(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 873 851 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
26.03.2014 Bulletin 2014/13

(21) Application number: **06747756.2**

(22) Date of filing: **19.04.2006**

(51) Int Cl.:
H01M 10/05 (2010.01) *H01M 10/38* (2006.01) *H01M 10/0562* (2010.01) *H01M 4/04* (2006.01) *H01M 4/136* (2010.01) *H01M 4/58* (2010.01) *H01M 4/38* (2006.01)

(86) International application number:
PCT/RU2006/000197

(87) International publication number:
WO 2006/112757 (26.10.2006 Gazette 2006/43)

(54) METHOD FOR PRODUCING A SECONDARY SOLID-STATE BATTERY

VERFAHREN ZUR HERSTELLUNG EINER SEKUNDÄREN FESTKÖRPERBATTERIE

PROCEDE DE FABRICATION D'UNE BATTERIE SECONDAIRE À L'ETAT SOLIDE

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

(30) Priority: **21.04.2005 RU 2005111721**

(43) Date of publication of application:
02.01.2008 Bulletin 2008/01

(73) Proprietor: **The Potanin Institute Limited**
Dublin 1 (IE)

(72) Inventor: **Potanin, Aleksander Arkadievich**
Nizhegorodskaya obl., 607190 (RU)

(74) Representative: **Reichert, Werner Franz et al**
Reichert & Kollegen
Bismarckplatz 8
93047 Regensburg (DE)

(56) References cited:
EP-A1- 1 981 107
EP-A2- 0 915 526
GB-A- 1 524 126
JP-A- 2001 066 353
RU-C- 1 804 252
SU-A1- 1 106 382
US-A- 2 689 322
US-A- 4 216 279
US-A- 4 222 000

EP 1 873 851 B1

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

[0001] The invention relates to electrotechnology area, and in particular, to production of secondary solid-state current sources (storage batteries).

[0002] The invention proposes the method for production of safe solid-state batteries with high energy capacity and includes the following steps:

[0003] Ensuring contact between a current collector, a solid anode, a solid electrolyte, a solid cathode, and one more current collector in the mentioned order. At that, the reversible solid-phase fluorination/defluorination processes occur at both the cathode and the anode, and the electrolyte has the high fluoride-ion conductivity along with the low electronic conductivity in the solid phase.

[0004] Baking a current source consisting of the current collector, the anode, the electrolyte, the cathode and the current collector by means of baking and thermoelectric influence.

[0005] According to the present invention, "the current source" is both a separate galvanic cell consisting of the current collector, the anode, the electrolyte, the cathode and the other current collector, connected in the mentioned order and a battery, consisting of several galvanic cells, connected in parallel or in series.

[0006] In their composition anode, electrolyte, and cathode in the presented method of production of solid-state secondary current source with high specific energy capacity can correspond to composition of the current source from application RU Patent № 2005111722, issued on 21.04.2005, wherein

[0007] The anode is a metal (or its alloy) selected from the group consisting of Li, K, Na, Sr, Ba, Ca, Mg, Al, Ce, La or their alloys, or from the alloys of the listed metals with the metals, selected from the group of Pb, Cu, Bi, Cd, Zn, Co, Ni, Cr, Sn, Sb, Fe; and in the charged state the anode consists of the fluorides of the aforementioned metals, correspondingly.

[0008] In the charged state the cathode is made from the simple fluorides, such as MnF_2, MnF_3, TaF_5, NdF_5, VF_3, VF_5, CuF, CuF_2, AgF, AgF_2, BiF_3, PbF_2, PbF_4, CdF_2, ZnF_2, CoF_2, CoF_3, NiF_2, CrF_2, CrF_3, CrF_5, GaF_3, InF_2, InF_3, GeF_2, SnF_2, SnF_4, SbF_3, MoF_5, WF_5, fluorinated black lead or the alloys based on them, or their mixtures; and in the discharged state it can be made from the metal selected from the group of Mn, Ta, Nd, VF, Cu, Ag, Bi, Pb, Cd, Zn, Co, Ni, Cr, Ga, In, Ge, Sn, Sb, Mo, W, black lead, or the listed metal alloys, or the mixture.

