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(54) Title: ELECTRODE FOR LITHIUM PRIMARY AND SECONDARY (RECHARGEABLE) BATTERIES AND THE METHOD OF ITS PRODUCTION

(57) Abstract: Field of application: the invention relates to electrodes of lithium primary and secondary (rechargeable) batteries and methods of their production. It can be used in the power sources with non-aqueous electrolytes. Point of invention: the electrode includes metal current collector which is covered by electro active composition comprising active material capable of lithium intercalation/de-intercalation, conductive additive with electron conductivity and two binders selected from groups of PVDF and PTFE. The binder selected from PVDF group is soluble in the process of electro active composition slurry preparing and is introduced into the suitable solvent selected from the group N-methyl-2-pyrrolidone, acetone, dimethylacetamide (mainly, dimethylacetamide), dimethylformamide. The binder selected from PTFE group is insoluble in the process of electro active composition slurry preparation, and as a powder with the particle size from 0.2 up to 4 µm is introduced into the blend of dry components at the stage of prior mixing. The electro active composition in the form of slurry is applied on a current collector by extrusion method, dried for solvent removing and objected to subsequent compressing using calendaring for optimal density and porosity. Advances: the invention enables decreasing cathode production complexity; expansion of the area of active cathode material applications, improving electrochemical characteristics and adhesion properties of coating, its flexibility and the contact between the current collector and cathode material that leads to decreasing transition resistance.

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**Electrode for lithium primary and secondary (rechargeable) batteries and the method of its production**

5       The invention relates to electrodes of lithium primary and secondary (rechargeable) batteries and the methods of their production. It can be used in the power sources with non-aqueous electrolytes.

      Lithium and lithium-ion power sources are widely used in the various areas where energy storage and independent power consumption are needed. The requirements for such power sources are constantly increased. It is necessary to extend  
10      the temperature range of battery application to increase their capacities and charge/discharge currents.

      Li-metal or Li-Al alloy is the active anode material of lithium power sources.  $\text{MnO}_2$ ,  $\text{FeS}_2$ ,  $\text{TiS}_2$ ,  $\text{MoO}_3$ ,  $\text{CF}_x$  and others are widely used as a cathode material. As a  
15      rule, such batteries are used as primary ones. Graphite intercalated by lithium is the active anode material of lithium-ion power sources; and the compound oxides like  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ , spinel form  $\text{LiMn}_2\text{O}_4$  and others are usually used as active cathode materials. Besides the active materials, electrode compositions contain  
20      conductive additives providing electron conductivity and the binder responsible for coating mechanical durability, for its flexibility and adhesion to a current collector.

      Electrode production technology for lithium and lithium-ion sources can be divided into two groups:

1. Application of the lamination technology of rubber-like mass on a current collector.
- 25      2. The coating technology of cathode composition slurry on a moving current collector in the form of foil or grid followed by the stages of drying and calendaring (compacting).

Tetrafluoroethylene resin (hereinafter referred to as PTFE) in the form of powder or aqueous suspension is used at the first group of electrodes' production technologies, which particular property is the high level of PTFE fibrillation. Since the electrode mass produced by such a way is quite rigid, it is applied on a current collector by lamination. This electrode production method was historically used in the batteries with alkaline electrolyte / US 4,216,045; JP 62-243264; JP 64-086449; JP 10-083830; McGraw-Hill: "Handbook of Batteries"/. At present, this technology is mainly utilized for the production of coin-cells, prismatic and cylindrical batteries based on  $\text{MnO}_2$  /US 5,849,044; US 5,863,675; US 5,667,909; JP 63-236258; JP 55-043766; JP 55-126964; JP 11-273665/. Water, ethyl alcohol or isopropanol is a dispersion medium at this technology. Various thickeners and stabilizers are also used.

The authors of US patent 5,543,249 used the surface-active materials of polyglycol group for PTFE -based suspension stabilization. The high level of PTFE fibrillation makes difficulties for homogeneous cathode masses establishing so that additional homogenization is necessary.

For regulation of fibrillation level, the authors of US patent 5,707,763 propose the combined binder, which particles consist of the nucleus of fibrillating PTFE and a shell - of non- fibrillating polymer.

Disadvantage of this technology consists in the difficulty of thin coating production due to PTFE bad adhesion. The other disadvantage consists in incompatibilities of some active cathode materials with regard to water and stabilizers.

Polyvinyliden fluoride (PVDF) homopolymer or polyvinylidene fluoride hexafluoropropylene (PVDF/HFP) copolymer is used at the second group of electrode production technologies. These polymers are dissolved into such solvents as N-methyl-2-pyrrolidone, acetone, dimethylformamide, dimethylacetoamide. The mixture of active materials and electro- conductive additives is introduced into polymer solution and slurry is prepared by mixing and homogenization. Then the slurry is

applied by extrusion method on the current collector in the form of foil or grid. Then the coating should be dried and compressed before electrode manufacturing for lithium-ion batteries (Walter A. van Schalkwijk, Bruno Scrosati: "Advances in Lithium-Ion Batteries"; JP 04-249860; JP 08-022841; JP 04-095363; JP 08-264181; 5 JP 11-307099; US 5,707,758; US 5,168,019; US 5,478,675). Special machines are used at this technology. These machines exhibit higher productivity in comparison with lamination technology and maintain uniform thickness for width of coating up to 20 centimeters under practically unlimited resources as regards thickness. In spite of the fact that fluorine polymers of PVDF-group have better adhesion capability, the 10 problems with adhesion and flexibility still take places. Moreover, there is a risk of PVDF/HFP-copolymers swelling in the electrolyte of galvanic cell. Attempts to solve these problems are mainly connected with binder modification and plasticizer utilization (US 6,265,107; US 6,001,507; US 5,961,671).

PVDF -based electrode production technology is the most progressive in 15 comparison with the technology of PVDF-based cathode masses lamination. Therefore, it is quite natural the new polymer-solvent system appearance with the object of adaptation of the materials used at lamination technology to extrusion technology.

Search of new polymer-solvent systems for  $\text{MnO}_2$ -cathode was demonstrated at 20 US Patent Application 20040091773. Its authors propose as binders, linear tri- block styrene-ethylene-butylene copolymer cross-linked by melamine formaldehyde resin, EPDM - caoutchouc- tri-block fluorocarbon polymer, hydro- nitrile caoutchouc, PVdF copolymers, thermoplastic polyurethanes and olefins. Normal and branched hydrocarbons, cyclic paraffinic solvents and aromatic hydrocarbons were used as 25 solvents. The authors underlined compatibility of cathode production technology with traditional one for the lithium-ion system based on PVDF: preparing cathode composition slurry based on binder-solvent solution and coating on a current collector

followed by drying. Although the authors covered entirely the wide class of polymers and solvents, they did not notice their compatibility with  $\text{MnO}_2$ . Correspondingly, electrochemical properties of cathodes and batteries are not presented.

