

Description

Title: Battery with improved electrolyte and improved electrodes

Technical field

5 [1] This disclosure relates to the field of batteries, whether in the form of a primary cell, fuel cell, or rechargeable battery.

Prior art

10 [2] Document WO-2018/060656 presented a particularly promising material for forming the electrolyte of a supercapacitor, this material being a crystalline solid with a $A_2B_2O_5$ structure, where A can be an alkali metal and B can be titanium. The performance of this material led the inventors named in that document to consider an application in batteries, which is mentioned in that document (specifically on page 12, lines 15-30, with reference to FIG. 8 of the document).

15 [3] However, the aim of the embodiment presented was to consider the entire electrolyte, in contact with the two electrodes, as a "pseudo-battery" in the sense that the electrical discharge ("rapid, on the order of a few minutes, then relatively slow thereafter, on the order of a few hours") could not be perfectly controlled, and jackets of piezoelectric elements PZ1, PZ2, PZ3, etc., remained necessary to mechanically constrain or relax the material in order to block or release the electrical charges.

[4] Typically, the materials provided for the electrodes were carbon, or a metal such as copper, silver, gold, or platinum, simply for collecting electrons.

Summary

20 [5] The present disclosure improves the situation.

[6] It proposes retaining a similar material for the electrolyte but improving the materials chosen for the electrodes, in order to better manage the charging/discharging of the device and increase the energy density that can be stored, by bringing into play a controlled chemical interaction between the material of an electrode and ions capable of moving within the material of the electrolyte.

25 [7] The aim is therefore a battery device comprising:

- electrodes comprising an anode and a cathode, and
- an electrolyte, between the electrodes, comprising a crystalline material having the composition $M_2B_2O_5 \cdot x(HOH) \cdot y(NOH)$, where M and N are alkali metals or hydrogen or mixtures of alkali metals or hydrogen, B is titanium, O and H respectively denote the elements oxygen and hydrogen, and x and y are between 0 and 4 and indicate the presence of H^+ , OH^- , N^+ ions capable of migrating in the crystalline material,

30 a device wherein at least one of the ions among H^+ , OH^- , N^+ and M^+ is mobile so as to migrate in the crystalline material towards at least one of the electrodes, and said at least one of the electrodes is made of a material suitable for carrying out a chemical interaction with at least one of said H^+ , OH^- , N^+ and M^+ ions.

35

[8] As used above, "chemical interaction" is understood to mean an intercalation of the ion migrating towards the electrode, or a chemical reaction between this ion and the material of the electrode. Thus, the aforementioned chemical interaction comprises one among:

- an intercalation of said at least one of the H^+ , OH^- , N^+ and M^+ ions into said at least one of the electrodes, and
- a chemical (typically electrochemical) reaction of said at least one of the OH^- , N^+ and M^+ ions with the material of said at least one of the electrodes.

[9] In the device described in the aforementioned document WO-2018/060656, the migrating ion species accumulated in the vicinity of the electrodes, thus generating a charge accumulation that allowed for the collection, storage, and release of electrical energy, but in a purely electrostatic form. Therefore, the amount of energy stored in the device constructed according to the teachings of document WO-2018/060656 remained limited by the electrostatic nature of the storage.

[10] Here, the chemical interaction with the electrode allows controlling the charging/discharging more efficiently and allows increasing the energy storage density.

[11] The prior art cited above does not envisage that the electrodes could be composed of materials that are specifically ion-intercalating or that give rise to electrochemical reactions with the migrating ionic species. Thus, it did not consider that migrating species in the electrolyte (in particular OH^- , H^+ , O^{2-}) could chemically react with the component materials of the electrodes or could intercalate into them.

[12] By means of the present implementation, the battery device of the present description is accorded the microscopic faradaic mechanisms usually present in rechargeable battery, primary cell, or fuel cell designs, allowing fine control over the charging or discharging of such a device. More specifically, the energy density is improved here by adding mechanisms of intercalation, ion absorption, or electrochemical reactions at the surface of the electrodes used, as well as by broadening the choice of migrating species in the electrolyte. The choice of component materials of the electrodes was then made to be adapted to the migrating species in the electrolyte, in order to create a rechargeable battery device, a primary cell, or a fuel cell.

