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(71) Applicant: **PRESIDENT AND FELLOWS OF HARVARD COLLEGE** [US/US]; 17 Quincy Street, Cambridge, MA 02138 (US).

(72) Inventors: **XI, Dawei**; 9 Oxford St, Cambridge, MA 02138 (US). **AZIZ, Michael, J.**; 63 Granville Road, Cambridge, MA 02138 (US). **YANG, Zheng**; 17 Quincy Street, Cambridge, MA 02138 (US).

(74) Agent: **MCDONALD, J., Cooper et al.**; Clark & Elbing LLP, 101 Federal Street, 15th Floor, Boston, MA 02110 (US).

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(54) Title: PH DECOUPLED REDOX FLOW BATTERIES

(57) Abstract: The present invention provides a single-membrane pH-decoupling redox flow batteries (e.g., aqueous redox flow batteries) that employ electrolytes of differing pH to develop a cell with high round-trip energy efficiency at an open-circuit voltage greater than the voltage for water splitting. Further, the invention provides an acid-base regeneration system to restore the negolyte and posolyte pHs to their initial values to compensate for any long-term acid/base crossover.

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pH DECOUPLED REDOX FLOW BATTERIES**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH**

This invention was made with government support under DE-AC05-76RL01830 awarded by U.S. Department of Energy (DOE). The government has certain rights in this invention.

5 BACKGROUND OF THE INVENTION

The need for decarbonization, the advantages of electrical-grid decentralization, and the intermittency of wind and solar energy are motivations for the development of grid-scale storage technologies. The aqueous redox flow battery (ARFB) is a promising solution, featuring safety, the decoupling of energy and power capacities, and potential long lifetime, recyclability, and low cost. Redox-active materials have
10 been rapidly developed to approach the requirements for practical grid-scale storage. Despite the advantages of ARFBs, the 1.23 V thermodynamic water splitting window presents practical challenges. Competing water splitting reactions can compromise the Coulombic efficiency of the cell and rapidly drive the two sides of the cell out of balance, greatly cutting the operational lifetime. Operation of ARFBs at higher voltage output is a potential pathway to achieving increased energy density, higher output power,
15 and lower capital cost, all of which improve the techno-economy and operational flexibility of the cell. Efforts have been put into designing redox-active species that allow higher cell voltage and developing conditions in which water-splitting kinetics remain sluggish. ARFBs known in the art suffer from short lifetimes and low overall energy efficiency, both of which must be improved in a commercially viable ARFB.

20 Accordingly, there is a need for new redox flow batteries and method of use thereof.

SUMMARY OF THE INVENTION

The present invention features a single-membrane, pH-decoupling redox flow batteries (e.g., aqueous redox flow batteries) that employ a negolyte comprising a solution of a first redox active species at a first pH (e.g., acidic, such as mildly acidic, e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, e.g., a pH of
25 about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7, or basic, e.g., mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13) and a posolyte comprising a solution of a second redox active species at a second pH (e.g., acidic, such as mildly acidic, e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, e.g.,
30 a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7, or basic, e.g., mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13), that is at least 0.5 (e.g., at least 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, or 6) pH units lower than the first pH, resulting in a cell with high round-trip energy efficiency at an
35 open-circuit voltage greater than the thermodynamic voltage for water splitting (e.g., greater than about 1.2 V, e.g., about 1.3 V, about 1.4 V, about 1.5 V, about 1.6 V, about 1.7 V, about 1.8 V, or about 1.75 V). ARFBs of the present invention may maintain this open circuit voltage for long durations without degradation by, in part, including a pH rebalancing means. The pH rebalancing means enables the pH of

both the negolyte and/or the posolyte to remain at or near their initial values, thereby compensating for any acid/base crossover. In some embodiments, the first and second pHs are >7 , e.g., 9-12 and 12-14.

In an aspect, the invention provides a flow battery including a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, a single membrane disposed between the negolyte and the posolyte, and a pH rebalancing means. The membrane is a cation exchange membrane that allows the passage of one or more cationic charge carriers other than proton or hydronium. The negolyte includes a solution of a first redox active species at a first pH (e.g., acidic, such as mildly acidic, e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, e.g., a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7 or basic, e.g., at least 7 or mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13). The posolyte includes a solution of a second redox active species at a second pH (e.g., mildly acidic, e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, e.g., a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7 or basic, e.g., mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13). In some embodiments, the pH of the posolyte is at least 0.5 (e.g., at least 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, or 6) pH units lower than the pH for the negolyte. The pH rebalancing means is configured to supply hydroxide ions to the negolyte and protons to the posolyte. In some embodiments, the negolyte pH is from about 10.5 to about 14.5. In some embodiments, the first and second pHs are >7 , e.g., 9-12 and 12-14.

