



(72) FRIEDRICH, HOLGER, DE
(72) PFEFFINGER, JOACHIM, DE
(72) LEUTNER, BERND, DE
(71) BASF AKTIENGESELLSCHAFT, DE
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(54) **PROCEDE DE PRODUCTION DE SELS DE LITHIUM DE
GRANDE PURETE**
(54) **METHOD FOR PRODUCING HIGHLY PURE LITHIUM SALTS**

(57) L'invention concerne un procédé de production d'un sel de lithium de grande pureté à partir de carbonate de lithium. Ce procédé consiste A) à traiter une composition de carbonate de lithium et d'eau au CO₂ pour obtenir une composition aqueuse contenant de l'hydrocarbonate de lithium; B) à faire transiter la composition aqueuse contenant de l'hydrocarbonate de lithium par un module d'échange d'ions; C) à extraire par précipitation le carbonate de lithium de la composition contenant l'hydrocarbonate de lithium obtenue en B après traitement à l'aide du module d'échange d'ions et D) à retraiter le carbonate de lithium précipité ou transformer le carbonate de lithium précipité en un autre sel de lithium de grande pureté.

(57) The invention relates to a method for producing a highly pure lithium salt using lithium carbonate. Said method comprises the following steps: A: treating a mixture comprising lithium carbonate and water with CO₂ to produce an aqueous mixture containing lithium hydrogencarbonate; B: passing the aqueous mixture containing lithium hydrogencarbonate through an ion-exchange module; C: precipitating out the lithium carbonate from the aqueous mixture containing lithium hydrogencarbonate obtained in step B after treatment with the ion-exchange module and D: reprocessing the precipitated lithium carbonate or converting the precipitated lithium carbonate into another highly pure lithium salt.



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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) Internationales Aktenzeichen: PCT/EP99/01322</p> <p>(22) Internationales Anmeldedatum: 1. März 1999 (01.03.99)</p> <p>(30) Prioritätsdaten: 198 09 420.5 5. März 1998 (05.03.98) DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AK- TIENGESSELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE).</p> <p>(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): FRIEDRICH, Holger [DE/DE]; Roxheimer Strasse 66, D-67240 Boben- heim-Roxheim (DE). PFEFFINGER, Joachim [DE/DE]; Bessemerstrasse 20, D-67063 Ludwigshafen (DE). LEUTNER, Bernd [DE/DE]; Taunusstrasse 17, D-67227 Frankenthal (DE).</p> <p>(74) Anwalt: ISENBRUCK, Günter; Bardehle, Pagenberg, Dost, Altenburg, Geissler, Isenbruck, Theodor-Heuss-Anlage 12, D-68165 Mannheim (DE).</p> </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(81) Bestimmungsstaaten: CA, CN, ID, JP, KR, MX, RU, SG, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p> </td> </tr> </table>			<p>(21) Internationales Aktenzeichen: PCT/EP99/01322</p> <p>(22) Internationales Anmeldedatum: 1. März 1999 (01.03.99)</p> <p>(30) Prioritätsdaten: 198 09 420.5 5. März 1998 (05.03.98) DE</p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): BASF AK- TIENGESSELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE).</p> <p>(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): FRIEDRICH, Holger [DE/DE]; Roxheimer Strasse 66, D-67240 Boben- heim-Roxheim (DE). PFEFFINGER, Joachim [DE/DE]; Bessemerstrasse 20, D-67063 Ludwigshafen (DE). LEUTNER, Bernd [DE/DE]; Taunusstrasse 17, D-67227 Frankenthal (DE).</p> <p>(74) Anwalt: ISENBRUCK, Günter; Bardehle, Pagenberg, Dost, Altenburg, Geissler, Isenbruck, Theodor-Heuss-Anlage 12, D-68165 Mannheim (DE).</p>	<p>(81) Bestimmungsstaaten: CA, CN, ID, JP, KR, MX, RU, SG, US, europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Veröffentlicht <i>Mit internationalem Recherchenbericht.</i></p>
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<p>(54) Title: METHOD FOR PRODUCING HIGHLY PURE LITHIUM SALTS</p> <p>(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON HOCHREINEN LITHIUMSALZEN</p> <p>(57) Abstract</p> <p>The invention relates to a method for producing a highly pure lithium salt using lithium carbonate. Said method comprises the following steps: A: treating a mixture comprising lithium carbonate and water with CO₂ to produce an aqueous mixture containing lithium hydrogencarbonate; B: passing the aqueous mixture containing lithium hydrogencarbonate through an ion-exchange module; C: precipitating out the lithium carbonate from the aqueous mixture containing lithium hydrogencarbonate obtained in step B after treatment with the ion-exchange module and D: reprocessing the precipitated lithium carbonate or converting the precipitated lithium carbonate into another highly pure lithium salt.</p> <p>(57) Zusammenfassung</p> <p>Verfahren zur Herstellung eines hochreinen Lithiumsalzes ausgehend von Lithiumcarbonat, das die folgenden Stufen A bis D umfaßt: A: Behandlung eines Gemischs, das Lithiumcarbonat und Wasser umfaßt, mittels CO₂, wobei ein Lithiumhydrogencarbonat enthaltendes wäßriges Gemisch erhalten wird; B: Durchleitung des Lithiumhydrogencarbonat enthaltenden wäßrigen Gemischs durch ein Ionenaustauscher-Modul; C: Ausfällen von Lithiumcarbonat aus dem in Stufe B erhaltenen, mittels einem Ionenaustauscher-Modul behandelten Lithiumhydrogencarbonat enthaltenden Gemisch; und D: Aufarbeiten des ausgefallten Lithiumcarbonats oder Überführen des ausgefallten Lithiumcarbonats in ein anderes hochreines Lithiumsalz.</p>				

