



(51) International Patent Classification:

H01M 8/18 (2006.01)

(21) International Application Number:

PCT/SG2019/050312

(22) International Filing Date:

24 June 2019 (24.06.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/688,575

22 June 2018 (22.06.2018)

US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: AN AQUEOUS REDOX FLOW BATTERY

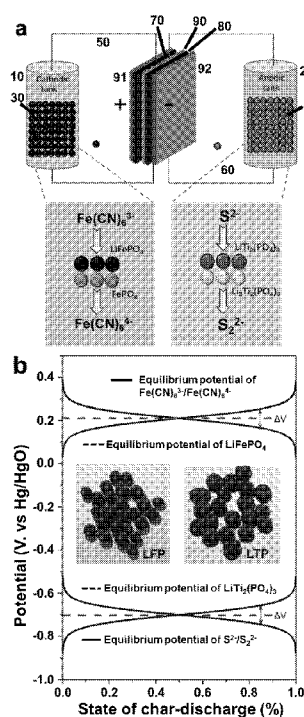


FIG. 1

(57) Abstract: Disclosed herein is a flow battery comprising solid energy storage materials in both the catholyte and anolyte storage tanks, a liquid catholyte, a liquid anolyte comprising an n-type redox mediator selected from one or more of the group consisting of $(\text{NH}_4)_2\text{S}_x$, viologens, Li_2S_x , Na_2S_x , and K_2S_x , wherein x is less than or equal to 8 and greater than or equal to 1.

Published:

— *with international search report (Art. 21(3))*

An aqueous redox flow battery

Field of Invention

5 This invention discloses a new flow battery system which comprises an aqueous catholyte, aqueous anolyte, cathodic and anodic energy storage materials in a flow battery apparatus. The cathodic and anodic energy storage materials are statically stored in cathodic and anodic tanks, respectively. The electrolytes are pumped through the battery stacks and tanks of the flow battery apparatus to generate electricity during discharge and store energy during the
10 charging process.

Background

The listing or discussion of a prior-published document in this specification should not
15 necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

A flow battery is generally considered to be a rechargeable fuel cell in which an electrolyte containing one or more dissolved electroactive elements flows through an electrochemical cell
20 that reversibly converts chemical energy directly to electricity. Additional electrolyte is stored externally, generally in tanks, and is usually pumped through the cell (or cells) of the reactor, although gravity feed systems are also known. Flow batteries can be rapidly "recharged" by replacing the electrolyte liquid (in a similar way to refilling fuel tanks for internal combustion engines) while simultaneously recovering the spent material for re-energization.

25 In other words, a flow battery is just like an electrochemical cell, with the exception that the electrolyte is not stored in the cell around the electrodes. Rather, the ionic solution is stored outside of the cell, and can be fed into the cell in order to generate electricity. The total amount of electricity that can be generated depends on the size of the storage tanks.

30 Examples of conventional redox flow batteries are the vanadium redox flow battery, polysulfide bromide battery, and (less typically) a uranium redox flow battery. Such redox flow batteries are generally have a low specific energy and low specific power, which makes them too heavy for use in a vehicle and too expensive for stationary energy storage.

35 Recently, organic redox flow batteries have been developed, which appear to overcome these problems. Organic redox flow batteries could be further classified into two categories:

Aqueous Organic Redox Flow Batteries (AORFBs) and Non-aqueous Organic Redox Flow Batteries (NAORFBs). AORFBs use water as solvent for electrolyte materials while NAORFBs employ organic solvents to dissolve redox active materials. However, these batteries tend to have low power performance.

5

As an example of such a system, reference is made to Jia C, Pan F, Zhu Y G, et al. High-energy density non-aqueous all redox flow lithium battery enabled with a polymeric membrane. Science Advances, 2015, 1(10): e1500886, which discloses a redox targeting-based non-aqueous flow battery which uses organic solvent in the electrolyte. Such a system has low power density.

10

As such, there is still a need to develop newer materials that have a higher energy density than conventional flow batteries and better power performance compared with the organic redox flow batteries. Such a battery system could find application in large-scale stationary energy storage, such as power grid, distributed energy storage for PV and wind farm, as well as household energy storage applications.

15

Summary of Invention

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In a first aspect of the invention, there is provided a flow battery system comprising:

- a solid cathodic energy storage material stored within a catholyte tank;

- a liquid catholyte that flows through a fluid pathway from the catholyte tank to a cathode and back to the catholyte tank;

- a solid anodic energy storage material stored within an anolyte tank;

25

- a liquid anolyte that flows through a fluid pathway from the anolyte tank to an anode and back to the anolyte tank;

- an ion selective membrane disposed between the cathode and anode; and

- a current collector surrounding the cathode and anode, wherein

the liquid anolyte comprises an n-type redox mediator selected from one or more of the group consisting of $(\text{NH}_4)_2\text{S}_x$ and, more particularly, viologens, Li_2S_x , Na_2S_x , and K_2S_x , wherein x is less than or equal to 8 and greater than or equal to 1.

30

In embodiments of the invention:

- (a) the solid cathodic energy storage material may be selected from one or more of the group consisting of LiFePO_4 , $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, NaFePO_4 , and Prussian blue (e.g. the solid cathodic energy storage material is LiFePO_4);

35

- (b) the solid cathodic energy storage material may be provided as granules;

(c) the liquid catholyte comprises a p-type redox mediator that may be selected from one or more of the group consisting of ferricyanide ($M_3Fe(CN)_6$), ferrocyanide ($M_4Fe(CN)_6$), ferrocene ($C_{10}H_{10}Fe$) and derivatives thereof (e.g. di(ethylsulfonic sodium) ferrocene ($C_{14}H_{16}FeS_2O_6Na_2$)), and iodide (I), where in each case M is independently selected from the group consisting of Li, Na, K and NH_4 , optionally wherein the p-type redox mediator is selected from one or more of the group consisting of, and iodide (I) (e.g. ferricyanide ($M_3Fe(CN)_6$) and/or ferrocyanide ($M_4Fe(CN)_6$)), where in each case M is independently selected from the group consisting of Li, Na, K and NH_4 ;

(d) the total concentration of the p-type redox mediator present in the catholyte 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;

(e) the solid anodic energy storage material may be selected from one or more of the group consisting of $LiTi_2(PO_4)_3$, TiP_2O_7 , and $NaTi_2(PO_4)_3$ (e.g. the solid anodic energy storage material is $LiTi_2(PO_4)_3$);

(f) the solid anodic energy storage material may be provided as granules;

(g) the total concentration of the n-type redox mediator present in the anolyte may be from 0.5 M to 3 M, such as from 0.75 M to 2 M, such as around 1 M;

(h) the liquid in the catholyte and anolyte may comprise water alone or in combination with an organic solvent suitable for use in a battery (e.g. the liquid in the catholyte and anolyte may be independently selected from water or water in combination with tetraglyme).