In a further aspect, the invention provides a flow battery including a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode; a single membrane disposed between the negolyte and the posolyte; and a pH rebalancing means. The membrane is an anion exchange membrane that allows the passage of one or more anionic charge carriers other than hydroxide. The negolyte includes a solution of a first redox active species at a first pH, e.g., of from 7 to about 13. The posolyte includes a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH, e.g., of at most 7. The pH rebalancing means is configured to supply hydroxide ions to the negolyte and protons to the posolyte. In some embodiments, the posolyte pH is from 0 to about 4.

In some embodiments of a preceding embodiment, the flow battery includes a posolyte storage reservoir and/or a negolyte storage reservoir.

In some embodiments, the pH rebalancing means includes a sub-cell including: (a) the negolyte in contact with a second negolyte electrode; (b) the posolyte in contact with a second posolyte electrode; and (c) a membrane separating the negolyte and the posolyte. In some embodiments, the membrane is a bipolar membrane including an anion exchange membrane in contact with the negolyte and a cation exchange membrane in contact with the posolyte.

In some embodiments, the sub-cell further includes a voltage source in electrical contact with the second negolyte electrode and the second posolyte electrode, wherein the voltage source is of sufficient potential

to perform a water-dissociation reaction, producing hydroxide ions in the negolyte and producing protons in the posolyte.

In some embodiments, the sub-cell further includes a voltage source, wherein the voltage source is of sufficient potential to perform a proton coupled electron transfer (PCET) reaction, wherein the proton coupled electron transfer reaction results in the generation of protons from water in the posolyte and/or hydroxide from water in the negolyte. In some embodiments, the PCET reaction includes a hydrogen evolution reaction, an oxygen evolution reaction, a hydrogen oxidation reaction, or an oxygen reduction reaction.

In some embodiments, the flow battery further includes a second negolyte electrode in contact with the negolyte, a second posolyte electrode in contact with the posolyte, and a voltage source in electrical contact with the second negolyte electrode and the second posolyte electrode, wherein the voltage source is of sufficient potential to perform a PCET reaction, wherein the PCET reaction results in the generation of protons from water in the second posolyte and/or hydroxide from water in the second negolyte.

In some embodiments, the PCET reaction includes a hydrogen evolution reaction, an oxygen evolution reaction, a hydrogen oxidation reaction, or an oxygen reduction reaction.

In some embodiments, the pH rebalancing means maintains the concentration of hydroxide ions in the negolyte to within 0.01 M of its original value. In some embodiments, the pH rebalancing means maintains the concentration of protons in the posolyte to within 0.01 M of its original value. In some embodiments, the flow battery includes an open circuit voltage of at least 1.3 V (e.g., at least 1.75 V). In some embodiments, the flow battery can be continuously operated for at least 7 days (e.g., at least 18 days) with an energy efficiency loss of at most 20%.

In some embodiments, the first redox active species includes a quinone, an anthraquinone, a naphthoquinone, a phenazine, a phenoxazines, a phenothiazine, a diquaternized bipyridine, a metal chelate, or a reduced form thereof, e.g., an anthraquinone.

In some embodiments, the second redox active species includes aluminum, vanadium, chromium, cobalt, iron, manganese, cobalt, nickel, copper, or lead, or an oxide thereof. In some embodiments, the second redox active species includes bromine, chlorine, iodine, molecular oxygen, ferricyanide or ferrocyanide, a ferrocene derivative, $\text{Fe}(\text{Bhmbpy})_3$ and salts or ions thereof; aluminum(III) biscaltrate monocatecholate, or a benzoquinone, e.g., ferricyanide or ferrocyanide.

In some embodiments, the first redox active species is an anthraquinone, and the second redox active species is ferricyanide or ferrocyanide.

In a further aspect, the invention provides a method of maintaining the pH of a flow battery including: (a) providing the flow battery as described herein; (b) allowing the battery to discharge for a duration; and (c) operating the pH rebalancing system, returning the pH of the negolyte to the first pH and/or returning the pH of the posolyte to the second pH.

In a further aspect, the invention provides a method of maintaining the pH of a flow battery including: (a) providing the flow battery of a preceding embodiment; and (b) allowing the battery to discharge for a

duration, wherein the pH of the first negolyte is maintained at about the first pH for the duration, and/or the pH of the first posolyte is maintained at about the second pH for the duration.

In some embodiments, the concentration of hydroxide ions in the negolyte varies by less than 0.01 M from its initial value throughout the duration.

- 5 In some embodiments, the concentration of protons in the posolyte varies by less than 0.01 M from its initial value throughout the duration.

In a further aspect, the invention provides a pH-rebalancing redox flow battery including a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, and a single cation exchange membrane disposed between the negolyte and the posolyte, wherein: the negolyte includes a
10 solution of a first redox active species at a first pH, e.g., of from about 10.5 to 14.5, and the posolyte includes a solution of a second redox active species at a second pH, e.g., of from about 1 to 4, that is at least 0.5 pH units lower than the first pH; and the cation exchange membrane allows the passage of one or more cationic charge carriers other than proton or hydronium.