Also, the other binder-solvent systems were proposed, which suppose  
5 utilization of the analogous technology similar to that for PVDF. The applications of latex binder based on carboxylated styrene-butadiene copolymer and styrene-acrylate copolymer /US 6,399,246/, acrylonitrile-butadiene rubber with carboxymethylcellulose /US 6,183,907/ were described for non-aqueous electrolyte systems. Water was the dispersion medium of the both examples. As pH of latex  
10 emulsion is about 8-10, it is not always acceptable for some active cathode materials due to decreasing their electrochemical activity.

The point of this invention is Modification of the traditional PVDF- production technology of cathodes for Li-ion system with non-aqueous electrolyte in such a way that it, improving mechanical and electrochemical properties of the cathodes  
15 based on such usual cathode materials as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ ,  $\text{LiMn}_2\text{O}_4$  will become acceptable for cathode production on the basis of such active materials as  $\text{MnO}_2$ ,  $\text{FeS}_2$ ,  $\text{TiS}_2$ ,  $\text{MoO}_3$ ,  $\text{CF}_x$  which were traditionally used in lamination technology is the task of invention.

This problem is solved by using two binders in the electrode for primary and  
20 secondary lithium batteries composed of metal current collector with the coated cathode composition including active material and electro conductive additive. One of these binders is soluble during preparation of slurry of electro active composition; and the other is insoluble and introduced into slurry composition during process of prior dry components mixing.

25 - current collector is a metallic foil or grid;

- active material is a compound sort oxides, sulphides, intercalated by lithium oxides, metal-complexes, spinels, fluorinated carbon or carbon-based compounds;
- content of conductive additive with electron conductivity ranges from 5 up to 7 % of the total mass of electro active composition;
- blend of carbon black and graphite taken in the ratio from 2:1 to 1:1 by mass is a conductive additive;
- as one of the conductive additive with electron conductivity there is used the carbon material, produced from graphitized carbon black with specific surface area ranging from 40 up to 70 m<sup>2</sup>/g and 50 % of material has the particle size up to 3 microns;
- the binder soluble during preparation of electro active composition slurry is the PVDF class compound;
- the binder of the PVDF class is the copolymer with the molecular weight at least 3\*10<sup>5</sup> (5) mol;
- the compound of the PVdF class is the binder insoluble in the production process of electro-active composition slurry;
- the binder of PTFE class is used as the powder of particle sizes 0.2 – 4 microns;
- the binder of PTFE class is introduced into the composition of dry components in the process of preliminary mixing;
- the mass ratio between PVDF and PTFE ranges from 1.2 up to 1.7 in the content of electro active composition;
- where PVDF solution is a dispersion medium during the process of slurry preparation in the appropriate solvent selected from the group: N-methyl-2-pyrrolidone, acetone, dimethylformamide, dimethylacetoamide (mainly dimethylacetoamide);

- where the mixture of active material, conductive additives and the binder of PTFE class is a continuous phase ;
- Electrode production method for primary and secondary lithium batteries includes preparing the blend of solid-phase components of electro active composition in a suitable solvents; combination and homogenization of solid-phase components and solution of soluble binder; slurry degassing; applying a slurry on a metal current collector; drying of coating; compressing by calendering; removing the residual amount of water and solvent.
- preparation of the mixture of solid phase components of electro- active composition includes mixing active material powders, conductive additive with electron conductivity and the binder powder from the PTFE class using a ball mill;
- preparation of soluble binder solution includes dissolving of PVDF polymer class into an appropriate solvent selected from the group of N-methyl-2-pyrrolidone, acetone, dimethylformamide, dimethylacetoamide (mainly dimethylacetoamide) under intermediate heating up to 60 °C using paddle type disperser;
- blend of solid phase components is introduced into the solution of soluble binder by 10 – 15 % portions of the total amount of dry components using low-speed mixer with anchor or Z-type paddles;
- solution of a soluble binder is introduced into the blend of solid phase components under continuous mixing using low-speed mixer anchor or Z-type paddles;
- product of combining solid phase component blend and the solution of soluble binder is subjected to homogenization using a high-shear mixer with

speed changing from 1500 up to 8000 rpm during 30 - 45 minutes under cooling;

- homogenized slurry of the electro active composition is subjected to degassing by vacuum under continuous mixing using low-speed mixer anchor or Z-type paddles;
- amount of solid phase components in a slurry is 30-60 % by mass;
- slurry viscosity ranges from 5000 up to 12000 cp at 23 °C, measured by Brookfield DV III, 20 rpm, spindle # 31;
- slurry of electro active composition is applied on a current collector by extrusion;
- electro active composition coating is dried immediately after coating under gradual temperature changing from 80 up to 120°C and solvent vapors exhaust by hot air blow;
- dried coating of electro active composition on metal current collector is compressed by calendaring under gradual thickness decrease so that total thickness decreasing as compared with initial thickness is 20-25 % increasing electrode mass density is 30-45 % at coating porosity 20-40%;
- cut-to cell dimensions electrode is dried at 125-170°C in air at continuous gas re-cycling through the systems of residual moisture and organic solvent vapor removal;
- cut-to cell dimensions electrode is dried at 125-170°C under inert gas re-circulated through the system of residual moisture and organic solvent vapor removal;
- cut-to cell dimensions electrodes is dried at 125-170°C under vacuum condition;

The proposed technology allows:

- to decrease the production complexity of cathode manufacturing



- to extend the range of active cathode materials applications;
- to improve the electrochemical properties of cathode, particularly, to extend the temperature range of productivity from  $-40^{\circ}\text{C}$  up to  $+70^{\circ}\text{C}$  and to increase discharge current up to 12-20 mA/cm<sup>2</sup>;
- 5      - to improve coating adhesion properties and flexibility, as well as the contact between current collector and electrode material resulting to transition resistance decrease.

Moreover, this technical solution allows producing thin flexible electrodes with one or both side coating on the current collector made of foil or grid (preferably  
10      aluminum). Made by this way cathodes can be utilized at prismatic or spiral wound cells without coating mechanical cracking. Flexibility of coating provides spiral wounding around 3 mm rod without any cracking and peeling from current collector. It is possible to produce the coatings with the density ranging from 1 up to 45 mg/cm<sup>2</sup>.

The stated advances are achieved at the cost of using:

- 15      - high-molecular PVDF or PVDF/HFP;
- dimethylacetoamide as a solvent;
- powder of PTFE as a second insoluble binder which acts as a plasticizer;
- high-shear technology of mixing.

Thus, the used electrode composition slurry and its temperature range of drying  
20      are fully acceptable for processing by usual extrusion machines used for coating.

Electrochemical cell of lithium or lithium-ion battery contains anode with negative tab; cathode with positive tab, separator, electrolyte or electrolyte system with dissociated lithium salt.

Lithium-metal or Li-Al alloy with Al content up to 5 % can be used as an  
25      active anode material; for lithium-ion system, graphite or other material capable of intercalating can be utilized.

$\text{MnO}_2$ ,  $\text{CF}_x$ ,  $\text{FeS}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$  and other materials used in lithium or lithium-ion system can be used as an active cathode material.

Selgar sort polypropylene film or others providing similar properties can be used as a separator.

