reduction, i.e. the lithium hydroxide formed in the compartment of the positive electrode during discharge of the battery.

So that the battery has the highest possible specific capacity, it is desirable to strongly limit the volume of aqueous electrolyte and to use the most concentrated solutions possible.

However, the inventors have shown that the presence of lithium ions in the aqueous electrolyte has a blocking effect on oxygen release during recharge of the battery. This blocking effect had already been observed in the past, but in a very different context: lithium had been used in the aqueous electrolyte of nickel batteries as an additive to prevent oxygen release when this reaction competes with the reaction of nickel electrodes (Constantin et al, "The influence of some additives on the electrochemical behaviour of sintered nickel electrodes in alkaline electrolyte", *Journal of Power Sources*, 74 (1998), 188-197). On the contrary, in the context of the present invention, and in particular in the context of lithium-air batteries, the blocking effect of the lithium ions is detrimental because it necessitates the application of an additional overvoltage across the terminals of the battery during recharge. The energy efficiency of the battery, i.e. the ratio (electrical energy flowing out of the battery when discharging / electrical energy consumed to recharge the battery), is thus decreased.

To improve the energy efficiency of the battery, it is therefore desirable to decrease the concentration of lithium ions in the aqueous electrolyte.

From these observations it transpires that the improvement in the specific capacity of the battery and in the energy efficiency of the battery seem to be two irreconcilable goals. In spite of this, the inventors have succeeded in improving the energy efficiency of a lithium-air type battery using an aqueous electrolyte without decreasing its specific capacity.

According to a first aspect~~The subject~~ of the present invention, a rechargeable lithium-air battery is described, the rechargeable ~~is a~~ lithium-air battery comprising:

- a negative-electrode compartment containing lithium metal;

- an aqueous solution containing lithium hydroxide and at least one additive decreasing the solubility of the lithium ions;

- a positive-electrode compartment comprising at least one positive air electrode, in contact with ~~an~~ the aqueous solution ~~containing lithium hydroxide~~; and

- a solid electrolyte separating, in a gas- and liquid-tight manner, the negative-electrode compartment from the positive-electrode compartment.~~:~~

~~characterized in that the aqueous solution containing lithium hydroxide further contains at least one additive decreasing the solubility of the lithium ions.~~

The documents US 4 684 584 and US 5 427 873, which refer to an additive decreasing the solubility of lithium ions, relate to lithium-water cells and not lithium-air batteries. These cells are not intended to be recharged. The problem of energy efficiency does not therefore arise. Moreover, these cells do not comprise any positive air electrode.

The solubility of a compound denotes the maximum concentration of this compound that can be solubilized in a solvent. The additive present in the aqueous solution has the effect of decreasing the solubility of the lithium ions, and of decreasing the concentration of lithium Li^+ ions in an aqueous solution saturated with lithium.

The solubility limit of lithium hydroxide in water is 5.2 mol/L at 20 °C (according to D.R. Lide, *CRC Handbook of Chemistry and Physics*, New York, 2005). The presence of an additive according to the invention advantageously makes it possible to decrease this solubility limit of lithium hydroxide. The solubility limit of lithium hydroxide in the aqueous solution containing the additive is preferably below 4 mol/L, more preferably below 3 mol/L, and more preferably still below 2 mol/L. The solubility limit is however preferably maintained above 1 mol/L, at lower values issue of re-solubilization of the lithium hydroxide when recharging the battery can occur. Advantageously, the solubility limit of lithium hydroxide in the aqueous solution containing the additive according to the invention can lie between 1 mol/L and 2 mol/L.

This additive can be chosen by those skilled in the art from among the known chemical compounds having a solubility in water above the solubility of lithium and forming a salt with the hydroxide ions. Preferably, the additive is an alkali metal hydroxide. More preferably, the additive decreasing the solubility of the lithium ions is

chosen from the group formed by potassium hydroxide and sodium hydroxide. More preferably still, the additive is potassium hydroxide.

The concentration of the additive decreasing the solubility of the lithium ions in the aqueous solution is fixed by those skilled in the art, as a function of the nature of this additive, so as to lower the solubility limit of lithium hydroxide down to the values described above. When the additive is potassium, its concentration in the aqueous solution containing lithium hydroxide can lie between 1 mol/L and 10 mol/L, more preferably between 4 mol/L and 9 mol/L, and more preferably still between 7 mol/L and 8 mol/L.