In a further aspect, the invention provides a pH-rebalancing redox flow battery including a negolyte in
15 contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, and a single anion exchange membrane disposed between the negolyte and the posolyte, wherein: the negolyte includes a solution of a first redox active species at a first pH, e.g., of from about 7 to 13, and the posolyte includes a solution of a second redox active species at a second pH, e.g., from about 0 to 4, that is at least 0.5 pH
20 units lower than the first pH; and the anion exchange membrane allows the passage of one or more anionic charge carriers other than hydroxide.

Definitions

By “about” is meant $\pm 10\%$ of a recited value.

By “in fluid communication with” is meant any connection between at least two device elements that allows for fluid flow therebetween. Fluid communication between the at least two device elements may
25 allow the composition of a fluid disposed within the device elements (e.g., the posolyte or negolyte) to be identical between the at least two device elements.

By “electrical contact” is meant any form of contact between two materials that allows the unrestricted or partially restricted flow of electrons between the materials. For example, the two materials may be connected by one or more of a conductive wire, a semiconductive wire, a battery, or an electrical load.

30 By “pH rebalancing means” is meant a component of a device or system configured to maintain or restore the pH of a solution (e.g., the negolyte and the posolyte of an ARFB). The pH rebalancing means may include, e.g., a secondary electrochemical cell. In some embodiments, the pH rebalancing means may perform a chemical reaction, e.g., a chemical reaction producing protons (e.g., hydrogen oxidation reactions or oxygen evolution reactions) or hydroxide ions (e.g., oxygen reduction reactions or hydrogen
35 evolution reactions).

BRIEF DESCRIPTION OF THE DRAWINGS

FIGs. 1A-1B show a schematic plot of a single-membrane, pH-decoupling, aqueous redox flow battery (ARFB). **FIG. 1A** shows an ARFB including a cation exchange membrane (CEM). A positive charge carrier (M^+) is allowed to cross the CEM. The proton concentration in the acidic electrolyte may be at least 10 times lower than the concentration of M^+ . **FIG. 1B** shows an ARFB including an anion exchange membrane (AEM). A negative charge carrier (X^-) is allowed to cross the AEM. The hydroxide concentration in the acidic electrolyte may be at least 10 times lower than the concentration of X^- .

FIG. 2 shows a schematic plot of a bipolar membrane (BPM) pH recovery sub-cell.

FIG. 3 shows a mild-pH decoupling ARFB of the present invention. The posolyte of the ARFB includes a first redox active species, has, e.g., a pH of from 3 to 7, and is in contact with an electrode. The half-cell is in fluid communication with a posolyte storage tank, which in turn is in fluid communication with a pH rebalancing sub-cell. The negolyte of the ARFB includes a second redox active species, has, e.g., a pH of from 7 to 14, and is in contact with an electrode. The half-cell is in fluid communication with a negolyte storage tank, which in turn is in fluid communication with the pH rebalancing sub-cell. A single membrane (in the present embodiment, a cation exchange membrane (CEM)) separates the posolyte and the negolyte. The negolyte and posolyte of the sub-cell are separated by a bipolar membrane (BPM). It should be understood that an ARFB including an anion exchange membrane (AEM) instead of a cation exchange membrane could be constructed similarly, by utilizing an AEM instead of a CEM, with a pH, e.g., of from 0 to 7, for the posolyte, and a pH, e.g., of from 7 to 11, for the posolyte.

FIG. 4 shows a schematic plot of a pH recovery cell that uses PCET to generate protons and hydroxide ions. Protons may be generated by a hydrogen oxidation reaction (Eq. 1) or an oxygen evolution reaction (Eq. 2). Hydroxide ions may be generated by an oxygen reduction reaction (Eq. 3) or a hydrogen evolution reaction (Eq. 4).

DETAILED DESCRIPTION

AFRBs have emerged as promising systems for energy storage from intermittent renewable sources. The usable voltage from an AFRB is dependent, in part, on the range of voltages under which the aqueous solvent does not undergo oxidation and reduction. To expand this window, the linear dependence of the water splitting voltage on pH can be exploited. By introducing a pH difference between the posolyte and the negolyte, the total achievable voltage out of a battery may be increased. However, operating an ARFB with a pH difference between the negolyte and the posolyte requires the pH to be maintained during operation, or performance suffers. Complicating matters further, the pH difference between the posolyte and the negolyte is often lost during operation as a result of acid/base crossover, thereby causing overall poor energy efficiency and short battery lifetimes. Simply restoring the pH of the posolyte or negolyte (e.g., by replenishing a supply of acid or base to the posolyte or negolyte) has further proven to be a cost and energy inefficient means of prolonging battery life.

