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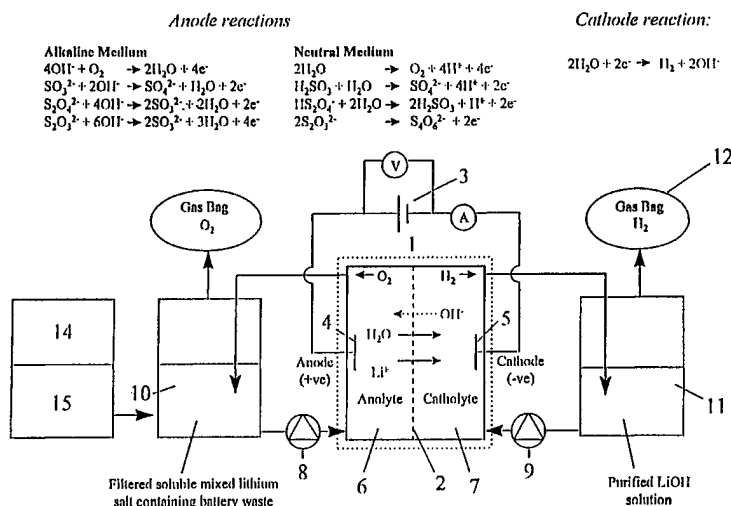
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(54) Title: LITHIUM RECOVERY AND PURIFICATION



(57) Abstract

This invention relates to a method and apparatus for the recovery and/or purification of lithium, particularly from lithium battery waste material. The method involves an electrolytic process in which a lithium containing slurry is filtered and washed to separate insoluble materials from the soluble lithium components, the filtered soluble mixed lithium salt containing battery waste solution is provided as an anolyte in the anode compartment of an electrolytic cell, the anode compartment is separated from the cathode compartment with a cation exchange membrane having a porosity to selectively allow the passage of lithium ions and inhibit the passage of others, a current is passed through the electrolytic cell and substantially pure lithium hydroxide solution is withdrawn from the cathode compartment. The method may further include a nanofiltration process in which the substantially pure lithium hydroxide solution is passed against a nanofiltration membrane having a stability at a pH of at least 11, under pressure, and the permeate is collected, being a further purified lithium hydroxide solution. The nanofiltration process may be employed for the purification of other monovalent lithium salt solutions.

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LITHIUM RECOVERY AND PURIFICATION

BACKGROUND

This invention relates to a method and apparatus for the recovery and/or purification of lithium from, in particular, although not necessarily solely, crushed, alkali hydrolysed primary and secondary lithium battery waste. The principles can be applied to any water soluble lithium sources.

In the case of recycling battery materials, the prior art has focused on the recovery of materials other than lithium from various battery sources (US 5437705, US 5173277, US 5478664 and US 5248342), and where lithium batteries have been recycled, lithium salt recovery from the waste material has not been addressed (US 5491037 and US 5612150).

A number of different techniques have been used for the recovery of lithium as high purity lithium hydroxide or for the recovery of other alkali metals as alkali metal hydroxide. Examples are described in US Patent Nos. 4036713, 4337216 and 4636295. Each of these use an electrical potential gradient to convert lithium salts or other alkali metal salts into their corresponding hydroxides. Such techniques require substantial inputs of energy much of which may be expended in producing gases at each of the electrodes. Furthermore, solution pre-concentration, chemical pretreatment, high feed temperature or even double-pass electrodialysis are required to achieve high product quality.

A single-pass electrolytic process effectively generates lithium hydroxide by splitting the lithium salt and water fed to the unit. The salt and water splitting steps require significant energy. Consequently, double-pass or multi-pass electrodialysis is not a good way to further purify lithium hydroxide in terms of energy consumption.

Other purification techniques include that described in US Patent No. 4565612 which uses the propensity of sodium carbonate to form a double salt with sodium sulphate to remove sulphate from a sodium hydroxide solution.

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Although this technique may be used to reduce sulphate concentrations, it cannot be used to reduce concentrations to small trace levels. Furthermore, such an operation can only be used once in the purification technique. Repetition of the step does not provide further purification.

Other techniques for purification include the use of nanofiltration. Examples are described in US Patent Nos. 5254257 and 5587083. Each of these processes utilise nanofiltration which utilises pressure rather than an electrical potential gradient to drive the separation. Without the need to perform salt and water splitting, further energy savings can be made through the use of nanofiltration. Nanofiltration is also a technique which can be performed repeatedly to obtain desired solution purities.

The difficulty with these prior art uses of nanofiltration is that the feed solutions are generally acidic or very slightly alkaline. In particular lithium hydroxide is highly alkaline. A typical feed solution of lithium hydroxide may have a pH of 14 or greater. As such, the nanofiltration membranes utilised in such prior art apparatus are generally unable to process lithium hydroxide solutions due to the instability of the membrane at such high pH levels.

OBJECT OF THE INVENTION

It is an object of the present invention to provide a method and/or apparatus for the recovery and/or purification of lithium in a high value form from recycled primary and secondary lithium battery waste which will overcome some of the disadvantages of the prior art or at least provide the public with a useful choice.

Other objects of the invention may become apparent from the following description which is given with reference to particular examples.

