

METHODS OF RECYCLING ALKALI METAL ION BATTERIES

FIELD OF INVENTION

The invention relates to a method of recovering one or more metals from at least two active materials obtained from an alkali metal ion battery.

BACKGROUND

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Alkali metal-ion batteries (AMIBs), in a particular lithium-ion batteries (LIBs), sodium-ion batteries (SIBs), potassium-ion batteries (KIBs), and calcium-ion batteries (CIBs), are important battery technologies.

Lithium ion batteries (LIBs) are currently the primary choice of power source for portable devices and they are increasingly in demand for applications such as electrical energy storage (EEs) and electric vehicle (EV). SIBs, KIBs, and CIBs have shown promise and potential for further development.

The widespread application of LIBs has resulted in two issues of particular concern: (1) the price of Li and Co raw materials (Li_2CO_3 and Co_3O_4) have been raised to \$24,000 and \$33,000 per ton, respectively, due to the large demand for cathode materials such as Li_2CoO_2 and LiFePO_4 ; (2) it is evident that LIBs will generate a large amount of waste at the end of their lifetime. This is of great concern to the environment, and the increased demand for the materials will speed up depletion of Li and other metal resources if they are not properly reused. Lithium and cobalt have been recognised as strategic resources as these elements are relatively rare in the earth's crust. Moreover, spent battery materials comprise valuable metals such as Al, Cu, Co, in addition to the alkali metal (i.e. Li, Na, K and Ca), and the concentration of these elements is much higher than that in natural ores.

Given the increase in demand for AMIBs, and the accumulation of waste generated from spent AMIBs, there is increasing importance for a viable recycling process for extracting metal elements from spent AMIBs for the sustainable deployment of these technologies. Some companies and institutions have established pilot lines for AMIBs recycling based on the traditional hydrometallurgical extraction process, in particular for LIBs and SIBs. The typical hydrometallurgical extraction process consists of the following steps: (1) releasing residual

electricity of spent batteries by discharge pre-treatment; (2) removing plastic packaging and casings from the batteries and separating out the cathode and anode electrodes; (3) scraping cathodic and anodic active materials from the electrodes; (4) dissolving the cathodic active material (such as LiCoO_2) using a strong acid (e.g. HCl or H_2SO_4) to form a solution containing Co^{2+} , Li^+ , SO_4^{2-} ions (leaching process); (5) adding NaOH to the resulting solution to precipitate $\text{Co}(\text{OH})_2$, leaving Li^+ , Na^+ , OH^- , SO_4^{2-} ions in the solution, and then adding Na_2CO_3 to the solution to precipitate Li_2CO_3 (metal separation process).

The above hydrometallurgical extraction process suffers from the following issues. Firstly, the process is complicated and involves many steps. In addition, it requires addition of a large amount of chemicals such as HCl , H_2SO_4 , NaOH and Na_2CO_3 , and in connection to this addition, generates a large amount of waste material after Li_2CO_3 has been precipitated, resulting in secondary pollution. Furthermore, traditional hydrometallurgical extraction processes are unable to effectively extract or leach LiFePO_4 because this material does not dissolve in acid, which is problematic because LiFePO_4 is a widely-used cathode material for electrical energy storage (EEs) and electric vehicle (EV).

There is therefore a need for an improved, simpler and low-cost process for recycling AIMIBs, in particular for LIBs and SIBs, or at least a need for useful alternatives.

SUMMARY OF INVENTION

Aspects and embodiments of the invention will now be described by reference to the following numbered clauses.

1. A method of recovering one or more metals from at least two active materials obtained from an alkali metal ion battery, the method comprising:

(a) providing a first active material and a second active material, each of the active materials comprising alkali metal ions, the first active material having a reduction potential greater than the reduction potential of the second active material;

(b) adding the first and second active materials to a redox mediator solution that comprises a solvent and a redox mediator to form a redox mediator solution comprising alkali metal ions in a first tank,

wherein the redox mediator has a reduction potential that is less than the reduction potential of the first active material and greater than the reduction potential of the second active material, such that the redox mediator reduces the first active material and oxidises the

second active material, thereby releasing the alkali metal ions from the first and second active materials;

(c) (i) once substantially all the first active material is reduced and/or substantially all the second active material is oxidised, moving the redox mediator solution from the first tank to a second tank, the second tank being fluidly connected to a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply; or

(ii) once substantially all the second active material is oxidised, or substantially all the first active material is reduced and substantially all the second active material is oxidised, moving the redox mediator solution from the first tank to a second tank, the second tank being fluidly connected to a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply;

(d) moving the redox mediator solution from the second tank through the redox flow cell, thereby enabling transport of the alkali metal ions through the ion selective membrane into the cathode compartment which comprises an aqueous catholyte solution;

(e) capturing the alkali metal ions as an alkali metal hydroxide in the cathode compartment through an electrochemical reaction on the cathode electrode and transferring the resulting aqueous catholyte solution containing the alkali metal hydroxide to a third tank;

provided that when the method comprises step (c)(i), the redox flow cell comprises a central compartment disposed between the anode and cathode compartments and separated from the anode compartment by a first ion selective membrane and separated from the cathode compartment by a second ion selective membrane, and step (d) comprises moving the redox mediator solution from the second tank to the central compartment of the redox flow cell enabling transport of the alkali metal ions through the second ion selective membrane into the cathode compartment; and

provided that when the method comprises step (c)(ii), the first and second active materials are present in the redox mediator solution in step (b) at equimolar amounts relative to each other, or the first active material is present in the redox mediator solution in step (b) at a molar excess relative to the second active material.

2. The method according to clause 1, wherein the redox mediator solution that has moved through the redox flow cell is returned to the second tank, followed by repeating steps (d) and (e) until substantially all the alkali metal ions are captured as the alkali metal hydroxide in the cathode compartment.

3. The method according to clause 1 or clause 2, wherein the pH of the redox mediator solution in the first tank is maintained at a pH of less than about 4.
4. The method according to any one of clauses 1-3, wherein the pH of the redox mediator solution in the second tank is adjusted to greater than about 4.
5. The method according to clause 4, wherein the pH of the redox mediator solution in the second tank is adjusted to a pH of from about 5 to about 6 (e.g. about 5.5), and then adjusted to a pH of from about 10 to about 12 (e.g. about 11).
6. The method according to clause 4 or 5, wherein the pH is adjusted by addition of the alkali metal hydroxide into the second tank.
7. The method according to any one of the preceding clauses, wherein when the method comprises step (c)(ii), the redox flow cell comprises a central compartment disposed between the anode and cathode compartments and separated from the anode compartment by a first ion selective membrane and separated from the cathode compartment by a second ion selective membrane, and
wherein step (d) comprises moving the redox mediator solution from the second tank to the central compartment of the redox flow cell enabling transport of the alkali metal ions through the second ion selective membrane into the cathode compartment.
8. The method according to clause 7, or the method according to any one of clauses 1-6 when the method comprises step (c)(i), wherein a hydrogen oxidation reaction (HOR) or oxygen evolution reaction (OER) on the anode electrode produces H^+ ions which are transported through the first ion selective membrane into the central compartment of the redox flow cell.
9. The method according to clause 7 or 8, wherein the anode compartment is supplied with hydrogen gas, and wherein a HOR on the anode electrode produces H^+ ions which are transported through the first ion selective membrane into the central compartment of the redox flow cell.
10. The method according to any one of the preceding clauses, wherein the first tank contains the first and second active materials at equimolar amounts relative to each other.

11. The method according to any one of clauses 1 to 9, wherein the first tank contains a molar excess of the first active material relative to the second active material, and wherein the method further comprises a step following step b) and before step c) of:

(I) moving the redox mediator solution through a redox flow cell fluidly connected to the first tank and comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply, and

the redox mediator solution is subjected to an electrochemical reaction on the cathode electrode, where the electrochemical reaction on the cathode electrode:

reduces the redox mediator, which is then returned to the first tank to reduce any remaining first active material;

step (I) being optionally repeated until substantially all the first active material is reduced.

12. The method according to clause 11, wherein, once substantially all the first active material is reduced, the redox mediator solution in the first tank is moved to the second tank according to step c).

13. The method according to clause 11 or 12, wherein a HOR or OER on the anode electrode of redox flow cell fluidly connected to the first tank produces H^+ ions which are transported through the ion selective membrane into the cathode compartment and to the first tank.

14. The method according to any one of the preceding clauses, wherein the electrochemical reaction on the cathode electrode in step (e) is a hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) which produces OH^- ions.