The present invention provides batteries that circumvent these problems by utilizing a negolyte under a first pH (e.g., acidic, such as mildly acidic, e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, e.g., a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7 or basic, e.g., mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13,

e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13) and/or a posolyte under a second pH (e.g., acidic, such as mildly acidic, e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, e.g., a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7, or basic e.g., mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13), that is at least 0.5 (e.g., at least 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, or 6) pH units lower than the first pH. In some embodiments, the difference in pH between the first and second pHs is 0.5 to 7 units, e.g., 0.5 to 5, 0.5 to 3, 0.5 to 1, 1 to 7, 1 to 5, 1 to 3, 2 to 7, 2 to 5, 2 to 3, 3 to 7, 3 to 5, 4 to 7, 4 to 5, or 6 to 7 units. In some embodiments, the first and second pHs are >7, e.g., 9-12 and 12-14. The resulting ARFBs are characterized by a high round-trip energy efficiency at an open-circuit voltage greater than the thermodynamic voltage for water splitting (e.g., greater than about 1.2 V, e.g., at least 1.3 V, at least 1.4 V, at least 1.5 V, at least 1.6 V, at least 1.7 V, or at least 1.75 V). Further, the present invention includes a pH rebalancing means that allows the pH of both the negolyte and the posolyte to remain at or near their initial values, thereby compensating for any acid/base crossover.

Aqueous Redox Flow Batteries

The present invention features a single-membrane, pH-decoupling, redox flow batteries (e.g., aqueous redox flow batteries (ARFBs)) with posolytes having a pH that is at least 0.5 (e.g., at least 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, or 6) pH units lower than the pH of the negolytes. ARFBs of the present invention may further include a pH rebalancing means, suitable for maintaining the pH of the negolyte and/or the pH of the posolyte.

The operation of ARFBs is dependent on the voltage range the ARFB may operate under. This voltage range is typically limited by the operable range of the water ARFBs utilize (i.e., the voltage range within which water does not undergo oxidation or reduction). The voltage of the water splitting window varies linearly with pH; whereas crossover fluxes vary exponentially. Accordingly, the utilization of mildly acidic (e.g., a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or about 7) and/or basic (mildly basic, e.g., a pH of at most 13, e.g., a pH of 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13) electrolyte can increase the operable voltage of the ARFB (e.g., to at least 1.3 V, at least 1.4 V, at least 1.5 V, at least 1.6 V, at least 1.7 V, or at least 1.75 V).

Operating an ARFB with a maximum pH difference between the posolyte and the negolyte is not sufficient to create an energetically and commercially viable battery. In highly basic and/or acidic electrolyte solutions, proton and/or hydroxide ions become the majority charge carriers of the battery, and therefore typically traverse an ion exchange membrane during battery discharge, neutralizing the pH difference. Further, there exists a thermodynamic driving force for protons and/or hydroxide ions to traverse the ion exchange membrane and neutralize the pH difference, driving additional crossover. Over prolonged operation, eventual acid-base crossover and electrolyte neutralization is unavoidable.

The present invention provides ARFBs that overcome this limitation. The electrolytes may be mildly acidic and/or mildly basic and may include significantly higher concentrations of supporting electrolytes (e.g.,

NaCl). For example, a mildly acidic posolyte with NaCl supporting salt will not have large amount of crossover of protons through a cation exchange membrane (CEM), because the main charge carrier will be Na^+ ions. Additionally, hydroxide ions in the basic negolyte solution are precluded from crossing over as the negatively charged hydroxide ion cannot traverse the CEM. This holds even if the negolyte includes large concentrations of hydroxide (i.e., is very basic). The same result can be achieved using an anion exchange membrane (AEM) in combination with a mildly basic negolyte and an acidic posolyte. Utilizing this design, acid-base crossover rates may be decreased to less than 200 nmol/s/cm^2 (e.g., less than 100 nmol/s/cm^2 , less than 50 nmol/s/cm^2 , less than 25 nmol/s/cm^2 , less than 10 nmol/s/cm^2 , less than 5 nmol/s/cm^2 , less than 1 nmol/s/cm^2 , less than 0.9 nmol/s/cm^2 , less than 0.8 nmol/s/cm^2 , less than 0.7 nmol/s/cm^2 , less than 0.6 nmol/s/cm^2 , less than 0.5 nmol/s/cm^2 , less than 0.4 nmol/s/cm^2 , less than 0.3 nmol/s/cm^2 , less than 0.2 nmol/s/cm^2 , less than 0.1 nmol/s/cm^2 , etc.).

The present invention further provides ARFBs including a pH rebalancing means configured to restore the negolyte and posolyte pH to their desired values. Exemplary pH rebalancing means of the present invention include (1) a bipolar membrane (BPM) sub cell resulting in water dissociation and (2) a cell with a single membrane employing proton coupled electron transfer (PCET) reactions which generate protons and/or hydroxide ions (e.g., oxygen evolution reactions, hydrogen evolution reactions, oxygen reduction reactions, or hydrogen oxidation reaction). In a BPM sub-cell, the protons and hydroxide ions are generated in a secondary electrochemical cell including the BPM. In a pH rebalancing means including a cell with a single membrane, the PCET reaction may be performed in the ARFB posolyte and negolyte directly (with the battery electrodes or a secondary set of electrodes) or in a separate sub-cell.