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STATEMENTS OF INVENTION

Accordingly, in a first aspect, the invention may broadly be said to consist in a method for the recovery and purification of lithium from lithium battery waste including:

- processing said lithium battery waste into a lithium containing slurry;
- filtering and washing the lithium containing slurry to separate the insoluble materials from the soluble lithium components;
- providing an electrolytic cell consisting of an anode and a cathode;
- separating anode and cathode compartments with a cation exchange membrane having a porosity to selectively allow the passage of lithium ions and inhibit the passage of others;
- providing the filtered soluble mixed lithium salt containing battery waste solution as an anolyte in the anode compartment;
- passing a current through the electrolytic cell; and
- withdrawing substantially pure lithium hydroxide solution from the cathode compartment.

Preferably, the anolyte may have a pH greater than 7.

Preferably, the anolyte and catholyte may be circulated through their respective anode and cathode compartments.

Preferably, the method may further include the step of keeping separate any gases produced at the anode and cathode.

In one preferred form the method may include further purification of the lithium hydroxide solution by nanofiltration, including the steps of:

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- providing a nanofiltration membrane having stability at a pH of at least 11;
- passing the lithium hydroxide solution against the membrane under pressure; and
- removing a permeate being a further purified lithium hydroxide solution from an opposed side of the membrane from the feed stock.

Accordingly, in a further aspect, the invention may broadly be said to consist in a method for the purification of monovalent lithium salt solutions comprising the steps of:

- providing a nanofiltration membrane having stability at a pH of at least 11;
- providing a feed stock of solution containing said monovalent lithium salt;
- passing said feed solution against said membrane under pressure; and
- removing a permeate being a purified monovalent lithium salt solution from a distal side of said membrane from said feed stock.

Preferably, the feed stock solution may have a temperature of substantially greater than or equal to 5°C.

Preferably, the feed stock may be provided at a pressure of greater than 5 Bar, and more preferably greater than 15 Bar.

Accordingly, in a further aspect, the invention may broadly be said to consist in an apparatus for the recovery of lithium from lithium battery waste including:

- a solid/liquid filter and which incorporates solids washing apparatus;

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- an electrolytic cell;
- anode and cathode compartments within said electrolytic cell divided by a cation exchange membrane having a porosity to selectively allow the passage of lithium ions;
- a power supply to said electrolytic cell to pass a current through said cell;
- filtered soluble mixed lithium salt containing battery waste solution within said anode compartment; and
- means to withdraw substantially pure lithium hydroxide solution from said cathode compartment.

Preferably, the cation exchange membrane may comprise a Nafion 350 membrane.

Accordingly, in a further aspect, the invention may broadly be said to consist in an apparatus for the purification of monovalent lithium salt solutions including:

- a filtration unit;
- a nanofiltration membrane within said filtration unit having a stability at pH levels of at least 11;
- pressurising means to feed a monovalent lithium salt solution into said filtration unit under pressure; and
- an outlet from the filtration unit on an opposed side of the nanofiltration membrane from the inlet.

Preferably, the nanofiltration membrane is stable at a pH of at least 14.

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Further aspects of the invention may become apparent to those skilled in the art to which the invention relates upon reading the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described with reference to the drawings in which:

Figure 1:

Is a schematic diagram of a general arrangement of the invention for performing the recovery of lithium by electrodialysis;

Figure 2:

Is a schematic diagram of one preferred embodiment of the process of purification of LiOH by nanofiltration.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The invention involves two parts. The first part principally relates to a method and apparatus for the production of substantially pure lithium hydroxide from primary and secondary lithium battery waste. The lithium hydroxide thus obtained can be further purified using the second part of the invention, or can be converted into different high purity lithium salts, including lithium carbonate for the manufacture of lithium battery materials.

The second part of the invention relates to the purification of lithium hydroxide solution by nanofiltration, whilst the first process involves the use of an electrolytic cell.

Referring to Figure 1, the general arrangement can be seen to include an electrolytic cell 1 having a membrane 2 which will allow the passage of lithium ions but generally keep the liquid and gas in the anode and cathode compartments separate from one another. A power source 3 is provided to

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pass a current from the anode 4 to the cathode 5 through the anolyte and catholyte 6 and 7; respectively.

Due to the reaction taking place within the electrolytic cell, lithium ions migrate from the anode compartment, through the cation exchange membrane 2, to the cathode compartment. It should be noted that the membrane 2 also serves to separate any gases which are produced at either electrode. The membrane also prevents the back migration of the hydroxy ions from the catholyte as well as the diffusion of contaminating anions into the catholyte from the anolyte. The membrane 2 can achieve this through the selective choice of membrane having a suitable porosity for the passage of lithium while reducing the ability of other cations to diffuse through the membrane. Additionally the membrane holds a negative charge which discourages the passage of anions.

The lithium containing battery waste may be processed into a slurry and then filtered in a solid/liquid filter 14. This is then followed by a washing step in a solids washing apparatus 15 to recover further lithium bound up in the material. This results in a filtered soluble mixed lithium salt containing battery waste. Typically this solution would have a pH in the range 11.5 to 12. The efficiency of the process is dependent on the starting pH of the solution, the higher the pH the more efficient the process. A pH of 7 or more is preferred.

It can be seen that the filtered soluble mixed lithium salt containing battery waste solution can be supplied as the anolyte in the cell and is pumped through the anode compartment by a pump 8. In the cathode compartment, a substantially pure lithium hydroxide solution is circulated under the influence of a pump 9.

Separate chambers 10 and 11 may be provided interconnected with the anode and cathode compartments respectively.