[13] The solid electrolyte may be in the form of single crystals, ceramics, pressed powders, membranes, or thin films. Its general formula is $M_2Ti_2O_{5.x}(H_2O)$ or $M_2Ti_2O_{5.x}(NOH)$, where M is one or more alkali metals (and/or hydrogen); N is one or more alkali metals (and/or hydrogen); and x can be equal to 0. For brevity, this electrolyte material is denoted hereinafter as "MTO".

[14] The electrode materials may be in solid, liquid, or gaseous form, as described below.

[15] In a typical embodiment, the battery device may comprise an anode made of a material comprising a metal hydride, for a chemical reaction with migrating OH^- ions.

[16] Alternatively, the anode may be made of a material comprising at least one element among zinc, iron, and aluminum (or also sodium or lithium), for a chemical reaction with migrating OH^- ions.

[17] In yet another alternative, the anode may be made of a material comprising dihydrogen, for a chemical reaction with migrating OH^- ions.

[18] As for the cathode, it may comprise a mixture of oxygen and water.

[19] For example, the cathode may be made of a material comprising nickel oxide hydroxide (NiOOH).

5 **[20]** Alternatively, the cathode may comprise silver oxide (AgO).

[21] In such an embodiment, the cathode may initially be made of a material comprising silver (Ag), and silver oxide (AgO) may then form at an interface with the electrolyte, typically when the cathode is exposed to ambient air (in particular to provide the aforementioned mixture of oxygen and water), in accordance with the embodiment described further below with reference to FIG. 6.

10 **[22]** In one particular embodiment, the device may make use of migrating H^+ and OH^- ions in the electrolyte, and comprise:

- a cathode made of a material that comprises silver and intercalates OH^- ions, and
- an anode made of a material having a $\text{M}_2\text{B}_3\text{O}_7$ type structure, where M is an alkali metal or mixtures of alkali metals, B is titanium, and O is oxygen, for intercalating H^+ ions.

15 **[23]** Alternatively, the device may comprise:

- a cathode made of a material that comprises silver and intercalates OH^- ions, and
- an anode made of a material that comprises graphite and intercalates H^+ ions.

[24] In yet another alternative, in a battery device where $x=0$ and M and/or N comprise at least one element selected among sodium and lithium, the device may comprise:

- 20 - an anode made of a material comprising an element among sodium and lithium (for example in metal form), respectively, and
- a cathode allowing the incorporation of lithium and/or sodium ions.

[25] For example, such a cathode may be made of a material selected among graphite and an $\text{M}'_2\text{B}_3\text{O}_7$ type structure where M' is an alkali metal or mixtures of alkali metals, B is titanium, and O is oxygen, for intercalating the migrating M^+ and/or N^+ ions.

25

[26] In one or more of the embodiments described above, the anode material and the electrolyte material may be successively deposited in the form of respective thin layers (this embodiment typically being easy to implement when the anode is made of a material having the $\text{M}_2\text{B}_3\text{O}_7$ structure).

[27] In one or more of the embodiments described above, at least the anode is encapsulated in a resin-type material or equivalent, so as to be sealed against air and moisture.

30

[28] In addition, the entire device (anode, electrolyte, and cathode) may be encapsulated in a resin-type material or equivalent, so as to be sealed against air and moisture.

[29] When the electrode materials are in solid form, or when one of the electrodes simply consists of ambient air (for example, the cathode in some of the embodiments described above), it is then possible to create a so-called "all-solid-state" battery.

35

[30] More generally, the choice of materials for the anode and cathode can be made as follows: the value of the standard redox potential of the couple at the anode (E_{0a}) must be lower than the value of the standard redox potential of the couple at the cathode (E_{0c}). Depending on the choice of electrodes, it is then possible to classify the embodiments by the nature of the migrating species within the electrolyte.

[31] In one embodiment which makes use of the **migration of OH^- ions**, the material of the electrolyte will create high-mobility hydroxide ions (OH^-) through spontaneous hydration.

