

(19)



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie

(11)

N° de publication :

LU509199

(12)

BREVET D'INVENTION

B1

(21)

N° de dépôt: LU509199

(51)

Int. Cl.:
H01M 10/42, H01M 10/54

(22)

Date de dépôt: 04/12/2024

(30)

Priorité:
25/09/2024 CN 202411341092.X

(72)

Inventeur(s):
AN Yong – China

(43)

Date de mise à disposition du public: 05/06/2025

(74)

Mandataire(s):
IP SHIELD – 1616 Luxembourg (Luxembourg)

(47)

Date de délivrance: 05/06/2025

(73)

Titulaire(s):
CHONGQING VOCATIONAL INSTITUTE OF
ENGINEERING – 402260 Chongqing (China)

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REPAIR SOLUTION AND AN IN-SITU REPAIR AND REGENERATION METHOD FOR SPENT LITHIUM IRON PHOSPHATE BATTERIES.

(57)

The present invention discloses a repair solution and an in-situ repair and regeneration method for spent lithium iron phosphate batteries. The in-situ repair and regeneration method for spent lithium iron phosphate batteries includes the following steps: S100, performing deep discharge of the spent lithium iron phosphate batteries using a small current, with a discharge rate of 0.001C-0.5C and a cut-off discharge voltage of 2.0-2.6V; S200, preparing the repair solution; S100 and S200 are not required to follow a specific sequence; S300, injecting the repair solution into the battery; S400, charging the battery to a fully charged state using a small current, with a charging rate of 0.001C-0.5C and a cut-off charging voltage of 3.6-4.0V; S500, repeating S100 and S400. This invention does not require the disassembly of the battery followed by calcination and reassembly processes, enabling the in-situ repair and regeneration of spent lithium iron phosphate batteries. It eliminates the need for complex processes such as disassembly, acid washing, alkali washing, high-temperature calcination, and battery reassembly. Consequently, the method is simple, energy-efficient, effective in repair, and highly efficient. Furthermore, the crystal structure of the cathode is restored, the cycling performance of the battery is enhanced, and the overall cost is low.

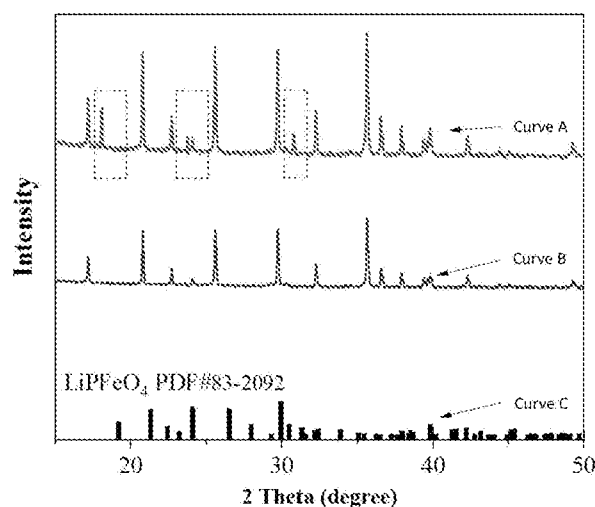


FIG.1

REPAIR SOLUTION AND AN IN-SITU REPAIR AND REGENERATION METHOD FOR SPENT LITHIUM IRON PHOSPHATE BATTERIES

Technical Field

5 The present invention relates to the field of lithium battery recycling and reuse, particularly to a repair solution and an in-situ repair and regeneration method for spent lithium iron phosphate batteries.

Background Technology

10 With the growing market demand for lithium iron phosphate (LiFePO_4 or LFP) batteries, the handling of spent batteries has become a significant challenge. Currently, the recycling and regeneration methods for lithium iron phosphate batteries are as follows:

15 First, the battery is physically disassembled to separate the mixed electrode powder, battery casing, copper foil, aluminum foil, and separator.

20 Second, the separated mixed electrode powder is dissolved in an alkaline solution to remove residual aluminum (Al) elements. It is then placed in an organic acid solution of a specific concentration to leach lithium (Li), iron (Fe), and phosphate (PO_4^{3-}), followed by filtration to remove insoluble graphite, thereby separating the cathode material from the anode graphite material.

25 Third, a certain proportion of lithium source is directly added to the spent lithium iron phosphate material and regenerated into lithium iron phosphate cathode material through high-temperature calcination.