In a specific embodiment of the invention, which may be combined with any technically sensible combination of embodiments (a) to (h) above, the battery provided may be one in which: the solid cathodic energy storage material is $LiFePO_4$; the solid anodic energy storage material is $LiTi_2(PO_4)_3$; the aqueous catholyte comprises $K_4Fe(CN)_6$ at a concentration of 0.3 M; and the aqueous anolyte comprises Li_2S_2 at a concentration of 1 M.

Drawings

Figure 1. Is a schematic illustration of a redox targeting-based aqueous flow lithium battery full cell. (a) Configuration of the cell with $LiFePO_4$ and $LiTi_2(PO_4)_3$ as cathodic and anodic energy storage materials in tanks, paired with redox mediator $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ and S^{2-}/S_2^{2-} in catholyte and anolyte, respectively. (b) Potential profiles of $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ and S^{2-}/S_2^{2-} as a function of activity, and comparison with the potential of $LiFePO_4$ and $LiTi_2(PO_4)_3$. The insets show the photograph of $LiFePO_4$ and $LiTi_2(PO_4)_3$ granules with diameter of 1.0 mm and 1.5 mm, respectively.

Figure 2. Depicts cyclic voltammograms (CV) of redox mediators and the paired solid Li⁺-storage materials used in the aqueous RFLB. The CV curves of Li₂S₂ and LiTi₂(PO₄)₃ were measured in 0.1 M LiOH aqueous solution, while those of K₄[Fe(CN)₆] and LiFePO₄ were obtained in 0.1 M LiOH solution with mixed H₂O and TEGDME (30 vol.%). The concentration of the respective redox species is 10 mM and the scan rate are 5 mV s⁻¹.

Figure 3. Cell performance of single molecule aqueous redox targeting flow batteries (ARTFBs). (a) Charge-discharge profile of the full cell. (b) Cycling performance of the full cell.

Description

This disclosure provides a rechargeable electrochemical energy storage device, i.e., a redox flow battery system that can be configured for different applications, such as powering portable electronic devices and electrical vehicles, storing energy generated from remote power systems such as wind turbine generators and photovoltaic arrays, and providing emergency power as an uninterruptible power source.

It has been surprisingly found that the use of solid active materials placed within the anolyte and catholyte storage tanks can provide increased power performance while delivering a smaller footprint/energy density, when coupled with particular redox mediators. As such, there is disclosed herein a flow battery system comprising:

- a solid cathodic energy storage material stored within a catholyte tank;
 - a liquid catholyte that flows through a fluid pathway from the catholyte tank to a cathode and back to the catholyte tank;
 - a solid anodic energy storage material stored within an anolyte tank;
 - a liquid anolyte that flows through a fluid pathway from the anolyte tank to an anode and back to the anolyte tank;
 - an ion selective membrane disposed between the cathode and anode; and
 - a current collector surrounding the cathode and anode, wherein
- the liquid anolyte comprises an n-type redox mediator selected from one or more of the group consisting of (NH₄)₂S_x, viologens, Li₂S_x, Na₂S_x, and K₂S_x, wherein x is less than or equal to 8 and greater than or equal to 1.

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*.

5

The separator divides the cathode from the anode. It can be an electro-active ion conducting membrane (e.g., a lithium or sodium ion conducting membrane). The separator 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 separator 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.

15

Both electrodes in the battery system, i.e., the cathode and the anode, can be a carbon, a metal, or a combination thereof. Preferably, these 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).

20

A flow battery according to the current invention is depicted in Fig. 1a. As shown, there is a flow battery system that includes a solid cathodic energy storage material 30 stored within a catholyte tank 10. A fluid pathway 50 that runs from the catholyte tank 10 to a cathode 70 and back to the catholyte tank 10 and is intended, which is intended to enable the circulation of a liquid catholyte from the storage tank 10 to the cathode 70 and back again. The cathode 70 is separated from the anode 80 by an ion selective membrane 90 disposed therebetween. A fluid pathway 60 runs from the anode 80 to the anolyte tank 20, which holds a solid anodic energy storage material. The fluid pathway 60 is intended to circulate a liquid anolyte from the storage tank 20 to the anode 80 and back again. Surrounding the cathode 70, anode, 80 and membrane 90, is a current collector 91, 92. As will be appreciated, the catholyte and anolyte may be circulated through the fluid pathways by any suitable means, such as by use of a suitable pumping system. As will be appreciated, the anode and cathode may be porous to allow flow of the respective electrolytes.

35

When used herein “solid cathodic energy storage material” refers to a material that can lose alkali metal ions in a charging cycle and regain said alkali metal ions in a discharging cycle of a battery. Any suitable solid cathodic energy storage material may be used in the current invention.

5

The cathodic energy storage material can be a metal fluoride (e.g., CuF_2 , FeF_2 , FeF_3 , BiF_3 , CoF_2 , and NiF_2), a metal oxide (e.g., MnO_2 , V_2O_5 , V_6O_{11} , Li_2O_2), $\text{Li}_{1-x-z}\text{M}_{1-z}\text{PO}_4$, $(\text{Li}_{1-y}\text{Z}_y)\text{MPO}_4$, LiMO_2 , LiM_2O_4 , Li_2MSiO_4 , a partially fluorinated compound (e.g., LiMPO_4F and LiMSO_4F , preferably, LiVPO_4F , LiFeSO_4F), Li_2MnO_3 . M is Ti, V, Cr, Mn, Fe, Co, or Ni; Z is Ti, Zr, Nb, Al, or Mg; x is 0 to 1; y is 0 to 0.1; and z is -0.5 to 0.5. Preferably, the cathodic energy storage material is a nanostructured material with a flat potential. The porosity, particle size, morphology, and microstructure of the solid cathodic electro-active material can be optimized to ensure an effective redox reaction with a p-type redox mediator in the electrolyte. Other suitable materials include $\text{Na}_a[\text{Cu}_b\text{Fe}_c\text{Mn}_d\text{Ni}_e\text{Ti}_f\text{M}_g]\text{O}_2$ (where: $0 \leq a \leq 1$; $0 \leq b \leq 0.3$; $0 \leq c \leq 0.5$; $0 \leq d \leq 0.6$; $0 \leq e \leq 0.3$; $0 \leq f \leq 0.2$; and $0 \leq g \leq 0.4$, and M is selected from one or more of the group consisting of Mo, Zn, Mg, Cr, Co, Zr, Al, Ca, K, Sr, Li, H, Sn, Te, Sb, Nb, Sc, Rb, Cs, and Na), or more particularly, $\text{M-Na}_2\text{Fe}_2(\text{CN})_6 \cdot 2\text{H}_2\text{O}$; $\text{R-Na}_2\text{Fe}_2(\text{CN})_6$, NVP, and $\text{Na}_4\text{Mn}_3(\text{PO}_4)_2(\text{P}_2\text{O}_7)$. Particularly suitable materials that may be mentioned herein include, but are not limited to LiFePO_4 , $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, NaFePO_4 , Prussian blue and combinations thereof.