METHOD FOR PRODUCING HIGHLY PURE LITHIUM SALTS

The present invention relates to a process for preparing a high purity lithium salt from lithium carbonate by subjecting an aqueous mixture comprising lithium bicarbonate to a treatment with an ion exchanger module.

10 High purity lithium compounds have become important in connection with the development of lithium secondary cells in particular, since such cells utilize, for example, LiPF_6 or LiPF_4 conducting salts. These or similar conducting salts are generally prepared from lithium salts, for example lithium fluoride (LiF) or lithium chloride (LiCl), which in turn are obtained from lithium carbonate (Li_2CO_3). To be able to prepare conducting salts useful for the above purposes from the lithium salts mentioned, the latter must already be very pure. More particularly, it is desirable for the foreign metal ion content to be not more than 1 ppm.

Accordingly, the literature discloses a number of processes for obtaining high purity lithium salts, especially from lithium fluoride.

20 The preparation of high purity lithium fluoride by the Stockbarger process, a zone melting process for preparing LiF in the form of single crystals, is described in Gmelin, 8th edition, Vol. 6, VCH-Verlag Weinheim, 1960, pages 305-327. However, this process, which is used to obtain lithium fluoride in the form of single crystals for optical purposes, is very complicated and costly and accordingly unsuitable for the production of large amounts of LiF .

US 3 839 546 describes a process for preparing high purity alkali metal halides by reacting an alkali metal alkoxide with gaseous halides such as HCl or SiCl_4 . This process is likewise relatively complicated and costly, especially because elemental alkali metal is used as starting material for the alkali metal alkoxide.

30 DE-A 195 41 558 describes a process for purifying lithium chloride solutions, where the focus is mainly on removing undesirable sodium chloride contents. The lithium chloride solutions obtained therein by evaporation with yields of $\geq 99\%$

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using a specific procedure are indeed essentially free from sodium chloride. The lithium chloride solutions obtained are said to have a sodium chloride content of less than 0.3% by weight. An NaCl content of 0.2% is exemplified.

5 Processes for preparing high purity lithium salts by treatment with an ion exchanger are likewise known. However, lithium chloride solutions are treated in every case (Hydrometallurgy, 27 (1991), 317-325, US 4 859 343 and US 4 929 588).

10 It is an object of the present invention to provide a simple process for preparing high purity lithium salts, especially from lithium fluoride, lithium carbonate and lithium chloride, on a large industrial scale.

We have found that this object is achieved by a process for preparing a high purity
15 lithium salt from lithium carbonate, said process comprising steps A to D as hereinbelow defined:

A: treating a mixture comprising lithium carbonate and water by means of CO₂ to obtain an aqueous mixture comprising lithium bicarbonate,

20

B: passing said aqueous mixture comprising lithium bicarbonate through an ion exchanger module,

C: precipitating lithium carbonate from the ion exchanger module treated
25 lithium bicarbonate mixture obtained in step B, and

D: working up the precipitated lithium carbonate, i.e., essentially by separating it off, optionally washing with H₂O or an H₂O-comprising solvent and drying, or converting the precipitated lithium carbonate into some other
30 high purity lithium salt.

As is evident from the above, the process of the present invention starts from lithium carbonate, which is dispersed in water or in an aqueous solvent mixture

35 with, for example, an alcohol, a ketone or aldehyde and converted by means of CO₂ into the water-soluble lithium bicarbonate. The concentration of lithium carbonate/

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lithium bicarbonate in the respective aqueous mixture is within the range from about 0.5 to about 30%, preferably within the range from about 3 to about 20%, by weight.

