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(54) **PRODUCTION OF DILUTE PB (0.2 TO 1.1 WT %) - LI ALLOYS**

HERSTELLUNG VON VERDÜNNTEN (0,2 BIS 1,1 WT %) PB-LI-LEGIERUNGEN

PRODUCTION D'ALLIAGES DILUÉS DE PB (0,2 À 1,1 % EN POIDS) -LI

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EP 3 841 231 B1

Description**FIELD OF INVENTION**

5 **[0001]** The present invention relates to fused salt electrolysis method which provide such dilute Pb- (0.2 wt% to 1.1 wt%) Li alloys according to claim 1 and the apparatus for the the method of claim 1 as claimed in claim 15.

BACKGROUND AND PRIOR ART

10 **[0002]** Conventionally the Pb-Li alloys are produced by slowly injecting Li in the electromagnetically stirred liquid lead. This process involves meticulous loading of Li by dosimeters and precise electromagnetic mixing of Pb and Li to achieve homogeneity. This methodology of production is essentially adopted to avoid the formation of undesirable intermetallics of Pb and Li. To our best knowledge, Latvia is the only country in the world which has developed the aforementioned complex technology for the production of the dilutes Pb-Li alloy.

15 **[0003]** However, such process has many drawbacks and some of them are enumerated below:

i. Very large differences between the densities of Pb and Li results in considerable stratification. In the aforementioned technique developed by Latvia, the problem is addressed by precise mixing at component level by magnetic stirring (Magnetic hydrodynamic process; MHD process).

20 ii. In order to avoid formation of intermetallics, such as Li_4Pb , Li_7Pb_2 , Li_3Pb , Li_5Pb_2 , at any point of mixing, high concentration of Li in liquid Pb is avoided. This demands for a close control of Li dosing during magnetic stirring making entire process complicated.

25 iii. Preparation of the alloy by the Latvian process requires handling of highly inflammable and chemically active metallic liquid lithium. This makes the process accident prone. Extensive infrastructure and safety criteria need to be followed in adopting the MHD technology. This, in turn, unnecessarily increases complexity of the process and the manufacturing cost of the final alloy.

iv. Scaling up of the production of Pb-Li alloy by the Latvian process is not straight forward process.

30 **[0004]** Thus there is need to provide a method that would provide dilute Pb- Li alloys such that the concentration of the solute (here Lithium) is close to 1% in comparison with the solvent (here lead) which is about 99%. Fused salt electrolysis methods for Pb-Li-alloys are known from US1360269, GB389150 and US4455202.

OBJECTS OF THE PRESENT INVENTION

35 **[0005]** Accordingly, an object of the invention is to avoid the drawbacks of the prior art.

[0006] A further objective of the present invention is to produce Pb-Li alloy by avoiding the involvement of metallic lithium. This technology can, in fact, be extended to prepare other lithium or lead based alloys.

SUMMARY OF THE INVENTION

40 **[0007]** According to claim 1 of the present invention there is provided a process production of dilute Pb-(0.2 wt% to 1.1 wt %) Li alloys, by fused salt electrolysis.

[0008] A further aspect is to provide an apparatus for fused salt electrolysis method of preparing Pb-Li alloy said apparatus according to claim 15.

DETAILED DESCRIPTION OF THE INVENTION

45 **[0009]** In the known art Pb-Li alloy is prepared by MHD (Electromagnetic) mixing of elemental Pb and Li. The process involves meticulous loading of Li by dosimeters and precise electromagnetic mixing of Pb and Li to provide homogeneity and avoids formation of intermetallic of Pb and Li.

[0010] On the contrary the present invention utilizes fused salt electrolysis process to prepare Pb-Li alloy. The process uses Lithium salts like LiCl provided as mixture of salt in defined proportion such as LiCl - KCl as a source of lithium and thus eliminates the necessity of handling of highly active lithium element.

50 **[0011]** More specifically eutectic composition of LiCl-KCl salt mixture is used in the present invention because it has low melting point (353°C) while pure LiCl has melting point of 610°C and pure KCl melting point is 770°C. Composition other than eutectic composition can also be used to supply the lithium but it will require higher temperature of operation as it will have higher melting point. If pure LiCl is taken then the temperate of operation has to necessarily above 610°C which will require higher energy input from the furnace. Apart from higher energy input, higher temperature of operation

may cause other problems like faster corrosion of structural materials thereby limiting the life of the retort and cage. It has been observed that at high temperature, susceptibility of cracking in alumina crucible also increases. Accordingly, LiCl-KCl salt mixture is found to be preferable.

[0012] The lead is allowed to melt and Li is allowed to diffuse into the liquid lead, atom by atom generated through the electrolysis process. After attaining certain concentration, the liquid bath is stirred with the help of a stir to homogenized the composition of the liquid alloy.

[0013] More specifically in the process of Pb-Li alloy making involves an electrolytic cell, a furnace, salts and Pb. In the present process melting of lead is carried out, preferably in small furnace. This is introduced into electrolytic cell. The said electrolytic cell includes outer container to hold salt mixture of LiCl and KCl uniformly mixed in ratio of from 44:56 to 46:54 and preferably at 45:55 (± 1) ratio. The furnace temperature is raised to 450°C - 550 °C. This temperature is critical as higher temperature of operation beyond 550 °C leads to increase in cost of the production. Lower temperature of 450 °C is required to ensure that the salts are molten (450 °C = 100 °C above the theoretical melting temperature of eutectic). Subsequent to attaining 550°C, time period of 30-45 minutes is provided to ensure complete melting of salt and lead. Pre electrolysis is done for 15-20 minutes at 2.5 - 3.5V

[0014] After pre-electrolysis, to start the electrolysis process polarity of electrodes is reversed. Electrolysis is carried out for 5-20 hrs-in at 4.5-4.8 V at temperature of 500-550 °C. The range of the voltage should be adequately above the decomposition voltage of LiCl taking into consideration the internal resistance of the system. The internal resistance may vary from system size, materials of construction and contact resistances. For present system (as provided herein), the voltage range of 4.5-4.8V has been found to be preferred.

[0015] Stirring is done at the interval of 2-3 hrs. After completion of electrolysis, stirring is carried out for about 15-20 minutes. Furnace temperature is subsequently lowered and the whole system was allowed to cool overnight. The lead lithium alloy thus formed is recovered and washed with acetone to remove the access salt which stick on the surface and kept safely by submerging under kerosene or any other chemical or container which can prevent the oxidation of the alloy.

[0016] In the present process scale up of the production is possible either by employing multiple parallel setups or by small modifications in the design of the process.

[0017] The concentration of Pb is taken as (100-concentration of Li, assuming the other impurities in the alloy as negligible).

[0018] In the present specification when "highly active lithium" is used the word "active" is basically the propensity of lithium to react with moisture or air.

[0019] However, when Li forms an alloy with lead, its activity to react with moisture or air is reduced. As the concentration of Li (0.2-1.1 wt%) is in the dilute range, the activity of Li in the alloy is expected to be low. However, the concentration range of Pb and Li as mentioned in the study are not critical from the activity (i.e., reaction with moisture etc) point of view. This range is important, as higher concentration of Li may form high melting intermetallics with lead and should be avoided.