15. The method according to any one of the preceding clauses, wherein the solvent is an aqueous acid solution, for example an acetic acid solution, a nitric acid solution, citric acid solution, oxalic acid solution, ascorbic acid solution, or sulphuric acid solution.

16. The method according to clause 15, wherein the aqueous acid solution is an acetic acid solution (e.g. a 3 M acetic acid solution) or a sulphuric acid solution (e.g. a 1 M to 3 M sulphuric acid solution).

17. The method according to any one of the preceding clauses, wherein the aqueous catholyte solution in step d) is initially selected from one of water, water comprising oxygen, water comprising air, water comprising oxygen and CO_2 , or water comprising air and CO_2 .

18. The method according to any one of the preceding clauses, wherein after step (e), the aqueous catholyte solution is an aqueous alkali metal hydroxide solution, an aqueous alkali metal hydroxide solution comprising oxygen, an aqueous alkali metal hydroxide solution comprising air, an aqueous alkali metal hydroxide solution comprising oxygen and CO₂ with alkali metal carbonate precipitate, or an aqueous alkali metal hydroxide solution comprising air and CO₂ with alkali metal carbonate precipitate.

19. The method according to any one of the preceding clauses, wherein the the alkali metal ions in the first and second active materials are lithium, sodium, potassium or calcium ions.

20. The method according to any one of the preceding clauses, wherein the alkali metal in the first and second active materials are lithium ions; the alkali metal hydroxide is LiOH; and the alkali metal carbonate precipitate in clause 18 is Li₂CO₃.

21. The method according to any one of the preceding clauses, wherein the first active material is LiNi_xCo_yMn_zO₂ (NCM, 0 ≤ x,y,z < 1), Li_xCoO₂ (0 ≤ x < 1), LiNi_xCo_yAl_zO₂ (NCA, x ≥ 0.8, z ≤ 0.05 and x + y + z = 1), Li_xMn₂O₄ (0 ≤ x < 1), Li_xNi_{0.5}Mn_{1.5}O₄ (0 ≤ x < 1), or a mixture of two or more thereof.

22. The method according to any one of the preceding clauses, wherein the first active material is LiCoO₂.

23. The method according to clause 22, wherein a precipitate of Co(OH)₂ is collected from the second tank.

24. The method according to any one of clauses 1-21, wherein the first active material is LiNi_xCo_yMn_zO₂ (NCM, 0 ≤ x,y,z < 1).

25. The method according to clause 24, wherein a precipitate of Ni_xCo_yMn_z(OH)₂ is collected from the second tank.

26. The method according to any one of the preceding clauses, wherein the second active material is LiFePO₄.

27. The method according to clause 26, wherein a precipitate of FePO₄ is collected from the first tank and/or second tank.

28. The method according to clause 27, wherein the precipitate of FePO_4 is collected from the first tank and/or second tank and subjected to a purification process to remove impurities, such as carbon-conductive additives (e.g. carbon black) and binders (e.g. PVDF).

29. The method according to any one of clauses 1 to 19, wherein the alkali metal ions in the first and second active materials are sodium ions; the alkali metal hydroxide is NaOH ; and the alkali metal hydroxide and alkali metal carbonate precipitate in clause 18 are NaOH and NaCO_3 or NaHCO_3 , respectively.

30. The method according to any one of clauses 1 to 19 or 29, wherein the first active material is NaCoO_2 .

31. The method according to any one of clauses 1 to 19, 29 or 30, wherein the second active material is NaFePO_4 , $\text{NaV}_2(\text{PO}_4)_3$, or a mixture thereof.

32. The method according to any one of the preceding clauses, wherein the redox mediator is hydroquinonesulfonic acid, anthraquinone-2,6-disulfonate, or a mixture thereof.

33. The method according to any one of the preceding clauses, wherein the total concentration of the redox mediator present in the redox mediator solution in the first tank is from about 0.01 M to about 1 M.

34. The method according to any one of the preceding clauses, wherein the first and/or second active material is/are attached to an electrode of a dismantled battery or provided free from the electrode.

DRAWINGS

Certain embodiments of the present disclosure are described more fully hereinafter with reference to the accompanying drawings.

FIG. 1 illustrates a redox flow system for recycling of spent Li-ion battery materials through bidirectional leaching of LiCoO_2 (LCO) and LiFePO_4 (LFP).

FIG. 2 illustrates a redox flow cell system for additional treatment of spent Li-ion battery materials containing an excess of LCO.

FIG. 3 shows (a) Cyclic voltammetry curves for 50 mM hydroquinonesulfonic acid in 3 M acetic acid solution compared with LCO and LFP in 3 M acetic acid; and (b) powder XRD results of the pristine LCO, LFP, FePO_4 (FP) and the powder after 24 h of leaching.

FIG. 4 shows (a) a schematic diagram of a 3-compartment redox flow cell for lithium removal; (b) the voltage profile of 50 mM hydroquinonesulfonic acid with Li^+ from leaching for lithium removal with hydrogen oxidation electrolytic cell paired with HER reaction at different current densities with a 3-compartment redox flow cell; (c) a schematic diagram of a 2-redox flow cell system for lithium removal; (d) the voltage profile of 50 mM hydroquinonesulfonic acid with Li^+ from the leachate for lithium removal with the 2-redox flow cell system at 50 mA/cm^2 .

FIG. 5 illustrates a purification process for FP.

FIG. 6 illustrates a hydrogen looping system for purification of FP.

FIG. 7 shows the voltage profile of the flow cell with dry H_2 and 10 mL 2 M NaCl as anolyte, 10 mL 2 M NaCl as catholyte and 10 mL 2 M NaCl as middle compartment electrolyte. Electrode area: 4 cm^2 .

FIG. 8 illustrates a purification process of FP from Li-extracted black mass. (a) FP added into the acidic solution ($\text{pH}=0.38$) obtained from the anode chamber of the above battery. (b) The leachate contained Fe^{3+} and $(\text{PO}_4)^{3-}$ after the binder and carbon black is filtered. (c) The mixture when an alkaline solution ($\text{pH}=13.32$) obtained from the cathode compartment of the above cell was added into the leachate. (d) The precipitated FePO_4 . (e) The leachate after precipitation.

FIG. 9 illustrates a decoupling hydrogen looping system for purification of FP.

FIG. 10 illustrates a system for recycling of spent Li-ion battery materials through bidirectional leaching of LiCoO_2 (LCO) and LiFePO_4 (LFP) black mass with FePO_4 recovery.

FIG. 11 illustrates a holistic recycling system for spent LiFePO_4 battery materials through acid leaching of black mass with FePO_4 recovery using a hydrogen looping system.

DESCRIPTION

It has been surprisingly found that alkali metal ions can be recovered by simultaneously processing two or more spent active materials from alkali metal ion batteries.

Thus, disclosed herein is a method of recovering one or more metals from at least two active materials obtained from an alkali metal ion battery, the method comprising:

- (a) providing a first active material and a second active material, each of the active materials comprising alkali metal ions, the first active material having a reduction potential greater than the reduction potential of the second active material;
- (b) adding the first and second active materials to a redox mediator solution that comprises a solvent and a redox mediator to form a redox mediator solution comprising alkali metal ions in a first tank,

wherein the redox mediator has a reduction potential that is less than the reduction potential of the first active material and greater than the reduction potential of the second active material, such that the redox mediator reduces the first active material and oxidises the second active material, thereby releasing the alkali metal ions from the first and second active materials;

- (c) (i) once substantially all the first active material is reduced and/or substantially all the second active material is oxidised, moving the redox mediator solution from the first tank to a second tank, the second tank being fluidly connected to a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply; or

(ii) once substantially all the second active material is oxidised, or substantially all the first active material is reduced and substantially all the second active material is oxidised, moving the redox mediator solution from the first tank to a second tank, the second tank being fluidly connected to a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply;

- (d) moving the redox mediator solution from the second tank through the redox flow cell, thereby enabling transport of the alkali metal ions through the ion selective membrane into the cathode compartment which comprises an aqueous catholyte solution;

- (e) capturing the alkali metals as an alkali metal hydroxide in the cathode compartment through an electrochemical reaction on the cathode electrode and transferring the resulting aqueous catholyte solution containing the alkali metal hydroxide to a third tank;

provided that when the method comprises step (c)(i), the redox flow cell comprises a central compartment disposed between the anode and cathode compartments and separated from the anode compartment by a first ion selective membrane and separated from the cathode compartment by a second ion selective membrane, and step (d) comprises moving the redox mediator solution from the second tank to the central compartment of the redox flow

cell enabling transport of the alkali metal ions through the second ion selective membrane into the cathode compartment; and

provided that when the method comprises step (c)(ii), the first and second active materials are present in the redox mediator solution in step (b) at equimolar amounts relative to each other, or the first active material is present in the redox mediator solution in step (b) at a molar excess relative to the second active material.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrases “substantially all the first active material is reduced” and “substantially all the second active material is oxidised” may be interpreted herein to refer to a majority of the first active material added to the first tank being reduced or a majority of the second active material added to the first tank being oxidised. For example, the greater than or equal to 50%, the greater than or equal to 60%, the greater than or equal to 70%, the greater than or equal to 80%, the greater than or equal to 90%, such as greater than 95% such as greater than 97%, such as greater than 99%, such as greater than 99.9%, such as greater than 99.99%, such as greater than 99.999%, such as 100%, of the first active material is reduced and/or second active material is oxidised.