As can be seen from Figure 1, the apparatus can also provide collection of the hydrogen gas produced as part of the electrolytic process and this may be collected in gas collector 12. If desired the hydrogen gas may be utilised in

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power generation to provide some further efficiencies on the apparatus as a whole.

To generate efficiencies with the electrolytic process, a number of factors need to be taken into account. Experiments were conducted using Nafion 350 and Neosepta CMS membranes, however other membranes of similar porosity may provide similar efficiencies.

In choosing the membrane, a number of factors need to be taken into account. It is desirable to utilise a membrane with a high current efficiency and which will reduce the migration of OH^- ions back towards the anolyte. A low electrical resistance is desirable as well as some resistance to heat. A low diffusion of ions other than lithium is preferable and low permeability of water may also be desirable.

To prevent undesirable back migration of the hydroxy ion from the cathode compartment to the anode compartment, the flow velocity may also need to be considered. The flow velocity may also enhance mixing, convection and the removal of gaseous products to overall reduce the resistance of the solution and enhance lithium extraction.

A matter specific to battery waste solutions is the presence of the sulphur oxyanions. Their oxidation at the anode will reduce the initial electrolysis voltage required and will prevent the production of oxygen. As the extraction process proceeds, the sulphur oxyanions will be consumed resulting in the consumption of hydroxide ions and water molecules. Both effects result in the production of oxygen and the reduction of anolyte pH. Furthermore, chloride present in the anolyte will be oxidized to chlorine during the process. On complete transfer of lithium from the anolyte to the catholyte, the residual anolyte will consist largely of concentrated sulphuric acid.

Example 1

In a laboratory trial, a battery waste solution was filtered to separate the insoluble battery waste materials. This yielded 2.3L filtrate with a lithium concentration of 2%.

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The electrolytic cell was assembled with the Nafion 350 membrane. Filtered soluble mixed lithium salt containing battery waste solution with an initial lithium concentration of 2% was circulated in the anode compartment, whereas lithium hydroxide solution of substantially lower lithium concentration was circulated in the cathode compartment to reduce the overall cell resistance. Flow rate optimization was performed by monitoring the cell voltage at different anolyte and catholyte flow rates.

Water migration could also be calculated by measuring the volume change of catholyte.

In passing the current through the electrolytic cell, gas bubbles are generated in both the cathode and latterly the anode compartments which increase the solution resistance. Solution flow rates may be employed to remove those gas bubbles so as to reduce the solution resistance and give a higher current. It has been found that lower flow rates for the anode compartment compared with the cathode compartment provide the optimum for electrical current during sulphur oxyanion oxidation, due to the lack of gas production. In a 10cm² cell, the anolyte flow rate was 0.32 L/min and the catholyte flow rate was 0.51 L/min. Towards the end of lithium extraction when most of the sulphur oxyanions have been oxidised and gas is being produced in the anode compartment, a higher anode compartment flow rate is optimal.

The cell characteristics of the trial were obtained using a Nafion 350 membrane and a current density of 2kA/m². When the catholyte concentration reached 20900 ppm lithium, the cell voltage was 5.3 volts with a current efficiency ranging from 91-74%. The energy consumption ranged from 39-34 gLi/kWhr.

These came from an electrolytic cell having an anolyte consisting filtered lithium battery waste solution with a lithium concentration of 2%. The catholyte concentration ranged between 6880 and 20900ppm lithium.

Example 2

In another laboratory trial, 480g solid battery waste was mixed with 500 mL deionized water. The mixture was stirred and was filtered to separate the insoluble battery waste materials. The residue was washed with deionized water. This yielded a filtrate with 3.2% lithium. 400 mL filtrate was used as the anolyte and 300 mL deionized water was used as the starting catholyte. The anolyte contained 150 ppm of monovalent cations (Na, K) and 38 ppm of total divalent and multivalent metal ions. A 10 cm² electrolytic cell assembled with the Nafion 350 membrane was used for the lithium extraction. A current density of 2.5 kA/m² was used. The volume of the anolyte was maintained by replenishing it with deionized water during the process.

The cathode gas, hydrogen, production rate was around 1200 L/m²/hr and approached 100% current efficiency. There was not much gas emission at the anode during the first 50% lithium transfer due to the preferential oxidation of sulphur oxyanions at the anode. The anode gas emission, essentially oxygen, reached a maximum of about 550 L/m²/hr at 70% lithium transfer.

The voltage dropped from 10 to 5.2 volts when the catholyte concentration reached 6.5% LiOH. It was found that the voltage went down further to 4.8 volts as the process proceeded even though the lithium concentration of the anolyte was decreasing. This was because the increase in acidity of the anolyte maintained or even increased the conductivity of the solution. However, the increase in acidity of the anolyte and the increase in hydroxide content of the catholyte caused lower current efficiency as a result of hydroxide ion back migration to the anolyte. This effect was found to be particularly pronounced at low anolyte pH values, typically found towards the end of the extraction process. The compositions of the feed and products at 90% lithium transfer are given in Table 1.