[32] In this case, in order to fabricate a rechargeable battery for example, it may be advantageous to choose:

- a metal hydride (such as MgH_2 for example) as the anode material, and
- nickel oxide hydroxide (NiOOH) as the cathode material.

[33] To fabricate another type of battery:

- a metal such as zinc (or iron or aluminum, or a mixture) may be used at the anode, and
- silver oxide (Ag_2O), or a mixture of $\text{O}_2 - \text{H}_2\text{O}$, may be used as the cathode material.

[34] To fabricate a fuel cell:

- dihydrogen may be used as the anode material, and
- a mixture of $\text{O}_2 - \text{H}_2\text{O}$ may be used as the cathode material.

[35] Furthermore, the generation of a **combined migration of both hydroxide ions OH^- and hydrogen ions H^+** is possible and may advantageously be used.

[36] Indeed, by including oxygen vacancies in the structure of the electrolyte material, it is possible to cause water vapor to dissociate into H^+ and OH^- . These two species can then migrate independently of each other, so that the following electrode choices are possible.

[37] A silver (Ag) cathode, for example, can typically react electrochemically with OH^- ions. At the anode, the intercalation or electrochemical reaction of H^+ ions can be ensured by graphite-based compounds, or by a solid material similar to that of the electrolyte, such as $\text{A}_2\text{Ti}_3\text{O}_7$ where A can be an element among sodium Na, potassium K, or rubidium Rb, or any type of material capable of intercalating H^+ .

[38] This embodiment has the advantage of causing to grow, on a suitable substrate, a first electrode (anode), for example $\text{K}_2\text{Ti}_3\text{O}_7$, having the property of intercalating protons, then the solid electrolyte, for example $\text{K}_2\text{Ti}_2\text{O}_5$, which is easy to grow on the anode given the similarities of the crystalline phases (and the lattice matching, for example), and finally a layer of Ag or graphite, which does not cause any deposition or interface issues on the solid electrolyte, to form the cathode.

[39] This design makes it possible to solve the problem frequently encountered in the field of all-solid-state batteries, which is the quality of the electrode/electrolyte interface when the two materials have crystallographic structures that are too different.

[40] The migration of other species present in the electrolyte, such as Na^+ , may also be utilized.

[41] By adding sodium to the chemical formula of MTO, we obtain for example the material $A_2B_2O_5(NaOH)$ or $A_{2-x}Na_xB_2O_5$, which possess highly mobile Na^+ ions in their structure.

[42] Thus, for a rechargeable battery:

- the anode material may comprise metallic sodium, and
- 5 - the cathode material may comprise a graphite-based compound, or $A_2Ti_3O_7$ where A can be [Na, K, Rb] or other types of materials capable of intercalating Na^+ .

[43] Depending on the migrating ion species, other embodiments are of course possible. For example, in order to utilize the migration of lithium ions Li^+ , it is possible to obtain the material $A_2B_2O_5(LiOH)$ or $A_{2-x}Li_xB_2O_5$ by adding lithium to the chemical formula of the electrolyte material,
10 each of these possessing highly mobile Li^+ ions in its structure.

[44] For a rechargeable battery, it is possible in the same manner to use:

- metallic lithium as the anode material, and
- a graphite-based compound as the cathode material, or $A_2Ti_3O_7$ where A can be [Na, K, Rb] or other types of materials capable of intercalating Li^+ .

15

Brief description of drawings

[45] Other features, details and advantages will become apparent upon reading the detailed description below and examining the accompanying drawings, in which:

Fig. 1

20 [46] [Fig. 1] shows the crystallographic structure of an MTO electrolyte material according to one embodiment.

Fig. 2

[47] [Fig. 2] shows the incorporation of a water molecule into such a material.

Fig. 3

25 [48] [Fig. 3] shows the gain in thermodynamic energy as a function of the hydration percentage of sites in the material's structure, which demonstrates that the more water molecules there are, the more stable they are.

Fig. 4

30 [49] [Fig. 4] shows a comparison between electrode arrangements in a "parallel" configuration of the material (figure on the left) and a "transverse" configuration (figure on the right).