The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, within 1%, within 0.5%, within 0.1%, within 0.05%, within 0.01%, within 0.005%, or within 0.001% of a stated value or of a stated limit of a range, and includes the exact stated value or range.

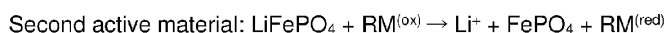
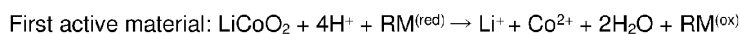
For the avoidance of doubt, the term “redox flow cell” as used may be used interchangeably with the terms “flow cell-type electrolyser”, “redox flow cell-type electrolyser” and “electrolyser”.

The process above is agnostic to whether the active material is obtained from a cathode and/or an anode. However, typically, the active materials are cathode active materials.

As will be appreciated, the process described above relates to the recovery of alkali metals from spent (retired) batteries or from waste materials produced during the manufacturing process. As such, the active materials referred to above may not be capable of functioning in a battery in their current form and so there is a need to recover the alkali metals for reuse.

An embodiment of the method of the invention is depicted in Figure 1. In Figure 1, the apparatus 10 comprises three tanks, a first tank 11, a second tank 21, and a third tank 31. The first tank 11 houses the first and second active materials comprising the alkali metal ions to be recovered, along with a solvent and a redox mediator, together forming a redox mediator solution. Typically, the solvent is an aqueous acid solution with a pH of less than about 7, for example a pH of about 1 to 4 (e.g. about 2). It should be understood that the redox mediator solution may also contain other relevant chemicals useful for the recovery of alkali metal ions. The second tank 21 may be in fluid connection with the first tank 11 and in fluid connection with a redox flow cell 100, which comprises an anode compartment 110 and a cathode compartment 120, and a central compartment 130, which is disposed between the anode and cathode compartments 110, 120 and separated from the anode compartment 110 by a first ion selective membrane 110a and separated from the cathode compartment 120 by a second ion selective membrane 120a. The anode compartment 120 includes an anode electrode 110b, while the cathode compartment 120 includes a cathode electrode 120b. The redox flow cell 100 also includes a power source 140 that is connected to the anode 110b and cathode 120b electrodes. The apparatus 10 also includes: a first fluid pathway 12 running from the first tank 11 to the second tank 21, the fluid pathway comprising a pump 13; a second fluid pathway 22 running from the second tank 21 to the central compartment 130 of the redox flow cell 100, and back to the first tank 11, the fluid pathway 22 comprising a pump 23. There is also a third fluid pathway 32 running from the third tank 31 to the cathode compartment 120a of the redox flow cell 100, and back to the third tank 31, the fluid pathway 32 comprising a pump 33. In Figure 1, hydrogen gas (H₂) may be supplied into the anode compartment 110.

In Figure 1, the first active material is LiCoO₂ (LCO) and the second active material is LiFePO₄ (LFP). The redox mediator (RM) reduces the first active material to form lithium ions and oxidises the second active material to form lithium ions. The reactions are as follows:



Analogous reactions will occur for other active materials subjected to the currently described method. As will be appreciated, the exact reactions will depend on the nature of the active material and the redox mediators used.

In Figure 1, once substantially all the first active material is reduced and/or substantially all the second active material is oxidised in the redox mediator solution contained in the first tank 11, the redox mediator solution is moved from the first tank 11 to the second tank 21 via fluid pathway 12, aided by pump 13. In the process shown in Figure 1, LiOH is added to the second tank which results in the pH of the redox mediator solution increasing to a pH of from about 5 to about 6 (e.g. about 5.5). At this pH, certain impurities (e.g. Al, Cu and Fe ions and/or Al, Cu and Fe containing compounds) may precipitate and be removed. The pH is then increased further by adding more LiOH until a pH of from about 10 to about 12 (e.g. about 11). At this pH, a precipitate of $\text{Co}(\text{OH})_2$ is formed in the tank, which may be collected. The LiOH added to the tank may be obtained from the third tank 31 following capture of lithium ions as LiOH. Other alkali metal hydroxides may be used depending on the active materials being processed. Once the pH in the second tank 21 is at about 10 to about 12, and optionally the $\text{Co}(\text{OH})_2$ has been collected, the redox mediator solution in the second tank 21 is moved from the second tank 21 (via fluid pathway 22 aided by pump 23) through the central compartment 130 of the redox flow cell 100, thereby enabling transport of the alkali metal ions (in Figure 1, Li^+ ions) through the ion selective membrane 120a into the cathode compartment 120 which comprises an aqueous catholyte solution. In the cathode compartment 120, the alkali metal ions are captured as an alkali metal hydroxide (in Figure 1, the alkali metal hydroxide is lithium hydroxide, LiOH) through an electrochemical reaction on the cathode electrode 120b. The resulting aqueous catholyte solution containing the alkali metal hydroxide is then transferred to a third tank via fluid pathway 32, aided by pump 33. The aqueous catholyte solution in the third tank 31 may be cycled between the third tank 31 and the cathode compartment 120 until substantially all the alkali metal ions are captured as the alkali metal hydroxide in the cathode compartment. The alkali metal hydroxide is collected from the third tank 31.

In Figure 1, hydrogen gas (H_2) may be supplied into the anode compartment 110. The hydrogen gas undergoes a hydrogen oxidation reaction (HOR) on the anode electrode 110b, which is equipped with a suitable catalyst (e.g. a Pt/C catalyst). The H^+ produced by the HOR are transported through the first ion selective membrane 110a into the central compartment 130 of the redox flow cell. This facilitates transport of the alkali metal ions (i.e. Li^+ ions) through the second ion selective membrane 120a into the cathode compartment 120. It also reduces the pH of the redox mediator solution before it is returned to the first tank 11 via fluid pathway 22. Alternatively, H^+ may be generated on the anode electrode 110b by an Oxygen Evolution

Reaction (OER). This is achieved by equipping the anode electrode 120b with a suitable catalyst (e.g. Ir-Ru alloy catalyst or $\text{Co}_3\text{O}_4\text{-CeO}_2$ composite oxide catalyst) and supplying the anode compartment 120 with water.

In Figure 1, FePO_4 (FP) may be collected from the first tank 11 and/or second tank 21 when the second active material is LiFePO_4 . The FePO_4 forms a precipitate at a pH of about 2 or above. If the pH of the redox mediator solution in the first tank is less than about 2, the FePO_4 may be precipitated and collected in the first and/or second tank by increasing the pH of the redox mediator solution to about 2 or above, for example by adding an alkali metal hydroxide such as LiOH . Typically, the step of precipitating FePO_4 is performed before the pH of the redox mediator solution is increased to about 5 to about 6 and then to about 10 to about 12 to precipitate of $\text{Co}(\text{OH})_2$. The FePO_4 precipitate may be collected with other impurities such as carbon-conductive additives (e.g. carbon black) and binders (e.g. PVDF). As such, the collected FePO_4 may be processed further to produce purified FePO_4 . Purified FePO_4 can be used for the resynthesis of LiFePO_4 , which could alleviate the global phosphorus demand caused by the decommissioning of LiFePO_4 containing batteries.

In certain embodiments, when the FePO_4 is collected with impurities such as carbon-conductive additives (e.g. carbon black) and binders (e.g. PVDF) it may be further purified by dissolving the FePO_4 in a suitable aqueous acid solution having a pH of below about 2 (e.g. a pH of about 1). At this pH, the FePO_4 dissolves but impurities such as carbon-conductive additives (e.g. carbon black) and binders (e.g. PVDF) do not. The FePO_4 may then be isolated (e.g. by filtration) from the other impurities for further use. Optionally, isolated FePO_4 dissolved in the aqueous acid solution may be precipitated by adding a suitable aqueous alkali solution to isolated FePO_4 solution to increase the pH to above at least 2. The precipitated may then be collected for further use.