[0009] The solid-state electrolyte can be made from either the fluorides of La, Ce or the compound fluorides based on them together with an alloying additives, such as fluoride/fluorides of alkaline-earth metals (LiF, KF, NaF) and/or alkaline-earth metal chlorides (LiCl, KCl, NaCl); or the compound fluorides based on the alkaline-earth metal fluorides (CaF_2, SrF_2, BaF_2) with an alloying additives of the rare-earth metal fluorides or/and the alkaline metal fluorides (LiF, KF, NaF); and (or) the chlorides of alkaline metals (LiCl, KCl, NaCl); or the compound fluorides based on PbF_2 containing SrF_2, or BaF_2, or CaF_2, or SnF_2 along with KF additive; or the compound fluorides based on BiF_3 containing SrF_2, or BaF_2 , or CaF_2, or SnF_2 along with KF additive; and the anode, the electrolyte and the cathode contain component or components that prevent destruction of a solid-state battery during charge/discharge cycles.

RU Patent № 2136083, HO1M6/18 (Informational Bulletin № 24, 1999) discloses the method for production of solid-state fluoride ion galvanic cells in the form of the multilayer structures using the technique of layer-by-layer pressing of the powders of the anodic, cathodic and electrolyte materials.

[0010] The drawback of the given method is that by using original solid ionic conductors with sufficiently high level of conductivity, resistance inside the produced current sources increases 100 and more times compare to resistance of the solid ionic conductors materials. This is associated with very high resistance at the particles' interface of the pressed structures (in particular of the electrolyte material) consisting of the powders of the solid-state ionic conductors. This is the widely known data for the polycrystalline structures made from the powders of the ionic conductors using pressing method (A.K. Ivanov-Shitz, I.V. Murin// Ionica of solid state, v.1., St. Petersburg University, 2000, pp 73-74.c.73-74).

[0011] At that, both the anode/electrolyte and the cathode/electrolyte interfaces have the high resistance, too. These resistances substantially determine the high internal resistance of the solid-state current sources produced by this technique. In that case the discharge power of the current sources at 25 °C is measured in microwatts. This fact essentially limits the application area of the batteries.

[0012] The method, which is the closest to this invention, is disclosed in RU Patent N 1106382, H01M 6/18, issued on 10.10.99. According to the method the chemical battery is made by coating both sides of solid electrolyte with electrode pastes that have different polarity. Then, the stack is burned under the thermoelectric influence of electric current passing through the electrodes with the voltage that does not exceed the destruction potential of the electrolyte.

[0013] U.S. patents US 2,689,322 A1 and US 422,200 A1 as well as Japanese patent JP 200166353 A respectively disclose a method for treating batteries which have already been completely manufactured before said treatment, partly by using alternating current.

[0014] The known method of producing the solid-state battery has the following disadvantages:

[0015] Coating both sides of solid electrolyte with electrode pastes that have different polarity (anode and cathode) does not allow production of high quality current sources usually because of high chemical activity of anode material. This leads to changes in chemical composition of electrodes that consequently leads to lower quality of production and degradation of characteristics of the current source, specifically increase in internal resistance of the current source, especially during baking at high temperatures.

[0016] The method is complex enough because of the special requirements to the battery baking which should be carried out in the inert atmosphere that meets the strict requirements with respect to the content of oxygen, nitrogen and moisture in order to prevent contamination of the electrode materials.

[0017] The battery thermoelectric treatment by direct current leads to the sintering of the electrode materials and the electrolyte along with the change in the chemical composition of the electrode materials. As a result, the battery quality deteriorates, and the internal resistance grows.

SUMMARY OF THE INVENTION

[0018] The object of the present invention is to provide a technically attractive method for manufacturing the secondary solid-sate current source allowing to improve the production quality and to decrease the battery internal resistance.

[0019] It is significant, that the problems concerned with the achievement of low internal resistance in the course of manufacturing a solid state current source are important today. Solid-state current sources that are based on solid super-ionic conductors usually have high internal resistance due to low ionic conductivity of solid ionic conductors and very high sensitivity of ionic conductivity to contamination of solid ionic conductors. This circumstance limits the area of applications and the development of solid-state current sources and a solution to lowering internal resistance has an important practical significance.