30 These methods are complex, consume large amounts of acids and bases, and require high-temperature calcination, leading to significant energy consumption. Therefore, for the recycling and upgrading of lithium iron phosphate batteries, it is urgently necessary to find more suitable methods.

Summary of the Invention

35 In view of the deficiencies in the prior art, the technical problem to be solved by the present invention is to provide a repair solution and an in-situ repair and

regeneration method for spent lithium iron phosphate batteries, characterized by a simple process, low energy consumption, and low cost.

To achieve the above objective, the present invention provides a repair solution comprising lithium salt, organic solvent, anode film-forming additives, and redox mediators. Using the organic solvent as a carrier, lithium salt, anode film-forming additives, and redox mediators are added sequentially, stirred evenly, and dissolved to achieve a lithium salt concentration of 0.1-5 mol/L, a mass fraction of the redox mediators of 0.01-3%, and a volume of the anode film-forming additive accounting for 0.1-10% of the total liquid volume.

The lithium salt is selected from one or any combination of lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium difluoro(oxalato)borate (LiODFB), lithium bis(oxalate)borate (LiBOB), lithium difluorophosphate (LiPO_2F_2), lithium hexafluorophosphate (LiPF_6), or lithium tetrafluoroborate (LiBF_4).

The organic solvent is selected from one or any combination of ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), or ethyl acetate (EA).

The anode film-forming additive is selected from one or any combination of vinylene carbonate (VC), fluoroethylene carbonate (FEC), vinyl ethylene carbonate (VEC), or 1,3-propane sultone (PS).

The redox mediator is selected from one or any combination of iodine (I_2), lithium iodide (LiI), copper iodide (CuI_2), cuprous iodide (CuI), or stannous iodide (SnI_2).

The role of the iodides in this context is based on the following principles:

$3\text{I}^- + 2\text{FePO}_4 + 2\text{Li}^+ \rightarrow 2\text{LiFePO}_4 + \text{I}_3^-$: In this process, the iodide ions in the repair solution react with ferric phosphate (FePO_4) produced at the cathode to form lithium iron phosphate (LiFePO_4), while generating triiodide ions (I_3^-).

$3\text{I}^- - 2\text{e}^- \rightarrow \text{I}_3^-$: In this process, the iodide ions in the repair solution are oxidized to form triiodide ions.

$\text{I}_3^- + 2\text{Li}^0 \rightarrow 2\text{Li}^+ + 3\text{I}^-$: In this process, the triiodide ions react with inactive lithium metal (Li^0), regenerating electrochemically active lithium ions (Li^+).

The present invention also discloses an in-situ repair and regeneration method for lithium iron phosphate batteries, comprising the following steps:

S100: Deep discharge of the spent lithium iron phosphate battery using a small current, with a discharge rate of 0.001C-0.5C and a cut-off voltage of 2.0-2.6V. The underlying principle is that after long-term cycling, the solid electrolyte interphase (SEI) layer on the battery anode thickens, consuming part of the Li^+ ions and transforming them into electrochemically inactive components. The purpose of this step is to partially decompose the SEI layer on the anode, releasing lithium ions and electrons.

S200: Preparing the repair solution. Steps S100 and S200 are not required to follow a specific sequence.

S300: Injecting the repair solution into the battery and allowing it to rest alternately on its positive and negative sides for a preset duration. The ratio of the repair solution mass to the nominal capacity of the battery is 0.1-5.00 g/Ah. This step is preferably performed in a low-humidity environment, with a dew point temperature $\leq -40^\circ\text{C}$. Initially, a hole is created on the battery cap with an area of less than 2 mm^2 , after which a specified amount of repair solution is injected, and the hole is sealed. Once sealed, the battery is rested alternately on its positive and negative sides for 12 hours each. Alternatively, it is also possible to inject the repair solution without creating a hole, as long as the solution can be added into the battery. The resting duration is not strictly limited; theoretically, any duration sufficient to achieve the repair effects described in this invention can be used. For practical implementation, while 12 hours each side is an empirical value, durations such as 9, 10, 11, 13, 14, 15, 20 hours or longer can be selected based on specific needs.