In particular embodiments that may be mentioned herein, the solid cathodic energy storage material may be LiFePO_4 . As will be appreciated, while the solid cathodic energy storage material may be provided in any suitable solid form (e.g. in the form of solid plates or a mesh), the material may be provided in the form of granules. When in the form of granules, the solid cathodic energy storage material may take any suitable size and shape. Examples of suitable size may include, but is not limited to, granules having an average diameter of from 0.2 mm to 2 mm, such as from 0.5 mm to 1.5 mm, such as from 0.75 mm to 1.25 mm, such as around 1 mm. As will be appreciated, when the solid cathodic energy storage material is in the form of granules, the outlet for the liquid catholyte may be smaller than the granules or may include a filter or pores that prevent the solid material from exiting the catholyte tank.

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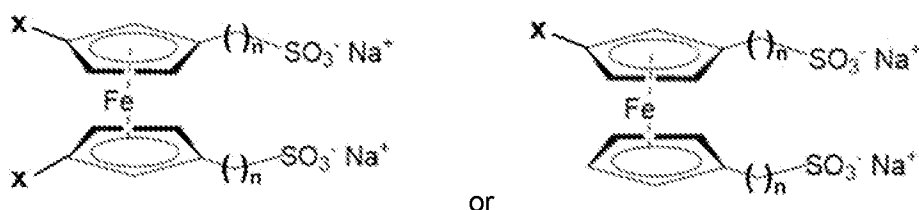
Given that the energy storage material is solid and is essentially held permanently within the catholyte tank of the flow battery, the liquid catholyte (i.e. the electrolyte in the cathodic portion of the flow battery) requires the presence of a redox mediator.

35

A redox mediator refers to a compound present (e.g., dissolved) in the electrolyte (catholyte or anolyte) that acts as a molecular shuttle transporting charges between the respective electrodes and the energy storage materials upon charging/discharging. A p-type redox

mediator transports charges between the cathodic electrode and the cathodic energy storage material. An n-type redox mediator transports charges between the anodic electrode and the anodic energy storage material. Not being bound by any theory, upon charging, the p-type redox mediator is reduced on the surface of the cathodic energy storage material and is oxidized on the surface of the cathodic electrode, and the n-type redox mediator is oxidized on the surface of the anodic energy storage material and is reduced on the surface of the anodic electrode. Upon discharging, the reverse processes take place.

Any suitable p-type redox mediator that is compatible with the solid cathodic energy storage material and the solvent used as the electrolyte base liquid may be used. Suitable p-type redox mediators that may be mentioned herein include, but are not limited to ferricyanide ($M_3Fe(CN)_6$), ferrocyanide ($M_4Fe(CN)_6$), ferrocene ($C_{10}H_{10}Fe$) 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 appreciated, any suitable concentration of the p-type redox mediators may be used. For example, the total concentration of the p-type redox mediator present in the catholyte 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. 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, NO_2 , COOR, C_{1-20} alkyl, CF_3 , and COR, in which R is H or C_{1-20} 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 ($FeCp_2PPh_2RCN$), 1,1-dimethylferrocene (DMFc), tetraferrocene, di(ethylsulfonic sodium) ferrocene ($C_{14}H_{16}FeS_2O_6Na_2$), and di(trimethanesulfonic sodium) ferrocene ($C_{16}H_{22}FeS_2O_6Na_2$).

In particular embodiments of the invention that may be mentioned herein, the derivative of ferrocene may be di(trimethanesulfonic sodium) ferrocene ($C_{16}H_{22}FeS_2O_6Na_2$) or di(ethylsulfonic sodium) ferrocene ($C_{14}H_{16}FeS_2O_6Na_2$).

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

When used herein “solid anodic energy storage material” refers to a material that can gain alkali metal ions in a charging cycle and lose said alkali metal ions in a discharging cycle of a
10 battery. Any suitable solid anodic energy storage material may be used in the current invention. Such materials include, but are not limited to a carbon-based material, a silicon-based material, a tin-based material, an antimony-based material, a lead-based material, a metal oxide (e.g. a lithium or sodium metal oxide), a sodium metal, and/or the like, which may be utilized singularly or as a mixture of two or more. The carbon-based material may be, for example,
15 soft carbon or hard carbon or a graphite-based material such as artificial graphite, natural graphite, a mixture of artificial graphite and natural graphite, natural graphite coated with artificial graphite, and/or the like. The silicon-based material may be, for example, silicon, a silicon oxide, a silicon-containing alloy, a mixture of the graphite-based material with the foregoing materials, and/or the like. The silicon oxide may be represented by SiO_x ($0 < x \leq 2$).
20 The silicon-containing alloy may be an alloy including silicon in the largest amount of the total metal elements (e.g., silicon being the metal element that is present in the largest amount of all the metal elements) based on the total amount of the alloy, for example, a Si-Al-Fe alloy. The tin-based material may be, for example, tin, a tin oxide, a tin-containing alloy, a mixture of the graphite-based material with the foregoing materials, and/or the like. Likewise for
25 antimony and lead-based materials. The lithium metal oxide may be, for example, a titanium oxide compound such as $Li_4Ti_5O_{12}$, $Li_2Ti_6O_{13}$ or $Li_2Ti_3O_7$. The sodium metal oxide may be, for example, a titanium oxide compound such as $Na_2Ti_3O_7$ or $Na_2Ti_6O_{13}$. Other metal oxides that may be mentioned herein as suitable include, but are not limited to, TiO_2 , Fe_2O_3 , MoO_3 . Particularly suitable materials that may be mentioned herein include, but are not limited to
30 $LiTi_2(PO_4)_3$, TiP_2O_7 , and $NaTi_2(PO_4)_3$ and combinations thereof. In particular embodiments that may be mentioned herein, the solid anodic energy storage material may be $LiTi_2(PO_4)_3$. As will be appreciated, while the solid anodic energy storage material may be provided in any suitable solid form (e.g. in the form of solid plates or a mesh), the material may be provided in the form of granules. When in the form of granules, the solid anodic energy storage material may take
35 any suitable size and shape. Examples of suitable size may include, but is not limited to, granules having an average diameter of from 0.5 mm to 2.5 mm, such as from 0.75 mm to 2 mm, such as from 1 mm to 1.75 mm, such as around 1.5 mm. As will be appreciated, when