The aqueous acid solution and aqueous alkali solution used in the further purification of the FePO_4 may be an aqueous hydrochloric acid solution and a suitable aqueous alkali metal hydroxide solution, respectively. In certain embodiments, the hydrochloric acid and alkali metal hydroxide (e.g. sodium hydroxide or lithium hydroxide) may be obtained from commercial sources. Additionally, or alternatively, the hydrochloric acid and the alkali metal hydroxide (e.g. sodium hydroxide or lithium hydroxide) may be generated from a NaCl solution or a LiCl solution by electrolysis using a suitable redox flow cell system. Examples of suitable redox flow cell systems are shown in Figures 6 and 9, and described in the Examples section disclosed herein.

When the first tank 11 contains a molar excess of the first active material relative to the second active material, the method of the invention may further comprise a step following step b) and before step c) of:

(l) moving the redox mediator solution to a redox flow cell fluidly connected to the first tank and comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply, and

the redox mediator solution is subjected to an electrochemical reaction on the cathode electrode, where the electrochemical reaction on the cathode electrode:

reduces the redox mediator, which is then returned to the first tank to reduce any remaining first active material;

step l) being optionally repeated until substantially all the first active material is reduced.

Figure 2 shows apparatus 20, which is suitable for performing step l) of the method of the present invention. The apparatus 20 comprises the first tank 11 and a fourth tank 41.

For the avoidance of doubt, the first tank 11 shown in Figure 1 is the same as the first tank 11 shown in Figure 1. However, it should be understood that another tank could be used in place of the first tank when performing step l), said other tank containing the redox mediator solution transferred from the first tank 11. Typically, step l) is performed using the first tank 11. Also for the avoidance of doubt, the first tank 11 in Figure 2 may remain connected to the second tank 21 during step l) or it may be disconnect from the second tank during step l).

In apparatus 20, the first tank 11 houses the redox mediator solution containing a molar excess of the first active material relative to the second active material. The first tank 11 may be in fluid connection with a redox flow cell 200, which comprises an anode compartment 210 and a cathode compartment 220, the anode and cathode compartments separated from each other by an ion selective membrane 230. The anode compartment 210 includes an anode electrode 110a, while the cathode compartment 220 includes a cathode electrode 220a. The redox flow cell 200 also contains a power source 240 that is connected to the anode 210a and cathode 220a electrodes. The apparatus 20 also includes: a first fluid pathway 14 running from the first tank 11 to the anode compartment 220 and back to the first tank 11, the fluid pathway comprising a pump 15; and a second fluid pathway 42 running from the forth tank 41 to the cathode compartment 210 and back to the fourth tank 41, the fluid pathway comprising a pump 43.

Typically, the process shown in Figure 2 is used once substantially all of the second active material in the first tank 11 has been oxidised by the redox mediator. As the first active material is in excess relative to the second active material, once substantially all the second active material has been oxidised, the first tank 11 contains remaining first active material yet to undergo reduction by the redox mediator.

Thus, typically, once substantially all of the second active material in the first tank 11 has been oxidised by the redox mediator, the redox mediator solution in the first tank 11 is moved from the first tank 11 through redox flow cell 200 via fluid pathway 14 which passes through the cathode compartment 220. When passing through the cathode compartment 220, the redox mediator in the redox mediator solution is subjected to an electrochemical reaction on the cathode electrode 220a, which reduces the redox mediator. The reduced redox mediator then returns to the first tank 11 via fluid pathway 14, where it can reduce any first active material remaining in the first tank. The redox mediator solution in the first tank 11 may be cycled between the redox flow cell 200 and the first tank 11 until substantially all the first active material is reduced by the redox mediator. At this stage, the redox mediator solution in the first tank 11 may be moved to the second tank 21 shown in Figure 1 via fluid pathway 12, where it may continue the process shown in Figure 1 until substantially all the alkali metal ions from the first and second active material are collected as an alkali metal hydroxide in the third tank 31.

In Figure 2, the fourth tank 41 contains water. The water is moved from the fourth tank 41 through redox flow cell 200 via fluid pathway 42 which passes through the anode compartment 210. When passing through the anode compartment 210, the water undergoes an Oxygen Evolution reaction (OER) on the anode electrode 210a, which produces H^+ ions that transport through the ion selective membrane 230 into the cathode compartment 220 and to the first tank 11, thereby facilitating reduction of the redox mediator and first active material. Alternatively, a Hydrogen Oxidation Reaction (HOR) may be used to generate H^+ on the anode electrode. When a HOR is used, the anode compartment is supplied with hydrogen gas.

Typically the electrochemical reaction on the cathode electrode in redox flow cell 100 is a hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) which produces OH^- ions. The OH^- ions being able to react with the alkali metal ions to form the alkali metal hydroxide.

In certain embodiments, any excess $LiFePO_4$ remaining from the methods described above may be purified using a process that comprises the steps of:

- A) providing a sample comprising LiFePO_4 and impurities such as carbon-conductive additives (e.g. carbon black), binders (e.g. PVDF), and redox inactive lithium compounds;
- B) separately generating an aqueous HCl solution and an aqueous LiOH from an aqueous solution of LiCl by electrolysis;
- C) adding the aqueous HCl solution generated in step A) to the sample comprising LiFePO_4 , thereby forming a precipitate of HFePO_4 ;
- D) oxidizing the precipitated HFePO_4 to form an aqueous HCl solution comprising Fe^{3+} and HPO_4 ;
- E) adding the aqueous LiOH solution generated in step B) to the aqueous HCl solution comprising Fe^{3+} and HPO_4 to form a precipitate of FePO_4 ; and
- F) optionally collecting the FePO_4 from step E) for further processing.

In the above process above, the aqueous HCl solution used in step C) preferably has a pH less than about 2 (e.g. about 1). In step E), preferably the aqueous LiOH is added to the aqueous HCl solution comprising Fe^{3+} and HPO_4 until the pH of the solution is about 2 or more. An apparatus suitable for performing steps A)-F) above is shown in Figure 11.

In the redox flow cells described herein, at least one ion selective membrane separates the cathode compartment from the anode compartment. The ion selective membrane is typically an electro-active ion conducting membrane (e.g., a lithium or sodium ion conducting membrane). The ion selective membrane prevents cross-diffusion of the redox mediator and allows for movement of the electro-active ions (e.g., lithium ions, sodium ions, magnesium ions, aluminum ions, silver ions, copper ions, protons, or a combination thereof). For example, the ion selective membrane may be a lithium phosphorus oxynitride glass, a lithium thiophosphate glass, sodium phosphorus oxynitride glass, a sodium thiophosphate glass, a NASICON-type lithium conducting glass ceramic, a NASICON-type sodium conducting glass ceramic, a Garnet-type lithium or sodium conducting glass ceramic, a ceramic nanofiltration membrane, a lithium or sodium ion-exchange membrane, or suitable combinations thereof.

Both electrodes in the redox flow cells described herein, i.e., the cathode and the anode, can be a carbon, a metal, or a combination thereof. Preferably, the two electrodes have high surface area, with or without one or more catalysts, to facilitate the charge collection process. They can be made of a carbon, a metal, or a combination thereof. Examples of an electrode can be found in Skyllas-Kazacos, et. al., Journal of The Electrochemical Society, 158, R55-79 (2011) and Weber, et. al., Journal of Applied Electrochemistry, 41, 1137-64 (2011). In certain embodiments, the anode electrode may comprise a catalyst to facilitate a HOR (e.g. a Pt/C

catalyst) In certain other embodiments, the anode electrode may comprise a catalyst to facilitate an oxygen evolution reaction (OER) (e.g. Ir-Ru alloy catalyst or Co_3O_4 - CeO_2 composite oxide catalyst). In certain embodiments, the cathode electrode may comprise a catalyst to facilitate a hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) to produce OH^- ions (e.g. a Pt/C catalyst).

The redox mediator used in the method of the present invention has a reduction potential that is less than the reduction potential of the first active material and greater than the reduction potential of the second active material. The redox mediator is therefore capable of reducing the first active material and oxidising the second active material. When the first active material is reduced and the second active material is oxidised, the alkali metal ions can dissociate from the other component parts of the respective active materials.