S400: Charging the battery to a fully charged state using a small current, with a charging rate of 0.001C-0.5C and a cut-off voltage of 3.6-4.0V. The purpose of this step is to replenish the lithium loss in the cathode, reduce Fe(III) to Fe(II) in the cathode, and eliminate antsite defects.

S500: Repeating steps S100 and S400 for 1-10 cycles. In practical implementation, the number of repetitions can be selected to achieve the desired repair effects. Theoretically, the number of repetitions is not limited.

The beneficial effects of the present invention are:

The present invention does not require disassembly, calcination, or reassembly of the battery, enabling in-situ repair and regeneration of spent lithium iron phosphate batteries. It eliminates complex processes such as disassembly, acid washing, alkali

washing, high-temperature calcination, and reassembly, resulting in a simple process with low energy consumption. Actual testing demonstrates that the invention has excellent repair effects, high efficiency, and achieves restoration of the cathode crystal structure, enhancing the cycling performance of the battery. Furthermore, the cost is significantly lower than that of existing technologies, making it better suited for the recycling, repair, and reuse of existing lithium iron phosphate batteries. The invention holds great technical value, economic benefits, and market application potential.

Description of the Drawings

Figure 1: an X-ray diffraction (XRD) pattern obtained by disassembling the battery in Example 7 and Comparative Example 2, extracting the lithium iron phosphate cathode sheets, and scraping off the powder for testing.

Detailed Embodiments

The following describes the technical solutions of the embodiments of the present invention clearly and completely with reference to the accompanying drawings.

Example 1:

A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 10.1Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.001C to 2.6V.

S200: Preparation of the repair solution:

S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC:EMC:EA = 1:1:1:1:0.5:0.5.

S220: LiPF_6 , (FEC, PS), and I_2 were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 1 mol/L, I_2 at a mass fraction of 0.01%, and FEC and PS accounting for 1% and 2%, respectively, of the total liquid volume. The repair solution preparation aimed only to achieve the specified component proportions and does not involve any specific process design; theoretically, as long as the solution with the required composition and proportions is achieved, the steps can

be flexible.

S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 15g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.01C to a voltage of 3.65V.

S500: Steps S100 and S400 were repeated 5 times.

Example 2:

A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 10.3Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.01C to 2.5V.

S200: Preparation of the repair solution:

S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC:EMC = 1:1:1:1.

S220: LiPF_6 , (VC, FEC, PS), and CuI_2 were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 1 mol/L, CuI_2 at a mass fraction of 1.5%, and VC, FEC, and PS accounting for 3%, 3%, and 4%, respectively, of the total liquid volume.

S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 45g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.1C to a voltage of 3.65V.

S500: Steps S100 and S400 were repeated 6 times.

Example 3:

A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 11.6Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.01C to 2.1V.

S200: Preparation of the repair solution:

S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC:EMC = 1:1:1:1.

5 S220: (LiPF_6 , LiFSI), VC, and CuI_2 were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 1 mol/L, LiFSI at 0.2 mol/L, CuI_2 at a mass fraction of 2%, and VC accounting for 3% of the total liquid volume.

10 S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 5g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.001C to a voltage of 3.65V.

S500: Steps S100 and S400 were repeated 5 times.

Example 4:

15 A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 10.6Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.01C to 2.2V.

S200: Preparation of the repair solution:

20 S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC = 1:1:1.

S220: LiPF_6 , FEC, and LiI were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 0.5 mol/L, LiI at a mass fraction of 0.01%, and FEC accounting for 5% of the total liquid volume.

25 S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 75g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.1C to a voltage of 3.7V.

30 S500: Steps S100 and S400 were repeated 5 times.

Example 5:

A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell)

recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 9.7Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.5C to 2.0V.

5 S200: Preparation of the repair solution:

S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC = 1:1:1.

10 S220: LiPF_6 , FEC, (SnI_2 , LiI) were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 0.1 mol/L, SnI_2 and LiI at a mass fraction of 1% each, and FEC accounting for 2% of the total liquid volume.

S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 2g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

15 S400: The battery was charged at a rate of 1.0C to a voltage of 3.7V.

S500: Steps S100 and S400 were repeated 5 times.

Example 6:

20 A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 9.8Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.01C to 2.1V.

S200: Preparation of the repair solution:

25 S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC = 1:1.

S220: LiPF_6 , FEC, and SnI_2 were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 3 mol/L, SnI_2 at a mass fraction of 3%, and FEC accounting for 5% of the total liquid volume.

