

# Liquid Metal Battery for Energy Storage

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**Abstract—** *The world is shifting towards renewable energy sources as it is well known that we are running out of conventional sources. But renewable sources are seasonal they are not available constantly all the time. This brings us the need for storage devices capable of handling huge power grids. From considering the above factor we came up with a new type of battery called Liquid Metal Battery. These batteries are possible candidates for massive and economically feasible large-scale stationary storage and as such could be key components of future energy systems based mainly or exclusively on intermittent renewable electricity sources.*

*The project at hand focuses on the possible material selection for making the battery, Cell chemistry, modelling of battery voltage and finally making a physical working model of the Liquid Metal Battery. All these followed with obtaining the designed battery's performance characteristics, allowing for more insight. Finally, the main intention for the development of this battery is for powering huge loads like cities when a large deficit exists between power generation from renewable sources and demand. Thereby reducing the requirement for conventional sources.*

**Keywords—** *Cell Voltage, Anode material, Cathode Material, Electrolyte, Outer Casing, Deep Cycling, Open Circuit Voltage*

## I. INTRODUCTION (HEADING 1)

Now a day's more demand for electricity because the world is developing day by day and also reducing the Non-renewable sources like coal, fuel, and gas. That's why, the world is shifting toward the development and utilization of renewable generation have attracted more and more attention in recent years the renewable source, such as wind power, solar power, and hydropower generation. But these renewable energy sources are located away from the city Centre, leading to discontinuity of generation energy. It requires to development of a kind of large-scale energy storage with security, stability, and sureness. Batteries come across as like to be the best choice for energy

storage because of their high energy efficiency, but traditional batteries like Nickel-cadmium (Ni-cd), lithium-ion (Li-ion), and Nickel-metal Hydride (Ni-MH) are not able to meet the low-cost, high-power density and long-life demands. As opposed to the traditional battery. To invite the new liquid metal battery (LMB) consists of two liquid metal electrodes and a molten salt electrolyte, which will be separated into three layers of different metals and densities. In this way, the LMB avoids the diaphragm and the structure deformation during charge-discharge cycles, granting itself a considerable long lifetime. Besides, most electrode materials are abundant and low-cost, further reducing the LMB's cost. All of the above characteristics make the LMB a good candidate for large-scale energy storage in the power grid.

The deployment of large-scale energy storage systems could support the grid, smoothing out fluctuations by injecting or accepting power. This is particularly important for use with energy generated by intermittent renewables, such as wind and solar. For instance, it is illuminating to compare the normalized electricity demand with the theoretical supply from wind and solar generators, and Power Supplied by Battery System is shown in Fig 1.1. Demand is high during the day and low at night. In contrast, electricity from wind or solar power generators is sporadic and inconsistent. At low levels of deployment, the fluctuating supply can be managed by conventional grid operations; however, beyond 30 % of installed grid capacity, the fluctuations become intolerable. Therefore, mass adoption of wind and solar requires a new approach. Large-scale storage is a promising solution, capable of smoothing out these curves by consuming electricity (charging) during periods of excess supply and returning it (discharging) when demand exceeds supply.

In general, grids typically attempt to utilize renewable energy as much as possible, so they use a minimum level of conventional (non-renewable) generation and then all the renewable generation possible. Final trimming/balancing can be performed with fast power units like combined cycle

Flex-Plants or simple cycle aero-derivative like an SGT-A65. In theory, this concept works very well. In practice, two main characteristics of renewable generation present problems to solve

Firstly, demand peaks in the early evening, when most people are getting home from work. Solar generation peaks around noon and wind generation peaks overnight. This means that when we need the power most, renewable generation sources are either not producing anything or an insufficient amount of electricity. Then, at times when we don't need as much electricity, renewables hit their peaks. Unfortunately, this (barring the incorporation of another technology) often results in a use-it-or-lose-it scenario.

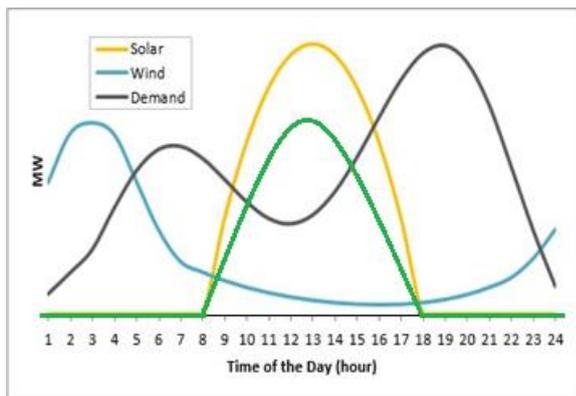


Fig. 1.1: Power Generation Curve of Solar & Wind, Power Supply by Battery and daily load curve

### 1.1 History

**Donald Robert Sadoway** (born 7 March 1950) is the current (as of January 2013) John F Elliott Professor of Materials Chemistry at the Massachusetts Institute of Technology. A faculty member in the Department of Materials Science Engineering, he is a noted expert on batteries and has done significant research on how to improve the performance and longevity of portable power sources. In parallel, he is an expert on the extraction of metals from their ores and the inventor of molten oxide electrolysis, which has the potential to produce crude steel without the use of carbon reductant thereby eliminating greenhouse gas emissions

In 2009, Sadoway disclosed the liquid metal battery comprising liquid layers of magnesium and antimony separated by a layer of molten salt that could be used for stationary energy storage. Research on this concept was being funded by ARPA-E and the French energy company Total S.A. Experimental data showed a 69% DC-to-DC storage efficiency with good storage capacity and relatively low leakage current (self-discharge).

