^3)	9,426.4
Active height (cm)	9.4
Volume cost (/cm^3)	$0.20
cm^3/kWh	1,178

Complete system

Electrode cost (/kWh)	$47.74
Electrolyte cost (/kWh)	$189.92
Enclosure cost (/kWh)	$105.12
Construction cost (/kWh)	$10.51
PCS cost (/kWh)	$31.25
BOP % total	*40%*
BOP cost (/kWh)	$97.92
Total cost (/kWh)	**$482.86**

Appendix B: Impact Projections



Assumptions	
Renewable Ramp (%/yr)	1.5%
Operating case*	0
Average Voltage (V)	Hi
Energy density (Wh/kg)	191
Units (Wh)	1.00E+09
Cation	Li
Anode	Li
Cathode	Sb
Current	Hi
Battery Name	*LiSbH4*
Cathode fraction	93%
Cation fraction	5%
Anode fraction	1%

*0=base, 1=700C, 2=intermetallic

Assumptions	
China annual growth	7.00%
US annual growth	3.00%
GDP Units ($)	1.00E+12

Regression Model

S = a*China_GDP + b*US_GDP + c + d*US_Consumption

	LCL	Avg	UCL	R^2
Sb_a	9.78E-09	2.15E-08	3.45E-08	0.842
Sb_b	3.77E-09	7.57E-09	1.14E-08	
Sb_c	-79039.6	-39790.72	-541.841	
Sb_d	1.5252	4.1062	6.6873	
Pb_a	0	0	0	0.945
Pb_b	-6.25E-08	-5.73E-08	-5.21E-08	
Pb_c	498592.4	597161.28	695730.1	
Pb_d	0.1369	0.2243	0.3116	
Bi_a	1.17E-09	1.52E-09	1.86E-09	0.764
Bi_b	-3.45E-10	-2.36E-10	-1.28E-10	
Bi_c	3890	4588	5286	
Bi_d	0	0	0	
Li_a	3.30E-08	5.18E-08	7.06E-08	0.916
Li_b	8.99E-09	1.49E-08	2.09E-08	
Li_c	-59939.1	-21694.29	16550.56	
Li_d	0	0	0	
Sr_a	0	0	0	0.967
Sr_b	4.97E-08	5.30E-08	5.64E-08	
Sr_c	-219322	-184340.7	-149360	
Sr_d	-3.148	-2.156	-1.164	

Sb Production (mt)

	Year	LCL	Avg	UCL
40				
41				
42				
43				
44				
45				
46	2015	72,684	290,719	517,541
47	2016	79,398	305,120	540,245
48	2017	86,503	320,372	564,302
49	2018	94,024	336,530	589,800
50	2019	101,989	353,652	616,831
51	2020	110,426	371,800	645,497
52	2021	119,365	391,042	675,903
53	2022	128,840	411,448	708,163
54	2023	138,884	433,094	742,399
55	2024	149,534	456,063	778,741
56	2025	160,831	480,439	817,328
	Average	***112,953***	***377,298***	***654,250***

Generation (BkWh)

Total	% Renewable	Renewable
4280.41	5.00%	214.02
4324.566	6.50%	281.10
4366.745	8.00%	349.34
4418.125	9.50%	419.72
4475.409	11.00%	492.29
4525.264	12.50%	565.66
4562.529	14.00%	638.75
4604.822	15.50%	713.75
4652.955	17.00%	791.00
4710.251	18.50%	871.40
4769.46	20.00%	953.89

Li Production (mt)

	Year	LCL	Avg	UCL
40				
41				
42				
43				
44				
45				
46	2015	325,176	596,485	869,354
47	2016	345,901	629,427	914,560
48	2017	367,889	664,365	962,495
49	2018	391,225	701,429	1,013,339
50	2019	415,995	740,760	1,067,280
51	2020	442,296	782,505	1,124,522
52	2021	470,226	826,823	1,185,282
53	2022	499,896	873,884	1,249,790
54	2023	531,418	923,869	1,318,296
55	2024	564,918	976,972	1,391,062
56	2025	600,525	1,033,400	1,468,371
	Average	***450,497***	***795,447***	***1,142,214***

This model, also developed in Microsoft Excel, uses regression analysis to project the future supply and future LMB demand of the metals selected for the cost model in Appendix A. The goal of this model is to estimate the impact that LMB demand will have on the metals' markets, indicating whether or not a particular candidate material is viable.