The negolyte includes, e.g., a redox active species dissolved or suspended in aqueous solution in contact with a negolyte electrode. The posolyte includes, e.g., a redox active species dissolved in an aqueous solution in contact with a posolyte electrode. The posolyte and the negolyte are separated by a membrane (e.g., an AEM or a CEM). In particular, the present invention provides ARFBs including a single membrane separating the posolyte and the negolyte.

Any suitable redox active species may be employed in the posolyte or the negolyte of the ARFB. Organic and inorganic redox active species may be employed. In some embodiments, the redox active species itself may undergo proton-coupled electron transfer (PCET) during oxidation or reduction. Organic species amenable to use as redox active species in the systems of the present invention include, but are not limited to, benzoquinones, naphthoquinones, anthraquinones, phenazines (e.g., 7,8-dihydroxyphenazine-2-sulfonic acid), alloxazines, isoalloxazines, phenoxazines, phenothiazine. The concentration of a redox active species may be any suitable amount. Ranges include, for example, from about 0.1 M to about 15 M.

The negolyte and/or the posolytes of the present invention include a solute (e.g., an electrolyte, e.g., salts including NH_4^+ , Li^+ , Na^+ , or K^+) which serves as the major charge carrier of the ARFB. By including a solute at a large concentration of, e.g., at least 10 times the concentration of hydroxide ions (e.g., 20 times, 50 times, 100 times, 500 times, or 1000 times) or at least 10 times the concentration of protons (e.g., 20 times, 50 times, 100 times, 500 times, or 1000 times), acid/base crossover is suppressed in favor of crossover of the charge carrier. In some embodiments, negolytes and/or posolytes of the present invention may include a cosolvent (e.g., an alcohol) to increase the conductivity of an electrode or

increase the solubility of a particular species. In some embodiments, the negolyte and/or posolyte may include a buffer. The buffer may be included in the pH rebalancing means or included in addition to the pH rebalancing means.

In some embodiments, the ARFBs described herein may include one or more redox mediators in contact with the negolyte, e.g., molecular oxygen, ferricyanide, potassium permanganate, DBEAQ (4,4'-([9,10-anthraquinone-2,6-diyl]dioxo)di-butyric acid), DPPEAQ ([9,10-dioxo-9,10-dihydroanthracene-2,6-diyl]bis[oxy]bis[propane-3,1-diyl])bis(phosphonic acid)), DPivOHAQ (3,3'-(9,10-anthraquinone-diyl)bis(3-methyl-butanoic acid)), DBAQ (4,4'-(9,10-anthraquinone-diyl)dibutanoic acid), DPAQ (anthraquinone-2,6-dipropionic acid), a benzoquinone, or a naphthoquinone.

In some embodiments, the ARFB may include one or more storage reservoirs. For example, the negolyte half-cell may be in fluid communication with a negolyte reservoir and the posolyte half-cell may be in fluid communication with a posolyte reservoir. In some embodiments, the negolyte half-cell of the sub-cell is in fluid communication with the negolyte half-cell of the ARFB via the negolyte reservoir. In some embodiments, the posolyte half-cell of the sub-cell is in fluid communication with the posolyte half-cell of the ARFB via the negolyte reservoir.

An ARFB of the invention may include additional components as is known in the art (e.g., additional reservoirs, pumps, flow plates, one or more additional electrodes, one or more additional negolyte solutions, one or more additional posolyte solutions, etc.). The reservoir may be recirculated by any means known in the art (e.g., convection, sonication, etc.). An ARFB may further include one or more pumps, e.g., to pump a solution from an external reservoir to the half-cell or sub cell. In some embodiments, a pump is used to transport a solution or suspension past one or both electrodes.

The balance of the system around the cell includes fluid handling and storage, and voltage and round-trip energy efficiency measurements can be made. Systems configured for measurement of the flow, pH, pressure, temperature, current density, or cell voltage of the negolyte or the posolyte may be included and used to evaluate cells. Fluid sample ports can be provided to permit sampling of both electrolytes, which will allow for evaluation of parasitic losses due to hydroxide crossover, proton or hydronium crossover, or side reactions. Electrolytes can be sampled and analyzed with standard techniques.

Suitable cells, electrodes, membranes, and pumps for ARFBs are known in the art, e.g., WO 2014/052682, WO 2015/048550, WO 2016/144909, and WO 2020/072406, the battery components of which are hereby incorporated by reference.

ARFBs of the present invention may have a cell voltage greater than the thermodynamic voltage of water splitting (e.g., at least 1.23 V, at least 1.3 V, at least 1.4 V, at least 1.5 V, at least 1.6 V, at least 1.7 V, or at least 1.75 V) and may be operated (e.g., continuously or periodically) for at least 1 day (e.g., at least 2 days, at least 3 days, at least 4 days, at least 5 days, at least 6 days, at least 7 days, at least 8 days, at least 9 days, at least 10 days, at least 11 days, at least 12 days, at least 13 days, at least 14 days, at least 15 days, at least 16 days, at least 17 days, or at least 18 days).