The technology was proposed in 2009 based on magnesium and antimony separated by molten salt. Magnesium was chosen as the negative electrode for its low cost and low solubility in the molten-salt electrolyte. Antimony was selected as the positive electrode due to its low cost and higher anticipated discharge voltage.

In 2010, with funding from Bill Gates and Total S.A., Sadoway and two others, David Bradwell and Luis Ortiz, co-founded a company called the Liquid Metal Battery Corporation (now Ambri) to scale up and commercialize the technology.

In 2011, the researchers demonstrated a cell with a lithium anode and a lead-antimony cathode, which had higher ionic conductivity and lower melting points (350–430°C). The main caveat of Lithium-ion chemistry is the higher cost. A Li/LiF + LiCl + LiI/Pb-Sb cell with about 0.9 V open-circuit potential operating at 450 °C had electroactive material costs of US\$100/kWh and US\$100/kW and a projected 25- year lifetime. Its discharge power at 1.1 A/cm<sup>2</sup> is only 44% (and 88% at 0.14 A/cm<sup>2</sup>).

Experimental data shows 69% storage efficiency, with good storage capacity (over 1000 mAh/cm<sup>2</sup>), low leakage (< 1 mA/cm<sup>2</sup>) and high maximal discharge capacity (over 200 mA/cm<sup>2</sup>). In October 2014 the MIT team has achieved an operational efficiency of about 70% at high charging/discharging rates of about 275 mA/cm<sup>2</sup>, similar to that of pumped-storage hydroelectricity and higher efficiencies at lower currents. Tests showed that after 10 years of regular use, the system would still retain about 89% of its actual initial capacity. In September 2014, a study described an arrangement using a molten alloy of lead-Antimony as the anode, liquid lithium for the negative electrode; and a molten mixture of lithium salts as the electrolyte.

## II. LITERATURE SURVEY

David J. Bradwell, Hojong Kim, Aislinn H. C. Sirk, and Donald R. Sadoway (2012) discuss the Magnesium – Antimony based Liquid Metal battery. The authors share the information about the process of making the battery, Material selection for Electrode, Electrolytes and outer body construction and finally tests which are being performed on the battery. In other words, the author shares the performance analysis of the battery, and the issues encountered during the procedures for making the battery.

Takanari Ouchi, Hong Kim,b, Xiaohui Ning, and Donald R. Sadoway (2014) discuss the performance of the Ca||Sb Liquid Metal Battery where Calcium-Antimony is a positive electrode material. The thermodynamic properties of the Ca||Sb battery by measuring terminal voltage and Kinetics of alloying and dealloying of the cell. In other words, the battery's performance improvement of the battery by replacing the Anode with Calcium.

Chunli Zhou and Tao Li (2019) disc the characteristics of a single sing Liquid metal Battery cell and the Series of those cells. The voltage curves deviation with and without equalization. Finally, the design of the equalizing management system helps us in battery management of the battery modules with accurate DC voltage measurements. They also discussed testing the Equalization system in experimental and verification platforms.

2.1 Magnesium–Antimony Liquid Metal Battery for Stationary Energy Storage

Batteries are an attractive option for grid-scale energy storage applications because of their small footprint and flexible siting. They also enhance the stability, security and reliability of the electrical grid. They improve the reliability of implementing renewable sources. The current battery called Magnesium-Antimony (Mg||Sg) liquid metal battery comprises of Magnesium anode, Antimony cathode and molten salt of magnesium (MgCl<sub>2</sub>-KCl-NaCl) as electrolyte. This battery operates at a high temperature (around 700 °C). Because of the density difference and immiscibility, the salt and metal phases are separated into three layers. The high-density Antimony in the bottle om, the medium-density electrolyte in the middle and low-density Magnesium whips are placed inside the outer casing as shown in fig 2.1. The density difference between the layers is maintained such that the layer’s separation increases.

During discharge, at the anode, Mg oxidizes to Mg<sup>+2</sup> ions, which dissolve into the electrolyte while the electrons are released into the external circuit. Simultaneously, these ions reduce to Magnesium, which gets deposited in Antimony to form a Magnesium - Antimony alloy.

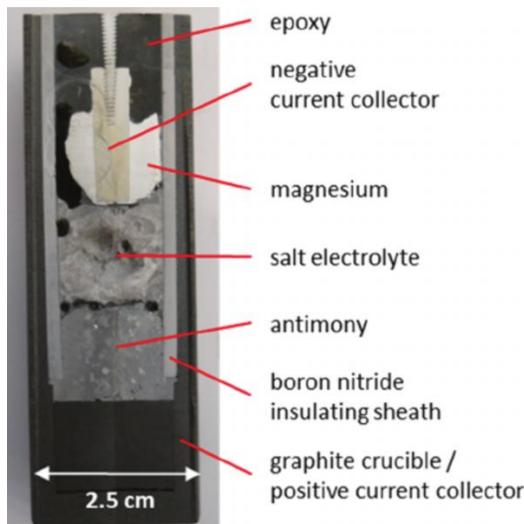
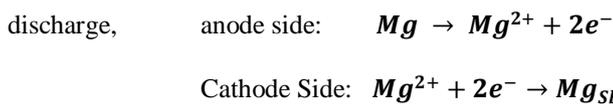