[0020] One of the main advantages of the process is that Dilute Pb-(0.2 wt% to 1.1 wt %) Li alloys in the batch of 20 kg scale, without using highly pyrophoric lithium metal, can be produced without involving very high technically qualified person. The process is much cheaper than the already existing MHD process, as (i) it uses cheaper input materials, like compound of Li (namely LiCl) as a source of lithium metal and (ii) does not require very stringent fire safety systems. The process also ensures regulated supply of in-situ produced lithium ions in a controlled manner to avoid formation of high melting lead-lithium intermetallics.

Some salient features of the present invention are as under

[0021]

- i. Cheaper input raw materials are available in open market.
- ii. The process can be easily scaled up.
- iii. The present invention can also be used to produce other lithium based alloys or lead base alloys also.

[0022] Regulated supply of Li is ensured by keeping the voltage constant, which provides a constant driving force for Li ions to move towards the lead cathode. The suitable conditions adopted in the process namely voltage and temperature as described in detail above, ensures non-aggregation of Li ions at any time which, in turns, does not allow formation of any high melting intermetallic phase. The compositions of the products are checked by two independent methods. In one, direct composition of the alloys is determined using ICP-AES and, in other, the melting point of the alloy, which is again, representative of the composition of the alloy, is determined by DSC.

[0023] In order to avoid the formation of Intermetallic phases, it is ensured that the concentration of Li should not exceed beyond 3.24 wt% (. The ICP-AES analyses of the samples collected from different locations showed maximum

concentration of Li as 1.1 wt%, which ruled out the formation of any intermetallic. The absence of intermetallic phases is also double checked by carrying out DSC where absence of any signature peaks of intermetallics reaffirms that there is no intermetallics.

[0024] The Pb-Li alloy formed by the present process has melting point of 232°C and having Pb at a concentration ranging from about 0.2 wt % to 1.1 wt % and Li at a concentration ranging from about 0.20 wt % to 1.10 wt%, preferably 0.65 wt%

[0025] The alloy formed by the present process is used as a coolant as well as a tritium breeder material for International Thermonuclear Experimental Reactor and future fusion reactors. The process of the present invention involves highly corrosive chloride based salts so commonly used stainless steel and iron based material will not be suitable as material of construction (MOC). They are easily corroded in the chloride atmosphere and would need to be replaced frequently. Moreover, corrosion of the component would also lead to contamination in the final product. Hence a special Ni based superalloy (Inconel 600) is selected as MOC for this purpose which has better corrosion resistance in chloride environment.

[0026] Though the process can run in any corrosion resistant apparatus, apparatus used in the present invention has a specially designed cage made of Inconel 600 which improves the ease of operation thereby improving the economy of the process. It is used to lift the product in the molten stage after the completion of the electrolysis. This helps in saving the consumables (graphite crucibles holding the salt) which can be used for future experimental runs. Otherwise, the product after cooling down would be stuck inside the solidified salt and the entire graphite needs to be broken to take out the product.

[0027] Another important feature of the setup is the use of Molybdenum stirrer for stirring the molten lead-lithium product intermittently. The stirring improved homogeneity of the product across the height. Molybdenum was selected as it has no solubility in molten lead, thereby preventing any contamination. It is to be noted that Inconel 600 made stirrers will not work because liquid lead has solubility of nickel.

[0028] The present invention is carried out in a specific apparatus which has retort and cage made of Inconel 600 as the same is corrosion resistant in chloride environment up to 600 °C. The Outer crucible to hold molten salts as well as Inner crucible to hold molten lead is made of graphite. Further the stirrer is made of molybdenum and the crucible for electrical insulation is made of high density alumina.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

[0029]

Fig. 1: Drawing of top flange for the Inconel retort (Fig 2). The top flange is used for insertion of Inconel cage, electrode (cathode and anode) assembly, mechanical stirrer and inert gas inlet/outlet.

Fig.2: Drawing of the Inconel retort used as container to hold graphite crucible, salt mixture and other paraphernalia

Fig.3: Drawing of Inconel cage used for lifting the lead cathode contained in graphite crucible above the molten salt level after the electrolysis.

Fig.4: Drawing of the outer graphite crucible which holds Inconel cage and salt mixture

Fig.5: Drawing of the alumina crucible (contained inside Inconel cage) which acts as an electric insulator.

Fig.5: Drawing of the alumina crucible (contained inside Inconel cage) which acts as an electric insulator.

Fig.6: Drawing of inner graphite crucible (kept inside the alumina crucible (Fig 5)) which holds the molten lead cathode

Fig.7: Schematic of graphite anode connected with Inconel rod (graphite anode assembly)

Fig.8: Drawing of molybdenum rod connector enclosed in alumina sleeve (molybdenum cathode assembly)

Fig.9: Schematic of molybdenum stirrer (2 mm thick) connected to Inconel rod (mechanical stirrer assembly)

Fig 10: The schematic of fused salt electrolysis assembly for lead lithium preparation. The table indicates the description of each part used in the assembly.

Fig. 11 Diagrammatic representation of the electrolysis process

Fig. 12: Typical Pb-Li alloy ingot obtained after electrolysis

[0030] The present invention is now described with reference to illustrative non-limiting examples and drawings

Example

[0031] Melting of small lead bricks with total weight of 18 Kg was taken in a 140 mm inner diameter, 170 mm height, 5 mm thick graphite crucible in a small furnace. The graphite crucible was kept in an alumina crucible having 160 mm inner diameter, 5 mm thick, 150 mm height. Alumina crucible along with graphite crucible was kept in an Inconel cage. An electrolytic cell of Inconel retort (as shown in figure 1) was employed with a outer graphite crucible as a container to hold the salt. Inconel cage consisting alumina crucible assembly was inserted in outer graphite crucible. Inconel retort

was kept in a furnace. A salt mixture of total 6 Kg weight consisting of LiCl and KCl uniformly mixed in the $45(\pm 1):55(\pm 1)$ ratio and poured into the outer graphite crucible till it fills the whole graphite crucible. Two graphite rods connected to Inconel rod, which serve as anode, was lowered to the salt level. A molybdenum rod sheathed with alumina sleeve was lowered to the lead level. A molybdenum stirrer connected to Inconel rod was also inserted. The stainless steel top flange was then closed and the entire cell was flushed with argon gas. Stirrer was locked into the top position. The furnace temperature was raised to 550 °C. Subsequent to attaining 550°C, time period of 30-45 minutes is provided to ensure complete melting of salt and lead. Pre electrolysis was done for 15-20 minutes at 3V by making graphite rod with Inconel negative and molybdenum rod as positive. After pre-electrolysis, to start the electrolysis process polarity of electrodes was reversed; molybdenum was made negative and graphite rod with Inconel made positive. Electrolysis was done for 16 hrs in at 4.5-4.8 V at temperature of 500-550 °C. Stirring was done at the interval of 3 hrs. After completion of electrolysis, 15 minutes stirring was done and then the cage which contains lead in graphite crucible, was lifted in hot condition till it gets above the salt surface. Graphite anodes and stirrer were locked into top position. Furnace temperature was lowered and the whole system was allowed to cool overnight. Cage was taken outside the retort and lead lithium alloy was recovered from graphite crucible with the help of hammer and chisel. The alloy was washed with acetone to remove the access salt stick on the surface and kept safely by submerging the ingot under kerosene. The samples taken from various locations of the alloy were analyzed for the composition using ICP-AES. In addition, melting point was determined through differential scanning calorimetric (DSC) analysis. Melting point was found 232°C and lithium composition was 0.65 ± 0.5 wt%.

