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A NOVEL APPROACH FOR LITHIUM EXTRACTION FROM SEA-WATER AND SUBSEQUENT BATTERY FABRICATION FOR SOLVING ENERGY CRISIS: "ENERGIZING THE EARTH FOR FUTURE DEARTH"

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ABSTRACT

The Environment seems to be in detrimental health conditions owing to extensive pollution from the vehicles using conventional sources of fuel energy. Renewable energy sources and technologies possess the acumen to provide solutions to the long-standing Global Energy problems and our paper unveils one such novel technique for the extraction of Lithium metal from Seawater (Renewable, Sustainable and Infinite Energy Resource), followed by the fabrication of Lithium batteries that would eventually be employed in the automobile and several other industries. The collected Seawater is first passed through a Graphene mesh network whereby, the water network bifurcates into two halves: one half consisting of pure water and the other half consisting of Brine which is our chief concern. This Brine contains Lithium in the form of insoluble Lithium Carbonate (Li_2CO_3) which when heated and then treated aptly, produces the target metal Lithium (discussed vividly with associate reactions in the full paper) which may be deployed in the manufacturing of rechargeable Lithium-ion Batteries (LIBs) for use in Green Vehicles. The formation of dendrites can be potentially done away with by effectively creating electrodes with Smoother Surface finishes. Furthermore, on adding small amounts of HF and H_2O in the electrolyte, the resultant formation of Li_2O and LiF coatings help to vanquish these dendrites and whiskers thereby making the procedure effective, efficient and void of any disparities.

Contribution/Originality: This paper's primary contribution is the introduction of a novel approach for the effective and efficient Lithium Extraction from Sea-water and consequent manufacturing of Lithium-Ion Batteries. The produced Lithium-Ion Batteries can be further utilized in Green Vehicles to promote a sustainable and environment-friendly transport system.

1. INTRODUCTION

The increased dependence of mankind on non-renewable Fossil fuels and Nuclear power has resulted in the energy industry being an important contributor to pollution and severe economic repercussions. These slow-moving but day-by-day increasingly severe crises, have affected larger populations across the world and have moved Researchers' & Industries' attention toward new, Sustainable and Renewable Energy Sources and materials which can be collected from the environment without affecting its natural components and surroundings. So, in this paper, a very simple and cost-effective Lithium metal Extraction procedure is introduced, in addition to an innovative technique of utilizing the extracted Lithium in an eco-friendly manner, which can be performed as long as seawater exists on the face of Earth. Practically speaking, this process doesn't utilize seawater directly; it is based on the by-product (Brine) of the RO Desalination process of seawater that produces drinking water. The novelty of the described methodology lies in its unique solution to the Energy crisis troubles, putting aside Environment Pollution.

2. RESEARCH ELABORATIONS

The processes involved in the extraction of Lithium from Seawater and subsequent Lithium-Ion Battery (LIB) production has been described by the flowchart in Figure 1:

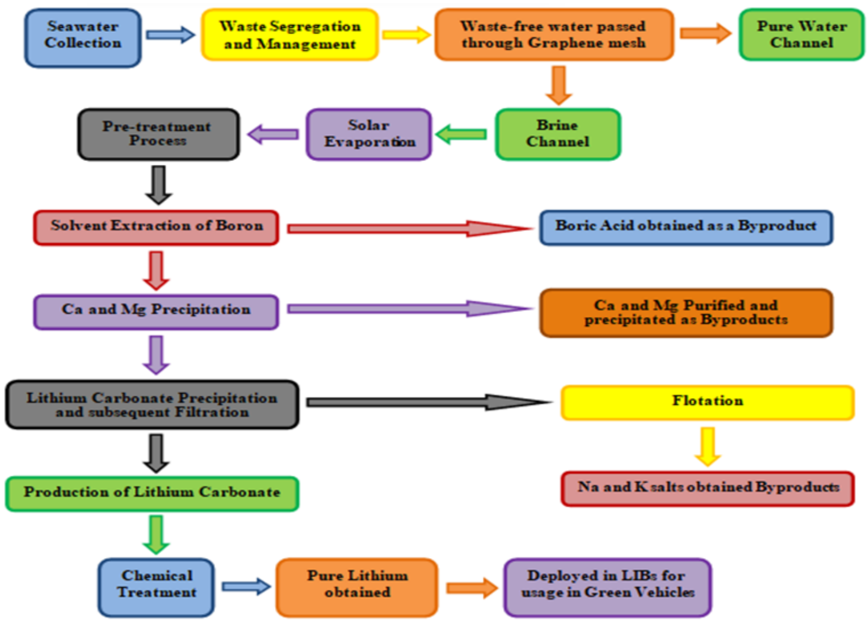

Figure-1. Flowchart demonstrating the Lithium extraction methodology.