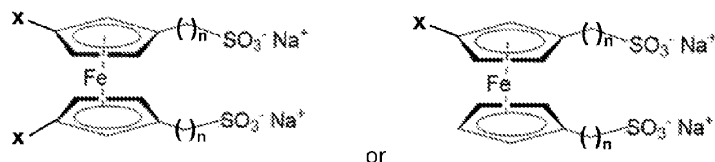
A redox mediator refers to a compound present (e.g., dissolved) in the solvent placed in the same tank (i.e. first tank) as the active materials that acts as a molecular shuttle to transport the alkali metal ions to the electrode in the flow cell to which the tank is connected.

The term "reduction potential" refers to the tendency of a compound to acquire electrons or lose electrons and thereby be reduced or oxidised respectively. A reduction potential of a given compound may be expressed in volts (V). Typically, a reduction potential is defined relative to a reference electrode, such as a standard hydrogen electrode (SHE), which is assigned an arbitrary half-cell potential of 0.0 V.

Any suitable redox mediator that is compatible with the active materials and the solvent used in the tanks may be used, provided it has a reduction potential that is less than the reduction potential of the first active material and greater than the reduction potential of the second active material.

Suitable redox mediators may include, but are not limited to, hydroquinonesulfonic acid, anthraquinone-2,6-disulfonate, ferricyanide ($\text{M}_3\text{Fe}(\text{CN})_6$), ferrocyanide ($\text{M}_4\text{Fe}(\text{CN})_6$), ferrocene ($\text{C}_{10}\text{H}_{10}\text{Fe}$) and derivatives thereof, iodide (I $^-$) and combinations thereof, where in each case M is independently selected from the group consisting of Li, Na, K and NH_4 . As will be understood, when the active material contains lithium, M may preferably be Li and when the active material contains sodium, M may be Na. Any suitable concentration of the redox mediators may be used. For example, the total concentration of the redox mediator present in the solvent may be from 0.05 M to 1.5 M, such as from 0.1 M to 1 M, such as from 0.3 M to

0.5 M, such as 0.2 M. Derivatives of ferrocene that may be mentioned herein include ferrocene derivatives having the structure:



In the above formulae, X is selected from H, F, Cl, Br, I, NO₂, COOR, C₁₋₂₀ alkyl, CF₃, and COR, in which R is H or C₁₋₂₀ alkyl; n is from 0 to 20.

Specific derivatives of ferrocene that may be mentioned herein include but are not limited to bromoferrocene, ferrocenylmethyl dimethyl ethyl ammonium bis(trifluoromethanesulfonyl)imide (Fc1N112-TFSI), *N*-(pyridin-2-ylmethylene)-1-(2-(diphenylphosphino) ferrocenyl) ethanamine (FcP₂PPh₂RCN), 1,1-dimethylferrocene (DMFc), tetraferrocene, di(ethylsulfonic sodium) ferrocene (C₁₄H₁₆FeS₂O₆Na₂), and di(trimethanesulfonic sodium) ferrocene (C₁₆H₂₂FeS₂O₆Na₂).

In particular embodiments of the invention that may be mentioned herein, the derivative of ferrocene may be di(trimethanesulfonic sodium) ferrocene (C₁₆H₂₂FeS₂O₆Na₂) or di(ethylsulfonic sodium) ferrocene (C₁₄H₁₆FeS₂O₆Na₂).

Further redox mediators that may be used in the current invention are described below with reference to WO 2013/012391.

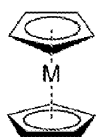
Further suitable redox mediators that may be mentioned herein include, but are not limited to (NH₄)₂S_x or, more particularly, viologens, Li₂S_x, Na₂S_x, and K₂S_x, wherein x is less than or equal to 8 and greater than or equal to 1.

Viologens are 1,1'-disubstituted 4,4'-bipyridinium ions (where the nitrogen atoms of the pyridine rings are substituted by an alkyl group (e.g. C₁ to C₁₂ alkyl)), with a suitable counterion (e.g. Cl⁻, F⁻, Br⁻ and I⁻). An example of a viologen of this type is paraquat. When used herein viologens may include related compounds, such as diquat and bipolaron.

Examples of redox mediators are discussed in depth in international application publication number WO 2013/012391, which is hereby incorporated by reference. For example, redox mediators disclosed in WO 2013/012391 include a metallocene derivative, a triarylamine

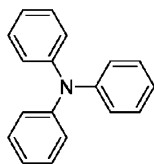
derivative, a phenothiazine derivative, a phenoxazine derivative, a carbazole derivative, a transition metal complex, an aromatic derivative, a nitroxide radical, a disulfide, or a combination thereof.

The metallocene derivative used as a redox mediator may have the following structure:



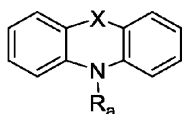
In the above formula, M can be Fe, Co, Ni, Cr, or V; each of the cyclopentadienyl rings, independently, can be substituted with one or more of the following groups: F, Cl, Br, I, NO₂, COOR, C₁₋₂₀ alkyl, CF₃, and COR, in which R can be H or C₁₋₂₀ alkyl.

The triarylamine derivative used as a redox mediator may have the following structure:



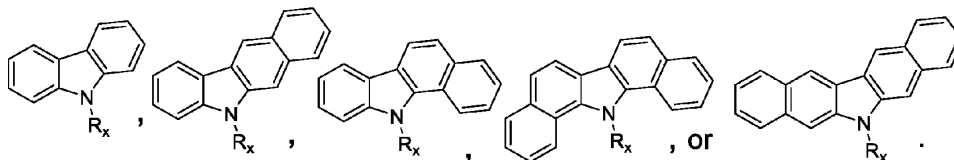
In the above formula, each of the phenyl rings, independently, can be substituted with one or more of the following groups: F, Cl, Br, I, NO₂, COOR, C₁₋₂₀ alkyl, CF₃, and COR, in which R can be H or C₁₋₂₀ alkyl.

The phenothiazine derivative and the phenoxazine derivative used as a redox mediator may have the following structure:



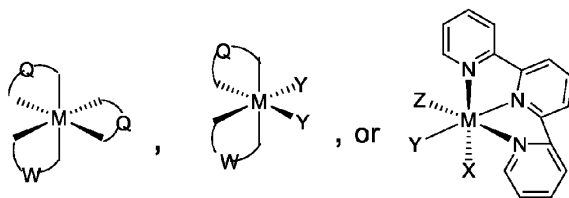
R_a can be H or C₁₋₂₀ alkyl, X can be O or S, each of the aromatic moieties is optionally substituted with one or more of the following groups: F, Cl, Br, I, NO₂, COOR, R, CF₃, and COR, in which R can be H or C₁₋₂₀ alkyl.

The carbazole derivative used as a redox mediator may have one of the following structures:

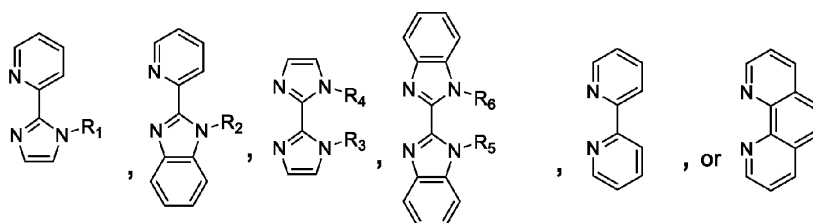


R_x can be H or C_{1-20} alkyl and each of the aromatic moieties is optionally substituted with one or more of the following groups: F, Cl, Br, I, NO_2 , $COOR$, C_{1-20} alkyl, CF_3 , and COR , in which R can be H or C_{1-20} alkyl.

The transition metal complex used as a redox mediator may have one of the following structures:



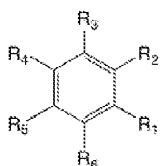
In the above formulae, M can be Co, Ni, Fe, Mn, Ru, or Os; each of the aromatic moieties is unsubstituted or is substituted with one or more of the following groups: F, Cl, Br, I, NO_2 , $COOR'$, R' , CF_3 , COR' , OR' , or $NR'R''$, each R' and R'' can independently be H or C_{1-20} alkyl; each of X, Y, and Z can independently be F, Cl, Br, I, NO_2 , CN, NCS, or NCO; and each Q and W can independently be selected from:



In these formulas, each of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 , can be F, Cl, Br, I, NO_2 , $COOR'$, R' , CF_3 , COR' , OR' , or $NR'R''$. Again, each of the aromatic moieties is optionally substituted with one or more of the following groups: F, Cl, Br, I, NO_2 , $COOR'$, C_{1-20} alkyl, CF_3 , COR' , OR' , or $NR'R''$, in which each of R' and R'' , independently, can be H or C_{1-20} alkyl. For the avoidance of doubt, the point of attachment of each Q and W to the metal is through the two nitrogen atoms present

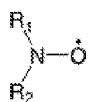
in each of the Q and W molecules above, thus Q and W act as bidentate ligands in the transition metal complex.