30 S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 1.5g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.5C to a voltage of 4V.

S500: Steps S100 and S400 were repeated 9 times.

Example 7:

5 A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 10.1Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.01C to 2.2V.

S200: Preparation of the repair solution:

10 S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC = 1:1:1.

S220: LiPF_6 , (VC, FEC, PS), and LiI were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 1 mol/L, LiI at a mass fraction of 0.5%, and VC, FEC, and PS each accounting for 1% of the total liquid volume.

15 S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 5g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.01C to a voltage of 3.8V.

20 S500: Steps S100 and S400 were repeated 10 times.

Example 8:

A rectangular aluminum-shell lithium iron phosphate battery (Gotion-15Ah cell) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., with an initial discharge capacity of 10.9Ah, was used.

25 S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.01C to 2.2V.

S200: Preparation of the repair solution:

S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC = 1:1:1.

30 S220: LiPF_6 , (VC, FEC, PS), and LiI were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 1 mol/L, LiI at a mass fraction of 0.5%, and VC, FEC, and PS each accounting for 1% of the total liquid volume.

S300: In an environment with a dew point temperature of -40°C , a hole with an area of 1mm^2 was created on the battery cap. Then, 5g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

5 S400: The battery was charged at a rate of 0.01C to a voltage of 3.8V.

S500: Steps S100 and S400 were repeated 10 times.

Example 9:

10 A rectangular aluminum-shell lithium iron phosphate battery (EVE-30Ah cell) recycled from Huizhou EVE Energy Co., Ltd., with an initial discharge capacity of 25Ah, was used.

S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.1C to 2.3V.

S200: Preparation of the repair solution:

15 S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC:EMC = 1:1:1:1.

S220: LiTFSI, VC, and CuI_2 were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiTFSI at 1 mol/L, CuI_2 at a mass fraction of 1.5%, and VC accounting for 3% of the total liquid volume.

20 S300: In an environment with a dew point temperature of -40°C , a hole with an area of 2mm^2 was created on the battery cap. Then, 3g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.01C to a voltage of 3.65V.

S500: Steps S100 and S400 were repeated 6 times.

25 **Example 10:**

A rectangular aluminum-shell lithium iron phosphate battery (EVE-30Ah cell) recycled from Huizhou EVE Energy Co., Ltd., with an initial discharge capacity of 18Ah, was used.

30 S100: The lithium iron phosphate battery was deeply discharged at a rate of 0.5C to 2.2V.

S200: Preparation of the repair solution:

S210: Preparation of the organic solvent by mixing the following components

uniformly in the specified volume ratio: EC:DMC:DEC:EMC = 1:1:1:1.

S220: (LiBF₄, LiODFB), VEC, and SnI₂ were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiBF₄ and LiODFB each at 0.5 mol/L, SnI₂ at a mass fraction of 2%, and VEC accounting for 2% of the total liquid volume.

S300: In an environment with a dew point temperature of -40°C, a hole with an area of 2mm² was created on the battery cap. Then, 15g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.5C to a voltage of 3.8V.

S500: Steps S100 and S400 were repeated 10 times.

Comparative Example 1:

A commercially available rectangular aluminum-shell lithium iron phosphate battery (15Ah) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., as used in Example 1, was used, with an initial discharge capacity of 10.2Ah. No further treatment was performed.

Comparative Example 2:

A commercially available rectangular aluminum-shell lithium iron phosphate battery (15Ah) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., as used in Example 2, was used, with an initial discharge capacity of 10.6Ah. No further treatment was performed.

Comparative Example 3:

A commercially available rectangular aluminum-shell lithium iron phosphate battery (15Ah) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., as used in Example 9, was used, with an initial discharge capacity of 10.8Ah. The battery was subjected to the following comparative steps:

S100: The battery was deeply discharged at a rate of 0.01C to 2.2V.

S400: The battery was charged at a rate of 0.01C to a voltage of 3.8V.

S500: Steps S100 and S400 were repeated 10 times.

Comparative Example 4:

A commercially available rectangular aluminum-shell lithium iron phosphate battery (15Ah) recycled from Hefei Gotion High-Tech Battery Technology Co., Ltd., as

used in Example 8, was used, with an initial discharge capacity of 10.8Ah. The battery was subjected to the following comparative steps:

S100: The battery was deeply discharged at a rate of 0.01C to 2.8V.