Fig. 5

[50] [Fig. 5] shows a battery type of device, in which the electrolyte is based on the aforementioned MTO material, according to one embodiment.

Fig. 6

[51] [Fig. 6] shows an embodiment of such a device in which the electrodes are based on zinc and silver (which oxidize at the interface with the electrolyte).

Fig. 7

[52] [Fig. 7] shows a device from the prior art within the meaning of document WO-2018/060656,
5 comprising identical electrodes, made of gold in this example embodiment.

Fig. 8

[53] [Fig. 8] shows a comparison of the electrical performance of the devices of FIGS. 6 and 7.

Description of embodiments

10 [54] The use of materials in the $M_2Ti_2O_5$ family (or "MTO" hereinafter) where $M = [Li, Na, K, Rb, H...]$ or a combination of these elements (having a structure similar to that described in document WO-2018/060656, and particularly $Rb_2Ti_2O_5$ and $K_2Ti_2O_5$, as a solid electrolyte for all-solid-state energy storage devices, is described below. More generally, the family of compounds having the formula $M_2Ti_xO_{2x+1}$, where x is greater than or equal to 2 and $M = [Li, Na, K, Rb]$, is considered here as
15 offering such properties.

[55] On a microscopic level, the MTO material is characterized by a lamellar structure with ionic bonds between the $Ti_2O_5^{2-}$ and Rb_2^{2+} planes. The material is lamellar and cleavable along the planes located between the Rb atoms.

[56] The non-hydrated or weakly hydrated material is capable of conducting ion species such as H^+ ,
20 K^+ , Rb^+ , Na^+ , Li^+ depending on the chemical formula of the compound, which may combine several cations in its composition, for example such as $(Na,K)_2Ti_2O_5$.

[57] In addition, there are the possibilities offered by the hydrated MTO material, which is indeed a highly hygroscopic material, especially in its powdered form, and has the property of spontaneously adsorbing water vapor. Ab initio simulations using density functional theory have shown that this
25 molecular water preferentially organizes into channels along the crystallographic direction corresponding to the b-axis. The water is incorporated into the structure by creating hydrogen bonds with the apical oxygen atoms of the perovskite structure, as shown in FIGS. 1 and 2, corresponding to the most probable configuration according to the simulations.

[58] The addition of a water molecule in this configuration thus represents an energy variation at $T=0$
30 of -0.5 eV (PBEsol method) or -0.25 (HSE method).

[59] FIG. 1 illustrates insertions of a water molecule creating very strong hydrogen bonds within the molecular structure of the material containing Rb atoms (one atom is shown in the upper right of FIG. 1), oxygen atoms O (one atom is shown in the center of FIG. 1), hydrogen atoms H (two of which are shown to the right of the central oxygen atom in FIG. 1), and titanium atoms Ti (in the lower right of
35 FIG. 1). This structure, having the general formula MTO, is more specifically referred to here as "RTO," as the M atom in the general MTO formula is an Rb atom. FIG. 1 thus illustrates the

incorporation of a water molecule into the RTO (or more generally, MTO) structure, creating two very short hydrogen bonds with the apical oxygen atoms of the structure. Furthermore, the simulations show that the energy gained by adding a water molecule to the structure increases with the number of water molecules in the same chain, as illustrated in FIGS. 2 and 3, discussed later, which favors
5 the creation of chains of water molecules that can lead, in particular, to a Grotthus-type proton conduction mechanism in water.

[60] More generally, the entities migrating within the intercalated water may be one of the following species: OH^- and/or M^+ where $\text{M} = [\text{H}, \text{Li}, \text{Na}, \text{K}, \text{Rb}]$ and/or O^{2-} .

[61] The hydrophilic nature of MTO favors the absorption of water.

10 **[62]** As illustrated in FIG. 2 for the MTO material where $\text{M}=\text{Rb}$, the water molecules are arranged in the MO planes (O1 designating the apical oxygens of the structure). The molecules organize themselves into chains in the ab planes (forming channels), preferentially oriented with the ab planes parallel to the deposition substrate (so-called "parallel" orientation), or with the ac planes parallel to the substrate plane (so-called "transverse" orientation), as respectively illustrated on the left and right
15 of FIG. 4, where the lines represent the ab planes of the lamellar compound.