Exemplary apparatus/device connections used for the Example:

Provided below is the specific apparatus used in the present invention.

[0032] The Inconel 600 retort and cage is specifically made for the present invention. Outer and inner crucible for holding molten salts and lead respectively and such crucibles being made of graphite. Further the stirrer used is of Molybdenum. The crucible for electrical insulation is made of high density alumina.

- Inconel retort and cage assembly
- Chlorine and Lead scrubber
- DC power supply
- Vertical furnace along with hydraulic lifting
- Small furnace for melting of pure lead

Details of Retort and cage assembly- Detailed Drawings are given in Fig 1-3.

[0033]

- | | | |
|----|---------------------------------------|--|
| 1. | Retort size | : ≈ 250 mm (OD) x 760 mm (H) x 7 mm (Thickness) |
| 2. | Retort Construction | : Inconel 600 |
| 3. | Flange of retort | : A double walled SS water-cooled flange fitted to the retort. The flange has many leak-tight ports as described below. |
| 4. | Ports in the Flange (as per drawing): | : 1. One number as gas inlet with valve
: 2. One number as gas outlet with valve
: 3. One number of wilson seal for cathode insertion with Teflon insert.
: 4. One number for stirrer immersion.
: 5. Two numbers for inserting solid rod arrangement to lift the crucible
: 6. Two number of wilson seal for anode insertion with Teflon insert. |
| 5. | Cage Size | : An inconel cage of 190 mm OD x 930 mm height x 6 mm thick and with 14 mm pore holes should be provided |
| 6. | Cage Material | : Inconel 600 |

Chlorine and Lead scrubber

[0034] The maximum flow of chlorine during the experiment should be **around 8 lpm**.

EP 3 841 231 B1

Design details

[0035]

Chlorine flow rate (max)	8 lpm (0.025 kg/min)
Chlorine gas temperature	200 °C
Scrubbing liquid	KOH (~25 wt %)
Separation efficiency	99.5 %

DC Power Supply

[0036]

Input Voltage	230V AC, $\pm 10\%$, 50Hz, 1phase
Output Voltage	0 to 32 V
Output Current	0 to 100 Amp
Line regulation CV	$\pm 0.01\% \pm 5\text{mV}$
Load regulation CV	$\pm 0.01\% \pm 5\text{mV}$
Line regulation CC	$\pm 0.1\% \pm 10\text{mA}$
Load regulation CC	$\pm 0.1\% \pm 10\text{mA}$
Remote sensing	Should be provided
Operating temperature	0 to 50 ° C
Protection	OL/SC current limit type
Indication (LED)	CV/CC
3 Digit DPM	V&I
Meter accuracy	± 3 count
Input On/Off	M.C.B.

Vertical Furnace

[0037]

HIGH TEMPERATURE CIRCULAR VERTICAL TYPE FURNACE WITH ONE END OPEN

1. Type of furnace : Circular vertical type furnace with one end open
2. Outside shell size : ≈ 500 mm (D) x 1000 mm (Height) Circular cross section
3. Useful volume (Hot Zone) : ≈ 500 mm dia x 450 mm height; Temperature uniformity should be $\pm 5^\circ\text{C}$ within this hot zone
5. Maximum operating temperature : : 1000°C
6. Continuous operating temperature : 50 - 600°C
7. Temperature control : Digital Temperature programmable controller
8. Temperature sensor : suitable Thermocouple along with display
9. Hydraulic lifting : It should have provision to lift 500 Kg weight

Small furnace for making Lead cathode in graphite crucible

[0038]

EP 3 841 231 B1

1. Type of furnace : Circular vertical type furnace with on end open and split type
2. Useful volume (Hot Zone) : ≈ 250 mm dia x 400 mm height
3. Maximum operating temperature : 800°C
4. Continuous operating temperature : 400°C
5. Temperature control : Digital Temperature programmable controller
6. Temperature sensor : Suitable Thermocouple along with display

Consumables required

[0039]

- Outer graphite crucible (Fig. 4)
- Inner graphite crucible (Fig. 6)
- Alumina crucible for electrical insulation (Fig. 5)
- High pure lead
- Lithium chloride salt (LiCl) and Potassium chloride salt (KCl)
- Molybdenum rod of 8 mm diameter and 1-meter length (Fig. 8)
- One-meter-long alumina sleeves to enclose molybdenum rod
- Two graphite rods (30 mm dia, 300 long) which is connected by threading with 1 mt long inconel rod (Fig. 7)
- A molybdenum stirrer connected to inconel rod (Fig. 9)

Outer graphite crucible

[0040]

1. Crucible size : $\approx 230\text{mm}$ (OD) x 215mm (ID) x 370 mm (Height) Circular cross section, bottom closed with thickness 10mm
2. Construction material : High density graphite (Density ≥ 1.85 gm/cc)

Note: 2 holes of 10 mm diameter in diametrically opposite direction should be provided at the top of graphite crucible (10 mm from top) for easy lifting.

Inner graphite crucible

[0041]

1. Crucible size : ≈ 150 mm (OD) x 170 mm (Height) x 5 mm (Thickness) Circular cross section, bottom closed with 10 mm thickness
2. Construction material : Density graphite (Density ≥ 1.80 gm /cc)

Alumina crucible for electrical insulation

[0042]

1. Crucible size : ≈ 170 mm (OD) x 150 mm (Height) x 5 mm (Thickness) Circular cross section, close end, bottom closed with 10 mm thickness
2. Construction material : Alumina (Density $\geq 99.9\%$)

High pure lead

[0043] 99.9% Pure Lead in the form of bricks of weight 5Kg with composition as given in table

Element	Composition (wt%)	Element	Composition (wt%)
Ag	<0.002	Bi	<0.03

(continued)

Element	Composition (wt%)	Element	Composition (wt%)
Cu	<0.002	Sn	<0.03
Nb	<0.002	w	<0.03
Pd	<0.002	As	<0.002
Zn	<0.002	Se	<0.002
Fe	<0.01	s	<0.002
Cr	<0.01	Cd	<0.002
Mn	<0.01	Te	<0.002
Mo	<0.01	Au	<0.002
Ni	<0.01	Al	<0.02
Si	<0.02		

LiCl & KCl

Purity: > 99%

Grade: AR grade

Claims

1. A process preparation of dilute Pb-(0.2 wt% to 1.1 wt %) Li alloys, by fused salt electrolysis, said process comprising
 - (i) providing molten lead;
 - (ii) providing salts of Lithium in defined proportion as a source of lithium;
 - (iii) subjecting fused salt to electrolysis wherein Lithium is allowed to diffuse into the liquid lead;
 - (iv) stirring intermittently during electrolysis to avoid formation of undesirable intermetallic compounds; and
 - (v) finally, stirring to homogenize the molten Pb-Li alloy of said concentration; wherein the stirrer is made of Molybdenum thereby preventing any contamination.
2. The process as claimed in claim 1 wherein salts of Lithium is provided as mixture of salts in defined proportion
3. The process as claimed in claim 2 wherein mixture of salts is LiCl -KCl
4. The process as claimed in claim 3 where LiCl-KCl mixture is provided in ratio 44:56 to 46:54 and preferably at 45: 55.
5. The process as claimed in any one of preceding claim wherein temperature achieved in this process is 550°C and maintained for 30 to 45 minutes allowing entire lead and lithium salt mixture to melt
6. The process as claimed in any one of preceding claim wherein Li is allowed to diffuse into the liquid lead, atom by atom generated through the electrolysis process
7. The process as claimed in any preceding claim wherein electrolysis is carried out for at 4.5-4.8 V
8. The process as claimed in any preceding claim where temperature is maintained at 500-550 °C during electrolysis.
9. The process as claimed in any one of preceding claim, wherein said electrolysis is performed after pre-electrolysis at 3V.
10. The process as claimed n claim 9 wherein said pre-electrolysis is carried out for a time of 15 minutes to 20 minutes.