5 One or several aprotic solvents like 1,2-dimethoxy ethane, propylene carbonate, ethylene carbonate, DMC, DEC, 1,3-dioxolane, tetrahydrofuran,  $\gamma$ -butyrolacton and others can be used as electrolytes.

$\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$  or  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and others can be used as a lithium salt.

10 The invention is explained by drawings presenting by:

Figure # 1: cathode production scheme.

Figure # 2: discharge characteristic of primary  $\text{Li/MnO}_2$  prismatic battery at 50 mA@23°C. Cathodes were produced in accordance with the method presented by this invention, example # 1.

- 15
- Dimension, mm: 34 x 60 x 3.8
  - Voltage range 3.3 – 1.5 V
  - Nominal capacity: 2 Ah@50mA to 1.5V@23°C
  - Energy : 5.2 Wh@50mA to 1.5V@23°C
  - Weight: 16 g
- 20
- Specific capacity of  $\text{MnO}_2$ , achieved during discharge: 260-270 mAh/g
  - Specific energy of battery: 325 mWh/g
  - Operating temperature range: from -40 up to 65°C
  - Temperature range of battery storage: from -40 up to 70°C
  - Package: laminated Al-foil.
- 25 Figure # 3: discharge curves of  $\text{MnO}_2$  –cathodes obtained in electrochemical cells with lithium anode (1 cathode & 2 anodes). Cathodes were prepared by the method of

this invention, example # 2. Size - 31x54 mm; two-sided coating on Al-grid; coating density - 15 mg/cm<sup>2</sup>. Electrolyte - PC, DME, TGF, 0.5 M LiClO<sub>4</sub>.

Table # 1

Curve #	Discharge current density, mA/cm <sup>2</sup>	Discharge current, C	Specific capacity of MnO <sub>2</sub> , mAh/g
1	0.15	0.05	260
2	1.5	0.5	216
3	3.0	1.0	193
4	4.5	1.5	187
5	6.0	2.0	165
6	12.0	4.0	127

5 Fig. # 4: Discharge curves of MnO<sub>2</sub>-cathodes obtained in electrochemical cells with lithium anode (two cathodes & three anodes) at -40 °C. Cathodes were produced by the method of this invention, example # 3. Dimension: 31x54 mm; two- sided coating on Al-foil; coating density - 15 mg/cm<sup>2</sup>. Electrolyte: PC, DME, TGF, 0.5 M LiClO<sub>4</sub> discharge cycles according to the diagram:

- 10
- 1<sup>st</sup>: duration is one hour at -40°C; final discharge voltage - 1.75 V.
  - From the 2<sup>nd</sup> to 8<sup>th</sup>: duration is one hour at -40°C; 10 min. discharge or up to 1.75 V ;
- 2,3,4,5,6,7,8: duration is 1 hour at -40°C, discharging – 10 min or up to 1.75 V.

15

Table # 2

cycle #	Discharge current density, mA/cm <sup>2</sup>	Discharge current, mA	Capacity at a circle, mAh
1	1.31	88	41.6
2	1.31	88	13.3
3	1.31	88	13.4

Continuation of Table # 2

4	1.22	81.6	13.6
5	1.22	81.6	13.6
6	1.22	81.6	13.6
7	1.22	81.6	13.6
8	1.22	81.6	13.6

Picture # 5: discharge curves of  $\text{CF}_x$  – the cathodes obtained in electrochemical cells with lithium anode (one cathode & two anodes). Cathodes were prepared by the method of this invention, example # 4. Two - sided coating on Al-foil.

- 5
- Curve # 1: 6 mA/cm<sup>2</sup>; discharge voltage - 2.23 V.
  - Curve # 2 : 12 mA/cm<sup>2</sup> ; discharge voltage - 2.1 V

Picture # 6: discharge curves of  $\text{LiMn}_2\text{O}_4$  –cathodes produced in electrochemical cells with lithium anode (one cathode & two anodes). Cathodes were prepared by the method of this invention, example # 5. Two-sided coating on Al-foil, 4.2 mg/cm<sup>2</sup>.

Table # 3

Curve #	Discharge current density, mA/cm <sup>2</sup>	Discharge current, C	Specific capacity of $\text{LiMn}_2\text{O}_4$ , mAh/g
1	0.24	0.5	111
2	0.53	1.1	108
3	2.65	5.5	97
4	5.30	10.9	91
5	7.60	15.8	84
6	10.0	20.6	76
7	12.4	25.5	69
8	14.7	30.4	61
9	17.7	36.5	51

The invention is realized through the following steps:

1. Powder-like blend preparing of the electrode components: active cathode material; conductive additive in the form of graphitized carbon black with specific surface area from 40 up to 70 m<sup>2</sup>/g and 50 % material has the particle size up to 3 micron or the mix of carbon black and graphite in the ratio from 2:1 up to 1:1 by mass; PTFE powder with the particle sizes from 0.2 up to 4 μm in proportion of total mass fraction

- active cathode material: 86-91 % ;
- graphitized carbon black or the mix of carbon black and graphite: 6-10 %;
- PTFE: 3-4 %.

Mixing of solid phase cathode materials is carried out using the ball mixer or the others designed for dry components mixing.

2. Preparing the solution of high-molecular PVDF or PVDF/HFP in dimethyl acetoamide in the proportion of total mass fraction

- PVDF or PVDF/HFP: 2-4%;
- DMAC: 96-98%.

PVDF or PVDF/HFP is dissolved using the paddle type mixer- emulsifier under moderate heating up to 60°C.

3. Mixing solid phase component blend with dimethylacetoamide solution of PVDF or PVDF/HFP that is carried out by one of two methods:

A - solid phase component blend is introduced into dimethylacetoamide solution of PVDF or PVDF/HFP by 10 – 15 % portions under continuous mixing using low-speed mixer with anchor or Z-type paddles<sup>1</sup>;

B - PVDF or PVDF/HFP solution is poured into solid phase component blend under continuous mixing using low-speed mixer with anchor or Z-type paddles<sup>1</sup>.

The ratio between solid phase component blend and dimethylacetoamide solution of PVDF or PVDF/HFP consist by mass of

- solid-phase component blend: 30 - 60 %
- dimethylacetoamide solution of PVDF or PVDF/HFP: 70 – 40 %

4. Homogenization of slurry under simultaneous effecting the three types of mixing<sup>1</sup>:

- 5     • agitation by low-speed mixer with anchor or Z-type paddles (Three Wing Anchor Agitator, 20-40 rpm)<sup>1</sup>;
- stirring by paddle type mixer - emulsifier (High Speed Dispenser, 200-300 rpm)<sup>1</sup>;
- dispersing by high-shear mixer (High Shear Rotor/Stator Mixer under gradual  
10    velocity increasing from 1500 to 8000 rpm)<sup>1</sup>.

Homogenization is carried out during 30-45 minutes under continuous cooling.

5. Degassing of homogenized slurry by applying moderate vacuum (10-50 mmHg) under constant agitation using low-speed mixer with anchor or Z-type paddles<sup>1</sup>.