[63] Characteristically, FIG. 3 shows the thermodynamic energy gain at temperature $T=0$ as a function of the hydration percentage of the sites in the structure.

[64] The MTO materials mentioned above may then be used as a solid electrolyte (therefore an ionic conductor), for example in micrometric or nanometric, planar, and crystalline configurations where
20 the electrolyte consists of a thin layer of MTO deposited on a substrate S, such as an integrated circuit, using deposition technologies such as PVD (Physical Vapor Deposition) or CVD (Chemical Vapor Deposition), for example including sputtering, pulsed laser deposition, atomic layer deposition, molecular-beam epitaxy, reactive plasma deposition, or others. The MTO layer is preferably monocrystalline and/or microcrystalline in regions.

25 **[65]** The electrolyte may alternatively consist of thin layers of MTO obtained by exfoliating sheets from a millimeter-sized crystal. This sheet, of nanometric thickness (up to a few hundred nm), can then be transferred onto an integrated circuit where it naturally adopts a parallel orientation.

[66] Referring to FIG. 5, in these two cases electrodes A and B are deposited (using vacuum deposition techniques) either on each side of the thin MTO layer in the case of parallel orientation,
30 or above and below the layer in the case of transverse orientation, so that ionic conduction preferentially occurs in the ab crystallographic plane (double arrow in FIG. 5).

[67] A step of controlled hydration of the thin layer may be implemented before or after the electrode deposition and before the possible encapsulation step. Finally, an encapsulant E (for example of silicone, epoxy resin, or a conformal coating, a polyurethane compound, or others) may be deposited
35 over the whole in order to "freeze" a chosen hydration level.

[68] Alternatively, the electrolyte may consist of MTO in bulk and crystalline form and may thus be composed of one or more oriented single crystals (stacked perpendicularly to the ab crystallographic

planes) and aggregated together in a polymer matrix (epoxy resin, silicone, or polyurethane compound). A step of controlled hydration of the crystals may be implemented before encapsulation in the matrix.

5 **[69]** Two electrodes A and B are deposited on either side of the encapsulated single crystals, so that ionic conduction occurs in the crystallographic ab plane, as illustrated by the double arrow in FIG. 5.

10 **[70]** Alternatively, the creation of a bulk device may use MTO cast in an encapsulant, the MTO material then having a crystalline form in membranes, ceramics, or others. For example, the electrolyte may be composed of MTO crystals mixed with at least one organic or aqueous solvent (for example 2-methylpyrrolidinone, water, ethanol, or others). A fluorinated compound dispersed in
15 the solvent may also be added (for example polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), or others) to increase the mechanical stability of the device. The size of the MTO crystals may vary from several mm to a few hundred nm. The volume percentage of MTO may be between 60% and 98% depending on the solvent chosen. A step of controlled hydration may be considered before mixing the powder with the solvent used. Depending on the solvent chosen for the fabrication
20 of the device, the mixing process may extend over several tens of hours and include annealing steps at temperatures up to 150°C. Depending on the intended application, the mixture may then be deposited on a non-adhesive substrate (such as a Teflon film) or on an electron-collecting electrode, which typically can interact with ions (for example, zinc, gold, silicon, sodium, and/or lithium (these being metallic), or silver oxide AgO, or others), as detailed below.

25 **[71]** For this purpose, deposition methods may include, for example, inkjet printing, spin coating, or doctor blade coating. A drying step may then take several tens of hours at a temperature that can reach up to 150°C. After evaporation of the solvent, a film having a thickness ranging from a few micrometers to several millimeters is obtained. Subsequently, if the film has been deposited on one electrode, the other electrode can then be deposited on top of the film. If the film has been deposited
30 on a non-adhesive substrate, then two electrodes are deposited, one on either side of the film. The film and its electrodes may then be encapsulated, the encapsulation providing good mechanical strength, as well as sealing against air and moisture.