The aromatic derivative used as a redox mediator may have the following structure:



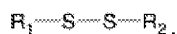
In these formulas, each of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 , can be C_{1-20} alkyl, F, Cl, Br, I, NO_2 , $COOR'$, CF_3 , COR' , OR' , $OP(OR')(OR'')$, or $NR'R''$, in which each of R' and R'' , independently, can be H, C_{1-20} alkyl.

The nitroxide radical used as a redox mediator may the following structure:



In these formulas, each of R_1 and R_2 , independently, can be C_{1-20} alkyl or aryl. R_1 , R_2 , and N together can form a heteroaryl, heteroaraalkyl, or heterocycloalkyl ring.

The disulfide used as a redox mediator may the following structure:



In these formulas, each of R_1 and R_2 , independently, can be C_{1-20} alkyl, $COOR'$, CF_3 , COR' , OR' , or $NR'R''$, in which each of R' and R'' , independently, can be H or C_{1-20} alkyl.

In certain embodiments, the redox mediator is hydroquinonesulfonic acid, anthraquinone-2,6-disulfonate, or a mixture thereof.

Any suitable concentration of the redox mediator may be used in the solvent present in the first tank. Examples of suitable concentrations include, but are not limited to, a total concentration of from about 0.01 M to about 1.5 M (e.g. 0.01 M to 1 M). When used herein,

the term "total concentration" is intended to mean that the sum of concentrations of redox mediators (when more than one redox mediator is present) fall within the cited range.

It is within the abilities of a person skilled in the art to select a suitable redox mediator based on the first and second active materials being processed according to the method of the present invention.

As will be appreciated, the method above also requires a solvent to be present in the tanks containing the active materials and the tank that collects the alkali metal ion to be recycled from said active materials. A suitable solvent is water, which may be used alone or in combination with an organic solvent suitable for use in a battery. Suitable organic solvents that may be mentioned herein include, but are not limited to a glyme solvent, a cyclic carbonate (such as propylene carbonate, ethylene carbonate, diethyl carbonate, butylene carbonate, fluoroethylene carbonate, chloroethylene carbonate, vinylene carbonate, and/or the like), a linear carbonate (such as dimethyl carbonate, diethyl carbonate, ethylmethyl carbonate, and the like), a cyclic ester (such as γ -butyrolactone, γ -valerolactone, and the like), a linear ester (such as methyl formate, methyl acetate, methyl butyrate, and the like), a cyclic or linear ether other than a glyme (such as tetrahydrofuran (and derivatives thereof), 1,3-dioxane, 1,4-dioxane, 1,2-dimethoxy ethane, 1,4-dibutoxyethane, and the like), a nitrile (such as acetonitrile, benzonitrile, and/or the like), dioxolane or a derivative thereof, ethylene sulfide, sulfolane, and sultone or a derivative thereof. These solvents may be used in any suitable weight ratio with respect to the glyme solvent (e.g. tetraglyme). For example, the additional solvents may be selected from one or more of the group selected from propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, ethyl methyl carbonate, tetrahydrofuran, sulfolane, and acetonitrile.

The glyme solvent may be selected from one or more of the group consisting of ethylene glycol dimethyl ether (monoglyme), diglyme, triglyme, tetraglyme, methyl nonafluorobutyl ether (MFE) and analogues thereof. Analogues of tetraglyme ($\text{CH}_3(\text{O}(\text{CH}_2)_2)_4\text{OCH}_3$) that may be mentioned include, but are not limited to, compounds where one or both of its CH_3 end members may be modified to either $-\text{C}_2\text{H}_5$ or to $-\text{CH}_2\text{CH}_2\text{Cl}$, or other similar substitutions. In certain embodiments of the invention that may be mentioned herein, the glyme solvent is tetraglyme.

In certain embodiments, the solvent in the first tank 11 is an aqueous acid solution. For example, the solvent may be an acetic acid solution (e.g. a 1 M, 2 M or 3 M acetic acid solution),

a nitric acid solution, a citric acid solution, a oxalic acid solution, a ascorbic acid solution, or a sulphuric acid solution (e.g. a 1 M to 3 M sulphuric acid solution).

In certain embodiments, the aqueous catholyte solution in the third tank 31 and/or fifth tank 51 is an aqueous alkali metal hydroxide solution, an aqueous alkali metal hydroxide solution comprising oxygen, an aqueous alkali metal hydroxide solution comprising air, an aqueous alkali metal hydroxide solution comprising oxygen and CO₂ with alkali metal carbonate precipitate, or an aqueous alkali metal hydroxide solution comprising air and CO₂ with alkali metal carbonate precipitate.

As noted above, the first and second active materials may come from a depleted (retired) battery or from the manufacturing processes to manufacture such batteries. Any form of the active materials may be used. For example, the active materials may still be attached to a electrode of a dismantled sodium- or lithium-ion battery or is provided free from the electrode.

Examples of suitable first active materials include, but are not limited to, LiNi_xCo_yMn_zO₂ (NCM, $0 \leq x, y, z < 1$), Li_xCoO₂ ($0 \leq x < 1$), LiNi_xCo_yAl_zO₂ (NCA, $x \geq 0.8$, $z \leq 0.05$ and $x + y + z = 1$), Li_xMn₂O₄ ($0 \leq x < 1$), Li_xNi_{0.5}Mn_{1.5}O₄ ($0 \leq x < 1$), NaCoO₂, or a mixture of two or more thereof.

Examples of suitable second active materials include, but are not limited to, Li_xFePO₄, NaFePO₄, NaV₂(PO₄)₃, or a mixture of two or more thereof.

Particular embodiments of the process described above are provided in the examples section below.

EXAMPLES

Example 1. Redox Mediator Selection

Stable RMs with reduction potentials between LCO and LFP should be used for bidirectional leaching. Here hydroquinonesulfonic acid was used as an example. The redox potential of hydroquinonesulfonic acid (HQS) was measured in 3 M acetic acid by cyclic voltammetry (CV) method. As shown in FIG. 3a, the redox potential of HQS is 0.64 V (vs. SHE), which is lower than that of LCO (0.89 V vs. SHE) and higher than that of LFP (0.39 V vs. SHE). This makes it suitable to be used as an RM for the bidirectional leaching of LCO and LFP together.

Example 2. Recycling Process of Spent LCO and LFP

Bidirectional Leaching of LCO and LFP

The bidirectional leaching of LCO and LFP was carried out in a reactor tank filled with 20 mL of 50 mM hydroquinonesulfonic acid in 3 M acetic acid solution. Spent LCO and LFP in a molar ratio of 1:1 was loaded into the tank. The reaction time was 24 h. After the reaction, LCO was dissolved in the electrolyte and LFP was decomposed into FP and Li^+ . The undissolved solids were subjected to X-ray powder diffraction (XRD) measurement to check their composition.

Removal of Co^{2+} and Li^+

After the leaching of LCO/LFP was finished, LiOH was added into the above leachate containing Li^+ , Co^{2+} and redox mediator. At $\text{pH} > 10$, Co^{2+} was completely precipitated as $\text{Co}(\text{OH})_2$, which was removed from the electrolyte solution by filtration to achieve the separation of cobalt ions.

The filtered solution containing Li^+ and RM (hydroquinonesulfonic) was directly used as electrolyte of the hydrogen flow electrolytic cell for Li^+ removal. A 3-compartment redox flow cell system was used with the detailed structure shown in FIG. 4a. A separate test with a two 2-compartment flow cell system with the structure shown in Figure 4(c) was also performed for comparison purpose.

Results and Discussions

XRD results of the undissolved solids shows it does not contain LCO or LFP, but only FP, which shows a complete leaching (FIG. 3b).

FIG. 4a shows the detailed structure of the 3-compartment redox flow system used. The average voltage plateau is around 1.70 V at a current density of 60 mA cm^{-2} (FIG. 4b).

In the separate test with the two 2-compartment redox flow cell system with the structure shown in FIG. 4c, the average voltage plateau was around 1.75 V and 0.05 V for the HER cell and HOR cell respectively at a current density of 50 mA cm^{-2} (FIG. 4d). The faradic efficiency reached as high as 92.4% by this approach from the ICP-OES measurements.