Fig.2.1: TS of Mg||Sb Liquid Metal Battery

The difference in chemical potentials of pure Mg and Mg dissolved in Sb generates a voltage that can be expressed as

$$E_{cell} = \frac{RT}{2F} \ln\left(\frac{a_{Mg(in\ Sb)}}{a_{Mg}}\right)$$

where R is the gas constant,

T is the temperature in Kelvins,

F is the Faraday constant,

$a_{Mg(in\ Sb)}$  is the activity of Mg dissolved in Sb and

$a_{Mg}$  is the activity of pure Mg

Way of Conduction:

The cell comprises 6 components graphite crucible, insulating sheath, current collector, current leads, and a cell cap. The graphite crucible is constructed from a 38mm diameter and 90mm long Graphite rod. To which 19mm diameter and 57mm deep hole was bored and 3mm thick Boron Nitrate (BN) rod was compression fit into the above graphite crucible. To the cell cap and bottom of the Graphite rod, 6mm diameter holes are drilled using a CNC machine and fitted with h 6mm diameter graphite rod and 1808 SS rod are tightly fit as shown ie fig 2.2 below. In the crucible Sb granules (Alfa-Aesar, 99.5 % purity) were placed at the bottom of the crucible, the electrolyte salts were added, and Mg slugs (Alfa Aesar, 99.95 % purity) were placed on top of the salt.

Recently there is work done on the Li-Ga battery which works under less internal temperature. But, they suffer mechanical failure by mechanisms such as electrode particle cracking. The liquid electrodes overcome this mechanical failure to complete reconstruction of electrodes during working helps in overcoming this issue of electrode failure and potentially endowing cells with unprecedented lifespans. Also, the liquid electrode facilitates inexpensive manufacturing of battery

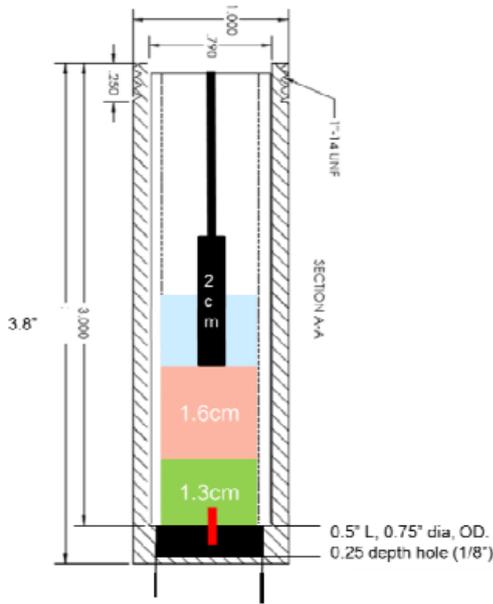


Fig. 2.2. Scaled Schematic of Mg||Sb cell (all units in mm)

**Characterization:**

Further electrochemical characterization was performed. Stepped-potential experiments indicated low leakage current densities of <math><1 \text{ mA/cm}^2</math> well below those of previously studied systems. This was attributed to the complexation of  $\text{Mg}^{2+}$  by ligand donors from the supporting electrolyte (NaCl, KCl) and the attendant suppression of metal solubility in its halide salts. Cells cycled at  $50 \text{ mA/cm}^2$  for a predefined discharge period of 10 h to a cut off charging voltage limit of 0.85 V achieved a round-trip Coulombic efficiency of 97% and a voltage efficiency of 71%, resulting in the overall energy efficiency of 69%.

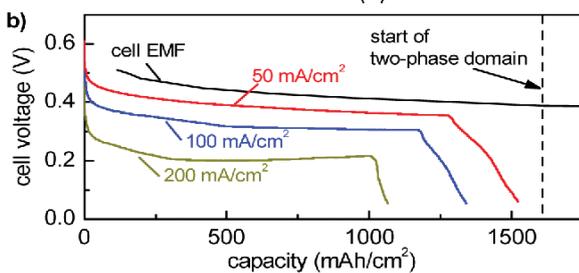
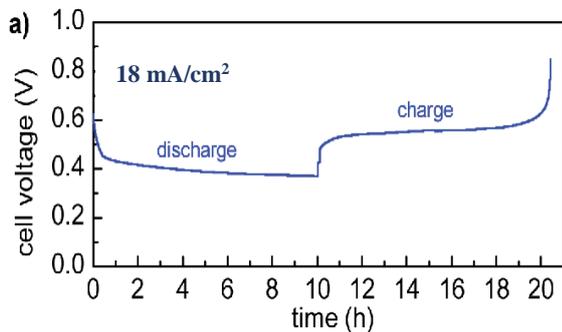


Fig. 2.3. a) cycling of Mg||Sb cell at  $i = 18 \text{ mA/cm}^2$  b) Discharge cycles of cell at current density  $i = 50 \text{ mA/cm}^2, 100 \text{ mA/cm}^2, 200 \text{ mA/cm}^2$

This low level of leakage current measured by two methods is impressive, and sufficiently low for grid-scale applications. As subsequent work on similarly constructed Na-based top electrode exhibited a significantly larger leakage current density ( $\sim 50 \text{ mA/cm}^2$ ), this suggests that the complexing of  $\text{Mg}^{2+}$  by NaCl and KCl ligand donors effectively suppressed Mg metal solubility in the electrolyte as predicted from literature.

III. MATERIAL CONSIDERATION

A liquid metal battery is a battery in which the electrodes are stacked vertically. Because the electrode materials inside the battery stay separated due to the density between the Anode electrode (A) and Cathode electrode (K). The material consideration so of the Anode, Cathode and Electrolyte material are given below but we need to keep a note that the selected material must have less melting point as well as be stable in high temperature i.e., in liquid form.