The additive can be added to the aqueous solution in any form. In particular, the additive can be added in the form of a hydroxide salt. If the additive is sodium, it is possible to add to the aqueous solution a sodium hydroxide salt. If the additive is potassium, it is possible to add to the aqueous solution a potassium hydroxide salt.

The inventors have observed that the presence of at least one additive according to the invention in the aqueous solution constituting the liquid electrolyte in a lithium-air battery has the effect of significantly reducing the charging voltage of the battery. Furthermore, the presence of the additive according to the invention has no impact on the energy released during discharge of the battery. As a consequence, the energy efficiency of the lithium-air battery is improved.

~~Another subject~~According to a second aspect of the present invention is ~~therefore a~~the use of at least one additive to reduce~~decreasing~~ the solubility of lithium ions ~~solubility to improve the energy efficiency of a lithium-air battery, the additive being~~ contained in an~~the~~ aqueous solution constituting a liquid electrolyte of a rechargeable lithium-air battery to improve the energy efficiency~~containing lithium hydroxide constituting the liquid electrolyte~~ of the rechargeable lithium-air battery.

Furthermore, the presence of at least one additive according to the invention in the aqueous solution constituting the liquid electrolyte in a lithium-air battery has no prohibitive impact on the specific capacity of the battery. Indeed, if the concentration of

the lithium hydroxide reaches and exceeds the saturation concentration, the alkali metal hydroxide precipitates. The formation of a precipitate is not problematic because, when

Claims

1. A rechargeable lithium-air battery comprising:

- a negative-electrode compartment containing lithium metal ;

- an aqueous solution containing lithium hydroxide and at least one additive decreasing the solubility of the lithium ions;

- a positive-electrode compartment comprising at least one positive air electrode, in contact with the aqueous solution; and

- a solid electrolyte separating, in a gas- and liquid-tight manner, the negative-electrode compartment from the positive-electrode compartment.;

2. The rechargeable lithium-air battery of claim 1, wherein the solubility limit of lithium hydroxide in the aqueous solution containing the additive is below 4 mol/L, more preferably below 3 mol/L, and more preferably still between 1 mol/L and 2 mol/L.

3. The rechargeable lithium-air battery of either one of claims 1 or 2, wherein the additive decreasing the solubility of the lithium ions is an alkali metal hydroxide.

4. The rechargeable lithium-air battery of claim 3, wherein the additive decreasing the solubility of the lithium ions is chosen from the group made up of potassium hydroxide and sodium hydroxide, the additive preferably being potassium hydroxide.

5. The rechargeable lithium-air battery of any claims 1 to 4, further comprising a means for preventing the formation of a dense crystalline layer of lithium hydroxide at the surface of the solid electrolyte.

6. The rechargeable lithium-air battery of claim 5, wherein the means for preventing the formation of a dense crystalline layer of lithium hydroxide at the surface of the solid electrolyte is a layer of an organic cation-conducting polyelectrolyte.

7. The rechargeable lithium-air battery of any claims 1 to 6, further comprising a positive oxygen releasing electrode, in contact with the aqueous solution.

8. The rechargeable lithium-air battery of any claims 1 to 7, wherein the positive air electrode further comprises an anion exchange polymer membrane forming a separation between the electrode material and the aqueous solution constituting the liquid electrolyte.

9. A method for storing and releasing electrical energy using ~~a~~ the rechargeable lithium-air battery of any claims 1 to 8, comprising the following successive steps :

(a) a discharging phase during which the lithium metal contained in the negative-electrode compartment oxidates and precipitates in the form of lithium hydroxide in the aqueous solution of the positive-electrode compartment;

(b) a recharging phase during which the lithium hydroxide solubilizes to release lithium ions which are reduced at the level of the negative electrode.

10. A use of at least one additive reducing the solubility of lithium ions contained in an aqueous solution constituting a liquid electrolyte of a rechargeable lithium-air battery to improve the energy efficiency of the rechargeable lithium-air battery.