35 **[72]** In one embodiment, the electrolyte consists of an MTO ceramic compacted at 10 tons for 2 hours at 150°C and sintered at 800°C for 10 hours. Alternatively, a mass fraction of 2 to 5% PTFE (polytetrafluoroethylene) may be added to the MTO powder to make the ceramic stronger without the sintering step. The electrodes are then deposited using a mixture of polymer-solvent-material (8% PVDF: polyvinylidene fluoride – 84% solvent: 1-methyl-2-pyrrolidinone – 8% material) and then dried for several hours at a temperature between 25 and 80°C. It is also possible to place the component powders for the electrodes A and B in the press system in order to fabricate the
40 electrodes simultaneously with the ceramic.

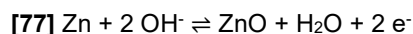
45 **[73]** The choice of possible electrodes for the different geometries of the energy storage devices described above must be made according to the migrating species in the electrolyte and the type of device chosen. In the configurations considered, the MTO material is used as a solid electrolyte

placed between an anode composed of a material having a standard redox potential E_{0a} , and a cathode composed of a material having a standard redox potential E_{0c} , where $E_{0a} < E_{0c}$.

[74] Various examples for fabricating the anode and cathode are presented below. Asymmetry may be created between the cathode and the anode by encapsulating one of the electrodes and leaving the other electrode "exposed to the air," which creates the possibility of supplying oxygen or water vapor to the device from only one side and results in supercapacitor effects.

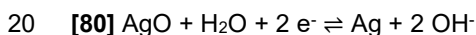
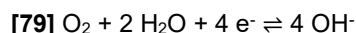
[75] The conduction of OH^- ions can be utilized in a (non-rechargeable) "Metal-Air" battery configuration. Materials that may be used as the anode include, for example, metallic zinc (Zn), metallic iron (Fe), metallic aluminum (Al), or a metal alloy composed of at least two of the materials mentioned above.

[76] One example of a redox reaction occurring at the anode is then:



[78] Materials that may be used as a cathode include, for example:

- silver oxide: AgO , or
- a mixture of $\text{N}_2/\text{O}_2/\text{H}_2\text{O}$ gases: ambient air may typically be used (with a humidity level greater than 5% and less than 95%, an oxygen (O_2) level greater than 15% and less than 25%, and a nitrogen (N_2) level greater than 75% and less than 85%), such that some examples of redox reactions occurring at the cathode can be:



[81] Other embodiments may utilize a NiMH (nickel-metal hydride) battery configuration. Materials that may be used as the anode include, for example:

- AB₅ type alloys, for example based on rare earth elements (La, Ce, Nd, Pr), such as LaNi_5 and its derivatives, or alloys comprising elements among Ni, Co, Mn, Al, Mg, Zr, C, Co, Fe, Ti.

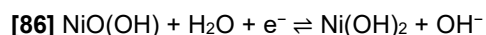
[82] One example of a redox reaction occurring at the anode can then be:

[83] $\text{OH}^- + \text{MH} \rightleftharpoons \text{H}_2\text{O} + \text{M} + \text{e}^-$, where M is a metallic element originally present in the form of a metal hydride MH (such as TiH_2 or MgH_2).

[84] Materials that may be used as the cathode include, for example:

- nickel oxide hydroxide (NiOOH), or
- a mixture of metal oxides (Ni-Co-Mg), or
- a Ni-Co-Al alloy.

[85] One example of a redox reaction occurring at the cathode can be:



[87] To make use of proton conduction, the materials that may be used as the anode (negative electrode) may include, for example:

- WO_3 , MoO_3 , TiO_2 , $\text{H}_2\text{Ti}_3\text{O}_7$, $\text{H}_2\text{Ti}_6\text{O}_{13}$, $\text{H}_2\text{Ti}_{12}\text{O}_{25}$ and other derivatives by substitution.

[88] Materials that may be used as the cathode (positive electrode) may be, for example:

- 5 - a metal oxide: RuO_2 , MnO_2 , V_2O_5 , PbO_2
- a protonated metal oxide: HCoO_2
- Prussian Blue Analog materials ("PBA"), for example $\text{A}_x\text{M}[\text{Fe}(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$
- or organic materials, for example PEDOT or HATN.