5 The resulting aqueous lithium bicarbonate mixture is then subjected to a treatment with an ion exchanger module (step B). According to the present invention, this step B is preferably carried out at from about 10 to about 70°C, more preferably at from about 20 to about 40°C.

10 Steps A and B are preferably carried out at superatmospheric pressure, since this makes it possible to achieve higher LiHCO_3 concentrations.

Commercially available ion exchange resins are used in this step B. Such ion exchange resins preferably consist of organic polymers having ion-active side
15 chains, for example sulfo or carboxyl groups.

In principle, any polymer-based ion exchanger can be used according to the present invention, i.e., not only weakly but also strongly acidic cation exchangers. Ion exchanger modules useful for the present invention include apparatus (a column,
20 for example) packed with the above-described cation exchangers in the form of powders, beads, granules, etc.

A particularly useful polymeric base material for such ion exchangers is a copolymer of styrene and divinylbenzene, especially a styrene-divinylbenzene
25 copolymer which has aminoalkylenephosphonic acid groups or iminodiacetic acid groups.

Specific examples are:

30 resins under the tradename of Lewatit[®] such as, for example, Lewatit[®] OC 1060 (AMP type), Lewatit[®] TP 208 (IDA type), Lewatit[®] E 304/88, Lewatit[®] TP 207, Lewatit[®] S 100;

those under the tradename of Amberlite[®], for example Amberlite[®] IR 120,
35 Amberlite[®] IRA 743;

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those under the tradename of Dowex[®], for example Dowex[®] HCR;

those sold under the tradename of Duolite[®], for example Duolite[®] C 20, Duolite[®] C 467, Duolite[®] FS 346; and

5

those under the tradename of Imac[®], for example Imac[®] TMR, the Lewatit[®] range being preferred.

10

Particular preference is given to using regenerated and hence relatively low sodium ion exchange resins of the Lewatit[®] type or other very low sodium ion exchange resins.

15

Further details concerning ion exchangers useful for the present invention are discernible inter alia from Ullmann's Encycl. of Industr. Chem., 5th edition, Vol. 14, pages 393-459, which reference shall be fully incorporated herein.

20

In the case of very impure lithium carbonate or bicarbonate or else to obtain particularly pure lithium compounds, step B may be carried out repeatedly, i.e., from two to 5 times, preferably from 2 to 3 times.

25

After passing through step B, the solution passes into a step C where lithium carbonate is reprecipitated, which may be done either by raising the temperature, preferably to the boiling point of the solution, and/or by reducing the CO₂ partial pressure. The temperature in step C is generally within the range from about 80 to about 100°C.

30

The lithium carbonate thus purified finally passes into a step D, where it is either directly worked up, i.e., essentially separated off, preferably filtered, optionally washed with H₂O or an H₂O-comprising solvent, and dried and/or recrystallized once more, in which case steps A to C are carried out again, or treated with appropriate reagents, for example aqueous hydrofluoric acid or hydrochloric acid, to convert it into whichever salt is desired.

35

The lithium carbonate thus obtained generally has a foreign metal ion content of less than 10 ppm, preferably less than 5 ppm, especially less than 1 ppm, and a

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chloride content of less than 30 ppm, preferably less than 10 ppm, especially less than 5 ppm.

5 To obtain lithium fluoride, for example, the precipitated lithium carbonate is dispersed in water and reacted with aqueous hydrofluoric acid to form LiF. The LiF is produced in the form of a solid and may be obtained by filtration and subsequent drying in pure form as a solid. CO₂ escapes as gas.

10 It is similarly possible to prepare LiCl, LiBr, Li₂SO₄, LiNO₃, Li₃PO₄, Li₂CO₃ and other lithium salts, for example LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₃, LiC(CF₃SO₂)₃, LiN(CF₃SO₂)₂, LiN(CF₃CF₂SO₂)₂, LiN(SO₂F)₂, LiAlCl₄, LiSiF₆, LiSbF₆. Especially the latter are highly useful as conducting salts, and among these preference is in turn given to LiPF₆, LiPF₄ and LiBF₄.

15 In a further embodiment of the process of the present invention, it is sufficient to carry out the dissolving with CO₂ in step A and the precipitating of the lithium carbonate in step C repeatedly - instead of the repeated performance of step B - if merely large sodium and/or potassium quantities are to be removed.

20 Accordingly, the following sequence of steps is also possible within the process of the present invention:

1. step A - step B - step C - step A - step C - step D; or
2. step A - step B - step B - step C - step A - step C - step D; or
- 25 3. step A - step B - step C - step A - step B - step C - step D.