11. The method as claimed in anyone of preceding claim, wherein stirring is carried out at a time interval of every 3 hours during electrolysis and for 15 minutes after completion of electrolysis.

12. The process as claimed in any one of preceding claim, wherein the obtained Pb-Li alloy is washed with acetone.

13. The process as claimed in claim 1, wherein the Pb-Li alloy obtained comprises Li at a concentration of 0.65 wt %.

14. The process as claimed in claim 1, wherein said Pb-Li alloy has melting point of 232°C.

15. An apparatus for fused salt electrolysis method of preparing Pb-Li alloy as claimed in claims 1 to 14, said apparatus comprising:

(a) a cathode (9);

(b) an anode (10),

(c) an inner graphite crucible (6) to hold molten lead (Pb);

(d) an outer graphite crucible (3) to hold molten salt mixture of LiCl-KCl;

(e) a stirrer (11);

(f) a Ni based superalloy retort (1) to hold outer and inner graphite crucible, salt mixture and other paraphernalia;

(g) a Ni based superalloy cage (4) to lift molten alloy in hot condition after completion of electrolysis process; and

(h) a top flange to cover retort (1) and cage (4) with a provision to insert cathode, anode and stirrer,

wherein the stirrer (11) is made of molybdenum.

16. The apparatus as claimed in claim 15, wherein the cathode (9) is made of molybdenum.

17. The apparatus as claimed in claim 16 where said Molybdenum cathode is fixed in alumina crucible (5).

18. The apparatus as claimed in any one of claims 15 to 17, wherein the anode (10) is made of graphite.

Patentansprüche

1. Prozess für eine Herstellung von verdünnten Pb(0,2 Gew.-% bis 1,1 Gew.-%)-Li-Legierungen mittels Salzschnmelzelektrolyse, der Prozess umfassend:

(i) Bereitstellen von geschmolzenem Blei;

(ii) Bereitstellen von Lithiumsalzen in definierten Anteilen als eine Lithiumquelle;

(iii) Unterziehen einer Salzschnmelze einer Elektrolyse, wobei Lithium ermöglicht wird, in das flüssige Blei zu diffundieren;

(iv) intermittierendes Rühren während der Elektrolyse, um die Bildung unerwünschter intermetallischer Verbindungen zu verhindern; und

(v) schließlich Rühren, um die geschmolzene Pb-Li-Legierung der Konzentration zu homogenisieren; wobei der Rührer aus Molybdän angefertigt ist, wobei dadurch jede beliebige Kontamination verhindert wird.

2. Prozess nach Anspruch 1, wobei Lithiumsalze als Mischung von Salzen in definierten Anteilen bereitgestellt werden.

3. Prozess nach Anspruch 2, wobei die Mischung von Salzen LiCl-KCl ist.

4. Prozess nach Anspruch 3, wobei das LiCl-KCl-Gemisch in einem Verhältnis von 44 : 56 bis 46 : 54 und bevorzugt von 45 : 55 bereitgestellt wird.

5. Prozess nach einem der vorhergehenden Ansprüche, wobei die in diesem Prozess erreichte Temperatur 550 °C beträgt und 30 bis 45 Minuten lang aufrechterhalten wird, um zu ermöglichen, dass die gesamte Blei- und Lithiumsalzmischung schmilzt.

6. Prozess nach einem der vorhergehenden Ansprüche, wobei dem Li ermöglicht wird, in das flüssige Blei Atom für Atom zu diffundieren, was durch den Elektrolyseprozess generiert wird.

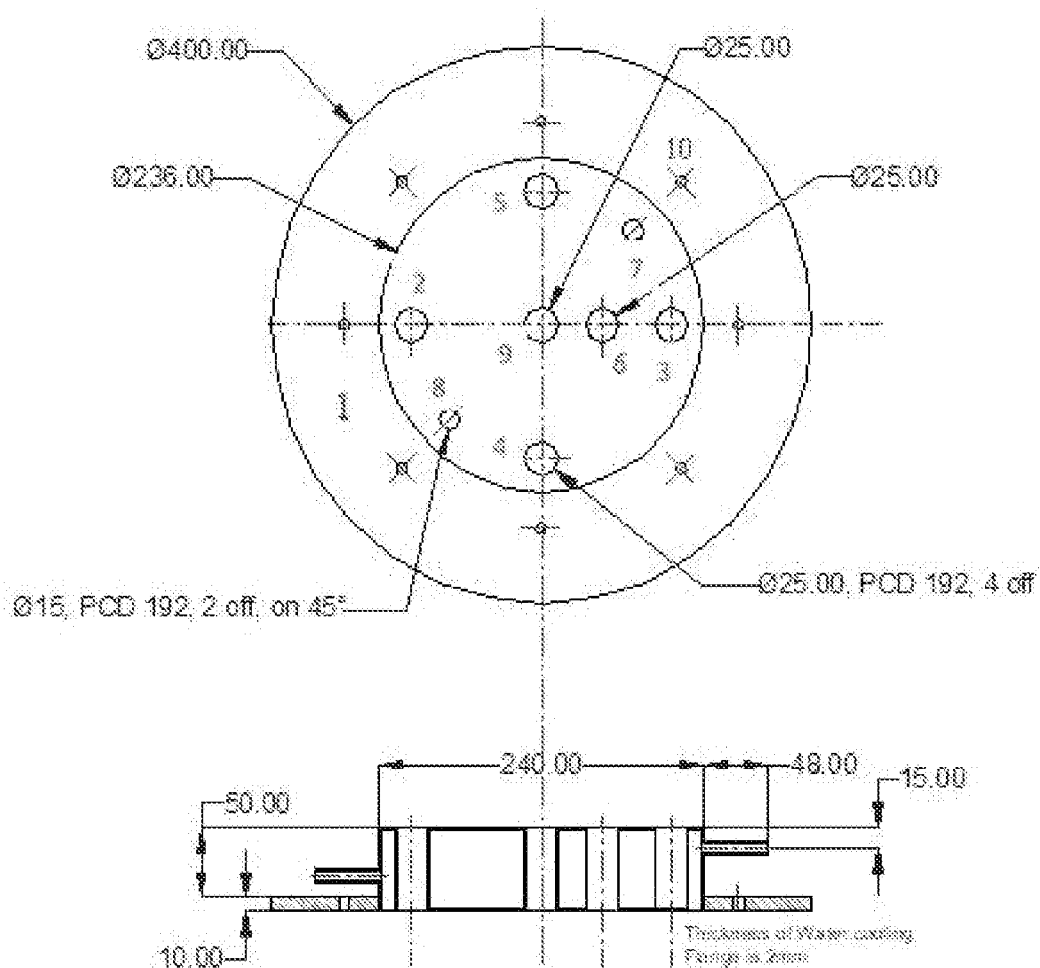
7. Prozess nach einem der vorhergehenden Ansprüche, wobei die Elektrolyse bei 4,5 bis 4,8 V ausgeführt wird.
8. Prozess nach einem der vorhergehenden Ansprüche, wobei die Temperatur während der Elektrolyse bei 500 bis 550 °C aufrechterhalten wird.
9. Prozess nach einem der vorhergehenden Ansprüche, wobei die Elektrolyse nach der Vorelektrolyse bei 3 V durchgeführt wird.
10. Prozess nach Anspruch 9, wobei die Vorelektrolyse für eine Zeit von 15 Minuten bis 20 Minuten ausgeführt wird.
11. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Rühren in einem Zeitintervall von alle 3 Stunden während der Elektrolyse und 15 Minuten lang nach Abschluss der Elektrolyse ausgeführt wird.
12. Prozess nach einem der vorhergehenden Ansprüche, wobei die erhaltene Pb-Li-Legierung mit Aceton gewaschen wird.
13. Prozess nach Anspruch 1, wobei die erhaltene Pb-Li-Legierung Li in einer Konzentration von 0,65 Gew.-% umfasst.
14. Prozess nach Anspruch 1, wobei die Pb-Li-Legierung einen Schmelzpunkt von 232 °C aufweist.
15. Einrichtung für ein Salzschnmelzelektrolyseverfahren für die Herstellung der Pb-Li-Legierung nach den Ansprüchen 1 bis 14, die Einrichtung umfassend:
 - (a) eine Kathode (9);
 - (b) eine Anode (10),
 - (c) einen inneren Graphittiegel (6), um geschmolzenes Blei (Pb) aufzunehmen;
 - (d) einen äußeren Graphittiegel (3), um eine geschmolzene Salzmischung aus LiCl-KCl aufzunehmen;
 - (e) einen Rührer (11);
 - (f) eine Ni-basierte Superlegierungsretorte (1), um einen äußeren und inneren Graphittiegel, die Salzmischung und anderer Utensilien aufzunehmen;
 - (g) einen auf Ni basierenden Superlegierungskäfig (4), um geschmolzene Legierung in heißem Zustand nach Abschluss des Elektrolyseprozesses zu heben; und
 - (h) einen oberen Flansch, um die Retorte (1) und den Käfig (4) abzudecken mit einer Vorrichtung, um die Kathode, die Anode und den Rührer einzusetzen, wobei der Rührer (11) aus Molybdän angefertigt ist.
16. Einrichtung nach Anspruch 15, wobei die Kathode (9) aus Molybdän angefertigt ist.
17. Einrichtung nach Anspruch 16, wobei die Molybdänkathode in einem Aluminiumoxidtiegel (5) befestigt ist.
18. Einrichtung nach einem der Ansprüche 15 bis 17, wobei die Anode (10) aus Graphit angefertigt ist.