10 **[89]** To make use of Li^+ ion conduction, the materials that may be used as anodes (negative electrode) are, for example:

- graphite carbon derivatives: carbon nanotubes, graphene, mesoporous carbon, etc.
- metallic lithium (Li).

[90] The materials that can be used to form the cathode (positive electrode) may be, for example:

- 15 - lithiated metal oxides, for example LiCoO_2
- lithium intercalation compounds (for example, a mixture of metal oxide (Ni-Co-Mg), a Ni-Co-Al alloy, PBA Prussian Blue structure materials, etc.).

[91] To make use of Na^+ ion conduction, the materials that may be used to form the anode (negative electrode) are, for example:

- 20 - carbon derivatives (graphite, carbon nanotubes, graphene, mesoporous carbon, etc.),
- metallic sodium (Na),
- sodium alloys: sodium-tin (Na-Sn), sodium-lead (Na-Pb), sodium-bismuth (Na-Bi),
- alloys of sodium and intercalated transition metals: Na-Mn-O, Na-Cr-S, Na-Ti-S,
- tin-based compounds: SnO_2 , SnSb ,
- 25 - lamellar titanium oxides of the form $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_4\text{Ti}_5\text{O}_{12}$, $\text{NaTi}_2(\text{PO}_4)_3$ in the family of the electrolyte's material and depositable as a solid thin film,
- vanadium or sodium oxides: NaV_2O_5

[92] The materials that may be used at the cathode (positive electrode) are, for example:

- structural materials such as Prussian blue PBA,
- 30 - TiSe_2
- sodium iron phosphate or sodium nickel phosphate: NaFePO_4 , NaNiPO_4
- sodium manganese oxide: NaMnO_2
- sodium nickel manganese oxide: $\text{Na}(\text{NiMn})\text{O}_2$
- sodium cobalt oxide or sodium chromium oxide: NaCoO_2 , NaCrO_2
- 35 - sodium-nickel-cobalt oxide: $\text{Na}(\text{NiCo})\text{O}_2$
- sodium copper oxide: NaCuO_2 .

Comparative examples

[93] FIG. 6 illustrates one example of a device according to the present description, in which:

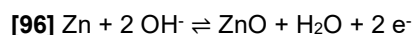
- the electrolyte comprises the MTO material obtained by implementing the method described above, starting with a single crystal or compacted polycrystals in a solvent and then dried, between two electrodes,
- 5 - the anode is made of a material containing zinc (Zn), and encapsulated in a resin E to prevent oxidation, and
- the cathode is initially made of a material containing silver (Ag) but without being encapsulated, so that the silver spontaneously oxidizes with the open air and in contact with the MTO, such that the cathode material is actually silver oxide (AgO), and the rest of the initial Ag material serves to
- 10 efficiently conduct charges to the cathode wire Fc (for example made of silver, similarly to the anode wire Fa).

[94] A device according to the prior art (FIG. 7) was fabricated under strictly the same conditions, in which:

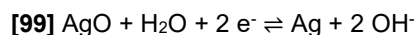
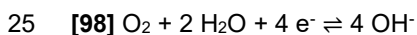
- the electrolyte comprises the MTO material obtained under the same conditions (starting with a
- 15 single crystal or compacted polycrystals in a solvent and then dried, between two electrodes),
- the anode and the cathode are made of a same material, containing gold (an excellent conductor but blocks ions), the anode being encapsulated in a resin E so as to be under the same experimental conditions as the device of FIG. 6, the anode and cathode wires being made of silver, as above.

[95] The embodiment according to FIG. 6 thus utilizes a migration of OH⁻ ions chemically reacting

20 with the Zn anode, according to an equation of the type:



[97] At the AgO cathode, as the ambient air naturally contains water vapor H₂O and oxygen O₂, the chemical equations are of the following type:



[100] FIG. 8 illustrates a comparison of the results and shows cyclic voltammetry curves of the devices in FIGS. 6 and 7.