[0020] The achievable technical result of the present invention is the following:

1. Retention of the chemistry of the anode and cathode during the baking;

2. Retention of the chemistry of the anode and cathode during the thermoelectric treatment.

3. Decrease of the battery internal resistance by upgrading the sintering of the anode, the cathode, and the electrolyte materials as well as the interfaces of the anode/electrolyte and the electrolyte/cathode.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] In order to accomplish the above-stated tasks and technical result the method for manufacturing a secondary solid-state current source by means of applying of the anodic and cathodic materials on the both sides of the solid-state electrolyte along with the subsequent baking and thermoelectric treatment under electric current with the electrodes' polarization potential lower than a decomposition potential of the electrolyte is suggested. At that, according to the invention the chemistry of the anode and cathode is the same as a composition of the anodic and cathodic materials in a fully discharged current source, and the thermoelectric effect is carried out by alternating current.

[0022] In the proposed method of production solid state current source according to the invention:

1. During application on both sides of electrolyte of anodic and cathodic electrodes in the form of materials with low chemical activity, corresponding to anodic and cathodic materials of a fully discharged current source, retention of chemical composition of anodic and cathodic materials during baking is ensured, this consequently ensures production quality increase and does not lead to increase in internal resistance of the current source.

2. During execution of thermoelectric treatment using alternating electrical current, the chemical composition of anodic and cathodic electrodes does not change. Quality increase in baking of anodic, cathodic and electrolytic materials and quality increase in the interfaces anode/electrolyte and electrolyte/cathode of solid-state current sources. During alternating electrical current, alternating temperature increase is observed in those localities of the current source, that have the highest resistance, this leads to intense sintering of these areas and decrease in resistance, which, at the end, is important for lowering resistance of a current source as a whole. Recurring heating of these areas is also important for the flow of mechanical relaxation processes, which take place during baking, that increase production quality during baking.

[0023] The thermoelectric influence can be effectively realized by alternating current of different polarity, or by sinusoidal alternating current, or by sinusoidal alternating current of industrial frequency. Use of sinusoidal alternating current of industrial frequency is the most attractive for the industrial production of the secondary solid-state battery in the frame of the present method.

[0024] According to the claimed method the thermoelectric influence can be carried out at the baking temperature and under the other conditions; simultaneously with baking or as an additional process, resulting in achievement of the formulated tasks and technological result.

A version of invention implementation

[0025] The industrial adaptability of the claimed method was determined experimentally. The LaF3-contining anode and the Ag-containing cathode were applied on the solid electrolyte of tysonite structure. The following baking at 800 °C along with the thermoelectric treatment by sinusoidal alternating current of industrial frequency allowed to produce a structure with low internal resistance. As a result, the current source with the OCV of 3.7 V had the stable discharge parameters at the discharge voltage up to 1.5 V under the subsequent charge/discharge cycles.

[0026] It will be understood that the particular method embodying the invention is not a limitation of the invention. The principles and features of this invention may be employed in various and numerous embodiments without departing from the scope of the claims.

Claims

1. A method of manufacturing a secondary solid state current source:

    characterized by the following steps:

    applying anodic material on one side of a solid electrolyte to form an anode and applying cathodic material on another side of the solid electrolyte to form a cathode; and
    subsequent baking and thermoelectric treatment of the anode and the cathode with an alternating current at such a polarization of the anode and the cathode which is lower than a voltage of decomposition of the solid electrolyte;
    wherein the secondary solid state current source is a galvanic cell or a secondary solid state battery; and
    the anodic material and the cathodic material have compositions corresponding to the compositions of the anodic material and the cathodic material of the secondary solid state current source in the fully discharged state during application of the anode and cathode materials, the baking and the thermoelectric treatment.

2. The method according to claim 1, wherein thermoelectric treatment of the anode and the cathode with the alternating current comprises the alternating electric current of different polarity.

3. The method according to claim 2, wherein thermoelectric treatment on the anode and the cathode with the alternating current comprises the alternating electric current of a sinusoidal form.

4. The method according to claim 3, wherein thermoelectric treatment on the anode and the cathode with the alternating current comprises alternating current of the sinusoidal form of an industrial frequency.

5. The method according to claim 1, wherein the subsequent baking and thermoelectric treatment of the anode and the cathode with the alternating current, those localities of the secondary solid state current source that have the highest resistance are recurringly heated.