- 15     6. Coating<sup>2</sup> of cathode composition slurry on the one or both sides of moved current collector in the form of foil or grid (preferable aluminum) by extrusion using extruder heads with variable slurry distribution through slots with fixed gap. The coated foil or grid (preferable aluminum) moves through two zones of drying by heated air blow at 80 and 120°C , respectively. Speed of tape movement is about 0.5 –  
20    1.0 meter per minute.

7. Calendering of cathode tape with gradual coating thickness reducing up to 20-25 %.

8. Final drying of cut-to element dimension electrodes that is carried out by one of the three methods:

- 25     • at 125-170°C under air re-circulated through the system of residual moisture and organic solvent vapor removal;

- at 125-170°C under inert gas re-circulated through the system of residual moisture and organic solvent vapor removal;
- at 125-170°C under vacuum condition;

Footnotes:

- 5 1 - ROSS Model VMC-100 VACUUM MIXER or similar.  
2 - HIRANO COATING MASHINE, TEXMAC. INC, or similar.

### Example 1.

10 Cathode with  $\text{MnO}_2$  as a active material. Cathode was produced by the above technology.

Content of electro active composition slurry:

PVDF – homopolymer (Solef® 6020, Solvay):	2.0 %
PTFE, (Zonyl® MP 1100, DuPont):	1.5 %
$\text{MnO}_2$ (CDM):	43.5 %
15 Graphite (ABG1005, Superior Graphite Co.):	1.0 %
Carbon black (Acetylene black AB55, Chevron Phillips Chemical Co.):	2.0 %
N,N-Dimethylacetamide (OMNISOLV):	50 %

Blend of solid-phase components of  $\text{MnO}_2$ , carbon black, graphite and PTFE was prepared by mixing during 5-6 hours using ball-mixer. N,N-Dimethylacetamide solution of PVDF was made by using ROSS Model 100L lab mixer with DL-attachment, 250 rpm, 3 hours under moderate heating up to 60°C. Slurry of electro active composition was prepared during three stages using ROSS Model VMC-100 VACUUM MIXER:

20

- Joining of PVDF solution and solid-phase components' blend. Three Wing Anchor Agitator was used at 20 - 40 rpm, mixing during 30 minutes.
- 25

- Homogenization by using Wing Anchor Agitator at 20-40 rpm; High Speed Disperser at 200-300 rpm; High Shear Rotor/Stator Mixer under gradual velocity increasing from 1500 to 8000 rpm. Mixing during 30-45 minutes under continuous cooling.
- Degassing during 30 minutes under moderate vacuum. Three Wing Anchor Agitator was used at 20 - 40 rpm.

Slurry was applied on both sides of 35 mkm thickness aluminum grid using HIRANO COATING MASHINE, TEXMAC INC., speed of tape's moving was 1 meter per minute with passing through 80 and 120°C zones of drying.

The produced cathodes were utilized at prismatic battery assembling consisting of 10 cathodes and 11 Li-anodes. Overall battery dimension was 34 x 60 x 3.8 mm; weight – 16 g. Cathode mass density was 2.7 – 2.8 g/cm<sup>3</sup>. Electrolyte: PC, DME, TGF, 0.5 M LiClO<sub>4</sub>. The battery was discharged by 50 mA current. MnO<sub>2</sub> specific capacity, achieved at discharging, was 270 mAh/g, Specific energy - 730 mWh/g. Discharge characteristic of battery is presented In Fig. # 2.

### Example 2.

Cathode with MnO<sub>2</sub> as an active material. Cathode was produced by the above technology.

Content of electro active composition slurry:

PVDF – homopolymer (Solef® 6020, Solvay):	2.0 %
PTFE, (Zonyl® MP 1100, DuPont):	1.5 %
MnO <sub>2</sub> (CDM):	42.5 %
Graphitized carbon black (SCD 315, Superior Graphite Co.):	4.0 %
N,N-Dimethylacetamide (OMNISOLV ) solvent :	50 %

Blend of the solid-phase components of MnO<sub>2</sub>, graphitized carbon black and PTFE was prepared by mixing during 5-6 hours using ball-mixer. N,N-Dimethylacetamide solution of PVDF was produced by using ROSS Model 100L lab



mixer with DL-attachment, 250 rpm, 3 hours under moderate heating up to 60°C. Slurry of electro active composition was prepared through three stage using ROSS Model VMC-100 VACUUM MIXER:

- Joining of PVDF solution and solid-phase components' blend. Three Wing Anchor Agitator was used at 20 - 40 rpm, mixing during 30 minutes.
- Homogenization by using Wing Anchor Agitator at 20-40 rpm; High Speed Disperser at 200-300 rpm; High Shear Rotor/Stator Mixer under gradual velocity increasing from 1500 to 8000 rpm. Mixing during 30-45 minutes under continuous cooling.
- Degassing during 30 minutes under moderate vacuum. Three Wing Anchor Agitator was used at 20 - 40 rpm.

Slurry was applied on the both sides of current collector from 35 mkm thickness aluminum grid using HIRANO COATING MASHINE, TEXMAC INC., speed of tape moving was 1 meter per minute with passing through 80 and 120 °C zones of drying.

The produced cathodes were utilized at assembling prismatic electrochemical cell consisting of 1 cathode and 2 Li-anodes. Electrolyte: PC, DME, TGF, 0.5 M LiClO<sub>4</sub>. The cells were discharged at room temperature at the current densities ranging from 0.15 mA/cm<sup>2</sup> up to 12 mA/cm<sup>2</sup>, that corresponded to the charge currents from 0.05 up to 4.0 C. Discharge characteristics are presented in Fig. # 3.

### **Example aprotic 3.**

Cathode with MnO<sub>2</sub> as an active material. Cathode was produced by the above technology.

Content of electro active composition slurry:

PVDF – homopolymer (Solef® 6020, Solvay):	2.0 %
PTFE, (Zonyl® MP 1100, DuPont):	1.5 %

MnO <sub>2</sub> (CDM):	42.5 %
Graphitized carbon black (SCD 315, Superior Graphite Co.):	4.0 %
N,N-Dimethylacetamide (OMNISOLV):	50 %

Blend of the solid-phase components MnO<sub>2</sub>, graphitized carbon black and PTFE was prepared by mixing during 5-6 hours using a ball mill. N,N-Dimethylacetamide solution of PVDF was prepared using ROSS Model 100L of the lab mixer with DL-attachment, 250 rpm, during 1 hour under moderate heating up to 60 °C. Slurry of electro active composition was prepared using ROSS Model 100L of the lab mixer with L-high-shear attachment with 8000 rpm during three 10-minute steps followed by periodical cooling. The slurry was applied on the both sides of 50 mkm thickness aluminum foil using lab coating machine Coatema.

The produced cathodes were utilized at assembling prismatic electrochemical cell consisting of 2 cathodes and 3 Li-anodes. Electrolyte: PC, DME, TGF, 0.5 M LiClO<sub>4</sub>. The cell was discharged by 1.31 and 1.22 mA/cm<sup>2</sup> currents at -40°C up to the 1.75 V voltage. Discharge characteristics of the cell are presented in Fig. # 4.