S200: Preparation of the repair solution:

5 S210: Preparation of the organic solvent by mixing the following components uniformly in the specified volume ratio: EC:DMC:DEC = 1:1:1.

S220: LiPF_6 , (VC, FEC, PS), and LiI were added to the organic solvent, stirred evenly, and dissolved. The final concentrations were: LiPF_6 at 1 mol/L, LiI at a mass fraction of 0.5%, and VC, FEC, and PS each accounting for 1% of the total liquid volume.

10 S300: In an environment with a dew point temperature of -40°C , a hole with an area of 2mm^2 was created on the battery cap. Then, 5g of repair solution was injected into the battery, and the hole was sealed. The battery was rested alternately on its positive and negative sides for 12 hours each.

S400: The battery was charged at a rate of 0.01C to a voltage of 3.8V.

15 S500: Steps S100 and S400 were repeated once.

Comparative Example 5:

A rectangular aluminum-shell lithium iron phosphate battery (30Ah, EVE-30Ah cell) recycled from Huizhou EVE Energy Co., Ltd., as used in Example 10, was used, with an initial discharge capacity of 19.7Ah. No further treatment was performed.

20 The parameter statistics for the implementation process of Examples 1-10 and Comparative Examples 1-5 are summarized in Table 1.

Table 1: Parameters of the Example and Comparison Process summarizing the key details

	Initial Capacity	S100 Discharge Rate & Voltage	S200 Repair Solution Composition	S300 Repair Solution Amount	S400 Charge Rate & Voltage	S500 Repetition Count
Example 1	10.1Ah	0.001C 2.6V	EC:DMC:DEC:EMC:EA=1:1:1:1:0.5:0.5; 1mol/L, LiPF_6 ; 1%FEC+2%PS; 0.01% I_2	15g	0.01C 3.65V	5
Example	10.3A	0.01C	EC:DMC:DEC:EMC=1:1:1:1;	45g	0.1C	6

2	h	2.5V	1mol/L, LiPF ₆ ; 3%VC+3%FEC+4%PS; 1.5%CuI ₂		3.65V	U509199
Example 3	11.6Ah	0.01C 2.1V	EC:DMC:DEC:EMC=1:1:1:1; 1mol/L, LiPF ₆ +0.2mol/LiFSI; 3%VC; 2.0%CuI ₂	5g	0.001C 3.65V	5
Example 4	10.6Ah	0.01C 2.2V	EC:DMC:DEC=1:1:1; 0.5mol/L, LiPF ₆ ; 5%FEC; 0.01%LiI	75g	0.1C 3.7V	5
Example 5	9.7Ah	0.5C 2.0V	EC:DMC:DEC=1:1:1; 0.1mol/L, LiPF ₆ ; 5%FEC; 1%SnI ₂ +1%LiI	2g	1.0C 3.7V	5
Example 6	9.8Ah	0.01C 2.1V	EC:DMC=1:1; 3mol/L, LiPF ₆ ; 5%FEC; 3%SnI ₂	1.5g	0.5C 4.0V	9
Example 7	10.1Ah	0.01C 2.2V	EC:DMC:DEC=1:1:1; 1mol/L, LiPF ₆ ; 1%VC+1%FEC+1%PS; 0.5%LiI	5.0g	0.1C 3.8V	10
Example 8	10.9Ah	0.01C 2.2V	EC:DMC:DEC=1:1:1; 1mol/L, LiPF ₆ ; 1%VC+1%FEC+1%PS; 0.5%LiI	5.0g	0.01C 3.8V	10
Example 9	25.0Ah	0.1C 2.3V	EC:DMC:DEC:EMC=1:1:1:1; 1mol/L, LiTFSI; 3%的 VC; 1.5%CuI ₂	3g	0.01C 3.65V	6
Example 10	18.0Ah	0.5C 2.2V	EC:DMC:DEC:EMC=1:1:1:1; 0.5mol/L, LiBF ₄ +0.5mol/LiODFB; 2%的 VEC; 2.0%SnI ₂	15g	0.5C 3.8V	10
Comparative Example 1	10.2Ah	None	None	None	None	None

Comparative Example 2	0.6Ah	None	None	None	None	None	U509199
Comparative Example 3	10.8Ah	0.01C 2.2V	None	None	0.01C 3.8V	10	
Comparative Example 4	10.8Ah	0.01C 2.8V	EC:DMC:DEC=1:1:1; 1mol/L, LiPF ₆ ; 1%VC+1%FEC+1%PS; 0.5%LiI	5.0g	0.01C 3.8V	1	
Comparative Example 5	19.7Ah	None	None	None	None	None	

Cycling performance test results of Examples 1-10 and Comparative Examples 1-5 at 25°C, 0.5C Charge/0.5C Discharge in Table 2.