3.1 Anode Electrode

The Anode metal must be a highly electropositive metal which must have a very high tendency to give away electrodes which constitutes a positive side of the battery also the Anode's density must be very low compared to the cathode electrode material. From the Periodic table shown below the anode, metal lies in the marked region.

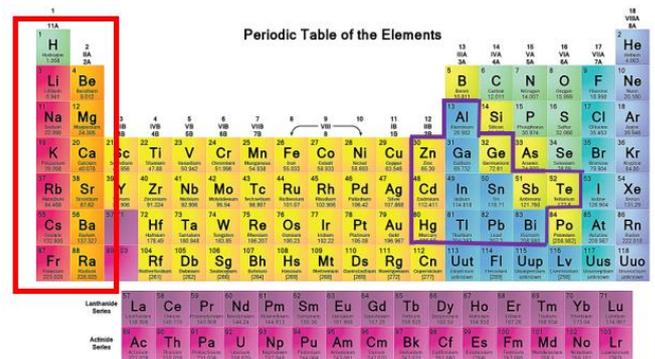


Fig. 3.1. Periodic table showing suitable elements for anode (Red box) and cathode (violet box)

From the above figure, Hydrogen is non-metal and hence excluded. Also, the metals in Group – I such as lithium (Li), sodium (Na) and potassium (K) are highly electropositive but they are highly reactive and show violent behaviour at high temperatures, using them as electrodes will be dangerous. So, Group – II metals can be considered the best option as Anode material. In a group, the electro positivity increases as we go down in the group. Hence, the metal we are going to select must

be nearer to the bottom of the group and should be stable at high temperatures.

Table 3.1. Electronegativity and price of the metals suitable for Anode electrode

Element	Electronegativity	Price (Rs/kilogram)
Lithium	0.98	30,000
Magnesium	1.31	3,000
Calcium	1	3,000
Sodium	0.93	4,000
Barium	0.89	12,000

From above all observations, Magnesium Beryllium and Calcium are the best options. Among all these calcium has less electronegativity and is available at a low price. This makes it the most desirable option for anode electrodes. In addition, with Calcium, a small quantity of pure Magnesium is also added to the anode as the Calcium has high dissolution properties with its salts. The added advantage is this by adding magnesium the melting point of calcium decreases a lot as Magnesium has a low melting point of about 650 °C whereas Calcium has about 860 °C. In addition to this the magnesium has the property to maintain a constant temperature for a long duration But, it reduces the output voltage of the battery a lot. Hence, a small amount of Magnesium is used for the anode

### 3.2 Cathode Electrode

The cathode is a highly electronegative metal which tends to accept electrons, also the cathode must have a high density compared to the anode to stay at the bottom of the battery. The possible area for a selection of cathode electrode materials is marked with a blue box as shown in the periodic table in violet colour.

The above materials selected are the only metals which have high electronegativity as in right most of the entire periodic table almost all the elements are non-metals. Among the selected metals Antimony (Sb) and Bismuth (Bi) will be best suitable which have electronegativity of 2.05 and 2.02 respectively. They also have a low melting point and remain stable at high temperatures which is desirable as reducing the operating temperature of the battery is more advantageous as it is easy to contain low-temperature materials.

Table 3.2. Electronegativity and price of the metals suitable for Cathode electrode

Element	Electron negativity	Price (Rs/kilogram)
Antimony	2.05	9,000
Bismuth	2.02	12,000
Tellurium	2.1	30,000

From all the above antimony is the one we are going to select for the battery as it has more electronegativity around 2.05. It also has a low melting point of about 630.76°C which is most desirable, as the operating temperature reduces with the reduction in anode melting point thereby reducing the heat losses of the battery.

### 3.3 Electrolyte Material

The electrolyte material of a Liquid metal Battery is generally a medium-density non-aqueous salt mixture, which majorly consists of the anode metal salt. The electrolyte salt of the Liquid Metal Battery is a special one it is required to have some properties which are discussed below

1. The electrolyte must have a low liquidus temperature possible to reduce the heat loss and to add simplicity to construction.
2. The salt should not dissolve the anode and cathode electrode materials, which may result in diffusion current and is not desired.
3. It must have a high electrochemical window as electrodes cannot act as electrodes.
4. It must have a high conductivity of ions of anode metals.

To meet the above demands the alkali-chlorides and Fluorides of the anode metals are the best options. The anode salt we are going to use is Calcium based salt which is calcium chloride (CaCl<sub>2</sub>). We are not going to use a pure form of salt, to improve the ion conductivity NaCl and KCl are added.

### 3.4 Ceramic Outer Casing

For any type of battery, the outer casing places a vital role during its operation of the battery. The outer casing not only provides mechanical stability to the battery but also provides protection from the external environment and avoids foreign materials entering the battery. This way protects the battery from conversion and other harmful effects posted by the outer environment thereby improving the lifespan of the battery. A liquid metal battery is a special type of battery in which the inner electrodes exist in a liquid state and the interior of the battery temperature exceeds 600 °C. Hence the outer casing of the liquid metal battery will also be made of a special material which must satisfy the below requirements

1. The outer casing must be capable of containing metals which exist in a molten state. i.e., the outer casing must

be capable of handling very high temperatures (above 1000 °C).