the solid anodic energy storage material is in the form of granules, the outlet for the liquid anodic may be smaller than the granules or may include a filter or pores that prevent the solid material from exiting the anolyte tank.

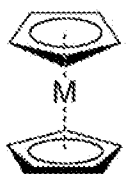
Given that the energy storage material is solid and is essentially held permanently within the anolyte tank of the flow battery, the liquid anolyte (i.e. the electrolyte in the anodic portion of the flow battery) requires the presence of an n-type redox mediator. Any suitable n-type redox mediator that is compatible with the solid anodic energy storage material and the solvent used as the electrolyte base liquid may be used. Suitable n-type redox mediators that may be mentioned herein include, but are not limited to $(\text{NH}_4)_2\text{S}_x$ or, more particularly, viologens, Li_2S_x , Na_2S_x , and K_2S_x , wherein x is less than or equal to 8 and greater than or equal to 1. As will be appreciated, any suitable concentration of the n-type redox mediators may be used. For example, the total concentration of the n-type redox mediator present in the anolyte may be from 0.5 M to 3 M, such as from 0.75 M to 2 M, such as around 1 M.

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. C_1 to C_{12} 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 p-type and n-type redox mediators are discussed in depth in international application publication number WO 2013/012391, which is hereby incorporated by reference. The p-type redox mediators mentioned in said document may be used in the currently disclosed battery system, which mediators are discussed below.

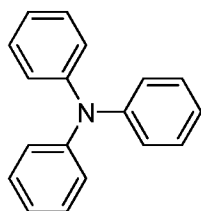
The p-type redox mediators disclosed in WO 2013/012391 may be a metallocene derivative, a triarylamine derivative, a phenothiazine derivative, a phenoxazine derivative, a carbazole derivative, a transition metal complex, an aromatic derivative, a nitroxide radical, a disulfide, or a combination thereof.

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



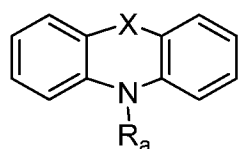
In the above formula, M can be Fe, Co, Ni, Cr, or V; each of the cyclopentadienyl rings, independently, can be substituted with one or more of the following groups: F, Cl, Br, I, NO₂, COOR, C₁₋₂₀ alkyl, CF₃, and COR, in which R can be H or C₁₋₂₀ alkyl.

- 5 The triarylamine derivative used as a p-type redox mediator may have the following structure:



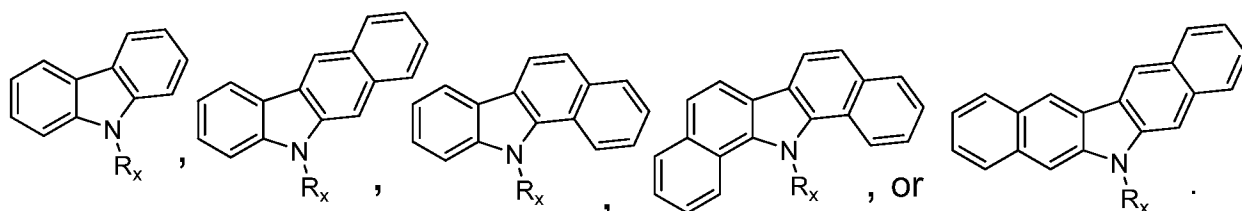
- 10 In the above formula, each of the phenyl rings, independently, can be substituted with one or more of the following groups: F, Cl, Br, I, NO₂, COOR, C₁₋₂₀ alkyl, CF₃, and COR, in which R can be H or C₁₋₂₀ alkyl.

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



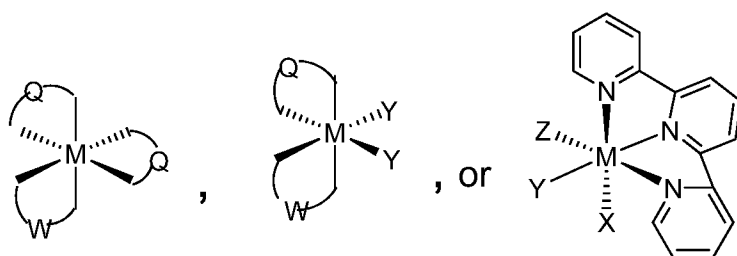
- 15 R_a can be H or C₁₋₂₀ alkyl, X can be O or S, each of the aromatic moieties is optionally substituted with one or more of the following groups: F, Cl, Br, I, NO₂, COOR, R, CF₃, and COR, in which R can be H or C₁₋₂₀ alkyl.

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

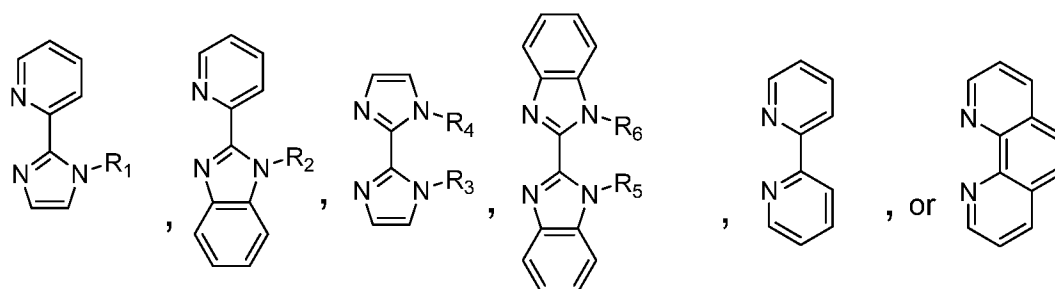


R_x can be H or C_{1-20} alkyl and each of the aromatic moieties is optionally substituted with one or more of the following groups: F, Cl, Br, I, NO_2 , COOR, C_{1-20} alkyl, CF_3 , and COR, in which R can be H or C_{1-20} alkyl.