#### Example 4.

Cathode with CF<sub>x</sub>-compound as an active material. The cathode was produced by the above technology.

Content of electro active composition slurry:

PVDF – homopolymer (Solef® 6020, Solvay):	1.4 %
PTFE, (Zonyl® MP 1100, DuPont):	1.0 %
CF <sub>x</sub> (ARS):	27.6 %
Graphitized carbon black (SCD 315, Superior Graphite Co.):	3.3 %
N,N-Dimethylacetamide (OMNISOLV) solvent :	66.7%

Blend of solid-phase components CF<sub>x</sub>, graphitized carbon black and PTFE was prepared by mixing during 5-6 hours using ball-mill. PVDF solution in N,N-Dimethylacetamide was prepared using ROSS Model 100L lab mixer with DL-

attachment, 250 rpm, 1 hour under moderate heating up to 60 °C. Slurry of electro active composition was prepared using ROSS Model 100L lab mixer with L-high-shear attachment at 8000 rpm in three stages, each duration is 10 minutes with periodical cooling. Slurry was applied on the both sides of 20 mkm thickness aluminum foil using lab coating machine Coatema.

The produced cathodes were utilized at assembling electrochemical cell of prismatic design consisting of 1 cathode and 2 Li-anodes. Electrolyte: PC, DME, TGF, 0.5 M LiClO<sub>4</sub>. The cell was discharged by the current densities 6 mA/cm<sup>2</sup> (discharge voltage 2.23 V) and 12 mA/cm<sup>2</sup> (discharge voltage 2.10 V) at room temperature. Cell discharge characteristics are presented in Fig. # 5.

#### Example 5.

Cathode with LiMn<sub>2</sub>O<sub>4</sub>-spinel as an active material. The cathode was produced by the above technology.

Content of electro active composition slurry:

PVDF/HFP – copolymer (Solef® 21216, Solvay):	1.4 %
PTFE, (Zonyl® MP 1100, DuPont):	1.0 %
LiMn <sub>2</sub> O <sub>4</sub> -spinel:	27.6 %
Graphitized carbon black (SCD 315, Superior Graphite Co.):	3.3 %
N,N-Dimethylacetamide (OMNISOLV) solvent :	66.7%

Blend of solid-phase component manganese spinel, graphitized carbon black and PTFE was prepared by mixing during 5-6 hours using ball-mill. N,N-Dimethylacetamide solution of PVDF was prepared using ROSS Model 100L lab mixer with DL-attachment, 250 rpm, for 1 hour under moderate heating up to 60 °C. Slurry of electro active composition was prepared using ROSS Model 100L lab mixer with L-high-shear attachment at 8000 rpm in three stages each duration is 10 minutes with periodical cooling. Slurry was applied on the both sides of 20 mkm thickness aluminum foil using lab coating machine Coatema.

The produced cathodes were utilized at assembling prismatic electrochemical cells consisting of 1 cathode and 2 Li-anodes. Electrolyte: EC, DMC, 1.0 M LiClO<sub>4</sub>. The cells were discharged by the current densities ranging from 0.24 up to 17.7 mA/cm<sup>2</sup>, that corresponded to discharge currents from 0.5 up to 36.5 C. Discharge characteristics are presented in Fig. # 6.

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## Claims.

1. Electrode for lithium primary and secondary batteries, consisting of metal current collector coated by electro active composition, comprising active material, conductive additive with electron conductivity, two binders, one of them is soluble during preparation of electro active composition slurry and other is insoluble and is introduced into slurry composition during the process of preliminary dry components mixing.
2. The electrode of claim 1, wherein the current collector is a foil or grid.
3. The electrode of claim 1, wherein the active material is the compound from the class of oxide, sulphides, lithiated oxides, metal complexes, spinels, fluorinated carbon, carbon or the compounds based on base carbon.
4. The electrode of claim 1, wherein the amount of conductive additive with electron conductivity ranges from 5 up to 7 % of the total mass of electro active composition.
5. The electrode of claim 1, wherein the conductive additive with electron conductivity is a blend of carbon black and graphite taken in the ratio from 2:1 to 1:1 by a mass.
6. The electrode of claim 1, wherein the one of conductive additive with electron conductivity is a carbon material made of graphitized carbon black.
7. The electrode of claim 1, wherein as graphitized carbon black is a carbon black with specific surface area ranging from 40 to 70 m<sup>2</sup>/g.
8. The electrode of claim 1, wherein 50 % of graphitized carbon black has particle size up to 3 microns.
9. The electrode of claim 1, wherein the total binders' amount does not exceed 5-7%.
10. The electrode of claim 1, wherein PVDF class compound is the binder soluble during preparation of electro active composition.
11. The electrode of claim 10, wherein copolymer with molecular mass of at least 3\*10<sup>5</sup> is a PVDF class binder.

12. The electrode of claim 10, wherein homopolymer with molecular mass of at least  $3 \cdot 10^5$  g/mol is a PVDF class binder.

13. The electrode of claim 1, wherein the PTFE class compound is the binder insoluble in the processes of electro-active slurry composition production.

14. The electrode of claim 13, wherein the PTFE class binder is used as a powder with the particle size 0.2 – 4 microns.

15. The electrode of claim 1, wherein the PTFE class binder is introduced into the blend of dry components at the stage of prior mixing.

16. The electrode of claim 1, wherein the mass ratio of PVDF to PTFE ranges from 1.2 up to 1.7 in electro active composition.

17. The electrode of claim 1, wherein for the slurry of electro-active composition, PVDF solution is a disperse medium in the appropriate solvent selected from the group: N-methyl-2-pyrrolidone, acetone, dimethylformamide, dimethylacetoamide (mainly, dimethylacetoamide).

18. The electrode of claim 1, wherein the mixture of active substance, conductive additives and the binder from PTFE is a dispersed phase of slurry.

19. Production method of the electrode for primary and secondary lithium batteries including preparation of solid-phase components blend of electro-active composition; solution of soluble binder from the group of PVDF in a suitable solvent; combination and homogenization of solid-phase components' mix and solution of soluble binder; slurry degassing; coating of current collector; coating drying; compressing by calendaring; removing the residual amount of water and solvent.

20. The process of claim 19, wherein the blend preparation of solid phase components of electro active composition includes mixing the active material powders, conductive additive with electron conductivity and the powder of PTFE class binder using a ball-mixer.

21. The process of claim 19, wherein solution preparation of soluble binder consists in PVDF dissolving into appropriate solvent selected from the group of

N-methyl-2-pyrrolidone, acetone, dimethylformamide, dimethylacetoamide (mainly dimethylacetoamide) at mild heating up to 60 °C using paddle type disperser.

22. The process of claim 19, wherein the blend of solid phase components is introduced into solution of soluble binder by the 10 – 15 % portions of the total amount of dry components.

23. The process of claim 22, wherein the low-speed mixer with anchor or Z-type paddles is used during introducing of solid phase components' mix into solution of soluble binder.

24. The process of claim 19, wherein solution of soluble binder is introduced into the blend of solid phase components under continuous mixing using low-speed mixer anchor or Z-type paddles.