Table 2: Performance Comparison of Examples and Comparative Examples

	Initial Discharge Capacity After Recycling	First Discharge Capacity After Repair	Capacity Recovery Rate (% of Nominal Capacity)	Cycle Count to 50% Capacity Degradation
Example 1	10.1Ah	13.7Ah	24.0%	1089
Example 2	10.3Ah	14.2Ah	17.3%	1358
Example 3	11.6Ah	13.2Ah	19.3%	1078
Example 4	10.6Ah	13.0	16.0%	978
Example 5	9.7Ah	12.7	20%	945
Example 6	9.8Ah	12.5	18%	956
Example 7	10.1Ah	13.1	16.7%	/
Example 8	10.9Ah	13.1	14.7%	1211

Example 9	25.0Ah	28.2Ah	20.7%	2305
Example 10	18.0Ah	26.2Ah	27.3%	1867
Comparative Example 1	10.2Ah	/	0%	367
Comparative Example 2	10.6Ah	/	0%	/
Comparative Example 3	10.8Ah	11.1Ah	2.0%	550
Comparative Example 4	10.8Ah	12.1Ah	8.67%	645
Comparative Example 5	19.7Ah	/	0%	548

From the comparison of cycling performance between Examples 1-10 and Comparative Examples 1, 2, and 5, it is evident that the discharge capacity of lithium iron phosphate batteries repaired using the present method is restored, and the cycle count until 50% capacity degradation is significantly improved.

5 By comparing Example 8 and Comparative Example 3, it can be observed that batteries without the repair solution exhibit significantly inferior repair effects compared to those with the repair solution.

By comparing Example 8 and Comparative Example 4, it is evident that batteries without deep discharge exhibit significantly inferior repair effects compared to those
10 subjected to deep discharge.

For Example 7 and Comparative Example 2, the batteries were disassembled, and lithium iron phosphate cathode sheets were extracted. The powder scraped from the sheets underwent X-ray diffraction (XRD) testing. The results are shown in FIG.1.

FIG.1: Curve A represents the XRD pattern of cathode powder repaired in Example
15 7. Curve B represents the XRD pattern of cathode powder from Comparative Example 2. Curve C represents the standard XRD card for lithium iron phosphate cathode

materials. The dashed rectangular box in the figure highlights impurity peaks generated during the usage of spent cathodes.

From the XRD results of the cathodes in Example 7 and Comparative Example 2, it is evident that the lithium iron phosphate cathode structure repaired by the present method is restored, and the ferric phosphate phases generated during usage are eliminated.

It is important to note that, unless otherwise specified, the technical terms or scientific terms used in this application should be understood as having the usual meanings as understood by those skilled in the art.

The above description represents the preferred specific implementation methods of this application. However, the scope of protection of this application is not limited to these implementations. Any variations or substitutions easily conceived by those skilled in the art within the technical scope disclosed in this application should be included within the scope of protection of this application. Therefore, the scope of protection of this application should be defined by the claims.

CLAIMS

1. A repair solution, characterized in that it comprises lithium salt, organic solvent, anode film-forming additives, and redox mediators; wherein the lithium salt, anode film-forming additives, and redox mediators are added to the organic solvent as a carrier, stirred evenly, and dissolved, resulting in a lithium salt concentration of 0.1-5 mol/L, a mass fraction of the redox mediator of 0.01-3%, and the volume of the anode film-forming additive accounting for 0.1-10% of the total liquid volume.

2. The repair solution according to Claim 1, characterized in that the lithium salt is selected from one or any combination of lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium difluoro(oxalato)borate (LiODFB), lithium bis(oxalate)borate (LiBOB), lithium difluorophosphate (LiPO₂F₂), lithium hexafluorophosphate (LiPF₆), or lithium tetrafluoroborate (LiBF₄).