Example 3. Chemical Purification Process of FePO_4 (FP)

Together with binder, carbon black and other impurities, FP was collected prior to the Co^{2+} precipitation described in Example 1. Herein a chemical purification method for FP according to the different solubilities of FP in acid and alkali was used. The flowchart in FIG. 5 illustrates the recycling process sequentially with the dissolution and precipitation of impure FP.

Purification Process of FePO_4 (FP)

The impurity-containing FP is firstly added to an acid solution ($\text{pH} \leq 2$), the FP is dissolved in the acid while the impurities remain. Then the impurities are filtrated, and the leachate is poured into an alkaline solution to reprecipitate the FP. After centrifugation and washings, high-purity FP can be obtained.

Results and Discussions

This process is conducted at room temperature with several steps and is therefore energy-efficient and easy to implement. The proposed method can be used for the recycling of FP from spent LFP material generated in LIBs industry, because most impurities are binders and carbon black, which are insoluble in the acid solution and thereby quite easy to be filtrated. The purified FP can be used for the resynthesis of LFP, which could alleviate the global phosphorus demand caused by the decommissioning of LFP batteries.

Example 4. A 3-Compartment Flow Cell Electrochemical Configuration for Recycling Process of FePO_4 (FP)

Recycling of FP could also be accomplished with two different electrochemical configurations, requiring only water and electricity supplies and no additional continuous consumption of acid and alkali, thus reducing the environmental impact and overall cost of FP whole recycling process.

General Setup of a 3-Compartment Flow Cell for the Recycling Process of FePO_4 (FP)

The setup comprises a flow cell with three compartments as shown in FIG. 6. At the anode, both hydrogen and NaCl solution are supplied, and HOR takes place at the catalyst site and releases protons. These protons dissolve in the flowing NaCl solution and combine with Cl^- transported from the middle compartment through the anion exchange membrane (AEM) to form HCl. With increasing acid concentration and at $\text{pH} < 2$, the solution can be used to dissolve the FP from the black mass. At the cathode, HER occurs with the assistance of catalyst. The generated OH^- will combine with Na^+ passing through the cation exchange membrane (CEM) from the middle compartment to form NaOH. The accumulation of OH^- contributes to an increased pH of the cathodic NaCl solution, which can be used to re-precipitate the FP dissolved in the acid solution from the anode side. Furthermore, hydrogen produced at the cathode can feed back to the anode side to compensate for the consumption of H_2 during HOR. The cation and anion exchange membranes in the flow cell allow the transportation of Na^+ and Cl^- from the middle compartment to achieve a charge neutrality in the three compartments.

Demonstration of a 3-Compartment Flow Cell for the Recycling Process of FePO₄ (FP)

To confirm the feasibility of the proposed strategy, a flow cell with 10 mL of 2 M NaCl as anolyte (supply H₂), 10 mL of 2 M NaCl as catholyte and 10 mL 2 M NaCl as middle compartment electrolyte was assembled. An AEM (AMV) near the anode compartment and a CEM (Nafion 212) near the cathode compartment were used in the cell. Pt/C coated SGL carbon paper was used as the anode and cathode electrode for HOR and HER. In addition, SGL carbon felt was used in the middle and anode compartments to prevent the excessive deformation of the membrane.

Results and Discussions

It can be seen from FIG. 7 that the cell could work steadily at 100 mA/cm² with a voltage of around 1.90 V. The slight decline of operation voltage may result from a reduction of membrane resistance due to the activation and wettability process of the membrane. After charging, the pH of the anolyte, electrolyte of the middle compartment and catholyte were determined to be -0.38, 0.27 and 13.32, respectively. The decrease in pH at the middle compartment indicates that some protons generated at the anode side migrate to the middle part through the CEM. Nonetheless, the concentrations of the obtained acid and alkaline solutions were sufficient to dissolve and precipitate FP.

FIG. 8 shows the purification of the FP from the Li-extracted black mass using the acid and alkali solutions obtained from the cell above. The FP in the black mass was successfully dissolved (FIG. 8b) and re-precipitated (FIG. 8d) with the assistance of the corresponding solution.

Example 5. Two 2-Compartment Flow Cell Electrochemical Configuration for Recycling Process of FePO₄ (FP)

In the device in Example 4, the current density is limited by the high resistance of the two membranes and multiple cell compartments, which will then hinder the production rate of protons and ⁻OH. To further increase the current density and speed up HER and HOR, the above three-compartment cell configuration can be separated into two individual cells with decoupled HER and HOR (FIG. 9). Both cells share the same electrolyte solution consisting of NaCl and a redox mediator (RM), which function as the anolyte in the HOR cell and catholyte in the HER cell.

Setup of the Two 2-Compartment Flow Cell System

Herein, anthraquinone-2,6-disulfonate (AQDS) is used as redox mediator. For the shared electrolyte, RM (in NaCl solution) is firstly oxidized at the anode electrode of the HOR cell (left

side), and then flow into the cathode of HER cell (right side) to participate in the reduction reaction. During the operation, Cl^- is transferred to the HOR side through AEM (AMV), while Na^+ is transferred to the HER side through CEM (Nafion 212) to balance the charges of the electrolyte of the two cells.

The catholyte of the HOR cell is dry H_2 and 10 mL of 2 M NaCl and the anolyte of the HER cell is 10 mL of 2 M NaCl. The hydrogen generated in HER can feed back to the HOR cell to compensate the hydrogen consumption.

Results and Discussions

In this design, only one membrane was used in each cell, enabling a more compact configuration without the need of the middle chamber. In principle, a higher current density can be achieved, which is beneficial also for the commercial application of this FP recovery method.

Example 6. Recycling Process Involving Redox Inactive Lithium Compounds

As LCO and LFP black mass usually contain other redox inactive lithium compounds, such as Li_3PO_4 , a strong acid, e.g. sulfuric acid can be used to replace the acetic acid in the leaching step in order to dissolve these species. With strong acid and redox mediator, the black mass is then decomposed into Li^+ , Co^{2+} , Fe^{3+} and PO_4^{3-} . By adjusting pH with addition of LiOH, Fe^{3+} and Co^{2+} can be precipitated sequentially as FePO_4 at pH=2 and $\text{Co}(\text{OH})_2$ at pH=10. Li^+ in the leachate can be similarly removed and collected as LiOH using the methods disclosed herein. After lithium removal, the pH of the electrolyte should be recovered as that before leaching. See FIG. 10.

Another case involves only the LFP black mass containing redox inactive lithium compounds. As shown in FIG. 11, in this case, a hydrogen looping system can be applied. In this case, two electrolyzers (A and B), A with an AEM and B with a CEM are required. As an example, LiCl solution is used as electrolyte in reactor tank I together with a suitable RM which shares by the two electrolyzers. Upon operation, HOR reaction happens in the anodic side of electrolyser A which drives Cl^- in reactor tank I across the AEM to form HCl with the H^+ produced by HOR in reactor tank III. HER occurs in the cathodic side of electrolyser B which produces OH^- and simultaneously drives Li^+ in reactor tank I across the CEM to form LiOH in reactor tank II. The RM is reduced in electrolyser A and oxidized in electrolyser B. In reactor tank III, LFP black mass together with the redox inactive lithium compounds is preloaded and leached by HCl to form Li^+ and insoluble HFePO_4 . The leachate is then pumped into tank IV where air is bubbled at alleviated temperature. Upon oxidation by O_2 , HFePO_4 will be dissolved into Fe^{3+} and

HPO_4^{2-} , and the leachate is pumped into tank V where part of LiOH obtained in tank II is added to precipitate the FePO_4 at $\text{pH}=2$. The electrolyte containing LiCl is then pumped back into tank I to replenish the Li^+ and Cl^- in the tank to achieve a continuous operation. Li^+ from LFP is recovered as the excess LiOH obtained in reactor tank II.