Revendications

1. Processus de préparation d'alliages de Pb-Li (0,2 % en poids à 1,1 % en poids) dilués, par électrolyse de sels fondus, ledit procédé comprenant
 - (i) la fourniture de plomb fondu ;
 - (ii) la fourniture de sels de lithium en proportion définie comme source de lithium ;
 - (iii) la soumission de sels fondus à une électrolyse, le lithium étant autorisé à se diffuser dans le plomb liquide ;
 - (iv) l'agitation par intermittence pendant l'électrolyse pour éviter la formation de composés intermétalliques indésirables ; et
 - (v) enfin, l'agitation pour homogénéiser l'alliage Pb-Li fondu de ladite concentration ; l'agitateur étant en molybdène, empêchant ainsi toute contamination.
2. Processus selon la revendication 1, des sels de lithium étant fournis sous forme de mélange de sels en proportion définie.

EP 3 841 231 B1

3. Processus selon la revendication 2, le mélange de sels étant LiCl-KCl.
4. Processus selon la revendication 3, le mélange LiCl-KCl étant fourni dans un rapport de 44:56 à 46:54 et de préférence de 45:55.
5. Processus selon l'une quelconque des revendications précédentes, la température atteinte dans ce processus étant de 550 °C et étant maintenue pendant 30 à 45 minutes, permettant à tout le mélange de plomb et de sels de lithium de fondre.
6. Processus selon l'une quelconque des revendications précédentes, le Li étant autorisé à se diffuser dans le plomb liquide, atome par atome généré par l'intermédiaire du processus d'électrolyse.
7. Processus selon l'une quelconque des revendications précédentes, l'électrolyse étant effectuée entre 4,5 et 4,8 V.
8. Processus selon l'une quelconque des revendications précédentes, la température étant maintenue entre 500 et 550 °C pendant l'électrolyse.
9. Processus selon l'une quelconque des revendications précédentes, ladite électrolyse étant réalisée après une pré-électrolyse à 3 V.
10. Processus selon la revendication 9, ladite pré-électrolyse étant effectuée pendant une durée de 15 minutes à 20 minutes.
11. Procédé selon l'une quelconque des revendications précédentes, l'agitation étant effectuée à un intervalle de temps de toutes les 3 heures pendant l'électrolyse et pendant 15 minutes après la fin de l'électrolyse.
12. Processus selon l'une quelconque des revendications précédentes, l'alliage Pb-Li obtenu étant lavé avec de l'acétone.
13. Processus selon la revendication 1, l'alliage Pb-Li obtenu comprenant du Li à une concentration de 0,65 % en poids.
14. Processus selon la revendication 1, ledit alliage Pb-Li ayant un point de fusion de 232 °C.
15. Appareil destiné à un procédé d'électrolyse de sels fondus pour la préparation d'un alliage Pb-Li selon les revendications 1 à 14, ledit appareil comprenant :
 - (a) une cathode (9) ;
 - (b) une anode (10),
 - (c) un creuset en graphite interne (6) pour contenir du plomb fondu (Pb) ;
 - (d) un creuset en graphite externe (3) pour contenir un mélange de sels fondus de LiCl-KCl ;
 - (e) un agitateur (11) ;
 - (f) une cornue (1) en superalliage à base de Ni pour contenir les creusets en graphite externe et interne, le mélange de sels et d'autres accessoires ;
 - (g) une cage (4) en superalliage à base de Ni pour soulever l'alliage fondu à chaud après la fin du processus d'électrolyse ; et
 - (h) un recouvrement supérieur pour couvrir la cornue (1) et la cage (4) avec un accès pour insérer la cathode, l'anode et l'agitateur,l'agitateur (11) étant en molybdène.
16. Appareil selon la revendication 15, la cathode (9) étant en molybdène.
17. Appareil selon la revendication 16, ladite cathode en molybdène étant fixée dans un creuset en alumine (5).
18. Appareil selon l'une quelconque des revendications 15 à 17, l'anode (10) étant en graphite.



