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54 ELECTROCHEMICAL GENERATOR WITH NON-AQUEOUS ELECTROLYTE

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FR A 2 168 866
FR A 2 277 898
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CHEMICAL ABSTRACTS, vol.89,
No.6, 7 August 1978, page 144,
abridgement 46261B Columbus,
Ohio, US J.O.BESENHARD:
"Chalcogenides of arsenic, anti-
mony and bismuth as positive
electrodes in lithium batteries"

COLLECTION CZECHOSLOV CHEM.COMMUN.,
vol. 33 No.3 1968 M.FRUMAR et al.:
"Synthese und elnige physikalische
Eigenschaften des Blei (II) -
Tetrathiodiantimonats (III), pages
683-690

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Electrochemical generator with non-aqueous electrolyte.

The present invention relates to an electrochemical generator (i.e. an electric cell) with a non-aqueous electrolyte, said electric cell being of the primary or of the secondary type and thus being optionally rechargeable and having a negative electrode including at least one alkali metal, and a positive electrode including an active compound in a layer configuration.

A number of investigations have been performed over the past few years on high energy density electric cells using positive electrodes that contain insertion compounds in which the negative active material is inserted during charging. The said negative active material is constituted by an alkali metal, in particular lithium. Such electric cells are described in particular in document FR-A-2 381 395.

Further, bismuth oxide Bi_2O_3 has also been recommended for use as a positive active material, as described in "Journal of the Electrochemical Society 1978, vol. 125 No. 1, p. 14" as has the use of compounds such as $\text{Pb}_2\text{Bi}_2\text{O}_5$ and PbBi_2O_4 as published in "The proceedings of the 11th International Power Sources Symposium No. 7, Brighton 1978", at page 623, published by Academic Press. Proposals have also been made to use Sb_2S_3 or Sb_2Se_3 (see document FR-A 2168866) and Bi_2S_3 or Bi_2Se_3 for lithium cells (see Chem. Abstr. vol. 89, 1978, p. 144 abstract No. 46216b).

However, such compounds which allow high energy density to be obtained are not suitable for producing rechargeable, or secondary electric cells.

The present invention remedies such drawbacks and produces a high energy density electric cell which is capable of undergoing a large number of charge/discharge cycles. Further, such an electric cell is not very expensive to produce.

The invention provides a primary or secondary electric cell which includes: a positive electrode whose active material is suitable for insertion into the negative active material and a negative electrode whose active material includes at least one alkali metal in contact with a non-aqueous electrolyte; characterized by the fact that the said positive electrode includes an active compound or solid solution whose general formula is

M_xX, R_yX_3 where:

M is an element chosen from lead and tin;
R is an element chosen from bismuth and antimony; and
X is an element chosen from sulphur and selenium, with x and y being greater than zero and having maximum values of $x = 1$ and $y = 2$.

Examples of the invention are described below with reference to the accompanying drawings and graphs in which:

Figure 1 is a cross-section through a button-type electric cell in accordance with the invention; and

Figures 2 and 3 are graphs which illustrate the electrical performance of electric cells in accordance with the invention.

An electric cell in accordance with the invention includes the following main components:

POSITIVE ELECTRODE

The active material of the positive electrode includes a compound whose general formula is the following:

M_xX, R_yX_3 .

In the above formula:

M represents an element chosen from lead and tin;
R represents an element chosen from bismuth and antimony;
X is an element chosen from sulphur and selenium; and
 x and y are greater than zero and have maximum values of $x = 1$ and $y = 2$.

By way of example, such compounds include PbBi_2S_4 and SnBi_2S_4 . 16

Such an active material can be used alone if it is sufficiently conductive or, if not, it should be used in association with an electronically conductive support such as carbon, copper, nickel, zinc, silver or the like, together with a bonding agent such as polytetrafluoroethylene which can be used to consolidate the structure.

Said active material is deposited on the support or forms a porous texture by being compressed onto a collector.

Said active material can also be mixed with a conductive powder such as carbon, graphite or a mixture thereof.

Generally, the structure of the positive active material is in layers based on the Schoenflies space group. These layers are interconnected by van der Waals forces. The individual layers form at least one sheet which contains metal atoms and is disposed between sheets of non-metal atoms. Insertion and de-insertion reactions take place between the layers and are made possible by the weakness of said van der Waals forces.

The speed of insertion and de-insertion (which corresponds to charging and discharging the electric cell) is considered to be an important factor for determining possibly appreciable concentration polarizations which may occur at the electrode during the electrochemical processes in presence of the compounds used as positive active materials.