3. The repair solution according to Claim 1, characterized in that the organic solvent is selected from one or any combination of ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), or ethyl acetate (EA).

4. The repair solution according to Claim 1, characterized in that the anode film-forming additive is selected from one or any combination of vinylene carbonate (VC), fluoroethylene carbonate (FEC), vinyl ethylene carbonate (VEC), or 1,3-propane sultone (PS).

5. The repair solution according to any one of Claims 1-4, characterized in that the redox mediator is selected from one or any combination of iodine (I₂), lithium iodide (LiI), copper iodide (CuI₂), cuprous iodide (CuI), or stannous iodide (SnI₂).

6. An in-situ repair and regeneration method for spent lithium iron phosphate batteries, characterized in that it comprises the following steps:

S100, performing deep discharge of the spent lithium iron phosphate batteries

using a small current, with a discharge rate of 0.001C-0.5C and a cut-off discharge voltage of 2.0-2.6V;

S200, preparing the repair solution according to any one of Claims 1-5; steps S100 and S200 are not required to follow a specific sequence;

5 S300, injecting the repair solution into the battery;

S400, charging the battery to a fully charged state using a small current, with a charging rate of 0.001C-0.5C and a cut-off charging voltage of 3.6-4.0V;

S500, repeating steps S100 and S400.

10 7. The in-situ repair and regeneration method according to Claim 6, characterized in that step S300 is carried out in a low-humidity environment, with a dew point temperature $\leq -40^{\circ}\text{C}$.

15 8. The in-situ repair and regeneration method according to Claim 6, characterized in that in step S300, after injecting the repair solution, the battery is placed in a static state for a preset duration.

20 9. The in-situ repair and regeneration method according to any one of Claims 6-8, characterized in that in step S300, the ratio of the mass of the repair solution to the nominal capacity of the battery is 0.1-5.00 g/Ah.

10. The in-situ repair and regeneration method according to Claim 6, characterized in that the number of repetitions in step S500 is 1-10 times.

REVENDICATIONS

1. Liquide de réparation, caractérisé en ce qu'il comprend un sel de lithium, un solvant organique, un additif de formation de film pour électrode négative et un médiateur redox ; le solvant organique étant utilisé comme support, le sel de lithium, l'additif de formation de film pour électrode négative et le médiateur redox sont ajoutés et mélangés uniformément jusqu'à dissolution complète, de manière à ce que la concentration en sel de lithium soit comprise entre 0,1 et 5 mol/L, la fraction massique du médiateur redox soit de 0,01 à 3 %, et le volume d'additif de formation de film représente 0,1 à 10 % du volume total du liquide.

2. Liquide de réparation selon la revendication 1, caractérisé en ce que le sel de lithium est choisi parmi le bis(fluorosulfonyl)imide de lithium (LiFSI), le bis(trifluorométhanesulfonyl)imide de lithium (LiTFSI), le borate d'oxalate difluoré de lithium (LiODFB), le borate d'oxalate de lithium (LiBOB), le phosphate de lithium difluoré (LiPO₂F₂), l'hexafluorophosphate de lithium (LiPF₆) ou le tétrafluoroborate de lithium (LiBF₄), pris individuellement ou en combinaison.

3. Liquide de réparation selon la revendication 1, caractérisé en ce que le solvant organique est choisi parmi le carbonate d'éthylène (EC), le carbonate de diméthyle (DMC), le carbonate de diéthyle (DEC), le carbonate de méthyle-éthyle (EMC) ou l'acétate d'éthyle (EA), pris individuellement ou en combinaison.

4. Liquide de réparation selon la revendication 1, caractérisé en ce que l'additif

de formation de film pour électrode négative est choisi parmi le carbonate de vinyle-éthylène (VC), le carbonate de fluoroéthylène (FEC), le carbonate de vinyle-éthylène (VEC) ou le 1,3-propane sultone (PS), pris individuellement ou en combinaison.

5 5. Liquide de réparation selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le médiateur redox est choisi parmi l'iode élémentaire (I_2), l'iodure de lithium (LiI), l'iodure de cuivre (CuI_2), l'iodure de cuivre (I) (CuI) ou l'iodure d'étain (SnI_2), pris individuellement ou en combinaison.

