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(54) **Titre :** PROCEDE POUR LA PRODUCTION DE $LIBF_4$ DE GRANDE PURETE
(54) **Title:** METHOD FOR PRODUCING HIGHLY PURE $LIBF_4$

(57) **Abrégé/Abstract:**

The invention relates to a method for producing highly pure $LiBF_4$ by preparing a solution of BF_3 etherate in diethyl ether, suspending LiF in this solution, converting same into solid $LiBF_4$ and then separating the resulting solid $LiBF_4$. The invention also relates to the use of $LiBF_4$ obtained in this manner for the production of lithium-ion batteries.

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(54) Title: METHOD FOR PRODUCING HIGHLY PURE $LiBF_4$

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON HOCHREINEM $LiBF_4$

(57) Abstract

The invention relates to a method for producing highly pure $LiBF_4$ by preparing a solution of BF_3 etherate in diethyl ether, suspending LiF in this solution, converting same into solid $LiBF_4$ and then separating the resulting solid $LiBF_4$. The invention also relates to the use of $LiBF_4$ obtained in this manner for the production of lithium-ion batteries.

(57) Zusammenfassung

Verfahren zur Herstellung von hochreinem $LiBF_4$ durch Bereiten einer Lösung von BF_3-Etherat in Diethylether, Suspendieren von LiF in dieser Lösung, Umsetzen zu festem $LiBF_4$, gefolgt von Abtrennen des gebildeten, festen $LiBF_4$. Verwendung des hergestellten $LiBF_4$ zur Herstellung von Lithiumionenbatterien.

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"METHOD FOR PRODUCING HIGHLY PURE $LIBF_4$"

The invention relates to a process for preparing highly pure $LiBF_4$ in diethyl ether, and also to its use for producing lithium ion batteries.

$LiBF_4$ can be used as a conducting salt for electrolytes in primary cells or secondary cells. In particular, it is used in rechargeable lithium ion batteries. The electrolytes are non-aqueous solutions of $LiBF_4$ in organic media, e.g. in diethyl carbonate, dimethyl carbonate, ethylene carbonate or propylene carbonate or others, or mixtures of the solvents mentioned.

Very high requirements are placed upon the purity of the $LiBF_4$ for this application. A particular requirement is that the $LiBF_4$ has a very low content of free hydrogen fluoride, very low water content, and only very small amounts of foreign metal ions. Contamination with organic carbon compounds also has to be avoided.

Various methods are known for preparing $LiBF_4$.

JP-A 61 151023 and JP-A 61 151024 describe processes in which LiF is reacted with BF_3 in liquid HF to give $LiBF_4$. Impurities then have to be removed in a second step by treatment with elemental fluorine in inert gases or in inert solvents. However, work with liquid HF and with elemental F_2 is dangerous, and complicated safety precautions are therefore necessary.

Preparation in organic solvents has also been described in order to avoid preparation in liquid HF.

SU 1013405 describes the preparation of $LiBF_4$ in tetrahydrofuran, in which $LiBF_4$ has good solubility, by reacting LiF with BF_3 in yields of from 86 - 89%. The product is isolated by concentrating the THF solution. This generally gives a product which still has considerable amounts of residual THF. To remove THF completely, drying in vacuo at from 70 to 80°C for from 10 to 15 hours using specific temperature programs is proposed. Procedures of this type are inconvenient and expensive.

JP-A 56 145113 discloses a process for preparing $LiBF_4$ by reacting LiF with BF_3 in non-aqueous organic solvents in which $LiBF_4$ has good solubility and which can form complexes with BF_3. Examples mentioned are tetrahydrofuran, dimethoxyethane, ethyl acetate and propylene carbonate. After the reaction of LiF with BF_3, impurities are filtered off. $LiBF_4$ is crystallized out from the filtrate by saturating the solution with BF_3. With the solvent BF_3 forms a complex in which $LiBF_4$ has low solubility, and crystallizes out. Problems with this process are the complete removal of any BF_3 adhering to the product and the need to use a considerable excess of BF_3. Diethyl ether is not used for the process mentioned since the solubility of $LiBF_4$ in diethyl ether at 25°C is only 1.3 g/100 ml (JACS, 75 (1953) 1753).

A process has also been disclosed (JACS, 75 (1953) 1753) for preparing $LiBF_4$ in diethyl ether by reacting lithium carbonate with boron trifluoride according to the reaction equation $3\ Li_2CO_3 + 8\ BF_3 \text{---->} 6\ LiBF_4 + 3\ CO_2 + B_2O_3$. The B_2O_3 formed as coproduct, and also undissolved $LiBF_4$, are filtered off and the filtrate is concentrated to obtain $LiBF_4$. Further amounts of $LiBF_4$ have to be isolated by extracting the filtered-off $B_2O_3/LiBF_4$ mixture with diethyl ether. However, this process is not cost-effective. Firstly, the low solubility of $LiBF_4$ in diethyl ether means that large amounts of solvent have to be used and then evaporated, and this does not remove the requirement for an additional extraction of the residue. Besides this, some of the BF_3 is converted into B_2O_3 coproduct .

It is an object of the present invention to provide a simple process for cost-effective preparation of highly pure $LiBF_4$ which can be used for producing lithium ion batteries.

We have found that this object is achieved by means of a simple and cost-effective process in which, despite the low solubility of $LiBF_4$ in diethyl ether, LiF can be reacted virtually completely with BF_3 etherate and $LiBF_4$ prepared with a high level of purity.