LMB Storage			LMB Demand (Cathode)		LMB % of annual production
% stored	Storage (BkWh)		Cumulative (mt)	Annual (mt)	
1.00%	2.14		10,458	10,458	3.6%
2.00%	5.62		27,472	17,014	5.6%
3.00%	10.48		51,213	23,740	7.4%
4.00%	16.79		82,041	30,828	9.2%
5.00%	24.61		120,282	38,242	10.8%
6.00%	33.94		165,849	45,566	12.3%
8.00%	51.10		249,707	83,858	21.4%
10.00%	71.37		348,780	99,073	24.1%
13.00%	102.83		502,491	153,711	35.5%
16.00%	139.42		681,307	178,816	39.2%
20.00%	190.78		932,258	250,951	52.2%
			Average	***84,751***	***20%***

LMB Demand (Cation)		LMB % of annual production
Cumulative (mt)	Annual (mt)	
597	597	0.1%
1,569	972	0.2%
2,925	1,356	0.2%
4,686	1,761	0.3%
6,871	2,184	0.3%
9,474	2,603	0.3%
14,264	4,790	0.6%
19,923	5,659	0.6%
28,703	8,780	1.0%
38,917	10,214	1.0%
53,252	14,335	1.4%

Appendix C: Electrolyte Salt Costs

	AA	AA Model	Bulk	In-House
KI	$2.12/g	$0.42/g	$22.60/kg	$0.21/g
KCl	$2.29/g	$0.75/g	$0.28/kg	$0.38/g
CaCl2	$5.25/g	$1.18/g	$0.31/kg	$0.59/g
NaF	$0.64/g	$0.02/g	$0.88/kg	$0.01/g
LiCl	$3.32/g	$0.81/g	$26.00/kg	$0.40/g
NaI	$2.47/g	$0.35/g	$31.92/kg	$0.17/g
NaCl	$2.43/g	$0.43/g	$0.02/kg	$0.22/g
NaBr	$3.34/g	$0.64/g	$12.89/kg	$0.32/g
KBr	$1.86/g	$0.40/g	$21.17/kg	$0.20/g
LiI	$2.95/g	$0.47/g	$199.20/kg	$0.23/g
LiBr	$2.82/g	$0.56/g	$29.31/kg	$0.28/g

Salt	Coeff	Exp
NaF	18.464	-0.507
NaI	16.118	-0.278
NaCl	13.471	-0.249
NaBr	17.838	-0.241
KCl	5.988	-0.15
KI	9.822	-0.229
LiCl	11.98	-0.195
LiI	19.386	-0.27
LiBr	12.951	-0.227
CaCl2	18.435	-0.199
KBr	6.434	-0.201

y = Ax^b
y - $/g
A - coefficient
b - exponent
x - quantity in grams

This model was developed in Microsoft Excel and is linked to the previous models to allow selection of any electrolyte. The four columns in the first box show the different pricing models allowed to be chosen. Here "AA" is the retail price obtained from Alfa-Aesar based on 1-kg quotes from the supplier. "AA Model" indicates prices determined by fitting a line to the commoditized graphs (like Figure 3.4) and using the parameters shown in the bottom box to calculate the expected price of a 1-ton quantity of the salt. The "Bulk" column consists of prices obtained either from bulk suppliers or USGS and "In-House" lists the expected costs of self-refining the salts instead of purchasing the pure materials from distributors.