10 6. Procédé de réparation et de régénération in situ d'une batterie usagée à base de phosphate de fer et de lithium, caractérisé en ce qu'il comprend les étapes suivantes :

S100 : décharger la batterie usagée à l'aide d'un faible courant jusqu'à une profondeur de décharge, avec un taux de décharge compris entre 0,001C et 0,5C, et
15 une tension de coupure de décharge comprise entre 2,0 et 2,6 V ;

S200 : préparer le liquide de réparation selon l'une quelconque des revendications 1 à 5 ; les étapes S100 et S200 n'ayant pas d'ordre requis ;

S300 : injecter le liquide de réparation dans la batterie ;

S400 : recharger la batterie avec un faible courant jusqu'à un état de pleine
20 charge, avec un taux de charge compris entre 0,001C et 0,5C, et une tension de coupure de charge comprise entre 3,6 et 4,0 V ;

S500 : répéter les étapes S100 et S400.

7. Procédé selon la revendication 6, caractérisé en ce que l'étape S300 est réalis
25 ée dans un environnement à faible humidité, la température de point de rosée de

cet environnement étant inférieure ou égale à -40°C .

8. Procédé selon la revendication 6, caractérisé en ce qu'après l'injection du liquide de réparation à l'étape S300, la batterie est laissée statique dans des positions alternées pendant une durée prédéterminée.

9. Procédé selon l'une quelconque des revendications 6 à 8, caractérisé en ce qu'à l'étape S300, le rapport entre la masse du liquide de réparation injecté et la capacité nominale de la batterie est compris entre 0,1 et 5,00 g/Ah.

10

10. Procédé selon la revendication 6, caractérisé en ce que le nombre de répétitions de l'étape S500 est compris entre 1 et 10 fois.

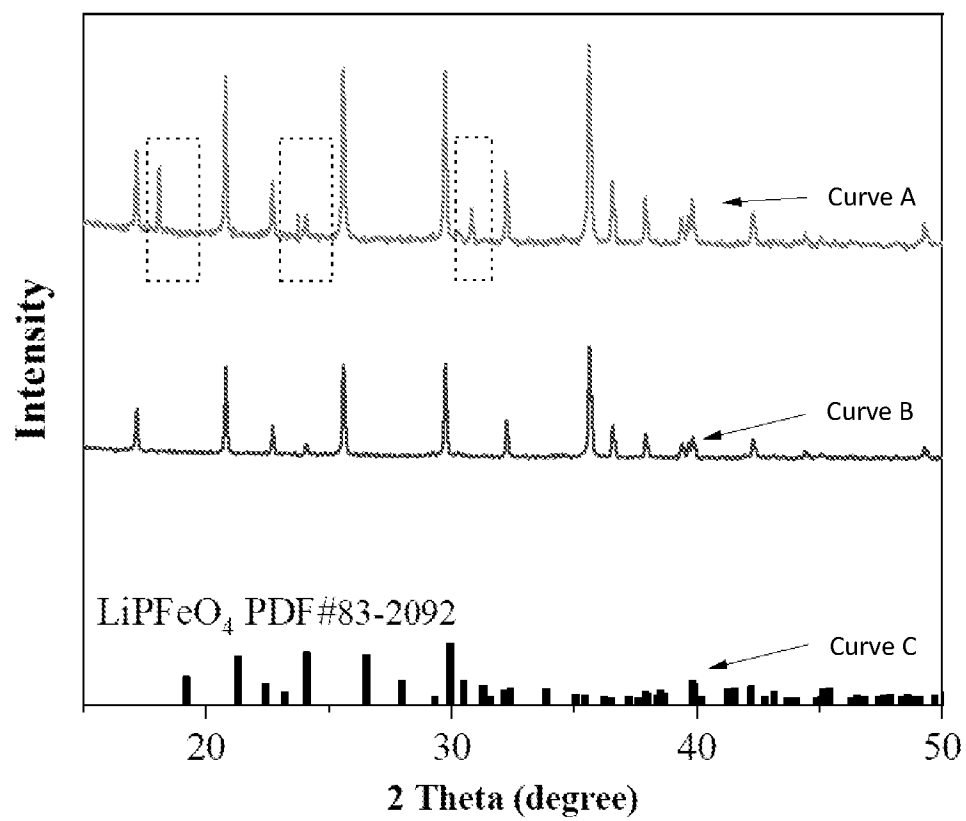


FIG.1