[101] The device in FIG. 6 shows a significant improvement compared to the prior art device (FIG. 7). In FIG. 8, redox peaks (dotted curve) show the presence of electrochemical reactions that control the charging and discharging of the device. The capacitance is improved by a factor of 10, and the energy density by a factor of 20. Furthermore, the reversibility observed in the electrical discharging/charging of the device makes it an ideal candidate for the fabrication of rechargeable batteries.

35 **[102]** The performance of a device as described herein may be further enhanced with very thin stackable layers of electrodes and electrolyte, allowing for greater densification and improved performance of the device per unit area.

Claims

- [Claim 1]** A battery device, comprising:
- electrodes comprising an anode and a cathode, and
 - an electrolyte, between the electrodes, comprising a crystalline material having the composition
- 5 $M_2B_2O_5 \cdot x(HOH) \cdot y(NOH)$, where M and N are alkali metals or hydrogen or mixtures of alkali metals or hydrogen, B is titanium, O and H respectively denote the elements oxygen and hydrogen, and x and y are between 0 and 4 and indicate the presence of H^+ , OH^- , N^+ ions capable of migrating in the crystalline material,
- a device wherein at least one of the ions among H^+ , OH^- , N^+ and M^+ is mobile so as to migrate within
- 10 the crystalline material towards at least one of the electrodes, and said at least one of the electrodes is made of a material suitable for carrying out a chemical interaction with at least one of said H^+ , OH^- , N^+ and M^+ ions.
- [Claim 2]** Device according to claim 1, comprising an anode made of a material comprising a metal hydride, for a chemical reaction with migrating OH^- ions.
- 15 **[Claim 3]** Device according to claim 1, comprising an anode made of a material comprising at least one element among zinc, iron, and aluminum, for a chemical reaction with migrating OH^- ions.
- [Claim 4]** Device according to claim 1, comprising an anode made of a material comprising dihydrogen, for a chemical reaction with migrating OH^- ions.
- 20 **[Claim 5]** Device according to one of the preceding claims, wherein the cathode comprises a mixture of oxygen and water.
- [Claim 6]** Device according to one of the preceding claims, wherein the cathode is made of a material comprising nickel oxide hydroxide ($NiOOH$).
- [Claim 7]** Device according to one of claims 1 to 5, wherein the cathode comprises silver
- 25 oxide (AgO).
- [Claim 8]** Device according to claim 7, wherein the cathode is made of a material comprising silver (Ag), and wherein silver oxide (AgO) is formed at an interface with the electrolyte.
- [Claim 9]** Device according to one of claims 5 to 8, wherein the cathode is exposed to ambient air.
- 30 **[Claim 10]** Device according to claim 1, wherein the ions migrating in the electrolyte are H^+ and OH^- , the device comprising:
- a cathode made of a material that comprises silver and intercalates OH^- ions, and
 - an anode made of a material that comprises a $M_2B_3O_7$ type structure, where M is an alkali metal or mixtures of alkali metals, B is titanium, and O is oxygen, for intercalating H^+ ions.
- 35 **[Claim 11]** Device according to claim 1, wherein the ions migrating in the electrolyte are H^+ and OH^- , the device comprising:
- a cathode made of a material that comprises silver and intercalates OH^- ions, and

- an anode made of a material that comprises graphite and intercalates H^+ ions.

[Claim 12] Device according to claim 1, wherein $x=0$ and M and/or N comprise at least one element selected among sodium and lithium, the device comprising:

- an anode made of a material comprising an element among sodium and lithium, respectively, and

5 - a cathode allowing the incorporation of lithium and/or sodium ions.

[Claim 13] Device according to claim 12, wherein the cathode is made of a material selected among graphite and an $M'_2B_3O_7$ type structure where M' is an alkali metal or mixtures of alkali metals, B is titanium, and O is oxygen, for intercalating the migrating M^+ and/or N^+ ions.

[Claim 14] Device according to one of the preceding claims, wherein the anode material and
10 the electrolyte material are successively deposited in the form of respective thin layers.

[Claim 15] Device according to one of the preceding claims, wherein at least the anode is encapsulated in a resin-type material so as to be sealed against air and moisture.

[Claim 16] Device according to one of the preceding claims, wherein the entire device is encapsulated in a resin-type material so as to be sealed against air and moisture.