Table 1**Composition of the feed and products at 90% lithium transfer.**

Parameters	Feed Anolyte	Finished Anolyte	Finished Catholyte
Major Component	battery waste	15% H ₂ SO ₄	6.4% LiOH
Li ⁺ (g)	12.9	1.7	11.6
Na ⁺ , K ⁺ (g)	0.059	0.003	0.058
Divalent & Multivalent metal ions (g)	0.015	0.010	0.006
SO ₄ ²⁻ (g)	42	72	1.1
S _x O _y ⁿ⁻ (as g SO ₄ ²⁻)	33	<0.004	<0.004
Cl ⁻ (g)	2.0	<0.004	<0.004

It was found that the divalent and multivalent metal ions did not deposit on the cation membrane, as indicated by the very good mass balance of these ions in both electrolytes before and after the process. Otherwise, membrane fouling will be observed with voltage increase during lithium transfer. Furthermore, the sulphur oxyanions, S_xO_yⁿ⁻, were oxidized to SO₄²⁻. The sum of the sulphate and sulphur oxyanions in the feed anolyte is very similar to the amount of sulphate in the finished anolyte. Chloride was oxidized to chlorine gas.

After the extraction process, a relatively pure and concentrated lithium hydroxide solution was produced as the catholyte. The finished anolyte consisted largely of concentrated sulphuric acid.

From the laboratory trials, the lithium hydroxide was carbonated using food grade carbon dioxide without product washing. The assay of the lithium carbonate obtained was 99.3%. The purity can be further increased by washing the product with deionized water but the product yield will be lower. Alternatively, the trace impurities in the lithium hydroxide can be removed through the use of ion exchange resins. However, the usable resin bed volume

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before column breakthrough is not economical and a large amount of chemical waste will be generated during resin regeneration. Consequently, the second part of the invention involves the purification of lithium hydroxide solution using a nanofiltration membrane. The nanofiltration technique is simple, offers high lithium recovery and high rejection for divalent and multivalent ions, and does not generate large amount of chemical waste.

The second part of the invention utilises a filter 21 containing a nanofiltration membrane 22, as shown in Figure 2. Nanofiltration membranes are generally, although not necessarily always, multiple layer thin film composites of polymers. The active membrane layer often consists of negatively charged chemical groups and are believed to be porous with an average pore diameter of 2 nanometers. As such, nanofiltration membranes will retain large molecules and certain multivalent salts such as MgSO_4 but pass substantial amounts of most monovalent salts and monovalent metal hydroxides. As a result, a monovalent lithium salt or lithium hydroxide can be purified using nanofiltration membranes to reject divalent ions.

As shown in Figure 2, the filter 21 and membrane 22 may be used in an overall apparatus to provide nanofiltration in batch mode. Alternatively, other configurations could allow continuous processing.

A feed solution of lithium hydroxide is provided in the container 23. The solution 24 may pass through a conduit or similar 25 and through a pump 26 to increase the pressure of the solution as it enters the filtration module 21. Although a variety of pressures may be used, pressure is an important component of the separation and the pressure is preferably greater than 10 Bar and, more preferably, approximately 20 Bar, although pressure as high as 40 Bar may be used.

As the solution passes over the membrane 22 towards the outlet 27, the solution is separated into a permeate and a retentate. The retentate may be passed through a conduit 28 to the container 23 and is preferably, though not necessarily, passed through a pressure valve 29 so that the pressure may be released.

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The permeate 30 may be drawn off through a separate outlet 31 on an opposed side of the membrane 22 from the inlet 32.

As can be seen, by operating in batch mode the retentate can be passed through the filtration unit 21 again until a sufficient concentration factor is obtained. In this example, the process was continued until a concentration factor being the ratio of the feed volume against the retentate volume had reached approximately 9.

It can also be seen that the temperature may be monitored and controlled by a sensor and/or heating means 33. Although shown in the container 23, the heating of the feed solution can be provided at any suitable point prior to entering the filtration unit 21.

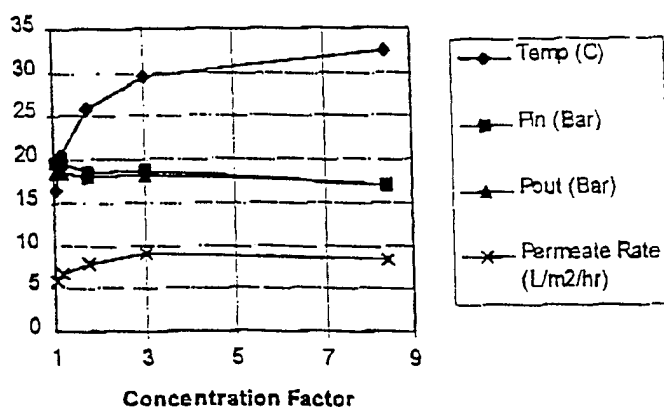
In a particular experiment conducted in batch mode as shown in Figure 2, a membrane area of 1.5m^2 was utilised and about 20L of sample was placed into the feed tank. The solution was pumped to the filtration unit 1 at a pressure of approximately 20 Bar until the concentration factor reached about 9. The feed, permeate and retentate were collected at different time intervals for analysis. Two varying trials were conducted and are discussed below.

Example 3

This trial utilised a 6.9% lithium hydroxide solution with dissolved lithium carbonate.