The table hereinbelow gives a few parameters of an active compound in accordance with the invention, i.e. PbBi_2S_4 , compared with already known compounds :

	d	m(g)	F/mole (primary)	Ah/kg	E(volts)	Wh/Kg	Wh/dm ³
Bi_2S_3	7.39	513.96	6	313.5	1.7	532.9	3938
PbBi_2S_4	7.3	753.15	8	284.7	1.6	455.5	3325
PbS	7.5	239.25	2	224	1.5	336	2520

In the above table :

d is density ;

$m(g)$ is molar mass;

F/mole (primary) is the number of Faradays;

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Ah/kg is the theoretical specific capacity;

$E/(\text{volts})$ is the initial voltage with respect to lithium;

Wh/kg is the energy density per unit weight;

Wh/dm^3 is the energy density per unit volume.

10 NEGATIVE ELECTRODE

The negative electrode includes at least one alkali metal.

Said metal can be used alone, deposited on an electronically conductive support made, for example, of copper, steel, nickel, carbon or the like.

15 An alloy of said alkali metal may also be used, providing the alloy is electronically conductive and capable of electrochemically releasing ions which react with the positive active material.

By way of example, the negative electrode may be made
20 of an alloy of lithium and aluminium thereby reducing the rate of dendrite formation and growth to a minimum during charging.

ELECTROLYTE

The electrolyte includes firstly a solvent which is chemically inert relative to the electrodes while allowing ions to
25 migrate towards the electrodes, and secondly an ionisable salt dissolved in said solvent. Such a salt has the following general formula:

$L Z$, where

L is a cation chosen from ions of alkali metals
30 and Z is at least one anion chosen from halides, sulphates, nitrates, phosphofluorides, thiocyanates, perchlorates, hexafluorophosphates and hydrocarbons.

Particularly advantageous salts are lithium perchlorate, lithium hexafluorophosphate and lithium thiocyanate, ammonium iodide and ammonium hexafluoroarsenide, hydrochloric acid, potassium thiocyanate or chloride and magnesium chloride.

5 The solvents used are polar organic compounds such as esters, ethers, organic carbonates, organic lactones, amides or sulfoxides.

Such solvents may be used either alone or in a mixture. The concentration of ionisable salt in the solvent is determined by its conductivity and by its chemical reactivity. In
10 mined by its conductivity and by its chemical reactivity. In general, concentrations of between 0.1 and 5 moles per litre are used.

It will also be noted that solid electrolytes such as beta alumina may be used. Likewise, molten alkaline halides
15 are also suitable.

A practical embodiment of a button type electric cell in accordance with the invention will now be described with reference to Figure 1.

Figure 1 illustrates a button type electric cell with
20 a negative active material 1, a positive active material 2 and a porous separator 3 which is impregnated with electrolyte. The positive collector 4 forms a cup and the negative collector 5 forms a cap.

The positive active material 2 is compressed in the cup 4
25 under a load of 800 kg and under a dry nitrogen atmosphere.

The negative active material 1 is compressed in the cap 5 under an argon atmosphere. The separator 3 is of the cellulose type and is impregnated with electrolyte. After crimping, the electric cell thus constituted is discharged
30 at 500 μ A then recharged at the same current intensity.

A few examples of electric cells will now be given.

1st EXAMPLE

The compound PbBi_2S_4 was prepared by heating a mixture of PbS and Bi_2S_3 at about 700°C for 2 weeks. A

1.5M solution of butyl-lithium in hexane was made to react with said mixture and the result analysed to verify that lithium had been inserted in said compound. Then, 500 mg of the substance was compressed in the cup 4 to form a button type electric cell such as described hereinabove, but assembled in the discharged state. The capacity of said electric cell after charging was 100 rechargeable milliamp-hours.

2nd EXAMPLE

The compound PbBi_2S_4 was prepared by heating a mixture of PbS and Bi_2S_3 to about 700°C for 1 week. The compound was then mixed with 15% by weight of a mixture of 70% graphite and 30% acetylene black. An electric cell such as described with reference to Figure 1 was then made with said compound, using a bimolar solution of LiClO_4 in dioxolane as the electrolyte. The equivalent capacity of such an electric cell was 90 mAh for a cathode with a surface of 1.2 cm^2 and 1.6 mm thick.

Figure 2 shows the discharge curve of said electric cell at an intensity of 200 μA (curve A) and 500 μA (curve B). The voltage E in volts as a function of the number of F/mole is plotted along the X-axis.

Figure 3 shows the cycle curve of such an electric cell, namely, the voltage E in volts as a function of the number of F/mole.

Such an electric cell has an energy-to-weight ratio of about 500 Wh/kg which is reversible.

The invention may advantageously be used in electric cells for watches or pacemakers, which cells are optionally rechargeable.