CLAIMS

1. A method of recovering one or more metals from at least two active materials obtained from an alkali metal ion battery, the method comprising:

(a) providing a first active material and a second active material, each of the active materials comprising alkali metal ions, the first active material having a reduction potential greater than the reduction potential of the second active material;

(b) adding the first and second active materials to a redox mediator solution that comprises a solvent and a redox mediator to form a redox mediator solution comprising alkali metal ions in a first tank,

wherein the redox mediator has a reduction potential that is less than the reduction potential of the first active material and greater than the reduction potential of the second active material, such that the redox mediator reduces the first active material and oxidises the second active material, thereby releasing the alkali metal ions from the first and second active materials;

(c) (i) once substantially all the first active material is reduced and/or substantially all the second active material is oxidised, moving the redox mediator solution from the first tank to a second tank, the second tank being fluidly connected to a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply; or

(ii) once substantially all the second active material is oxidised, or substantially all the first active material is reduced and substantially all the second active material is oxidised, moving the redox mediator solution from the first tank to a second tank, the second tank being fluidly connected to a redox flow cell comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply;

(d) moving the redox mediator solution from the second tank through the redox flow cell, thereby enabling transport of the alkali metal ions through the ion selective membrane into the cathode compartment which comprises an aqueous catholyte solution;

(e) capturing the alkali metal ions as an alkali metal hydroxide in the cathode compartment through an electrochemical reaction on the cathode electrode and transferring the resulting aqueous catholyte solution containing the alkali metal hydroxide to a third tank;

provided that when the method comprises step (c)(i), the redox flow cell comprises a central compartment disposed between the anode and cathode compartments and separated from the anode compartment by a first ion selective membrane and separated from the

cathode compartment by a second ion selective membrane, and step (d) comprises moving the redox mediator solution from the second tank to the central compartment of the redox flow cell enabling transport of the alkali metal ions through the second ion selective membrane into the cathode compartment; and

provided that when the method comprises step (c)(ii), the first and second active materials are present in the redox mediator solution in step (b) at equimolar amounts relative to each other, or the first active material is present in the redox mediator solution in step (b) at a molar excess relative to the second active material.

2. The method according to claim 1, wherein the redox mediator solution that has moved through the redox flow cell is returned to the second tank, followed by repeating steps (d) and (c) until substantially all the alkali metal ions are captured as the alkali metal hydroxide in the cathode compartment.

3. The method according to claim 1 or claim 2, wherein the pH of the redox mediator solution in the first tank is maintained at a pH of less than about 4.

4. The method according to any one of claims 1-3, wherein the pH of the redox mediator solution in the second tank is adjusted to greater than about 4.

5. The method according to claim 4, wherein the pH of the redox mediator solution in the second tank is adjusted to a pH of from about 5 to about 6 (e.g. about 5.5), and then adjusted to a pH of from about 10 to about 12 (e.g. about 11).

6. The method according to claim 4 or 5, wherein the pH is adjusted by addition of the alkali metal hydroxide into the second tank.

7. The method according to any one of the preceding claims, wherein when the method comprises step (c)(ii), the redox flow cell comprises a central compartment disposed between the anode and cathode compartments and separated from the anode compartment by a first ion selective membrane and separated from the cathode compartment by a second ion selective membrane, and

wherein step (d) comprises moving the redox mediator solution from the second tank to the central compartment of the redox flow cell enabling transport of the alkali metal ions through the second ion selective membrane into the cathode compartment.

8. The method according to claim 7, or the method according to any one of clauses 1-6 when the method comprises step (c)(i), wherein a hydrogen oxidation reaction (HOR) or oxygen evolution reaction (OER) on the anode electrode produces H^+ ions which are transported through the first ion selective membrane into the central compartment of the redox flow cell.

9. The method according to claim 7 or 8, wherein the anode compartment is supplied with hydrogen gas, and wherein a HOR on the anode electrode produces H^+ ions which are transported through the first ion selective membrane into the central compartment of the redox flow cell.

10. The method according to any one of the preceding claims, wherein the first tank contains the first and second active materials at equimolar amounts relative to each other.

11. The method according to any one of claims 1 to 9, wherein the first tank contains a molar excess of the first active material relative to the second active material, and wherein the method further comprises a step following step b) and before step c) of:

(I) moving the redox mediator solution through a redox flow cell fluidly connected to the first tank and comprising a cathode compartment, having a cathode electrode, and an anode compartment, having an anode electrode, separated by an ion selective membrane, where the cathode electrode and anode electrode are attached to a power supply, and

the redox mediator solution is subjected to an electrochemical reaction on the cathode electrode, where the electrochemical reaction on the cathode electrode:

reduces the redox mediator, which is then returned to the first tank to reduce any remaining first active material;

step (I) being optionally repeated until substantially all the first active material is reduced.

12. The method according to claim 11, wherein, once substantially all the first active material is reduced, the redox mediator solution in the first tank is moved to the second tank according to step c).

13. The method according to claim 11 or 12, wherein a HOR or OER on the anode electrode of redox flow cell fluidly connected to the first tank produces H^+ ions which are transported through the ion selective membrane into the cathode compartment and to the first tank.

14. The method according to any one of the preceding claims, wherein the electrochemical reaction on the cathode electrode in step (e) is a hydrogen evolution reaction (HER) or oxygen reduction reaction (ORR) which produces OH^- ions.

15. The method according to any one of the preceding claims, wherein the solvent is an aqueous acid solution, for example an acetic acid solution, a nitric acid solution, citric acid solution, oxalic acid solution, ascorbic acid solution, or sulphuric acid solution.

16. The method according to claim 15, wherein the aqueous acid solution is an acetic acid solution (e.g. a 3 M acetic acid solution) or a sulphuric acid solution (e.g. a 1 M to 3 M sulphuric acid solution).

17. The method according to any one of the preceding claims, wherein the aqueous catholyte solution in step d) is initially selected from one of water, water comprising oxygen, water comprising air, water comprising oxygen and CO_2 , or water comprising air and CO_2 .

18. The method according to any one of the preceding claims, wherein after step (e), the aqueous catholyte solution is an aqueous alkali metal hydroxide solution, an aqueous alkali metal hydroxide solution comprising oxygen, an aqueous alkali metal hydroxide solution comprising air, an aqueous alkali metal hydroxide solution comprising oxygen and CO_2 with alkali metal carbonate precipitate, or an aqueous alkali metal hydroxide solution comprising air and CO_2 with alkali metal carbonate precipitate.

19. The method according to any one of the preceding claims, wherein the the alkali metal ions in the first and second active materials are lithium, sodium, potassium or calcium ions.

20. The method according to any one of the preceding claims, wherein the alkali metal in the first and second active materials are lithium ions, the alkali metal hydroxide is LiOH , and the alkali metal carbonate precipitate in clause 18 is Li_2CO_3 .

21. The method according to any one of the preceding claims, wherein the first active material is $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM, $0 \leq x, y, z < 1$), Li_xCoO_2 ($0 \leq x < 1$), $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA, $x \geq 0.8$, $z \leq 0.05$ and $x + y + z = 1$), $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0 \leq x < 1$), $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($0 \leq x < 1$), or a mixture of two or more thereof.

22. The method according to any one of the preceding claims, wherein the first active material is LiCoO_2 .

23. The method according to claim 22, wherein a precipitate of $\text{Co}(\text{OH})_2$ is collected from the second tank.
24. The method according to any one of claims 1-21, wherein the first active material is $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM, $0 \leq x, y, z < 1$).
25. The method according to claim 24, wherein a precipitate of $\text{Ni}_x\text{Co}_y\text{Mn}_z(\text{OH})_2$ is collected from the second tank.
26. The method according to any one of the preceding claims, wherein the second active material is LiFePO_4 .
27. The method according to claim 26, wherein a precipitate of FePO_4 is collected from the first tank and/or second tank.
28. The method according to claim 27, wherein the precipitate of FePO_4 is collected from the first tank and/or second tank and subjected to a purification process to remove impurities, such as carbon-conductive additives (e.g. carbon black) and binders (e.g. PVDF).
29. The method according to any one of claims 1 to 19, wherein the alkali metal ions in the first and second active materials are sodium ions, the alkali metal hydroxide is NaOH , and the alkali metal hydroxide and alkali metal carbonate precipitate in clause 18 are NaOH and NaCO_3 or NaHCO_3 , respectively.
30. The method according to any one of claims 1 to 19 or 29, wherein the first active material is NaCoO_2 .
31. The method according to any one of claims 1 to 19, 29 or 30, wherein the second active material is NaFePO_4 , $\text{NaV}_2(\text{PO}_4)_3$, or a mixture thereof.
32. The method according to any one of the preceding claims, wherein the redox mediator is hydroquinonesulfonic acid, anthraquinone-2,6-disulfonate, or mixture thereof.
33. The method according to any one of the preceding claims, wherein the total concentration of the redox mediator present in the redox mediator solution in the first tank is from about 0.01 M to about 1 M.

34. The method according to any one of the preceding claims, wherein the first and/or second active material is/are attached to an electrode of a dismantled battery or provided free from the electrode.