The results of this trial are shown below:

Trial One, 6.9% LiOH with Dissolved Li_2CO_3



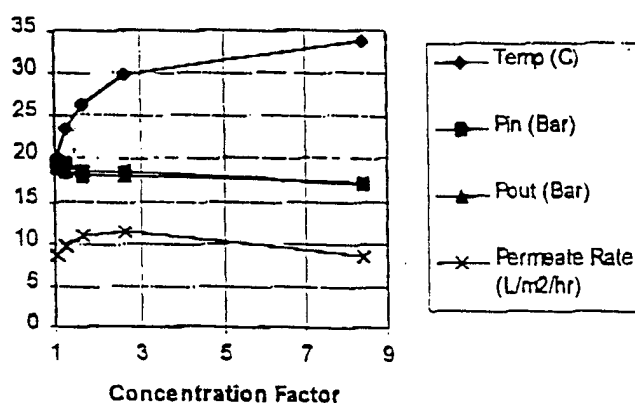
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It can be seen that as the filtration proceeded, the permeate rate increased because of higher solution temperature. The permeate rate rose to a maximum of approximately 9 L/m²/hr and dropped to about 8 L/m²/hr due to the high concentration factor and lower observed operating pressure at the end of the process.

Example 4

The second trial utilised 5.6% lithium hydroxide with no dissolved lithium carbonate. The results of this trial are also shown below:

Trial Two, 5.6% LiOH, No Dissolved Li₂CO₃



In this instance, the permeate rate rose to a maximum of approximately 12 L/m²/hr and again dropped back as with the previous trial. It was noticed that lower lithium hydroxide concentrations have higher permeate rates.

The permeate rates for water and lithium hydroxide and the battery waste were considered. It was found that water had the higher permeate rate of 25 L/m²/hr at 19°C and 18 Bar.

At temperatures of 19°C and a pressure of 19 bar, the limiting concentrations for lithium hydroxide were found to be 11% which is very similar to its aqueous solubility at room temperature.

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In consideration of temperature, it was found that the permeate rates were increased by 2-3% per degree Celsius rise in temperature.

The quality of the permeate was considered in each trial. The impurities for the permeate for the two trials are shown in Tables 2 and 3 below.

Table 2

Impurities of Trial One (6.9% LiOH with dissolved Li₂CO₃)

Values are in ppm except Li which is in %.

	Feed	Final Retentate	Bulk permeate	% Rejection
Zn	0.05	0.70	-0.05	189
Mn	0.01	0.07	0.00	136
Mo	0.00	0.05	0.00	129
Fe	0.61	3.66	-0.03	105
Ni	0.02	0.10	0.00	102
Cu	0.02	0.17	0.00	101
Be	0.00	0.02	0.00	98
Si	5.33	30.83	0.29	95
Cr	0.08	0.44	0.01	94
SO ₄	488	2002	36	93
Mg	0.21	0.58	0.03	84
Ca	0.56	2.41	0.14	75
Hg	0.53	0.43	0.19	63
B	0.06	0.26	0.02	57
Al	1.72	8.53	0.75	56
Pb	0.12	0.52	0.07	41
Na	93	72	64	32
K	2.41	2.48	2.35	3
Li	2.01	2.22	2.03	-1

Table 3**Impurities of Trial Two (5.6% LiOH without Li₂CO₃)**

Values are in ppm except Li which is in %.

	Feed	Final Retentate	Bulk permeate	% Rejection
Be	0.00	0.01	0.00	157
Mg	0.05	0.10	-0.01	121
Mo	0.01	0.05	0.00	117
Hg	0.50	0.57	0.05	91
Si	4.78	29.05	0.51	89
SO ₄	224	1609	25	89
Cu	0.02	0.14	0.00	89
Fe	0.39	2.24	0.04	89
Cr	0.05	0.17	0.01	85
Mn	0.02	0.11	0.00	85
Zn	0.11	0.76	0.02	83
Ni	0.01	0.09	0.00	83
Al	1.48	7.85	0.70	53
B	0.06	0.25	0.04	28
Ba	0.07	0.00	0.06	19
Ca	7.2	11.5	6.0	17
Pb	0.06	0.20	0.05	16
K	34	38	33	3
Na	221	243	216	2
Li	1.62	1.76	1.61	1

In the lithium hydroxide trials, it was found that the divalent and the multivalent ions were well rejected by nanofiltration and were within the specification for ultra high grade lithium carbonate following carbonation of the lithium hydroxide permeate.

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Monovalent ions such as sodium, potassium and chloride are not significantly rejected by nanofiltration. However monovalent contaminants may be addressed by washing the solid lithium carbonate with deionised water.

On the selection of the nanofiltration membrane 22, a suitable membrane is a Koch nanofiltration membrane. A membrane supplied by Koch such as the MPS-34 nanofiltration membrane is stable at the necessary pH conditions and provides operating conditions including the maximum pressure of 35 bar at 40°C or a maximum temperature of 70°C at 15 bar. Such a membrane would appear suitable for the purification of lithiums and monovalent salt solutions.

Thus it can be seen that the second part of the invention provides the process for the purification of lithium hydroxide and monovalent salts which utilises pressure for the separation. Furthermore, this selection of the membrane allows this process to be provided at suitable pH ranges for lithium hydroxide.

Where in the foregoing description reference has been made to specific components or integers of the invention having known equivalents then such equivalents are herein incorporated as if individually set forth.

Although this invention has been described by way of example and with reference to possible embodiments thereof it is to be understood that modifications or improvements may be made thereto without departing from the scope or spirit of the invention.