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



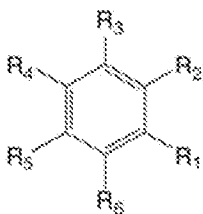
- 10 In the above formulae, M can be Co, Ni, Fe, Mn, Ru, or Os; each of the aromatic moieties is unsubstituted or is substituted with one or more of the following groups: F, Cl, Br, I, NO_2 , COOR', R', CF_3 , COR', OR', or $NR'R''$, each R' and R'' can independently be H or C_{1-20} alkyl; each of X,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



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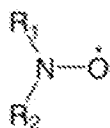
- 20 In these formulas, each of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 , can be F, Cl, Br, I, NO_2 , COOR', R', CF_3 , COR', OR', or $NR'R''$. Again, each of the aromatic moieties is optionally substituted with one or more of the following groups: F, Cl, Br, I, NO_2 , COOR', C_{1-20} alkyl, CF_3 , COR', 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.

- 25 The aromatic derivative used as a p-type redox mediator may have the following structure:



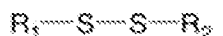
In these formulas, each of R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 , can be C_{1-20} alkyl, F, Cl, Br, I, NO_2 , $COOR'$, CF_3 , COR' , OR' , $OP(OR')(OR'')$, or $NR'R''$, in which each of R' and R'' , independently, can be H, C_{1-20} alkyl.

The nitroxide radical used as a p-type 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 p-type 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.

As will be appreciated, the catholyte and anolyte also require a solvent. 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 particular embodiments that may be mentioned herein the solvent used in the catholyte and anolyte may be water alone or water in combination with a glyme solvent (e.g. water and tetraglyme).

The catholyte and anolyte also contain a suitable salt to enable electro-active ions (e.g. Na^+ and Li^+) to be dissolved in the solvent. The source of the electro-active ion can be a salt of the electro-active ion. Suitable salts for lithium-based systems include LiClO_4 , LiCF_3SO_3 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$, $\text{LiN}(\text{SO}_2\text{F})_2$, $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{Li}[\text{N}(\text{SO}_2\text{C}_4\text{F}_9)(\text{SO}_2\text{F})]$, LiCl , LiBr , LiI , LiNO_3 , Li_2SO_4 , lithium bis(oxalato)borate (i.e., LiBOB), or a combination thereof. Suitable salts for sodium-based system include NaClO_4 , NaSCN , NaBr , NaI , Na_2SO_4 , $\text{Na}_2\text{B}_{10}\text{Cl}_{10}$, NaCl , NaNO_3 , Na_3PO_4 , $\text{Na}(\text{CF}_3\text{SO}_3)$, $\text{NaN}(\text{CF}_3\text{SO}_2)_2$, $\text{NaN}(\text{FSO}_2)$, $\text{NaN}(\text{C}_2\text{F}_5\text{SO}_2)_2$, $\text{NaN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$, $\text{NaC}(\text{CF}_3\text{SO}_2)_3$, $\text{NaC}(\text{C}_2\text{F}_5\text{SO}_2)_3$, sodium stearyl sulfonate, sodium octyl sulfonate, and sodium dodecylbenzene sulfonate. The above materials may be present in a concentration of from 0.5 to 2.5 M within the catholyte and anolyte.

The catholyte and anolyte may further include various suitable additives such as a negative electrode SEI (Solid Electrolyte Interface) forming agent, a surfactant, and/or the like. Such additives may be, for example, succinic anhydride, lithium bis(oxalato)borate, sodium bis(oxalato)borate, lithium tetrafluoroborate, a dinitrile compound, propane sultone, butane sultone, propene sultone, 3-sulfolene, a fluorinated allylether, a fluorinated acrylate, carbonates such as vinylene carbonate, vinyl ethylene carbonate and fluoroethylene carbonate and/or the like. The concentration of the additives may be any suitable one that is utilized in a sodium-ion battery. Particular additives that may be included in the electrolyte are

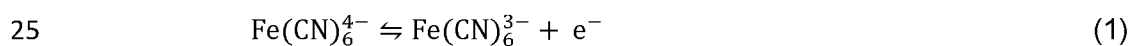
those selected from one or more of the group consisting of fluoroethylene carbonate (FEC), vinylene carbonate (VC), vinyl ethylene carbonate (VEC), and adiponitrile. The above additives may be present in any suitable weight ratio.

- 5 In certain embodiments that may be mentioned herein, the weight to weight ratio of the solid cathodic energy storage material to solid anodic energy storage material in the battery may be from 1:2 to 2:1, such as from 1:1.5 to 1:1, such as around 0.9:1. In further embodiments that may be mentioned herein, the volume to volume ratio of the catholyte to anolyte in the battery may be from 1:2 to 2:1, such as from 1:1 to 1.9:1, such as around 1.75:1.

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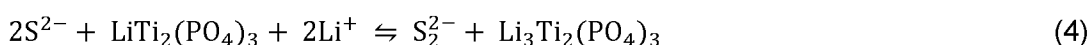
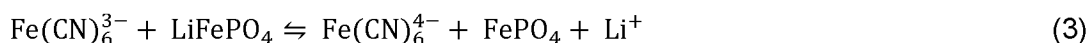
The catholyte and anolyte tanks, the cathode and anode, the ion selective membrane the current collector and the flow paths used herein may be any conventionally used in the field of flow batteries. No particular limitation is placed on these components.