25. The process of claim 19, wherein the product of mixing solid phase component blend and soluble binder solution is subjected to homogenization using rotor type high-speed mixer at changing a promptness from 1500 up to 8000 rpm during 30 - 45 minutes under cooling.

26. The process of claim 19, wherein the homogenized slurry of electro active composition is subjected to degassing by vacuum under continuous mixing using low-speed mixer anchor or Z-type paddles.

27. The process of claim 19, wherein the amount of solid phase components in slurry is 30-60 % by mass.

28. The process of claim 19, wherein slurry viscosity ranges from 5000 up to 12000 cp at 23 °C, measured by Brookfield DV III, 20 rpm, spindle # 31.

29. The process of claim 19, wherein the slurry of electro active composition is applied on a current collector by extrusion.

30. The process of claim 19, wherein the covering of electro active composition is dried immediately after coating under gradual temperature changing from 80 up to 120 °C and solvent vapors exhaust by hot air blow.

31. The process of claim 19, wherein the dried coating of electro active composition on a current collector is compressed by calendaring under gradual



thickness reducing by such a way that total thickness reducing is 20–25 % as compared to initial thickness and increasing electrode mass density is 30-45 % at 20-40% coating porosity ;

32. The process of claim 19, wherein the cut-to element dimensions electrode is dried at 125-170°C under air re-circulated through the system of residual moisture and organic solvent vapor removal.

33. The process of claim 19, wherein the cut-to element dimensions electrode is dried at 125-170°C under inert gas re-circulated through the system of residual moisture and organic solvent vapor removal.

34. The process of claim 19, wherein cut-to element dimensions electrode is dried at 125-170°C under vacuum condition.

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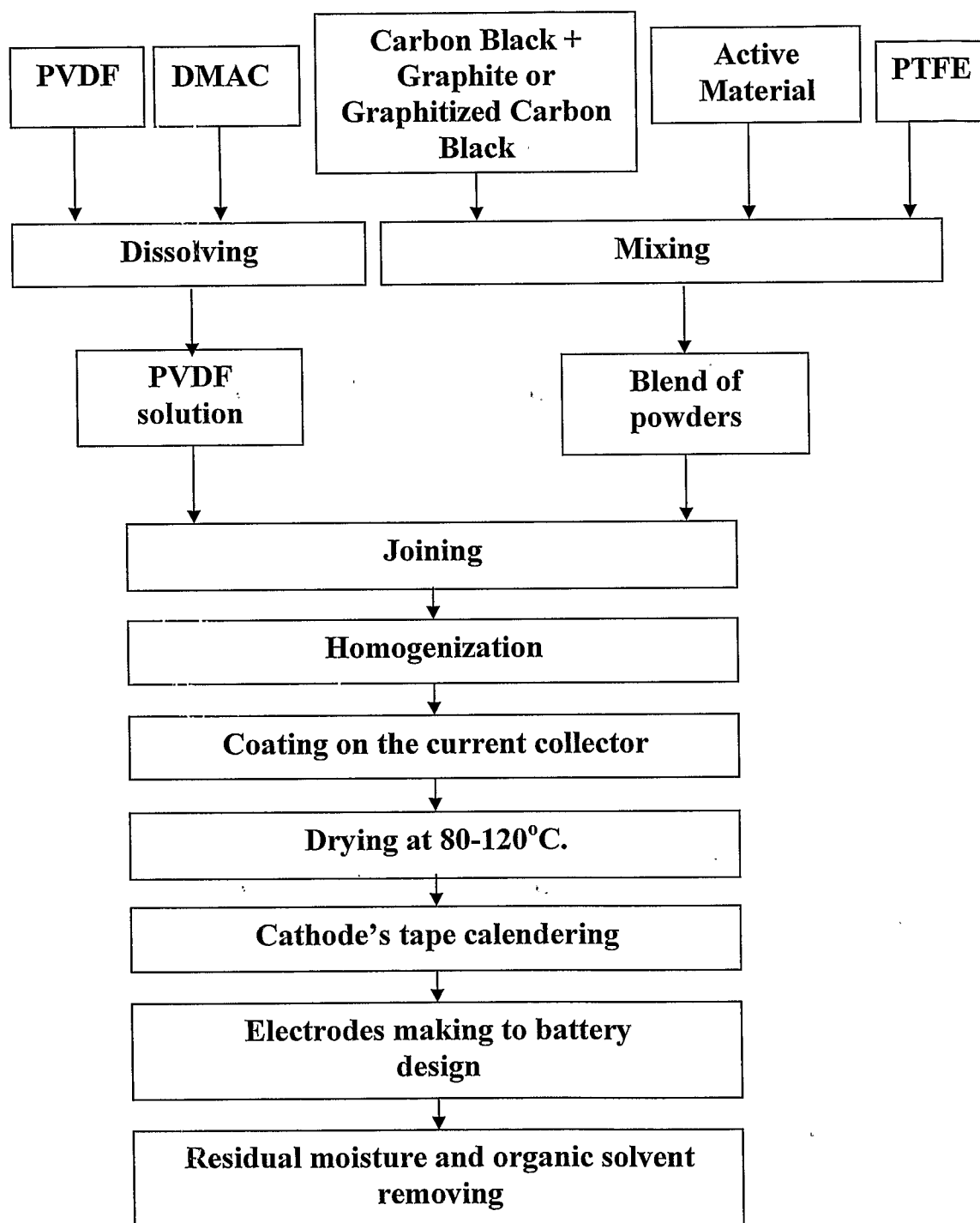


Fig.1

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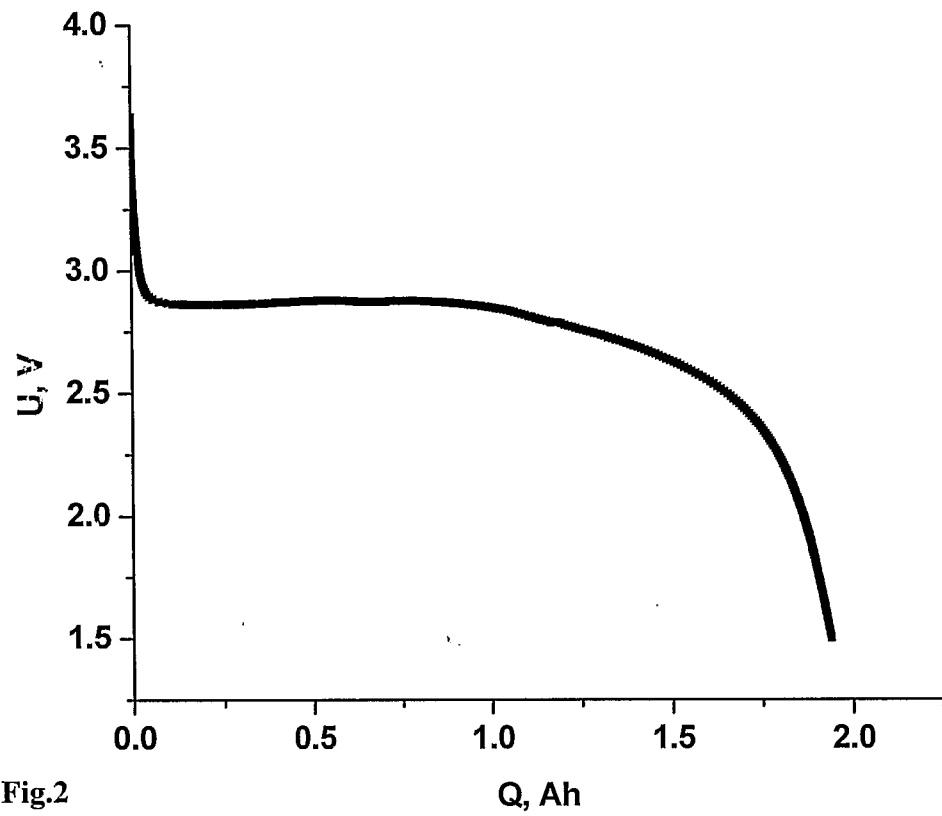