2. It must be chemically stable at high temperature and does not react with the electrodes which exist in a molten state.
3. It must be a bad conductor of electricity to avoid a short circuit. It must be mechanically strong to protect the battery from external shocks and jerks.
4. It must be capable of maintaining the inner temperatures of the battery constant for a long time thereby reducing heat losses

**Table 3.3. Mechanical properties of Alumina, Boron Nitrate and Zirconia**

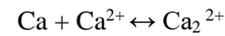
		Alumina (Al <sub>2</sub> O <sub>3</sub> )	Boron Nitrate (BN)	Zirconia (ZrO <sub>2</sub> )
<b>Density (g/m<sup>3</sup>)</b>		3.98	2.18	6.05
<b>Melting Point (°C)</b>		2,072	2,973	2,715
<b>Oxygen content (%)</b>		60	4.0	20.9
<b>Volume Resistivity (Ω. cm)</b>		>10 <sup>14</sup>	>10 <sup>14</sup>	>10 <sup>14</sup>
	Air	≤1575	≤900	≤1000
	Inert Gas	≤2100	≤2100	≤2100
	Vacuum	≤1925	≤1900	≤1500
<b>Bending Strength (Mpa)</b>		266.7 – 357.5	30	900 – 1200
<b>Coefficient of thermal expansion (10<sup>-6</sup>/°C)</b>		8.1	2.7	2.3
<b>Thermal Conductivity (W/m. K)</b>		18	50	2.5-3

Considering all the above requirements of the battery Ceramic based material might be the best option for the Liquid metal battery. There are many sorts of materials suitable for the outer casing material for Liquid Metal batteries some of them are Alumina, Boron Nitrate and Zirconia. The mechanical properties of these materials are tabulated below in table 3.3.

But the reason we are selecting Alumina based material is that the mechanical strength of the Alumina based material has reasonable mechanical strength. Also compared to others it's the per-unit cost is less near Rs.1200 whereas others cost an average of Rs.3000 to Rs. 6000. Also, the thermal conductivity of alumina is less which is the most required property to contain the inner temperature of the battery for a long time.

### 3.5 Adding Magnesium into Calcium Anode

Generally, to improve the battery voltage and reduction in calcium cost Calcium metal is chosen as an anode. But Calcium suffers from a property of high dissolution in its salts. This dissolution reduces the chemical potential of the battery. Due to this dis-charge currents increases by using calcium, hence the charge of the battery reduces over time very quickly, which is not a desirable one. The detrimental dissolution reaction of calcium in calcium salts can be represented by the following



Where calcium metal (Ca) reacts with calcium cations (Ca<sup>2+</sup>) to form sub-valent ions (Ca<sup>+</sup> or Ca<sup>2+</sup>). Using the above case as an example, the equilibrium constant of the dissolution reaction is therefore given by:

$$K_{eq} \propto a_{Ca^{2+}} / [a_{Ca^+} \cdot a_{Ca^{2+}}]$$

where a<sub>Ca<sup>2+</sup></sub> is the activity of dissolved sub valent calcium, a<sub>Ca<sup>+</sup></sub> is the activity of calcium metal in the negative electrode, and a<sub>Ca<sup>2+</sup></sub> is the activity of calcium cation in the electrolyte. Focusing on the contributions of the reactants, we reason that suppressing the activity of calcium metal in the negative electrode, a<sub>Ca<sup>+</sup></sub>, by alloying with more electronegative metals acting as diluents and lowering the activity of a<sub>Ca<sup>2+</sup></sub> in the electrolyte, a<sub>Ca<sup>2+</sup></sub>, by the introduction of other cations, should result in attendant reductions in the concentration of sub valent a<sub>Ca<sup>2+</sup></sub> while simultaneously reducing the reactivity and melting temperature of the negative electrode.

Due to this dis-charge currents increases by using calcium, hence the charge of the battery reduces over time very quickly, which is not a desirable one. To suppress this dissolution property of Calcium into its salts, a small amount of Magnesium is added. The magnesium suppresses the dissolution of calcium thereby improving battery performance. The magnesium also decreases the melting point of the Calcium to about 550 °C. But there is a small issue of the battery voltage reduced with the addition of the Magnesium which is depicted in below Fig 3.2.

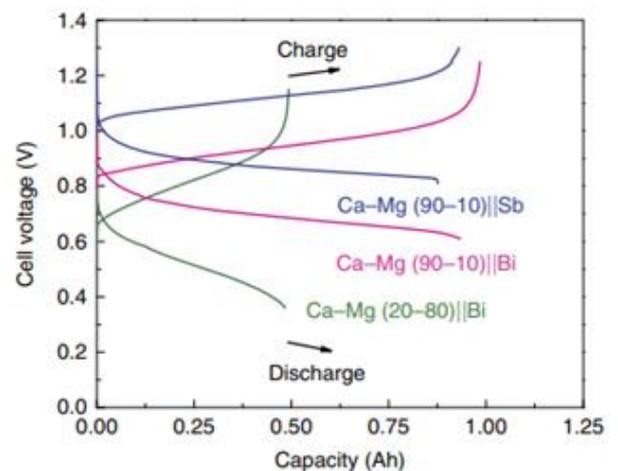
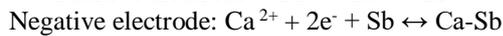
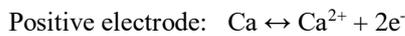


Fig. 3.2. Characteristics for cell voltage and Ah capacity of Calcium Anode Cell

Here from the above graph, it can be understood that with an increase in mole concentration of Magnesium in the Anode the cell voltage reduces but it is not significant. To avoid the reduction in cell voltage the Ca – Mg concentrations are maintained at 90 – 10 % mol. To balance between cell voltage and reduces the discharge current.