Negolytes

Negolytes of the present invention include a redox active species dissolved or suspended in an aqueous solution. In some embodiments, the aqueous solution is acidic (e.g., of a pH of at most 7, e.g., from 0 to 7, from 0 to about 6, from 0 to about 5, from 0 to about 4, etc.). In some embodiments, the aqueous solution is basic (e.g., of a pH of at least 7, e.g., from about 7 to about 14.5, e.g., from about 9 to about 14.5, from about 10 to about 14.5, or from about 10.5 to about 14.5). In some embodiments, the aqueous solution has a mildly acidic pH (e.g., e.g., a pH of at least 1, e.g., from about 1 to about 7, about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or about 7) or a mildly basic pH (e.g., a pH of at most 13, e.g., about 7 to about 13, e.g., about 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13). In some embodiments, the negolyte is basic. In some embodiments, the aqueous solution of the negolyte is at least 0.5 (e.g., at least 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 13.5, or 14) pH units higher than the posolyte solution. In embodiments utilizing an AEM separating the negolyte and the posolyte, the negolyte may be held at a mildly basic pH (e.g., a pH of at most 13, e.g., a pH of about 7 to about 13, e.g., about 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13). Negolytes of the present invention may include a base to modify the pH of the negolyte. In some embodiments the base may be a weak base (e.g., NH_4OH). In some embodiments, the base may be a strong base (e.g., LiOH , NaOH , or KOH).

In some embodiments, the negolyte includes an organic a redox active species. Exemplary organic redox active species include quinones (e.g., hydroquinones), anthraquinones (e.g., hydroanthroquinones, e.g., 9,10-anthraquinone, 2,6-dihydroxy-9,10-anthraquinone, 1,5-dimethyl-2,6-dihydroxy-9,10-anthraquinone, 2,3,6,7-tetrahydroxy-9,10-anthraquinone, 1,3,5,7-tetrahydroxy-2,4,6,8-tetramethyl-9,10-anthraquinone, and 2,7-dihydroxy-1,8-dimethyl-9,10-anthraquinone), naphthoquinones (e.g., a hydronaphthoquinones), reduced forms of phenazine (e.g., 7,8-dihydroxyphenazine-2-sulfonic acid), reduced monoquaternized or N,N'-diquaternized phenazines, reduced phenoxazines, reduced phenothiazine, or reduced form of diquaternized bipyridines (e.g., alkyl viologen radical monocations). In some embodiments, the negolyte of the present invention may include a metal chelate (e.g., an iron chelate (e.g., FeDIPSO) or a chromium chelate (e.g., CrPDTA). In some embodiments, the negolyte of the present invention may include a mixture of redox active species. Other redox active species suitable for use in negolytes of the invention are described in WO 2014/052682, WO 2015/048550, WO 2016/144909, and WO 2020/072406, the redox active species of which are incorporated by reference. The redox active species may be dissolved or suspended in solution (e.g., aqueous solution).

The concentration of each redox active species may be any suitable amount (e.g., from about 0.1 M to about 15 M, e.g., about 0.1 M, about 0.2 M, about 0.3 M, about 0.4 M, about 0.5 M, about 0.6 M, about 0.7 M, about 0.8 M, about 0.9 M, about 1 M, about 1.1 M, about 1.2 M, about 1.3 M, about 1.4 M, about 1.5 M, about 1.6 M, about 1.7 M, about 1.8 M, about 1.9 M, about 2 M, about 2.2 M, about 2.4 M, about 2.6 M, about 2.8 M, about 3 M, about 3.2 M, about 3.4 M, about 3.6 M, about 3.8 M, about 4 M, about 4.2 M, about 4.4 M, about 4.6 M, about 4.8 M, about 5 M, about 5.5 M, about 6 M, about 6.5 M, about 7 M,

about 7.5 M about 8 M, about 8.5 M, about 9 M, about 9.5 M, about 10 M, about 11 M, about 12 M, about 13 M, about 14 M, or about 15 M).

Posolytes

Posolytes of the present invention include a redox active species dissolved or suspended in an aqueous solution. In some embodiments, the aqueous solution is acidic (e.g., of a pH of at most 7, e.g., from 0 to 7, from 0 to 6, from 0 to 5, from 0 to 4, etc.). In some embodiments, the aqueous solution is basic (e.g., of a pH of at least 7, e.g., from 7 to about 14.5, e.g., from about 9 to about 14.5, from about 10 to about 14.5, or from about 10.5 to about 14.5). In some embodiments, the aqueous solution has a mildly acidic pH (e.g., e.g., a pH of at least 1, e.g., from about 1 to 7, about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or about 7) or a mildly basic pH (e.g., a pH of at most 13, e.g., from 7 to about 13, e.g., 7, about 7.5, about 8, about 8.5, about 9, about 9.5, about 10, about 10.5, about 11, about 11.5, about 12, about 12.5, or about 13). In some embodiments, the posolyte is acidic. In some embodiments, the aqueous solution of the posolyte is at least 0.5 (e.g., at least 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, 10.5, 11, 11.5, 12, 12.5, 13, 13.5, or 14) pH units lower than the negolyte solution. In embodiments utilizing an CEM separating the negolyte and the posolyte, the posolyte may be held at a mildly acidic pH (e.g., e.g., a pH of at least 1, e.g., a pH of from about 1 to 7, a pH of about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5, about 5, about 5.5, about 6, about 6.5, or 7). Posolytes of the present invention may include an acid to modify the pH of the posolyte. In some embodiments the acid may be a weak acid. In some embodiments, the acid may be a strong acid (e.g., HCl or H₂SO₄).