Numbers marked: 1: Stainless steel (SS 316) flange, 2-3: Ports for Inconel 600 cage, 4-5: Ports for graphite anode assembly, 6: Port for molybdenum cathode assembly connected to lead cathode, 7-8: Ports for gas inlet/outlet (SS 316), 9: Port for molybdenum stirrer assembly

Figure 1

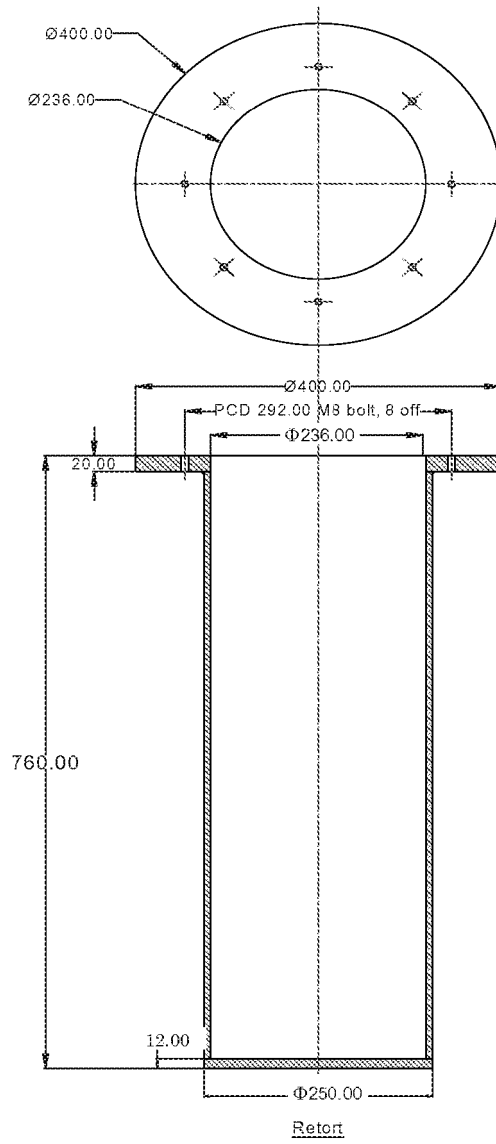