- 15 In a particular example, illustrated in Fig. 1a the flow battery disclosed herein may contain:
 LiFePO₄ as the solid cathodic energy storage material;
 LiTi₂(PO₄)₃ as the solid anodic energy storage material;
 an aqueous catholyte comprising K₄Fe(CN)₆ at a concentration of 0.3 M; and
 an aqueous anolyte comprising Li₂S₂ at a concentration of 1 M, where the solvent for
 20 the anolyte and catholyte may be water and teraglyme or only water. As illustrated in Fig. 1a, there are two sets of reactions concomitantly taking place at the electrodes and tanks which make this invention highly different from previous one. Equation (1) and (2) show the electrochemical reactions on the cathode and anode respectively:



The other set are the redox targeting reactions chemically happened in the cathodic and anodic tanks, as shown by equation (3) and (4), respectively:

30



- In the charge process, [Fe(CN)₆]³⁻ is generated on the cathode by the oxidation of [Fe(CN)₆]⁴⁻
 35 in the catholyte, which then flows into the cathodic tank and delithiates LiFePO₄ to form FePO₄. The reduced species is regenerated when circulates back to the cell, starting a new round of

reactions. Meanwhile, S^{2-} is formed on the anode by the reduction of S_2^{2-} in the anolyte, which then flows into the anodic tank and lithiates $LiTi_2(PO_4)_3$ to form $Li_3Ti_2(PO_4)_3$. During this process, the Li^+ ions extracted from $LiFePO_4$ in the cathodic tank constantly transport through the Li^+ -conducting membrane and are stored in $LiTi_2(PO_4)_3$ in the anodic tank. In the discharge process, all the above processes proceed conversely.

Advantages associated with the currently disclosed invention include:

- a) reducing the capital investment by using low cost active materials compared with a vanadium flow battery;
- b) improving power performance, which reduces the cost of a battery stack, and allows the stack to be compact in comparison to redox targeting-based non-aqueous flow batteries;
- c) when water or water and particular non-flammable organic solvents are used in the flow battery (e.g. tetraglyme), the batteries may be much safer to use;
- d) the batteries disclosed herein use an alkaline electrolyte, which is less corrosive than the acidic electrolytes used in vanadium flow batteries;
- e) the batteries disclosed herein use solid-state materials to store the electrical energy, which enables them to have a much higher volumetric capacity and energy density than conventional flow batteries.

All of the features disclosed in this specification may be combined in any combination. Each feature disclosed in this specification may be replaced by an alternative feature serving the same, equivalent, or similar purpose. Thus, unless expressly stated otherwise, each feature disclosed is only an example of a generic series of equivalent or similar features.

From the above description, one skilled in the art can easily ascertain the essential characteristics of the present invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

Hereinafter, embodiments of the invention are illustrated in more detail with reference to the following examples. However, the present disclosure is not limited thereto. Furthermore, what is not described in this disclosure may be sufficiently understood by those who have knowledge in this field and will not be illustrated herein.

Examples

Example 1

Cyclic voltammetry curves for Li_2S_2 and $\text{LiTi}_2(\text{PO}_4)_3$ were obtained using a 0.1 M LiOH aqueous solution. CV curves for $\text{K}_4[\text{Fe}(\text{CN})_6]$ and LiFePO_4 were obtained using a 0.1 M LiOH solution containing H_2O and tetraethylene glycol dimethyl ether (TEGDME; present in 30 vol.%). The concentration of the respective redox species was 10 mM and the scan rate was 5 mV s^{-1} .

Olivine LiFePO_4 and rhombohedral $\text{LiTi}_2(\text{PO}_4)_3$ have been shown to be robust cathode and anode materials, respectively, for aqueous lithium ion batteries. Their potentials are relatively flat, which is ideal for redox targeting reactions (e.g. see Fig. 1b and Fig. 2 versus Hg/HgO), and are well within the electrochemical window of water at alkaline conditions. These two materials were chosen for use as the cathodic and anodic energy storage materials, respectively in the battery described in Example 2.

The Cyclic voltammograms in Fig. 2 show the redox potential of LiFePO_4 is 0.21 V (vs. Hg/HgO) in a 0.1 M LiOH electrolyte, and that of $\text{LiTi}_2(\text{PO}_4)_3$ is -0.69 V (vs. Hg/HgO) in a 0.1 M LiOH electrolyte. A cathodic redox mediator that pairs with LiFePO_4 is $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$. For the anodic side, polysulfides are noted to have comparable redox potential to that of $\text{LiTi}_2(\text{PO}_4)_2$.

Example 2

A full cell with solid materials loaded in both the anodic and cathodic energy storage tanks was fabricated (as depicted in Figure 1a) to evaluate the cycling and power performance of a battery made using the materials discussed in Example 1. 7 mL 0.3 M $\text{K}_4\text{Fe}(\text{CN})_6$ catholyte and 4 mL 1 M Li_2S_2 anolyte were employed in the cell in conjunction with 0.9 g LiFePO_4 and 1.0 g $\text{LiTi}_2(\text{PO}_4)_3$ granules in the cathodic and anodic tanks, respectively. The cell had a discharge voltage of around 0.80 V at a current density of 5 mA cm^{-2} , and a capacity of 81 mAh of which 30.9% is contributed by the solid material in the catholyte (Fig. 3a). The cell also had a capacity retention of 94.1% after 30 cycles (Fig. 3b) and a maximum power density of 8 mW cm^{-2} at a current density of 20 mA cm^{-2} .

Claims

1. A flow battery system comprising:
 - a solid cathodic energy storage material stored within a catholyte tank;
 - a liquid catholyte that flows through a fluid pathway from the catholyte tank to a cathode and back to the catholyte tank;
 - a solid anodic energy storage material stored within an anolyte tank;
 - a liquid anolyte that flows through a fluid pathway from the anolyte tank to an anode and back to the anolyte tank;
 - an ion selective membrane disposed between the cathode and anode; and
 - a current collector surrounding the cathode and anode, whereinthe liquid anolyte comprises an n-type redox mediator selected from one or more of the group consisting of $(\text{NH}_4)_2\text{S}_x$, viologens, Li_2S_x , Na_2S_x , and K_2S_x , wherein x is less than or equal to 8 and greater than or equal to 1.
2. The battery according to Claim 1, wherein the solid cathodic energy storage material is selected from one or more of the group consisting of LiFePO_4 , $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, NaFePO_4 , and Prussian blue.
3. The battery according to Claim 2, wherein the solid cathodic energy storage material is LiFePO_4 .
4. The battery according to any one of the preceding claims, wherein the solid cathodic energy storage material is provided as granules.
5. The battery according to any one of the preceding claims, wherein the liquid catholyte comprises a p-type redox mediator selected from one or more of the group consisting of 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, and iodide (I), where in each case M is independently selected from the group consisting of Li, Na, K and NH_4 .
6. The battery according to Claim 5, wherein the active material is selected from one or more of the group consisting of, and iodide (I) (e.g. ferricyanide ($\text{M}_3\text{Fe}(\text{CN})_6$) and/or ferrocyanide ($\text{M}_4\text{Fe}(\text{CN})_6$)), where in each case M is independently selected from the group consisting of Li, Na, K and NH_4 .