CLAIMS

1. A method for the recovery and purification of lithium from lithium battery waste including the steps of:
 - processing lithium battery waste into a lithium containing slurry;
 - filtering and washing the lithium containing slurry to separate the insoluble materials from the soluble lithium components;
 - providing an electrolytic cell consisting of an anode and a cathode;
 - separating anode and cathode compartments with a cation exchange membrane having a porosity to selectively allow the passage of lithium ions and inhibit the passage of others;
 - providing the filtered soluble mixed lithium salt containing battery waste solution as an anolyte in the anode compartment;
 - passing a current through the electrolytic cell; and
 - withdrawing substantially pure lithium hydroxide solution from the cathode compartment.
2. A method according to claim 1 further including the step of replenishing the anolyte with deionised water.
3. A method according to claim 1 wherein the anolyte is provided having a pH of greater than 7.
4. A method according to claim 1 wherein sulphuric acid produced in the anolyte is used as a by-product.

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5. A method according to claim 1 further including the step of circulation of the anolyte and catholyte through their respective anode and cathode compartments.
6. A method according to claim 1 wherein the cation exchange membrane is a Nafion 350 membrane.
7. A method according to claim 1 wherein the method further includes the step of keeping separate any gases produced at the anode and cathode.
8. A method according to claim 7 wherein hydrogen produced during the electrolytic process is at least partially used in power generation for the method.
9. A method according to any one of the preceding claims including further purification of the lithium hydroxide solution by nanofiltration, including the steps of:
 - providing a nanofiltration membrane having stability at a pH of at least 11;
 - passing the lithium hydroxide solution against said membrane under pressure; and
 - removing a permeate being a further purified lithium hydroxide solution from an opposed side of said membrane from the feed stock.
10. A method according to claim 9 wherein the nanofiltration is performed on a solution having a temperature of substantially greater than or equal to 5°C.

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11. A method according to claim 9 wherein the feed stock is provided at a pressure of greater than 5 Bar.