Examples of redox active species for the posolyte include bromine, chlorine, iodine, molecular oxygen, vanadium, chromium, cobalt, iron (e.g., ferricyanide/ferrocyanide or a ferrocene derivative, e.g., as described in WO 2018/032003; Fe(Bhmbpy)₃ and salts or ions) aluminum, e.g., aluminum(III) biscitrate monocatecholate, manganese, cobalt, nickel, copper, or lead, e.g., a manganese oxide, a cobalt oxide, or a lead oxide. A benzoquinone may also be used as the redox active species. Other redox active species suitable for use in posolytes of the invention are described in WO 2014/052682, WO 2015/048550, WO 2016/144909, and WO 2020/072406, the redox active species of which are incorporated by reference. The redox active species may be dissolved or suspended in solution (e.g., aqueous solution).

In some embodiments, the negolyte of the present invention may include a mixture of redox active species. The concentration of each redox active species may be any suitable amount (e.g., from about 0.1 M to about 15 M, e.g., about 0.1 M, about 0.2 M, about 0.3 M, about 0.4 M, about 0.5 M, about 0.6 M, about 0.7 M, about 0.8 M, about 0.9 M, about 1 M, about 1.1 M, about 1.2 M, about 1.3 M, about 1.4 M, about 1.5 M, about 1.6 M, about 1.7 M, about 1.8 M, about 1.9 M, about 2 M, about 2.2 M, about 2.4 M, about 2.6 M, about 2.8 M, about 3 M, about 3.2 M, about 3.4 M, about 3.6 M, about 3.8 M, about 4 M, about 4.2 M, about 4.4 M, about 4.6 M, about 4.8 M, about 5 M, about 5.5 M, about 6 M, about 6.5 M, about 7 M, about 7.5 M about 8 M, about 8.5 M, about 9 M, about 9.5 M, about 10 M, about 11 M, about 12 M, about 13 M, about 14 M, or about 15 M).

Membranes

ARFBs of the present invention include one or more membranes, e.g., a membrane disposed between two reservoirs (e.g., between a reservoir including the negolyte and a reservoir including the posolyte), configured to allow the passage of certain materials while inhibiting the passage of other materials.

- 5 ARFBs of the present invention feature only a single membrane disposed between the posolyte and the negolyte. One or more additional membranes may be present throughout the ARFB (e.g., separating the negolyte of a sub-cell and the posolyte of a sub-cell).

In some embodiments, the membrane may be an ion exchange membrane. An ion exchange membrane (IEM) is a porous material designed to prevent the passage of non-ionic species through the membrane.

- 10 An IEM may be a cation exchange membrane (CEM) or an anion exchange membrane (AEM). IEMs are commonly made from polymeric materials with hydrophobic and hydrophilic domains. The hydrophilic domains are typically characterized by acidic groups (e.g., $-\text{SO}_3\text{H}$, $-\text{COOH}$, PO_3H_2 , etc.) alkyl- or arylammonium groups (e.g., piperidinium), alkyl- or arylphosphonium groups (e.g., triphenylphosphonium), or alkyl- or aryl sulfonium groups (e.g., sulfone) which allow for the shuttling of
15 ions through the hydrophilic domains of the polymer. An IEM may be pretreated (e.g., by soaking the IEM in a solution of an electrolyte (e.g., NaCl or KCl)) prior to usage.

- Exemplary CEMs include Nafion® (i.e., a sulfonated tetrafluoroethylene fluoropolymer, e.g., Nafion® 117), Ultrex CMI 7000 (polystyrene crosslinked with divinyl benzene with numerous sulfonic acid groups), Zirfon (a polysulfone matrix mixed with ZrO_2), Hyflon (a copolymer of tetrafluoroethylene and 2,2,4,4-trifluoro-5-trifluoromethoxy-1,3-dioxole), heteropolyacids (e.g., polymolybdates, polytungstates, etc.), and gelled acid electrolytes (e.g., borophosphates, borosulfonic acids, etc.). In some embodiments, the cation exchange membrane is soaked in an acid solution (e.g., H_2SO_4 , H_3PO_4 , acetic acid, etc.) prior to use. In some embodiments, the CEM is or includes polyethylene terephthalate (PET) (e.g., Fumasep® E-620k).