### 3.6 Cell Equation of Liquid Metal Battery

From the above material Considerations, we got finalized that we are about to make a battery based on Calcium and Antimony as electrode material. This battery can also be called a Calcium – Antimony Liquid Metal Battery. From them, the cell equation can be represented as



The general cell equation for any battery is given by

$$E_{cell} = E_{oxidation} - E_{reduction}$$

The oxidation happens in cathode side, hence  $E_{oxidation} =$

$$E_{Ca(inSb)}$$

The reduction happens in anode side, hence  $E_{reduction} =$

$$E_{Ca(inMg)}$$

Therefore,

$$E_{cell} = E_{Ca(inSb)} - E_{Ca(inMg)}$$

Therefore,

Where,  $E_{Ca(inSb)}$  is potential of calcium in Antimony

$E_{Ca(inMg)}$  is potential of calcium in Magnesium

$$E_{Ca(inSb)} = E^0_{Ca} + RT \ln a_{Ca(inSb)}$$

$$E_{Ca(inMg)} = E^0_{Ca} + RT \ln a_{Ca(inMg)}$$

Therefore,

$$E_{cell} = -\frac{RT}{nF} \ln \left( \frac{a_{Ca(inSb)}}{a_{Ca(inMg)}} \right)$$

Where,  $a_{Ca(inSb)}$  is activity of calcium in Antimony

$a_{Ca(inMg)}$  is activity of Calcium in Magnesium

R is the Gas Constant; and  $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

T is Temperature in kelvins

n is number of electrons in cell equation for this

battery  $n = 2$

F is Faraday Constant;  $F = 96485.332 \text{ C mol}^{-1}$

## IV. EXPERIMENTAL ANALYSIS AND RESULTS

### 4.1 Working Principle

Liquid Metal generally comprises liquid Anode, Electrolyte and Cathode layers respectively from top to bottom. Whenever the battery is heated above the melting points of the internal electrode materials. The metals melt and the electrode metals

atoms freely move in the metal soup forming the electrochemical battery as below.



Where, A is Anode

B is Cathode

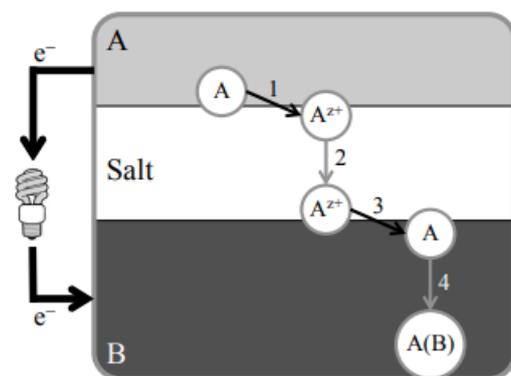
AX is electrolyte

*Charging:*

During Charging when an electric field is applied to the battery the freely moving anode metal atoms discharge electrons( $e^-$ ) to form Anode metal ions( $A^+$ ), which flow through the electrolyte towards the cathode side of the battery. At the same time, the electrons flow through the source and get to the cathode side where the Anode metal ions ( $A^{z+}$ ), electrons( $e^-$ ) and Cathode metal atoms (B) combine to form Anode-Cathode alloy (A-B alloy). In this process, the anode metal inside the battery is physically consumed finally leaving electrolyte and Anode-Cathode alloy.

*Discharging:*

During discharging when the load is connected the electrochemically unstable Anode-Cathode alloy (A-B alloy) discharges electron ( $e^-$ ) to disintegrate into Anode metal ions ( $A^{z+}$ ) and Cathode atoms (B). Due to the anode metal ions being less dense they flow back toward the top through the electrolyte. At the same time, the electrons flow through load and go to the anode side and recombine with anode metal ions to form Anode metal at the top layer. Thus, again forming the anode metal layer on the top layer.



(a)

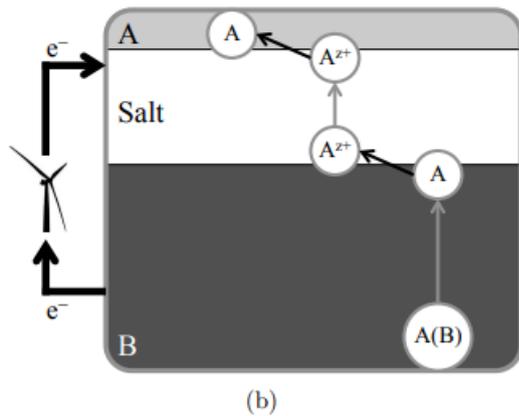


Fig. 4.1. schematic of liquid metal battery cell operation upon (a) discharge and (b) charge

#### 4.2 Way of Conduction

The cell model construction consists of Alumina Crucible and disk as outer material. The Electrode materials are Ca as anode and Antimony as a cathode. The Alumina Crucible of dimensions 24mm outer diameter, 18mm inner diameter and 100mm length is taken, to which a 5mm diameter hole is machine drilled at the bottom. The Alumina disk of diameter 25mm also the machine drilled a 5mm hole. Now the Crucible Graphite rod of 5mm diameter is tightly fixed in the hole at the bottom, and also 18/08 stainless steel rod of the diameter of 5mm is fitted in the disk hole as shown in fig 4.1. Initially, Antimony powder is poured into the crucible, then Calcium based salt electrolyte mixture (CaCl<sub>2</sub> 50%– KCl 30% – NaCl 20% mol) is poured and finally, Calcium and Magnesium (90% - 10%mol) are poured. The amount and concentration of the electrodes and electrolyte poured into the cell are described in the table below. Now the disk is properly placed on the crucible and sealed using Asahi Alumina Cement. Thus, the cell model is completed and proceeded for further processes to make it work.