12. A method according to claim 11 wherein the pressure is greater than 15 Bar.
13. A method according to any one of the preceeding claims wherein the lithium hydroxide solution is converted to a lithium salt.
14. A method according to claim 13 wherein the lithium salt is lithium carbonate formed by carbonation of the lithium hydroxide.
15. A method according to claim 14 wherein the lithium carbonate is washed with deionised water and subsequently dried.
16. A method for purification of monovalent lithium salt solution comprising the steps of:
 - providing a nanofiltration membrane having stability at a pH of at least 11;
 - providing a feed stock solution containing a monovalent lithium salt;
 - passing the feed stock solution against the membrane under pressure; and
 - removing a permeate being a purified monovalent lithium salt solution from an opposed side of the membrane from the feed stock.
17. A method according to claim 16 wherein the monovalent lithium salt is lithium hydroxide.

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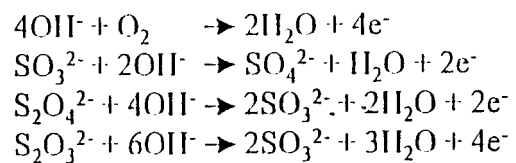
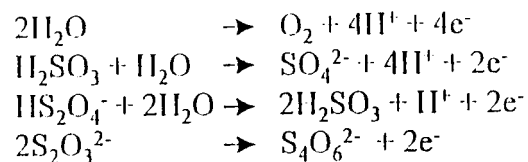
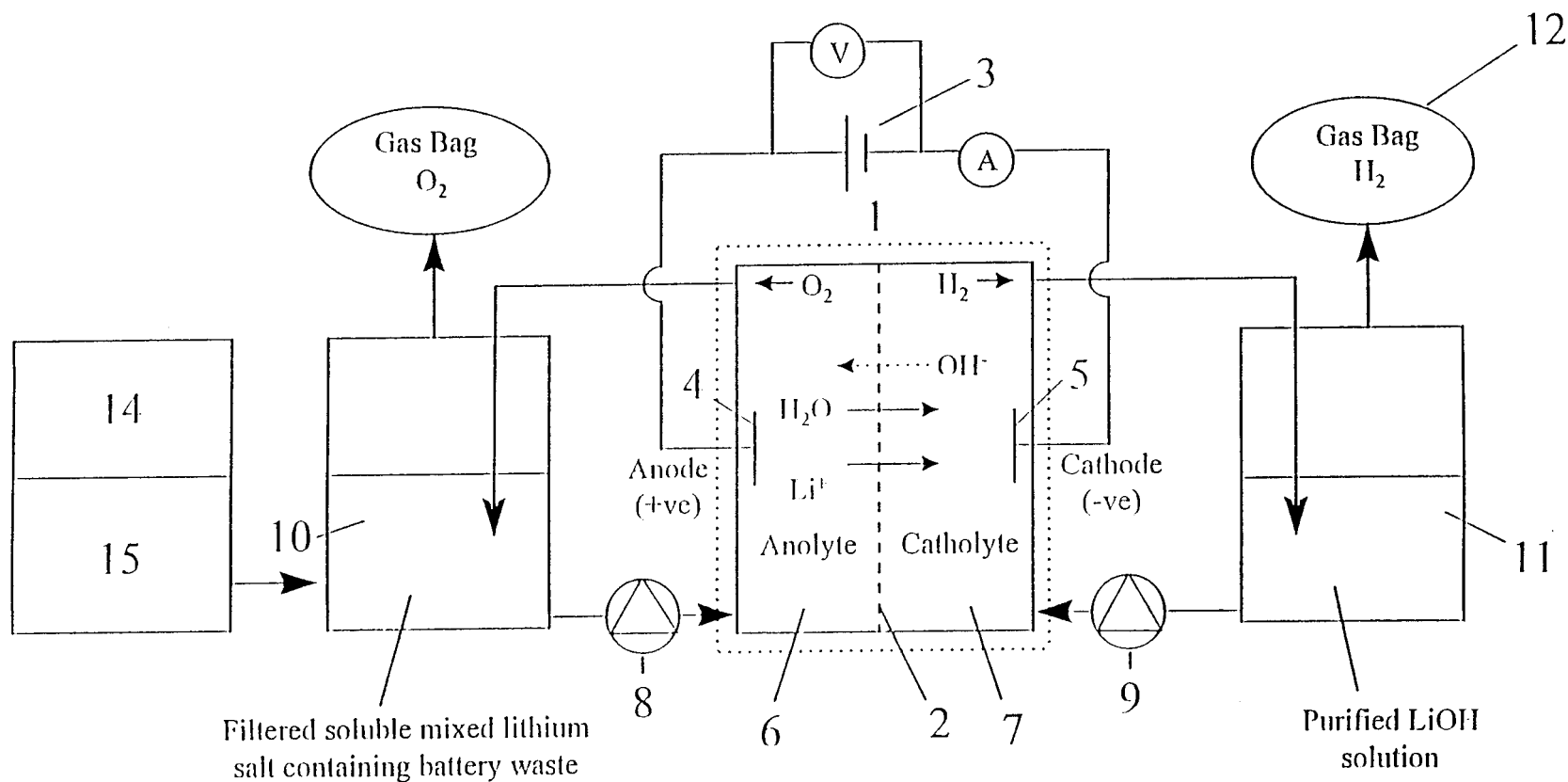
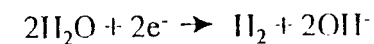
18. A method according to claim 17 wherein the nanofiltration is performed on a solution having a temperature of substantially greater than or equal to 5°C.
19. A method according to claim 18 wherein the feed solution is provided at a pressure of greater than 5 Bar.
20. A method according to claim 19 wherein the pressure is greater than 15 Bar.
21. Lithium recovery apparatus adapted for the recovery and purification of lithium from lithium battery waste, said apparatus including:
 - a solid liquid filter incorporating solids washing apparatus;
 - an electrolytic cell;
 - anode and cathode compartments within said electrolytic cell divided by a cation exchange membrane having a porosity to selectively allow the passage of lithium ions;
 - a power supply to said electrolytic cell to pass current through the cell;
 - filtered soluble mixed lithium salt containing battery waste solution within said anode compartment; and
 - means to withdraw substantially pure lithium hydroxide solution from the cathode compartment.
22. Apparatus according to claim 21 further including pumping means adapted to provide circulation of the anolyte and catholyte through their respective anode and cathode compartments.