In a further embodiment of the present invention, the process of the present invention is carried out as follows:

30 step A: semicontinuously, i.e., the dispersion comprising water and Li₂CO₃ is charged initially and CO₂ is passed in;

step B: continuously;

35

steps C and D: batchwise.

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As follows from the foregoing, the process of the present invention has the particular advantage that not only alkali metal cations, especially sodium ions, but also polyvalent cations, for example alkaline earth metal and transition metal ions, are very efficiently removable; the process of the present invention makes it possible to reduce the sodium concentration in Li_2CO_3 by a factor of up to more than 400; impurities due to polyvalent ions, for example calcium, magnesium, iron and/or aluminum, are virtually completely removed by the treatment with an ion exchanger as per step B. In addition, the product obtained is essentially free from chloride.

An embodiment of the present invention will now be more particularly described by way of example.

Example: (preparation and purification of LiF)

First, 100 g of Li_2CO_3 (technical grade) (1.353 mol) and 2000 g of distilled water were weighed into a 2 l glass bottle.

CO_2 gas was then introduced for six hours at room temperature (21°C) with stirring, until all the Li_2CO_3 had dissolved.

The solution obtained was filtered and pumped through an ion exchanger bed of regenerated Lewatit® TP 207 (100 ml), followed by washing with 100 ml of water.

The dosage rate through said Lewatit® TP 207 was 400 ml/h.

The solution obtained after passage through the ion exchanger bed was then boiled under reflux to cause the lithium bicarbonate (by detaching CO_2) to convert into lithium carbonate and precipitate.

The solution was cooled and filtered and the filter residue was washed with water and then dried at 300°C to leave 69.6 g of dry lithium carbonate.

Of this amount, 58.22 g (0.788 mol) were once more admixed with water (1106 g), dissolved by stirring and CO_2 gas absorption and then filtered again.

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This corresponds to a yield of 69.6%, based on the amount of lithium carbonate used.

5 The filtrate was admixed with 78.8 g of 40% strength by weight hydrofluoric acid (1.576 mol of HF), and the lithium fluoride was precipitated with CO₂ evolving. A pH of 7.5 was then set with ammonia solution, and the batch was filtered, and the filter residue was washed with water and dried at 300°C.

10 This gave about 39 g of lithium fluoride. This corresponds to a yield of 95.5%, based on the amount of lithium carbonate used after the treatment with the ion exchanger.

15 Accordingly, the overall yield of LiF based on the amount of Li₂CO₃ used is 66.4%.

The results with regard to the purity of the Li₂CO₃ and LiF obtained are shown in the table below.

	Li ₂ CO ₃ used [mg/kg]	Li ₂ CO ₃ 1st precipi- tation [mg/kg]	LiF [mg/kg]	Ratio of foreign metal ion concentration per mole of Li before/ after 1st precipitation
Foreign metal ion content				
Al	7	< 1	< 1	> 7
Ca	60	< 1	about 1	> 60
Fe	3	< 1	< 1	> 3
K	40	< 1	< 1	> 40
Mg	25	< 1	< 1	> 25
Na	480	about 1	< 1	480
Cl	55	< 5	< 5	55

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We claim:

- 5 1. A process for preparing a high purity lithium salt from lithium carbonate, said process comprising steps A to D as hereinbelow defined:
- 10 A: treating a mixture comprising lithium carbonate and water by means of CO₂ to obtain an aqueous mixture comprising lithium bicarbonate,
- 15 B: passing said aqueous mixture comprising lithium bicarbonate through an ion exchanger module,
- C: precipitating lithium carbonate from the ion exchange module treated lithium bicarbonate mixture obtained in step B, and
- 20 D: working up the precipitated lithium carbonate or converting the precipitated lithium carbonate into some other high purity lithium salt.
2. A process as claimed in claim 1, wherein said high purity lithium salt is lithium chloride, lithium fluoride, lithium bromide, lithium sulfate, lithium nitrate, lithium phosphate or lithium carbonate.
- 25 3. A process as claimed in claim 1, wherein said high purity lithium salt has a foreign metal ion content of less than 1 ppm.
4. A process as claimed in claim 1, wherein step B is carried out repeatedly.
- 30 5. A process as claimed in claim 1, carried out according to any of the following sequences 1 to 3:
1. step A - step B - step C - step A - step C - step D; or
2. step A - step B - step B - step C - step A - step C - step D; or
- 35 3. step A - step B - step C - step A - step B - step C - step D.

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6. A process as claimed in any of claims 1 to 5, wherein the ion exchanger used is a resin based on a styrene-divinylbenzene copolymer having aminoalkylenephosphonic acid or iminodiacetic acid groups.