The invention therefore provides a process for preparing highly pure $LiBF_4$ by preparing a solution of BF_3 etherate in diethyl ether, suspending LiF in this solution, reacting to give solid $LiBF_4$, and then separating off the solid $LiBF_4$ formed.

The novel process uses BF_3 etherate. The BF_3 etherate is preferably diluted with diethyl ether. The solution of BF_3 etherate in diethyl ether can be prepared by diluting pure BF_3 etherate with diethyl ether. It is also possible to pass the desired amount of gaseous BF_3 into diethyl ether. The molar ratio of diethyl ether to BF_3 etherate is preferably from 0.1 to 3, particularly preferably from 0.5 to 1.5.

Finely divided LiF is added to this solution and suspended in the solution. The LiF is advantageously ground before addition. However, it is also possible to suspend LiF in diethyl ether and to add this suspension to pure BF_3 etherate or to a solution of BF_3 etherate in diethyl ether, or to pass BF_3 gas into the suspension. The amount of BF_3 etherate used is at least stoichiometrically equivalent to that of LiF. It is advantageous to work with a small excess of BF_3 etherate, but the molar ratio of BF_3 etherate to LiF should not be greater than 1.2. The molar ratio of BF_3 etherate to LiF is preferably from 1 to 1.1.

The reaction is generally carried out with heating, preferably heating to reflux. The reaction time depends on the temperature selected. The reaction is generally allowed to continue for from 4 to 10 h. However, it is also possible to work at room temperature with a corresponding increase in reaction time.

The suspending of LiF and the reaction to give $LiBF_4$ are advantageously carried out with intensive mixing, for example with the aid of stirrers or of dispersing equipment. Mixing devices and apparatuses of this type are known per se.

The $LiBF_4$ obtained from the reaction, substantially suspended in diethyl ether, is separated off by processes known per se, such as filtration, pressure filtration, centrifuging or decanting, and dried. Before filtering off it is advantageous to cool the suspension at least to room temperature.

Surprisingly, in spite of the low solubility of $LiBF_4$ in diethyl ether, the suspended LiF reacts virtually completely with the BF_3 to give $LiBF_4$. The proportion of LiF in the final $LiBF_4$ product is not more than 2% by weight, generally less than 1%. The final product also has only low proportions of acid impurities, low moisture and low proportions of heavy metals. The highly volatile diethyl ether is easily removed from the final product. The residual proportion of organic carbon (total organic carbon, TOC) is less than 0.1% by weight.

This purity gives the $LiBF_4$ prepared by the novel process excellent suitability for use as a conducting salt in lithium ion batteries.

The following examples are intended to explain the invention in more detail without restricting its scope.

Example 1

BF_3 etherate (474.5 g; 3.24 mol) was diluted with 400 ml of diethyl ether (3.85 mol) and placed in the Teflon reactor (molar ratio of diethyl ether to BF_3 etherate: 1.19). Lithium fluoride from Merck, Suprapur (84 g, 3.24 mol) was introduced into this solution, with stirring and under a blanket of argon (molar ratio of BF_3 etherate to LiF: 1.0). The mixture was then stirred under reflux for 7 h, the reflux temperature reducing from 40 to 35°C. The suspension was cooled to 15°C, passed to a pressure filter and filtered. The filter cake was rewashed with diethyl ether. The crystals isolated were dried for 1 h in a current of nitrogen, and then under reduced pressure at 6 mbar.

Product isolated: 254 g of $LiBF_4$ (84% of theory). The B and F NMR spectra of the substance each showed a $LiBF_4$ peak.

Acid impurities (as HF): 100 ppm
LiF: 2%
Na, Fe, Ca and Al: each < 1 ppm
TOC: 0.02%
Moisture: < 100 ppm

Example 2

BF_3 etherate (461.0 g; 3.24 mol) was diluted, without pretreatment, with 400 ml of diethyl ether (3.85 mol) and placed in the Teflon reactor (molar ratio of diethyl ether to BF_3 etherate: 1.19). Lithium fluoride from Merck, Suprapur (84 g, 3.24 mol) was introduced into this solution, with stirring and under a blanket of argon (molar ratio of BF_3 etherate to LiF: 1.0). The mixture was then stirred under reflux for 5 h, the reflux temperature reducing from 42 to 35°C. The suspension was then filtered and the filter cake was washed with diethyl ether. Drying gave 240 g (81% of theory) of $LiBF_4$. The product was then slurried again in diethyl ether, filtered, washed with diethyl ether and dried as in Example 1.

F NMR showed the product to be pure $LiBF_4$.

Acid impurities (as HF): < 100 ppm
LiF: 0.78%
Na, Fe, Ca and Al: each < 1 ppm
TOC: 0.03%

To prepare an electrolyte solution, $LiBF_4$ was dissolved in a mixture of diethyl carbonate and ethylene carbonate (1 mol/l). The solution was filtered to remove residues of LiF. The water content of the solution was < 10 ppm. Residual acid (as HF):6 ppm.

We claim:

1. A process for preparing highly pure $LiBF_4$ in diethyl ether, which comprises preparing a solution of BF_3 etherate in diethyl ether, suspending LiF in this solution, reacting to give solid $LiBF_4$ and then separating off the solid $LiBF_4$ formed.

2. A process for preparing highly pure $LiBF_4$ in diethyl ether as claimed in claim 1, wherein the molar ratio of BF_3 etherate to LiF is from 1 to 1.2.

3. A process for preparing highly pure $LiBF_4$ in diethyl ether as claimed in claim 1 or 2, wherein the molar ratio of diethyl ether to BF_3 etherate is from 0.1 to 3.