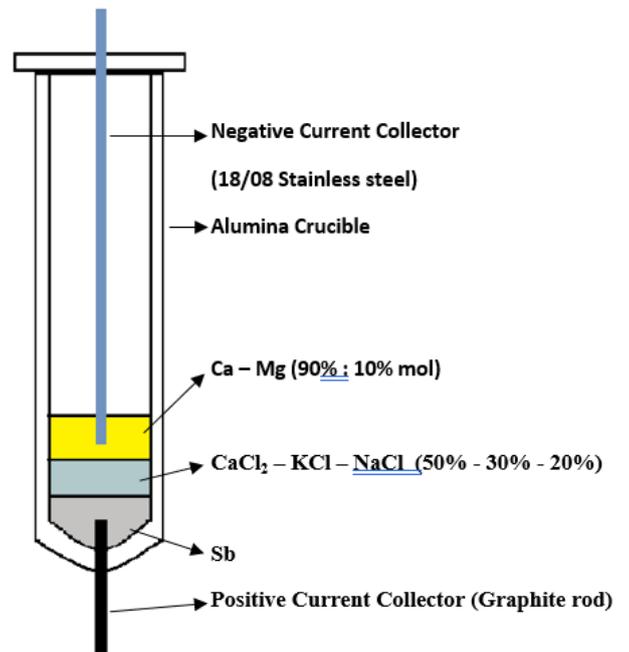


Fig. 4.2. Schematic of Ca-Sb Liquid Metal Battery

The above-prepared cell model is filled with some Argon gas to avoid oxygen exposure, then placed in a furnace and heated to 700 °C at a constant rate of 5 °C/min, above the melting point of Mg and Sb metal electrodes and salt electrolyte as shown in fig 4.2. The slow heating is for activation of the atoms to get ready for ions flow in the inside battery.

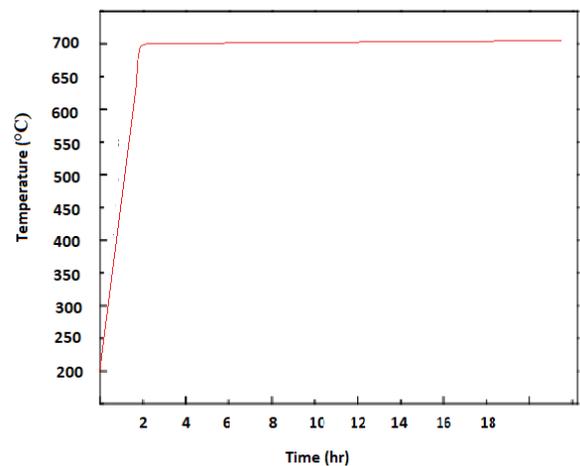


Fig. 4.3. Cell heating profile of the assembled battery

#### 4.2 Precautionary Measures

Making a new experimental prototype of a battery is a challenging task. It requires lots of work to achieve results while handling such prototypes most care must be taken to yield good results. Especially for this battery care towards the battery as well as ourselves is necessary for getting accurate results,

first the safety of the personnel around the battery. Below are the precautionary measures which are taken while making the battery,

- Maintain an inert environment while assembling the battery, it is preferable to maintain a vacuum while its assembly
- Maintain an inert environment while keeping it in a furnace to avoid air reacting with inner metal during heating
- Use gas masks as antimony releases toxic gases when heated
- Use thick gloves as we are handling metals at very high temperature, also it is preferred to use a tong to hold the battery after taking it out from the furnace
- At any point do not drop the battery or move quickly which may result in shaking of internal molten metals, they may lead to fire and in worst cases bursting of the battery
- While battery testing maintain the temperature of the battery using a blow torch or muffle furnace to avoid cooling the battery
- Always fully discharge the battery before keeping it idle for a long time

#### 4.3 Equipment and Testing

For the present model of battery, there need to be performed many tests such as cyclic voltammetry, electrochemical impedance spectroscopy, galvanostatic (constant current) battery cycling, etc. But due to cost and the drawback of handling high-temperature materials. We will perform two major for open-circuit voltage and deep cycling of battery at different.

##### 1. Open-circuit Voltage:

Open Circuit Voltage is the voltage of the battery after manufacture, it shows the battery voltage just after the manufacture without connecting any load. This open-circuit voltage shows how well the battery holds the charge for a long time for optimal conditions. It also tests how well the battery is working or whether the battery is working or not after making it.

The open-circuit voltage was measured for this battery before charging and discharging the battery. Initially, the cell was assembled with the required quantity of metals and heated as per the above process. The leads of the battery were connected to the multimeter in voltmeter mode. The voltage was measured every 10 minutes on a time scale to note down the battery voltage. This process was about performed for more than 5 hours.

##### 2. Deep cycling:

Deep cycling is the testing procedure to test the performance of the battery on load, charging and depletion. It is also done for inspection of battery for damage, and depletion of battery after usage. In deep cycling, the battery is fully charged and discharged up to its worst conditions to check the battery's robustness. For testing models or prototypes, deep cycling shows the charging and discharging characteristics which describe the battery performance during its rough usage. Generally, deep cycling is done at different current densities of battery and C rates to yield the battery performance under all conditions.

Deep cycling is the process of Charging and Discharging of battery to its limits. For any battery, this process reveals how immune is the battery to ageing and depletion. The process is conducted very simply. The battery is connected to a constant load of resistive type. The load is selected such that to perform this test in the required current densities. In the present test current densities for 20 mA/cm<sup>2</sup>, 100 mA/cm<sup>2</sup> and 250 mA/cm<sup>2</sup>. Initially, the battery is charged at any of these rates then the battery is connected to load which is selected as per the current densities we need to achieve and the battery was charged in the same current density using Regulated Power Supply.