a) *Seawater Collection and its Waste Treatment*: Firstly, Seawater containing various wastes is collected and then, the wastes are Segregated and Managed by several potent engineering techniques as described by Poddar, De, and Sarkar (2020).

b) *Usage of Graphene mesh network to procure Brine*: The Seawater after waste treatment is collected and passed through a Graphene sieve network (Ji et al., 2019) for filtration by using desalination of seawater leverage RO, whereby the water channel gets bifurcated into two streams; one of purified water and the other of concentrated Brine solution. This Brine obtained here, basically serves as the chief source of Lithium Carbonate which is insoluble in water.

c) *Pre-treatment of Brine*: After primary solar evaporation, chemical treatment of Brine is performed. During this pre-treatment procedure, Boric acid is obtained as a byproduct by Solvent Extraction method and with further treatment Calcium and Magnesium get precipitated as byproducts. Finally, we obtain filtered, water insoluble Lithium Carbonate (Li_2CO_3) after the Flotation process, whereby Sodium (Na) and Potassium (K) are received as byproducts.

d) *Extraction of Lithium from Li_2CO_3*: Lithium can be procured from Li_2CO_3 (obtained from the reject stream) by heating it with the aid of the following reactions. Alcohol can be also used to dissolve the Li salts. The vacuum thermal reduction helps to produce Li from CaO, which we can get by the cycle.

$$Li_2CO_3(s) \xrightarrow{\Delta} Li_2O(s) + CO_2(g)$$
$$2Li_2O(s) + Si(s) + 2CaO(s) \rightarrow 4Li(s) + Ca_2SiO_4(s)\,;\,\Delta G^\circ(1000K) = -351KJ$$
$$3Li_2O(s) + 2Al(s) + CaO(s) \rightarrow 6Li(s) + Ca(AlO_2)_2\,;\,\Delta G^\circ(298K) = +81KJ$$

e) *Lithium Battery Fabrication:* The extracted Lithium from the previous phase are compiled together and fabricated into Lithium Ion Batteries (LIBs) which contains Lithium-Metal Oxides (the metal being Manganese or Cobalt) as Cathode and metallic lithium or graphitic carbon or synthetic graphite as the Anode material. $LiClO_4$ or $LiCF_3SO_3$ is used as the Electrolyte. Several challenges are faced while researching for the discovery of efficient anode materials used in Li-ion batteries which can be applied in the future Electrical Vehicles or Green Vehicle (Lu, Chen, Pan, Cui, & Amine, 2018).

f) *Working of LIBs:* The Lithium-Ion Battery works based on the Intercalation principle during its charging and discharging. During discharging, the positive Lithium ion moves from the negative electrode (usually graphite) and enters the positive electrode (usually lithium metal oxide) through the electrolytic solution ($LiClO_4$ or $LiCF_3SO_3$). During charging, the reverse process occurs. Certain other Intercalation methods under research have been proposed which include i) *Graphite Intercalation Compounds (GICs)* and ii) *Pulsed Electrochemical Intercalation (PEI)* (Liu et al., 2020). In GICs, strong inter-planar covalent bonding exists between the anode carbon atoms and a weak Van der Waals force dominates between the Graphitic layers.

g) *Demerits of LIBs:* The major demerit of LIB is Dendrite and Whisker formation. In this failure, lithium from either of the electrodes begins to deposit by an electrochemical reaction over surface defects like pits, cracks or indentations that exist on the electrode leading to the initiation of dendrite formation by the metallic deposits. This deposition continues to build up and extend towards the other electrode over time causing catastrophic consequences like short circuit, poor recharge-ability etc.

h) *Novelties of this proposal:* The formation of dendrites can be potentially done away with by effectively creating electrodes with Smoother Surface finishes. Furthermore, on adding small amounts of HF and H_2O in the electrolyte, the resultant formation of Li_2O and LiF coatings help to vanquish these dendrites and whiskers thereby making the procedure effective, efficient and void of any disparities.

3. RESULTS

3.1. Controlling Factors of Lithium Extraction from Brine

Brine is a high-concentrated solution of salt in water ranging from about 3.5% up to about 26% (a typical saturated solution, depending on temperature).

Considering both Scientific and Economic perspectives, we must take into account certain controlling factors as follows:

- Suitability of pond soil and admissibility of the area for solar evaporation.
- Concentration of Lithium in Brine.
- The ratio of alkali metals and alkaline earth elements to Lithium.
- The complexity of the phase chemistry.

In the process of evaporation, about 50% of the original natural brine gets evaporated and lithium remains in the residual Brine. This expression has been ascribed to the retention of lithium by precipitated salts. Residual brine is highly loaded with Mg^{2+} ions as compared to K^+ and Na^+ ions. Murodjon, Yu, Li, Duo, and Deng (2020) The Table 1 shows various extraction process of lithium from Brine.