Patentansprüche

1. Verfahren zur Herstellung einer sekundären Festkörperstromquelle, **gekennzeichnet durch** die folgenden Schritte:

    Anbringen eines Anodenmaterials auf einer Seite eines festen Elektrolyten, um eine Anode zu bilden, und Anbringen eines Kathodenmaterials auf der anderen Seite des festen Elektrolyten, um eine Kathode zu bilden; und
    anschließende Sinterung und thermoelektrische Behandlung der Anode und der Kathode mit einem Wechselstrom, und zwar mit einer solchen Polarisation der Anode und der Kathode, die geringer ist als eine Zersetzungsspannung des festen Elektrolyten;
    wobei die sekundäre Festkörperstromquelle ein galvanisches Element oder eine sekundäre Festkörperbatterie ist; und
    das Anodenmaterial und das Kathodenmaterial während des Anbringens des Anodenmaterials und des Kathodenmaterials, der Sinterung und der thermoelektrischen Behandlung Zusammensetzungen aufweisen, die den Zusammensetzungen des Anodenmaterials und des Kathodenmaterials der sekundären Festkörperstromquelle im vollständig entladenen Zustand entsprechen.

2. Verfahren nach Anspruch 1, wobei die thermoelektrische Behandlung der Anode und der Kathode mit dem Wechselstrom einen elektrischen Wechselstrom mit unterschiedlicher Polarität umfasst.

3. Verfahren nach Anspruch 2, wobei die thermoelektrische Behandlung der Anode und der Kathode mit dem Wechselstrom einen elektrischen Wechselstrom in sinusförmiger Form umfasst.

4. Verfahren nach Anspruch 3, wobei die thermoelektrische Behandlung der Anode und der Kathode mit dem Wechselstrom einen Wechselstrom in sinusförmiger Form mit einer Industriefrequenz umfasst.

5. Verfahren nach Anspruch 1, wobei bei der anschließenden Sinterung und thermoelektrischen Behandlung der Anode und der Kathode mit dem Wechselstrom jene Stellen der sekundären Festkörperstromquelle, die den höchsten Widerstand aufweisen, wie-

derholt erhitzt werden.

Revendications

1. Un procédé de fabrication d'une source de courant secondaire à l'état solide :

   caractérisé par les étapes suivantes :

   L'application d'un matériel d'anode sur un côté d'un électrolyte solide pour former une anode et l'application d'un matériel de cathode sur un autre côté de l'électrolyte solide pour former une cathode ; et
   une cuisson subséquente et un traitement thermoélectrique de l'anode et la cathode avec un courant alternatif à une polarisation de l'anode et de la cathode qui soit inférieure à une tension de décomposition de l'électrolyte solide ;
   où la source de courant secondaire à l'état solide est une cellule galvanique ou une batterie secondaire à l'état solide ; et
   le matériel d'anode et le matériel de cathode ont des compositions correspondant aux compositions du matériel d'anode et du matériel de cathode de la source de courant secondaire à l'état solide dans l'état totalement déchargé pendant l'application des matériels d'anode et de cathode, la cuisson et le traitement thermoélectrique.

2. Le procédé selon la revendication 1, où le traitement thermoélectrique de l'anode et de la cathode avec le courant alternatif comprend le courant électrique alternatif de polarité différente.

3. Le procédé selon la revendication 2, où le traitement thermoélectrique sur l'anode et la cathode avec le courant alternatif comprend le courant électrique alternatif de forme sinusoïdale.

4. Le procédé selon la revendication 3, où le traitement thermoélectrique sur l'anode et la cathode avec le courant alternatif comprend le courant alternatif de forme sinusoïdale d'une fréquence industrielle.

5. Le procédé selon la revendication 1, où la cuisson subséquente et le traitement thermoélectrique de l'anode et la cathode avec le courant alternatif, les localités de la source de courant secondaire à l'état solide qui ont la plus grande résistance sont chauffées de façon récurrente.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- RU 2005111722 **[0006]**
- RU 2136083 **[0009]**
- RU 1106382 **[0012]**
- US 2689322 A1 **[0013]**
- US 422200 A1 **[0013]**
- JP 200166353 A **[0013]**

Non-patent literature cited in the description

- *Informational Bulletin,* 1999 **[0009]**
- **A.K. IVANOV-SHITZ ; I.V. MURIN.** *Ionica of solid state,* 2000, vol. 1, 73-74.c.7374 **[0010]**