Figure 2

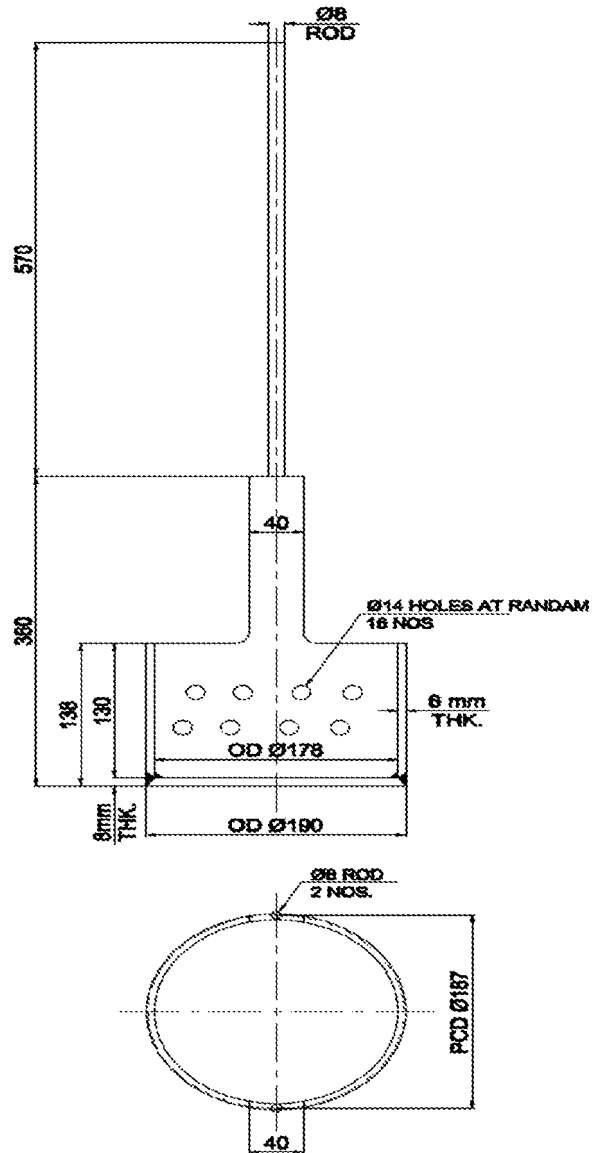


Figure 3

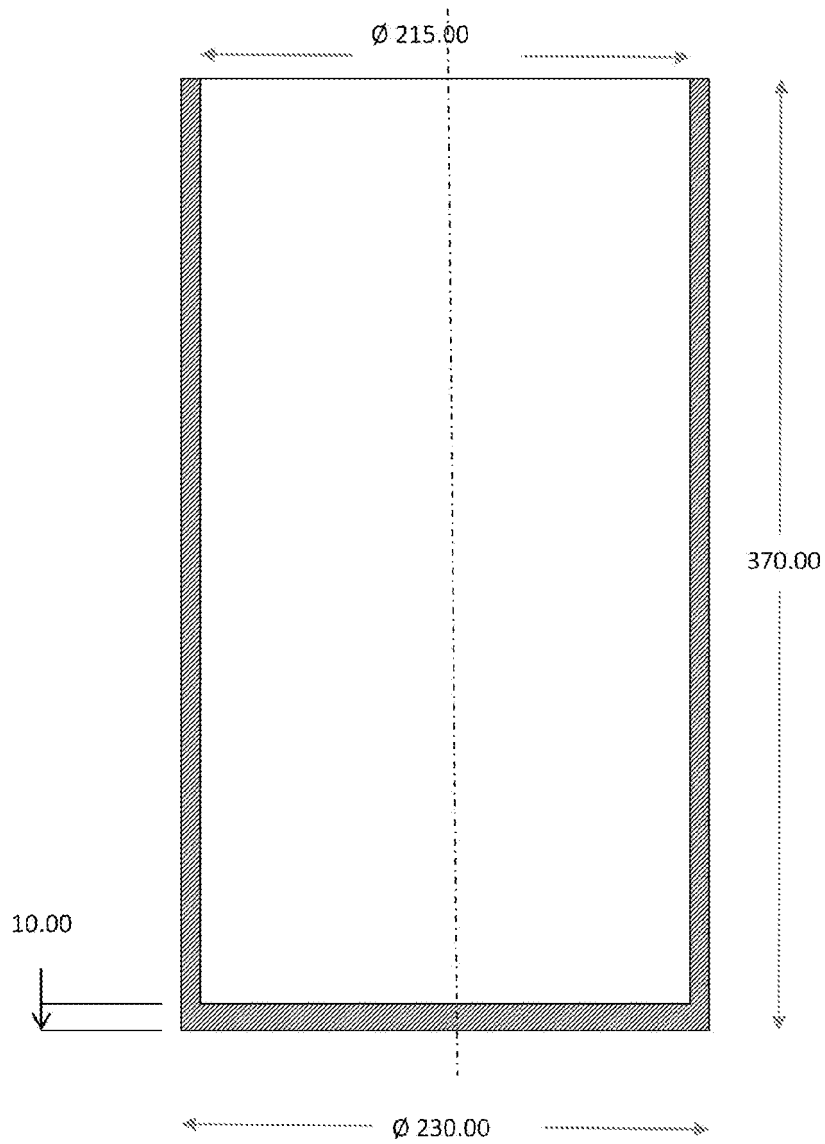


Figure 4

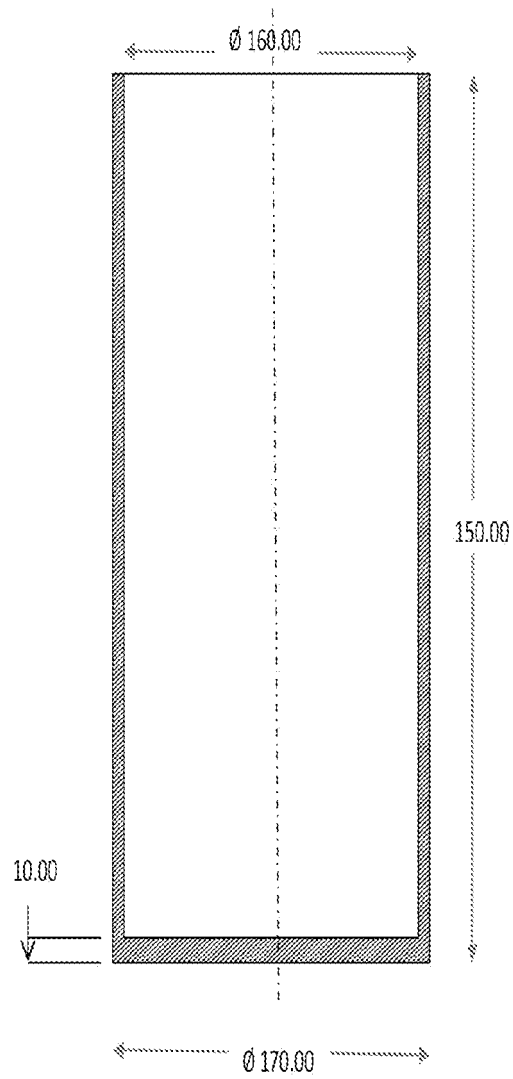


Figure 5

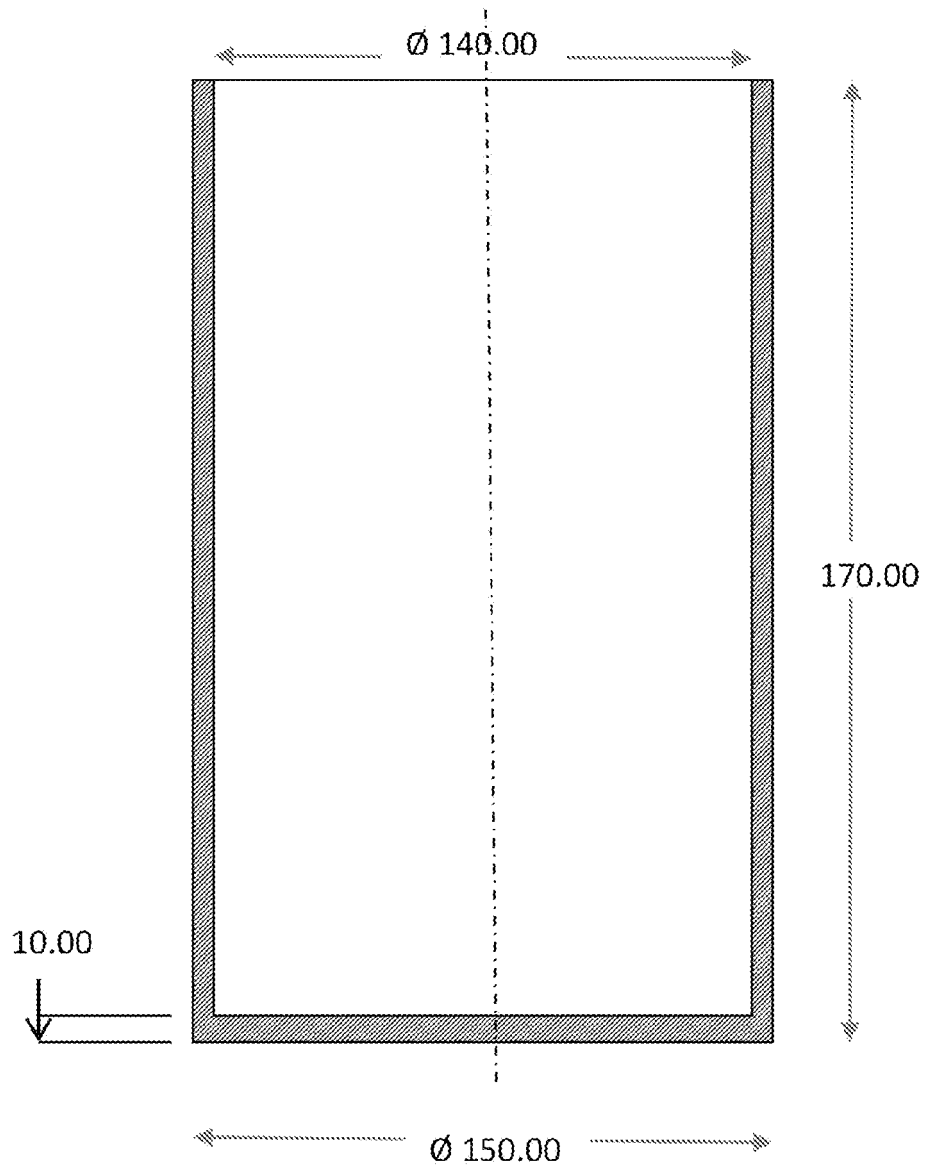


Figure 6

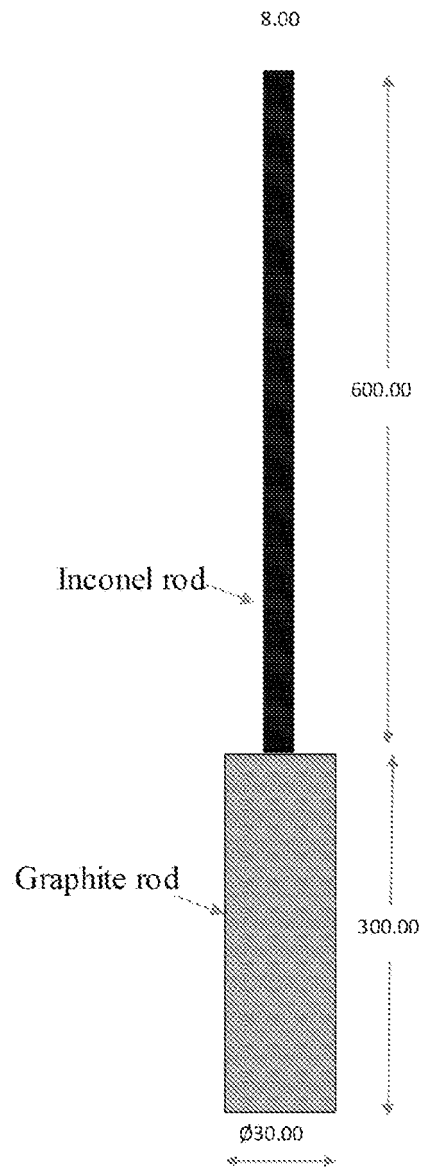


Figure 7