Fig.2

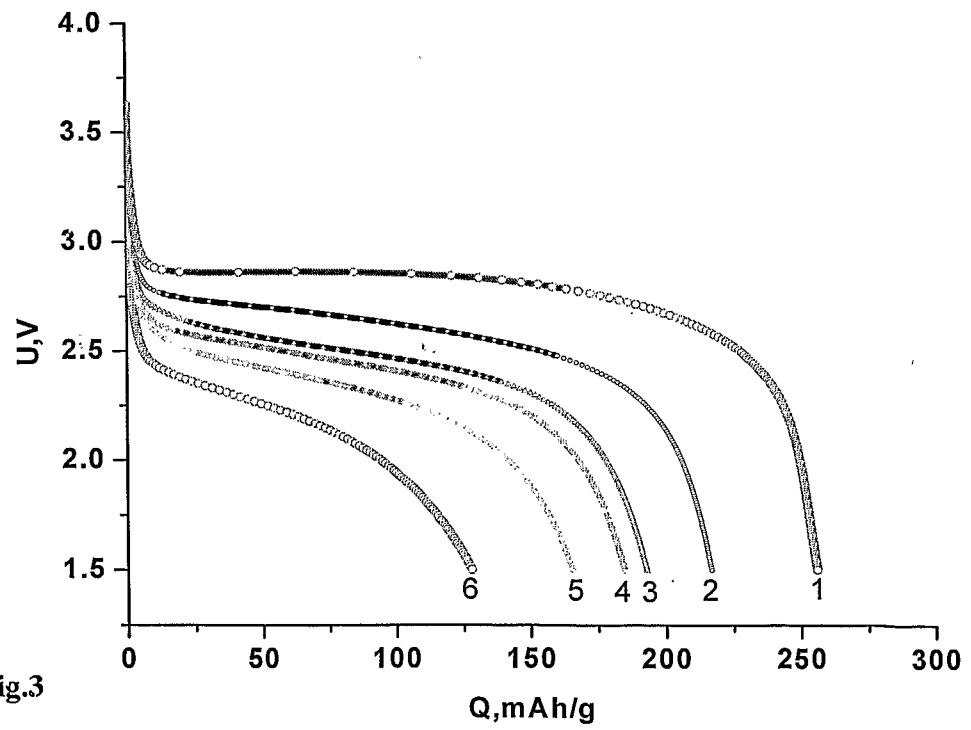


Fig.3

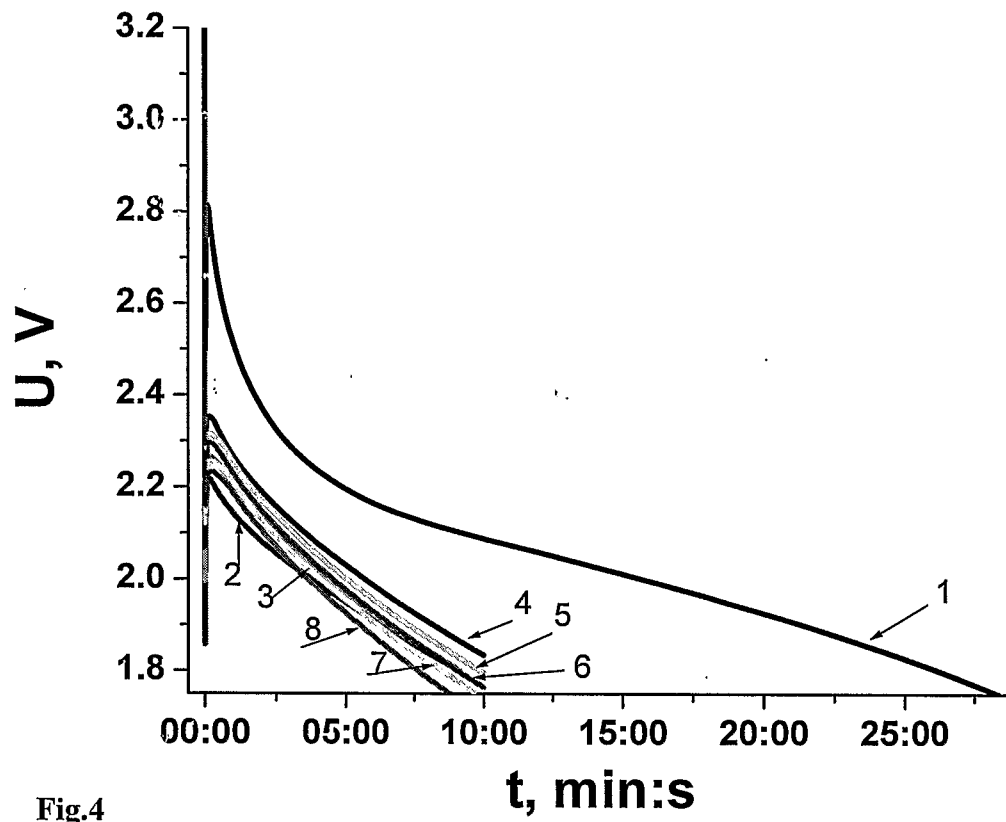


Fig.4

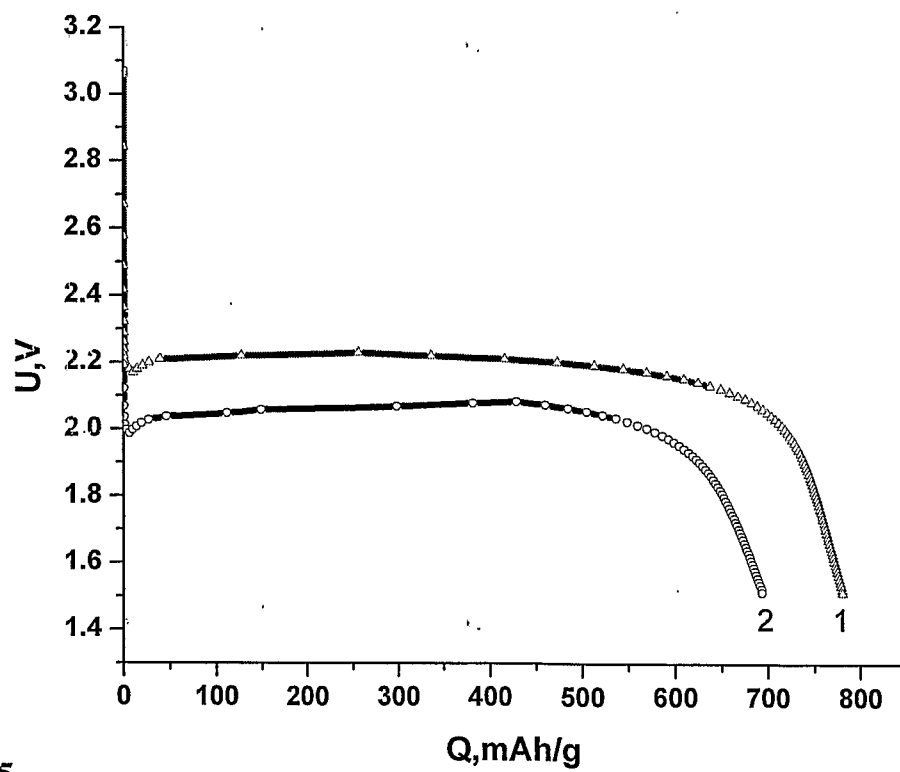


Fig.5

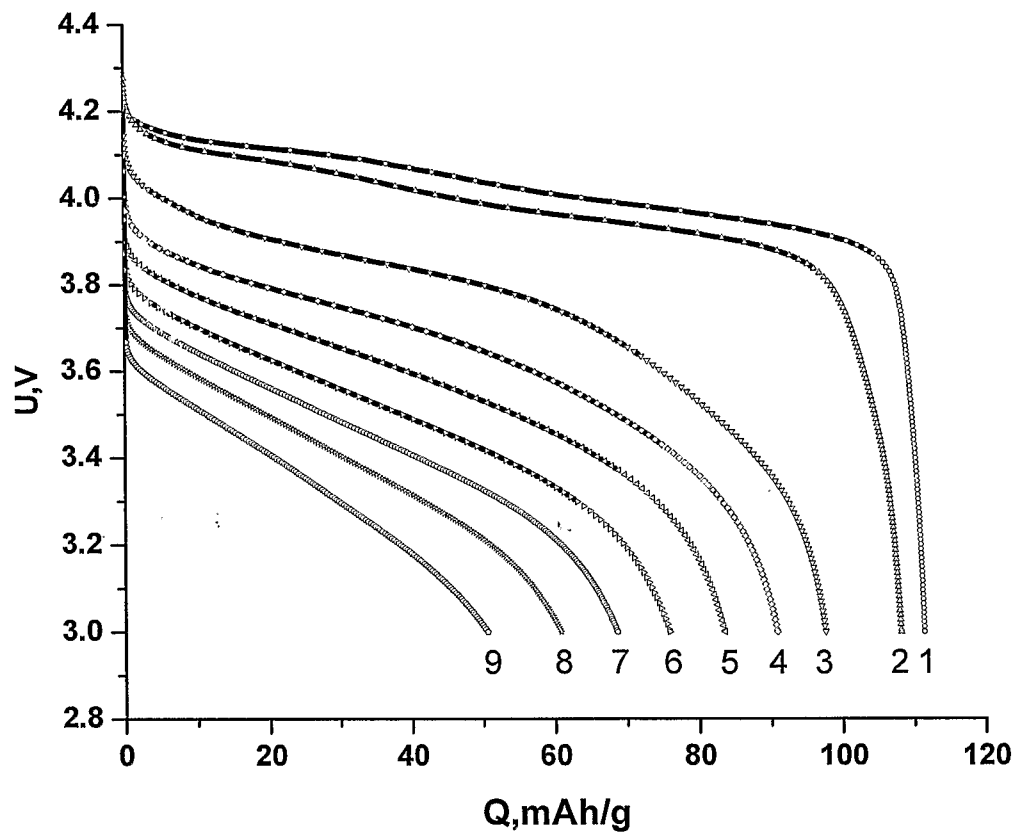


Fig.6

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/UA 2006/000055

## A. CLASSIFICATION OF SUBJECT MATTER

*H01M 4/02 (2006.01)*  
*H01M 4/62 (2006.01)*

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)

H01M 4/02, H01M 4/04, H01M 4/60, H01M 4/62, H01M 6/14, H01M 10/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PAJ, Esp@cenet, USPTO DB, БД Роспатента, EAPO

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RU 2143768 C1 (POLIPLYUS BATTERI KOMPANI, INK.) 27.12.1999, claims 1-16, 34-47	1-34
A	RU 2003111060 A (OOO INZHENERNAYA FIRMA "ORION KHIT") 20.11.2004, abstract	19-34
A	US 5707763 A (DAIKIN INDUSTRIES, LTD) 13.01.1998, col. 6, lines 8-57	1-18
A	EP 1179869 A2 (MATSUSHITA ELECTRIC INDUSTRIAL CO, LTD.) 13.02.2002, claim 9	1-18

<input type="checkbox"/> Further documents are listed in the continuation of Box C.	<input type="checkbox"/> See patent family annex.
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>	
Date of the actual completion of the international search report 28 November 2006 (28.11.2006)	Date of mailing of the international search report 18 January 2007 (18.01.2007)
Name and mailing address of the ISA/RU FIPS Russia, 123995, Moscow, G-59, GSP-5, Berezhkovskaya nab., 30-1 Facsimile No. 243-3337	Authorized officer  E. Kovaleva  Telephone No. 240-2591

H01M 4/04, 4/62

**Electrode for lithium primary and secondary (rechargeable) batteries and the method of its production**

5       The invention relates to electrodes of lithium primary and secondary (rechargeable) batteries and the methods of their production. It can be used in the power sources with non-aqueous electrolytes.

      Lithium and lithium-ion power sources are widely used in the various areas where energy storage and independent power consumption are needed. The  
10       requirements for such power sources are constantly increased. It is necessary to extend the temperature range of battery application to increase their capacities and charge/discharge currents.

      Li-metal or Li-Al alloy is the active anode material of lithium power sources.  $\text{MnO}_2$ ,  $\text{FeS}_2$ ,  $\text{TiS}_2$ ,  $\text{MoO}_3$ ,  $\text{CF}_x$  and others are widely used as a cathode material. As a  
15       rule, such batteries are used as primary ones. Graphite intercalated by lithium is the active anode material of lithium-ion power sources; and the compound oxides like  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ , spinel form  $\text{LiMn}_2\text{O}_4$  and others are usually used as active cathode materials. Besides the active materials, electrode compositions contain  
20       conductive additives providing electron conductivity and the binder responsible for coating mechanical durability, for its flexibility and adhesion to a current collector.

      Electrode production technology for lithium and lithium-ion sources can be divided into two groups:

1. Application of the lamination technology of rubber-like mass on a current collector.
- 25       2. The coating technology of cathode composition slurry on a moving current collector in the form of foil or grid followed by the stages of drying and calendaring (compacting).