Table-1. Various Processes involved for Extraction of Lithium from Brine.

Resources	Process	Reagent
Brine	Electro dialysis	Bipolar Membranes
Brine	Desalination	Nanofiltration Membrane
Brine	Liquid-liquid extraction	With Tributyl phosphate (TBP)
Synthetic Brine	Liquid-liquid extraction	n-Butanol

Source: Modified from Murodjon et al. (2020)

3.2. Eco-Friendly Solution of Energy Crisis by Lithium

Energy crisis is one of the biggest challenges now faced by the world's energy system that is arguably far greater than those of the 1970's energy crisis. So, the manufactured Lithium Battery can change the Future Energy Crisis issues with the consequent growing innovative Engineering techniques for improving energy density and efficiency to suffice the energy demand. The pi-charts shown below in Figure 2 demonstrate the relative growth in the use of LIBs with time.

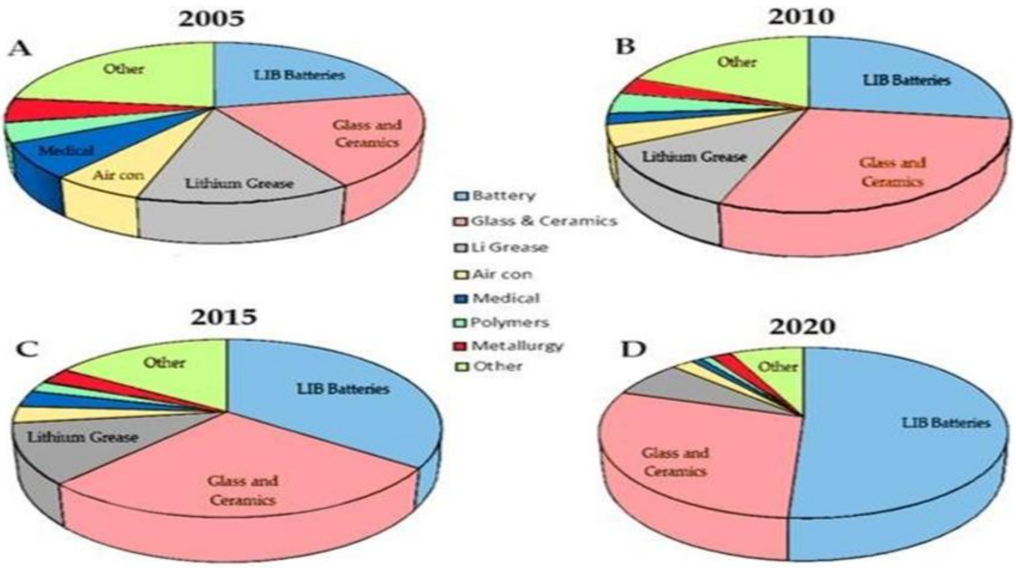

Figure-2. Statistical data showing growth of LIBs for Energy Storage.

This Lithium based Power storage battery can be easily recycled for the Future use effectively and efficiently without polluting the Environment as shown in Figure 3 below:

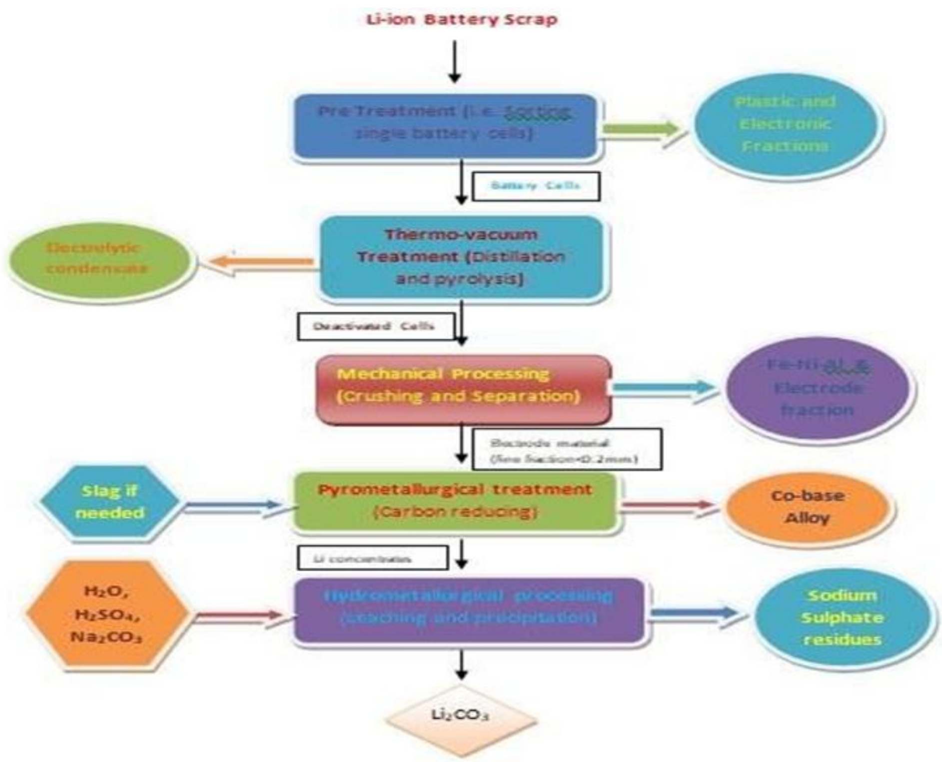

Figure-3. Flowchart showing the complete Recycling of LIB.

3.3. Field of Application

We can utilize the LIBs in Green vehicle or Electric Vehicle to promote a Sustainable medium of Transportation. From the range and performancepoint of view, the application of lithium-ion batteries seems to be prospective.

The following factors enumerate why our paper suggests Lithium-ion batteries prepared from seawater, as extremely suitable for these kinds of power trains:

- ***Energy-storing acumen:*** A high energy density combined with a high-power output is characteristic of LIBs.
- ***Weight:*** Lightweight LIBs aid the battery power in overcoming the vehicular inertia, for obtaining maximum mileage.
- ***Power:*** Since Lithium-ion cells do not have much of a "memory-effect", the battery- capacity remains undiminished and can thus be recharged and discharged way more swiftly than other battery technologies like NiMH batteries.

Production-cost isn't much of a concern here, because when more electric or hybrid vehicles would require more batteries, each individual battery is bound to become less expensive to manufacture.

3.4. Comparison among various Hybrid Lithium Batteries

The notion of an 'ideal contender' for the electric power train does not exist, and lithium-ion in general remains a good choice for the cathode in case of fabrication of batteries. However, on the basis of their desirability, keeping in mind the battery's- (i) ***Specific energy/Capacity*** (Energy held by the battery per unit weight), (ii) ***Specific Power*** (Capability of the battery to deliver high current as and when required and to exhibit potential vehicle acceleration),

(iii*)* ***Safety***, (iv) ***Cost*** (Technology feasibility and warranty included), (v) ***Life Span*** (cycle count and longevity), (vi) ***Overall Performance*** (inclusive of the battery conditions, the vehicle being driven in harsh climatic conditions), the following Table 2 has been devised to display which battery is superior to the other based on the above characteristic features (Miao, Hynan, von Jouanne, & Yokochi, 2019).

Table-2. Li-Ion Batteries and their comparison.

Perspective	$LiCoO_2$	LMO	NMC	LFP	LTO	NCA
1. Specific Energy (Capacity)						
2. Specific Power						
3. Cost						
4. Life Span						
5. Safety						
6. Overall Performance						

INDEX:
Maximum- (On a scale of 1 to 4, this grading implies a 4.)
High- (On a scale of 1 to 4, this grading implies a 3.)
Average/Low- (On a scale of 1 to 4, this grading implies a 2.)
Minimum- (On a scale of 1 to 4, this grading implies a 1.)
[The more the grade value, the better the Hybrid Lithium Battery]

3.5. Potential Risks and Design Considerations

Unlike the power trains of fuel-driven automobiles, the usage of Li-ion batteries in Electric and Hybrid vehicles possess a significant number of threats, as has been exhibited in Figure 4. Hence certain preventive measures are to be taken during the Design procedure of the Lithium battery (Hollmotz & Hackmann, 2011).

The electrical risks as mentioned in Figure 4 above can be caused out of internal and external short cuts (basically failures of the high voltage system), cell aging processes, overcharging and over-discharging, external high temperature or crash events as well. Fire and explosion, as mentioned above, can be caused by sparks arising from a local gas concentration in proximity to our batteries. As far as the Chemical reactions of cathode or anode or electrolyte materials of the battery is concerned, thermal accidents can often arise out of these in the Electric/Hybrid vehicles.

Figure-4. Potential risks and dangers of using Li-ion batteries in EVs/Hybrid vehicles.

3.6. Safety Measures

The Figure 5 focuses on the safety of vehicle using LIBs, keeping in mind their 3-Level Chemistry, Cell and Battery system.

Figure-5. Safety Considerations for LIBs.

4. CONCLUSION

In this pivotal stage of energy crisis situation, the extraction of Lithium from brine and its manifestation in the production of LIBs can prove to be the quintessential solution to the existing Energy-scarcity problems of the world. Our proposed application of those LIBs in Electric and Hybrid vehicles is not just the future of e-mobility; it is rather, the key. This paper also hints at the diversion of the extractive industry to lower grade, abundant ores like Lithium, thereby helping to generate higher economic returns in the near future.

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