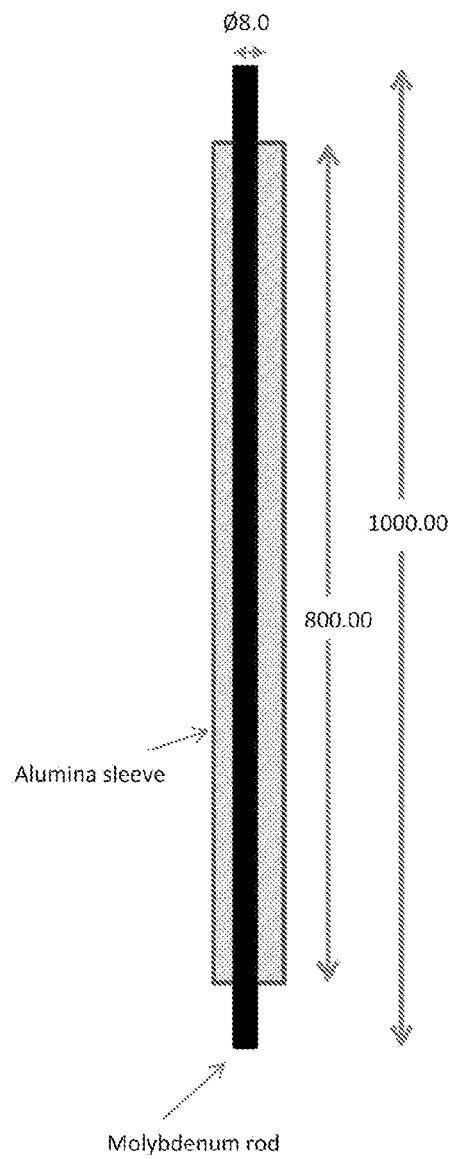


Figure 8

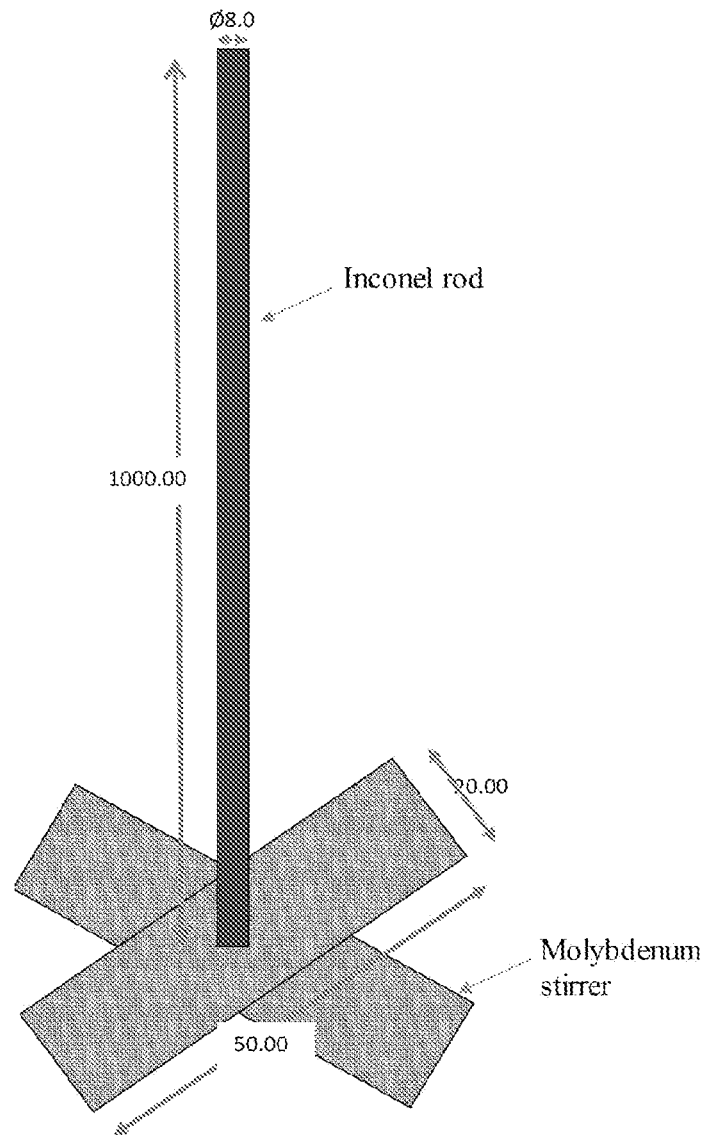


Figure 9

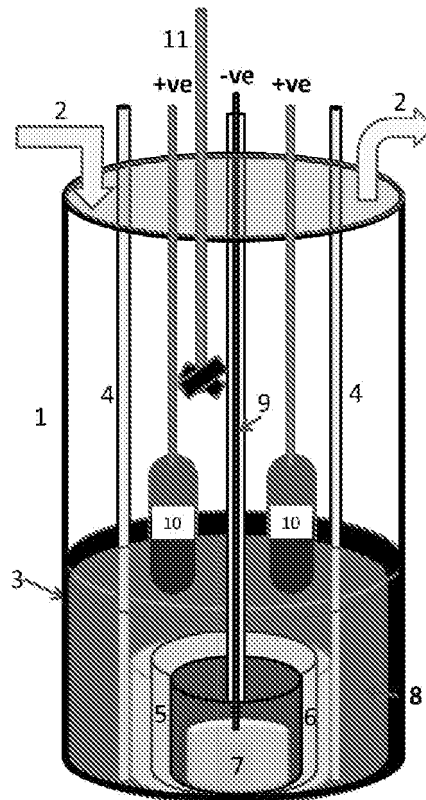


Figure 10

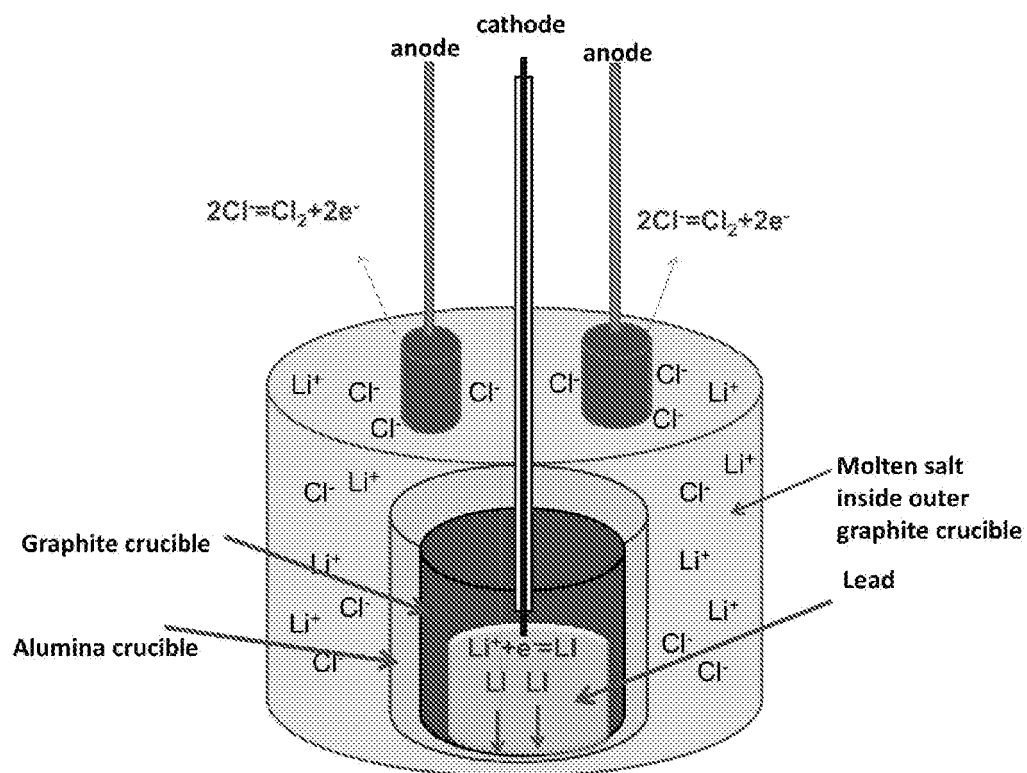


Figure 11



Figure 12

REFERENCES CITED IN THE DESCRIPTION

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