7. The battery according to Claim 5, wherein the derivative of ferrocene is di(ethylsulfonic sodium) ferrocene ($C_{14}H_{16}FeS_2O_6Na_2$).
8. The battery according to any one of Claims 5 to 7, wherein the total concentration of the p-type redox mediator present in the catholyte is from 0.05 M to 1.5 M.
9. The battery according to any one of the preceding claims, wherein the solid anodic energy storage material is selected from one or more of the group consisting of $LiTi_2(PO_4)_3$, TiP_2O_7 , and $NaTi_2(PO_4)_3$.
10. The battery according to Claim 9, wherein the solid anodic energy storage material is $LiTi_2(PO_4)_3$.
11. The battery according to any one of the preceding claims, wherein the solid anodic energy storage material is provided as granules.
12. The battery according to any one of the preceding claims, wherein the total concentration of the n-type redox mediator present in the anolyte is from 0.5 M to 3 M.
13. The battery according to any one of the preceding claims, wherein the liquid in the liquid catholyte and liquid anolyte comprises water alone or in combination with an organic solvent suitable for use in a battery.
14. The battery according to Claim 13, wherein the liquid in the catholyte and anolyte is independently selected from water or water in combination with tetraglyme.
15. The battery according to any one of the preceding claims, wherein the liquid anolyte comprises an n-type redox mediator selected from one or more of the group consisting of viologens, Li_2S_x , Na_2S_x , and K_2S_x , wherein x is less than or equal to 8 and greater than or equal to 1.
16. The battery according to any one of the preceding claims, wherein:
 - the solid cathodic energy storage material is $LiFePO_4$;
 - the solid anodic energy storage material is $LiTi_2(PO_4)_3$;
 - the aqueous catholyte comprises $K_4Fe(CN)_6$ at a concentration of 0.3 M; and
 - the aqueous anolyte comprises Li_2S_2 at a concentration of 1 M.