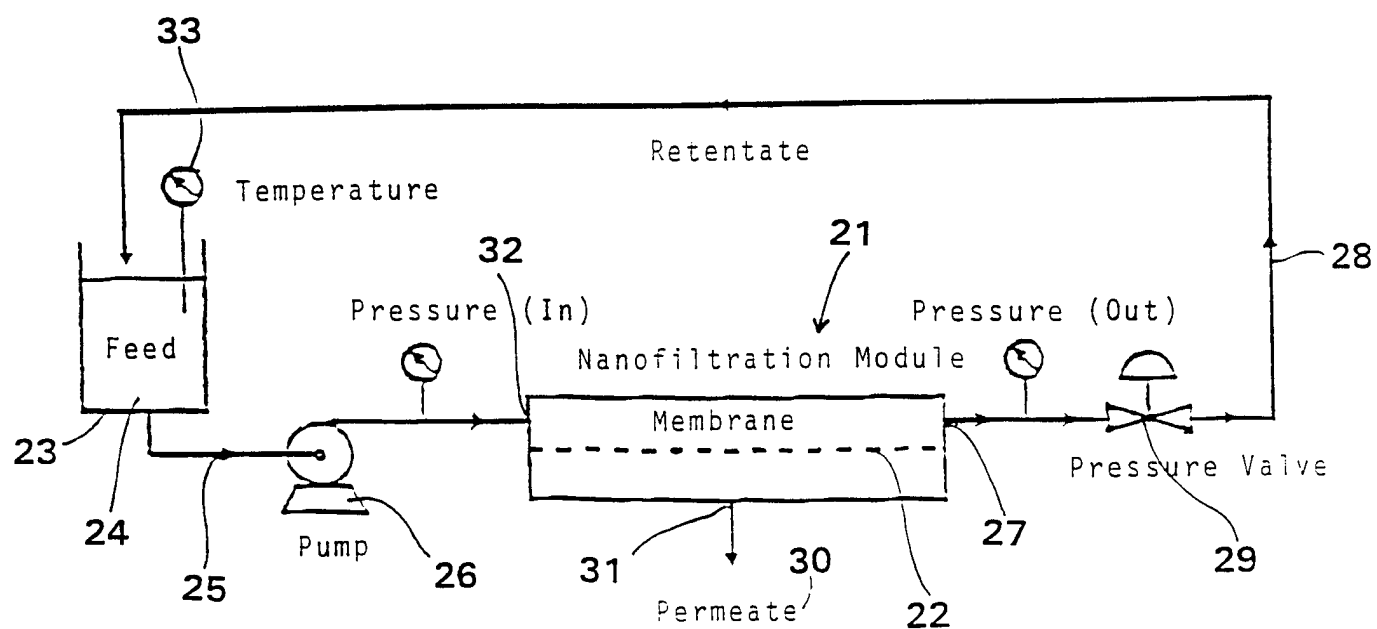
- 22 -

23. Apparatus according to claim 22 wherein the cation exchange membrane comprises a Nafion 350 membrane.
24. Apparatus according to claim 21 further including means for replenishing the withdrawn anolyte with deionised water.
25. Apparatus for the recovery of lithium according to claim 21 adapted to further purify recovered lithium hydroxide by including:
 - a filtration unit;
 - a nanofiltration membrane within said filtration unit having a stability at pH levels of at least 11;
 - pressurising means to feed the lithium hydroxide solution into the filtration unit under pressure; and
 - an outlet from the filtration unit on an opposed side of the nanofiltration membrane from the inlet.
26. Apparatus according to claim 25 wherein the nanofiltration membrane is stable at a pH of at least 14.
27. Apparatus according to claim 26 wherein the nanofiltration membrane comprises a single polymer film or a multiple layer thin film composite of polymers.
28. Monovalent lithium salt purification apparatus including:
 - a filtration unit;
 - a nanofiltration membrane within the filtration unit having a stability at pH levels of at least 11;

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- pressurising means to feed a monovalent lithium salt solution into the filtration unit under pressure; and
 - an outlet from the filtration unit on an opposed side of the nanofiltration membrane from the inlet.
29. A method for the recovery and/or purification of lithium from lithium battery waste substantially as herein described and with reference to the accompanying drawings and/or Examples.
30. Apparatus for the recovery and/or purification of lithium from lithium battery waste substantially as herein described and with reference to the accompanying drawings and Examples.

*Anode reactions***Alkaline Medium****Neutral Medium***Cathode reaction:***FIGURE 1**

**FIGURE 2**

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NZ 98/00087

A. CLASSIFICATION OF SUBJECT MATTER																						
Int Cl ⁶ : H01M 6/52, 10/54; B01D 61/14, 61/16, 61/18; C25B 1/16; C01D 15/02.																						
According to International Patent Classification (IPC) or to both national classification and IPC																						
B. FIELDS SEARCHED																						
Minimum documentation searched (classification system followed by classification symbols) Int Cl ⁶ IPC H01M 6/52, 10/54; B01D 61/14, 61/16, 61/18; C01D 15/02.																						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU: IPC as above 1975-1998																						
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent Online Abstracts (1) (H01M 6/52 or H01M 10/54) and keywords (Li or Lithium) (2) KEYWORDS (LITHIUM OR LI) AND (MEMBRANE OR NANOFILT:). Japio Online Abstracts (1) (H01M 6/52 or H01M 10/54) AND KEYWORDS (LI AND LITHIUM) (2) B01D AND KEYWORDS (LITHIUM OR LI) AND (MEMBRANE OR NANOFILT:) in all cases, period 1975-1998 searched.																						
C. DOCUMENTS CONSIDERED TO BE RELEVANT																						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																				
A	US 4036713 A (BROWN) 19 July 1977 See abstract	1																				
A	US 4636295 A (BALL et al) 13 January 1987 See abstract	1																				
☒ Further documents are listed in the continuation of Box C ☐ See patent family annex																						
* Special categories of cited documents: <table border="0"> <tr> <td>"A"</td> <td>Document defining the general state of the art which is not considered to be of particular relevance</td> <td>"T"</td> <td>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"E"</td> <td>Earlier document but published on or after the international filing date</td> <td>"X"</td> <td>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"L"</td> <td>Document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"Y"</td> <td>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"O"</td> <td>Document referring to an oral disclosure, use, exhibition or other means</td> <td>"&"</td> <td>document member of the same patent family</td> </tr> <tr> <td>"P"</td> <td>Document published prior to the international filing date but later than the priority date claimed</td> <td></td> <td></td> </tr> </table>			"A"	Document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"E"	Earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"L"	Document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"O"	Document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family	"P"	Document published prior to the international filing date but later than the priority date claimed		
"A"	Document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention																			
"E"	Earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																			
"L"	Document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																			
"O"	Document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family																			
"P"	Document published prior to the international filing date but later than the priority date claimed																					
Date of the actual completion of the international search 26 August 1998		Date of mailing of the international search report 10 SEP 1998																				
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 ODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929		Authorized officer GRAEME BROXAM Telephone No.: (02) 6283 2133																				

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NZ 98/00087

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 618633 A (HITACHI LTD.) 5 October 1994 See abstract, claims	1
A	US 4882017 A (WEAVER) 21 November 1989 See abstract	1-15
A	US 5254257 A (BRIGANO et al) 19 October 1993 See abstract	16-20
A	US 5587083 A (TWARDOWSKI) 24 December 1996 See abstract	16-20

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NZ 98/00087**Box I** Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Claims 1-15 relate to an electrolytic membrane separation process for the recovery of lithium from lithium battery waste. Claims 16-20 relate to a method of purifying a monovalent lithium salt solution using a pressure-driven nanofiltration system. The two groups of invention are not so linked as to form a single inventive concept.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Information on patent family members

International Application No.
PCT/NZ 98/00087

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	4036713	DE	2700748	JP	52119498		
US	4636295	CA	1272982				
EP	618633	JP	6338352	JP	6338353	US	5597526
		US	5628973	US	5714129	EP	673075
		US	5612150	US	5679477		
US	5587083	AU	52670/96	CA	2163480	EP	821615
		WO	9633005				
END OF ANNEX							