#### 4.4 Characterization

##### Open Circuit Voltage:

An open-circuit voltage test was performed in a controlled lab environment. The battery internal temperature was maintained at around 700°C using a muffle furnace that constantly maintains the chamber temperature at 700°C range. tests The battery cell voltage was constant and can be reproducible at the present temperature range of about 1.1V with a 7.244g of Ca and 0.481g of mg in the anode and 24.352g of Sb as shown in fig 4.3.

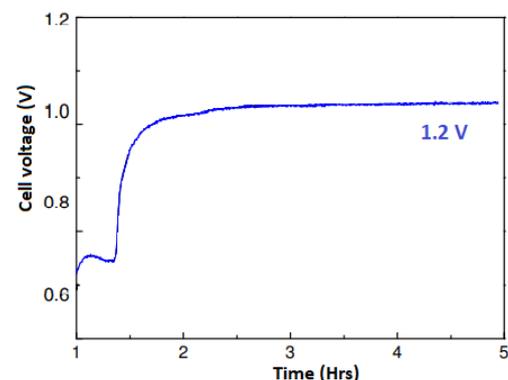


Fig. 4.4. Open Circuit voltage of (Ca-Mg)||Sb cell at 700°C

##### Deep Cycling Characteristics:

The deep cycling was performed in the inert environment using Argon gas and the temperature was also maintained constant at

700 °C. The deep cycling characteristics of the battery at different current densities are shown in fig 4.4

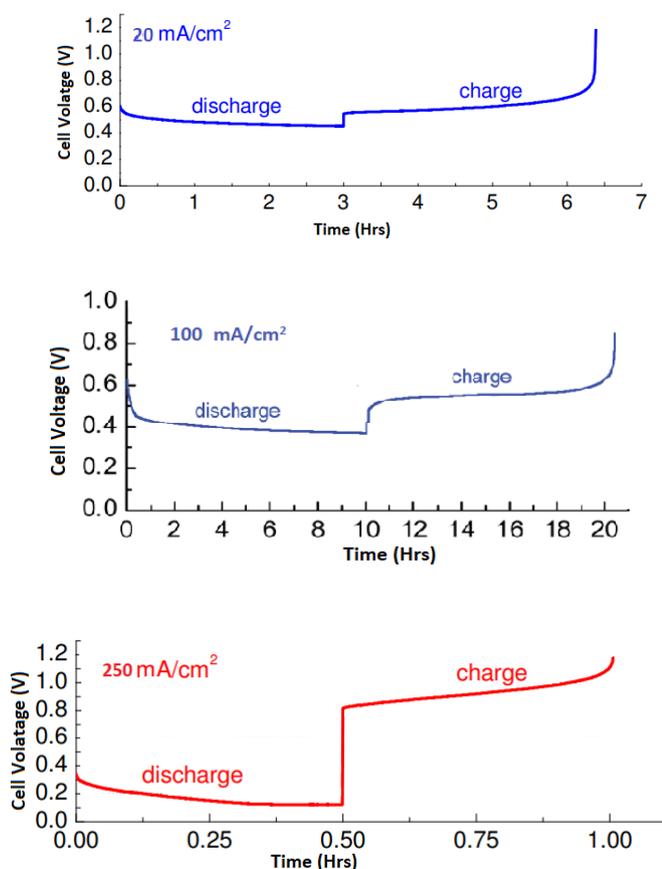


Fig. 4.5. Deep Cycling Characteristics of battery at current densities of 20 mA/cm<sup>2</sup>, 100 mA/cm<sup>2</sup> and 250 mA/cm<sup>2</sup>

#### 4.5 Analysis

The measurement of self-discharge current was performed after the cell reached the operating temperature and the current became steady at a constant applied voltage of 1.1 V. The charging and discharging voltage-time curves were measured at constant current densities of 20 mA/cm<sup>2</sup>, 100 mA/cm<sup>2</sup> and 250 mA/cm<sup>2</sup>. Data were acquired from instrumentation meant for battery testing (Model 4300, Maccor). Coulombic efficiency ( $\eta_Q$ ) was calculated from charging capacity ( $Q_C$ ) and discharging capacity ( $Q_D$ ), ( $\eta_Q = 100 Q_D/Q_C$ ) Energy efficiency ( $\eta_E$ ) was calculated from charging energy ( $Q_C$ ) and discharging energy ( $E_D$ ), ( $\eta_E = 100 \cdot E_D/E_C$ ). Discharge voltage ( $V_D$ ) was calculated from discharge capacity and discharge energy ( $V_D = Q_D/Q_C$ ). The theoretical discharge capacity of the cell was defined as the mole fraction of calcium, at which the nucleation of the Ca<sub>11</sub>Sb<sub>10</sub> phase occurs (25 mol% at 550°C and 27 mol% at 650°C) or the Ca<sub>11</sub>Sb<sub>10</sub> phase (23 mol% at 650°C) assuming that only calcium participates in charge/discharge reaction.

#### CONCLUSION

The performance of the cell was observed to be better compared to previous models Mg||Sb cell and Ca||Bi cell. The open-circuit voltage was observed to be 0.1V higher than Ca||Bi cell and the deep cycling characteristics are improved but not significantly large. In the present (Ca-Mg)||Sb cell, the performance is almost identical even though the Ca-Mg mole ratios are varied. The economy of the battery was improved and the way of conduction for making the battery was simplified by the usage of Alumina as an outer casing. The usage of earth-abundant metals makes the battery easily manufacturable at a low cost.

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