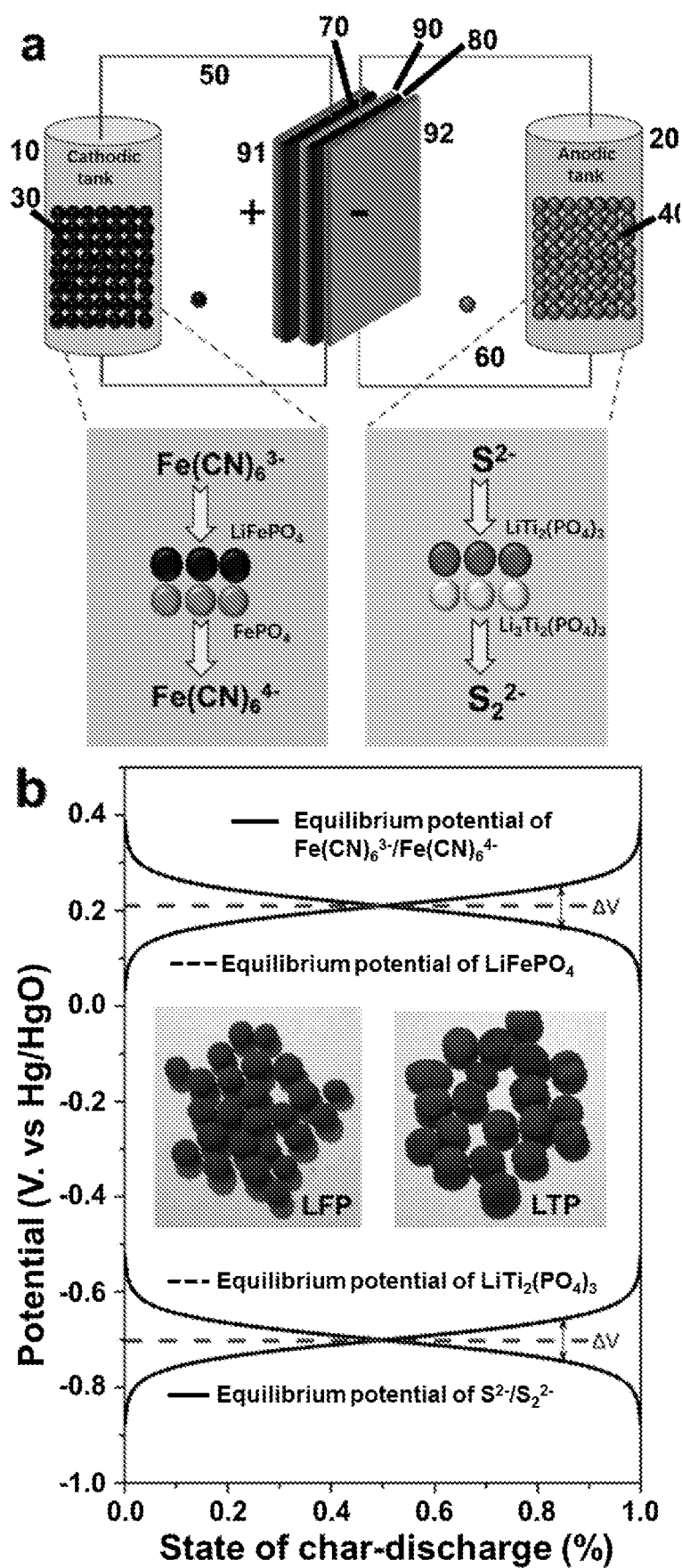


FIG. 1

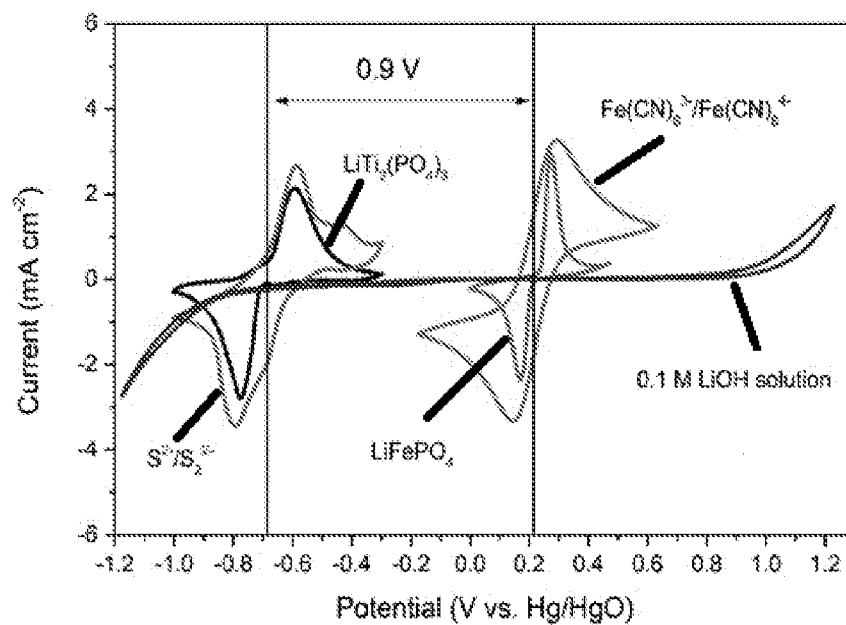


Fig.2

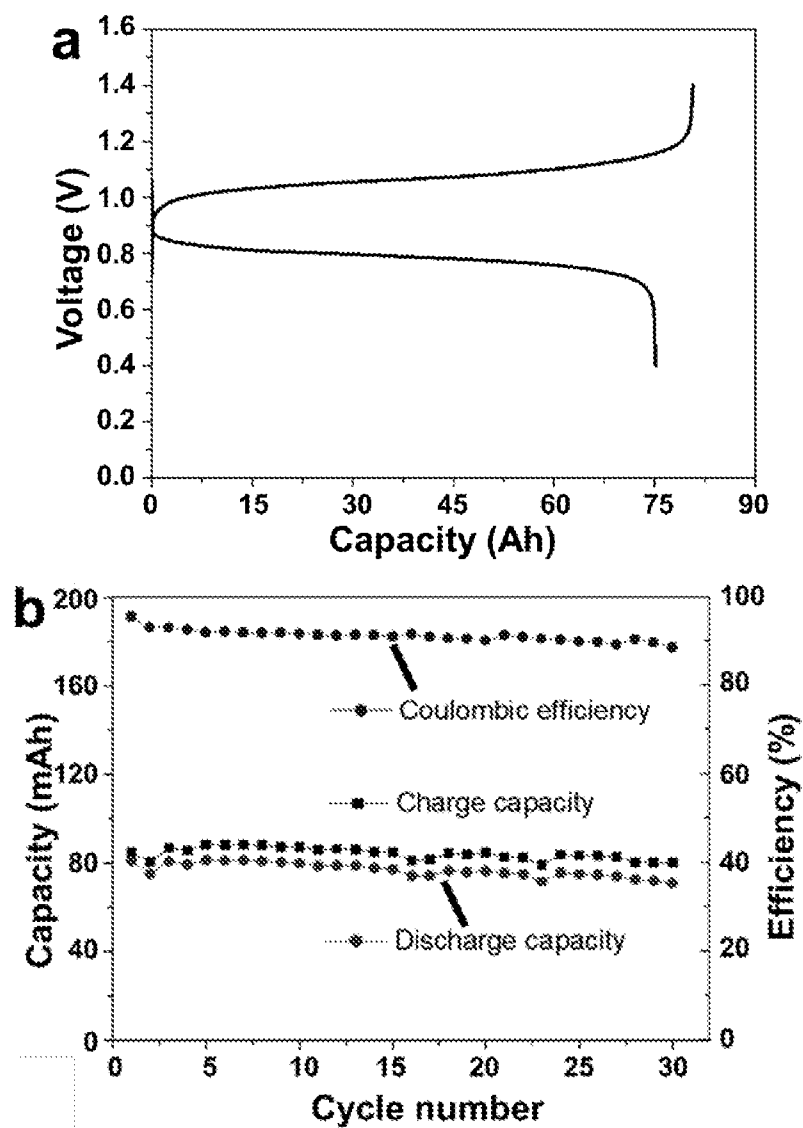


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050312

A. CLASSIFICATION OF SUBJECT MATTER**H01M 8/18 (2006.01)**

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: H01M 8/18, CPC: Y02E60/528

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

FAMPAT, CAPLUS, INSPEC, COMPENDEX, CNKI using Registry Numbers and keywords: battery, cell, flow, redox, mediate, solid, granule, energy, electrolyte, anolyte, catholyte, sulfide, viologen, pyridine, paraquat, diquat, bipolaron, ferrocene, iodide, 液流电池, 氧化还原介体, 固体, 阴极, 储能材料, 固态电极颗粒 and the like.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 103247816 A (BEIJING HAWAGA POWER STORAGE TECHNOLOGY COMPANY LTD.) 14 August 2013 paragraph [0009], [0022], Fig. 1, 2; of the original non-English language document (a machine translation is enclosed only for your reference)	1-16
A	ZHOU, M. ET AL., Nernstian-Potential-Driven Redox-Targeting Reactions of Battery Materials. <i>Chem</i> , 2 November 2017, Vol. 3, No. 6, pages 1036-1049 [Retrieved on 2019-08-30] <DOI: 10.1016/J.CHEMPR.2017.10.003> Fig. 2A, 2B; pg 1038	1-16
A	HUANG, Q. ET AL., Reversible chemical delithiation/lithiation of LiFePO ₄ : towards a redox flow lithium-ion battery. <i>Phys. Chem. Chem. Phys.</i> , , 13 December 2012, Vol. 15, No. 6, pages 1793-1797 [Retrieved on 2019-08-30] <DOI: 10.1039/C2CP44466F> Fig. 1A; pg 1794	-

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22/08/2019

(day/month/year)

Date of mailing of the international search report

16/09/2019

(day/month/year)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2019/050312

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/0244406 A1 (XIA, G. ET AL.) 27 September 2012 [0018]-[0019], Fig. 1, 2	-
A	US 2018/0072669 A1 (LIU, T. ET AL.) 15 March 2018 [0003], [0004], [0008], [0013], [0014]; Fig. 1	-
P,X	YU, J. ET AL., Redox Targeting-Based Aqueous Redox Flow Lithium Battery. <i>ACS Energy Lett.</i> , 6 September 2018, Vol. 3, No. 10, pages 2314-2320 [Retrieved on 2019-08-30] <DOI: 10.1021/ACSENERGYLETT.8B01420> Whole document	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2019/050312

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 103247816 A	14/08/2013	NONE	
US 2012/0244406 A1	27/09/2012	US 2014/0079976 A1 WO 2012/134553 A2	20/03/2014 04/10/2012
US 2018/0072669 A1	15/03/2018	NONE	