- Exemplary AEMs include polymers with cationic functional groups such as quaternary ammoniums (e.g.,
25 poly(fluorenyl aryl piperidinium)), imidazolium and benzimidazoliums (e.g., benzimidazolium poly(phenylene oxide)), guanidiniums (e.g., poly(aryl ether sulfone) hexaalkylguanidinium), pyridines (e.g., (poly(vinyl alcohol))-co-(4-formyl-1-methyl-pyridinium benzenesulfonate)), phosphoniums (e.g., tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternary phosphonium hydroxides), sulfoniums (e.g., poly(ether sulfone) hydroxide), and metal ions (e.g., dicyclopentadiene-co-bis(4'-(2-oxo-noborene)-
30 terpyridine ruthenium(II)). In some embodiments, the AEM is or includes a perfluorosulfonic acid membrane. In some embodiments, the AEM is or includes a polytetrafluoroethylene (PTFE) polymer backbone functionalized with sulfonium (e.g., Selemion® DSV-N).

- In some embodiments, the invention may further include a bipolar membrane (BPM), e.g., in a pH rebalancing sub-cell. A bipolar membrane is a two-layer composite including an AEM on a first side
35 (referred to as the anion exchange layer (AEL)) and a CEM on a second side opposite the first side (referred to as the cation exchange layer (CEL)). When a DC current is passed over the BPM, water is dissociated inside of the membrane into hydroxide and protons (e.g., as hydronium). Because of the bipolar nature of the membrane, hydroxides exclusively exit the membrane via the AEM side and protons exit the membrane via the CEM side. In some embodiments, the junction region between the AEL and

CEL may be a smooth junction (i.e., a junction including a clearly defined border between the AEL and the CEL), a grooved junction (i.e., a junction including a plurality of portions wherein continuous AEL material is disposed within the CEL and continuous CEL material is disposed within the AEL), or a heterogeneous junction (i.e., a junction including a region wherein discrete regions of CEL material and discrete regions of AEL material are mixed, and/or a chemical bond is formed between the AEL and the CEL (e.g., via crosslinking). In some embodiments, the BPM includes a polymer matrix with a vinyl monomer disposed throughout. In some embodiments, the base polymer matrix includes or is formed from polystyrene, sodium alginate, poly(phenylene oxide), chitosan, polyvinyl chloride, poly ethyl ether ketone, polysulfone, poly vinylidene fluoride, and copolymers thereof. In some embodiments, the CEL includes polymers functionalized with acidic functional groups (e.g., sulfonic acid or phosphonic acid) or negatively charged functional groups (e.g., carboxylate). In some embodiments, the AEL includes polymers functionalized with basic functional groups (e.g., tertiary amines, secondary amines, or diamines) or positively charged functional groups (e.g., quaternary ammonium ions).

BPMs suitable for the present invention include any BPM known in the art to be usable in aqueous media (see, e.g., Parnamae et al.; *Bipolar Membranes: A review on Principles, Latest Developments, and Applications*; J. Membr. Sci., 617 (2021); 118538, the BPMs of which are incorporated herein by reference). A BPM may be constructed by combining an AEM described herein with as the AEL, and a CEM described herein as the CEL. In some embodiments, the AEL is or includes a polysulfone backbone functionalized with quaternary ammonium ions; and the CEL is or includes a crosslinked poly-ether ether ketone backbone functionalized with sulfonic acid (e.g., Fumasep® FBM).

By separating the posolyte and the negolyte using an IEM membrane, significant crossover of select ions (e.g., hydronium or hydroxide) can be prevented. For example, by separating the posolyte and the negolyte with an AEM, crossover of positively charged ions (e.g., hydronium and/or acidic protons) may be reduced or prevented. This allows for the posolyte to be held at a highly acidic (i.e., a pH of at most 2, at most 1, or at most 0) pH while precluding crossover of hydronium and/or acidic protons. With a CEM, crossover of anions may be reduced or prevented, allowing for the negolyte to be held at highly basic (e.g., a pH of at least 12, at least 13, or at least 14) pH while precluding crossover of hydroxide.

Electrodes

Each of the negolyte and the posolyte are in contact with an electrode. Electrodes suitable for the invention include any carbon electrode, e.g., glassy carbon electrodes, carbon paper electrodes, carbon felt electrodes, or carbon nanotube electrodes. Other suitable electrodes may include metals such as stainless steel, copper, bismuth, or lead. Titanium electrodes may also be employed. Electrodes can also be made of a high specific surface area conducting material, such as a nanoporous metal sponge (T. Wada, A.D. Setyawan, K. Yubuta, and H. Kato, *Scripta Materialia* **65**, 532 (2011)), which has been synthesized previously by electrochemical dealloying (J.D. Erlebacher, M.J. Aziz, A. Karma, N. Dmitrov, and K. Sieradzki, *Nature* **410**, 450 (2001)), or a conducting metal oxide, which has been synthesized by wet chemical methods (B.T. Huskinson, J.S. Rugolo, S.K. Mondal, and M.J. Aziz, arXiv:1206.2883 [cond-mat.mtrl-sci]; *Energy & Environmental Science* **5**, 8690 (2012); S.K. Mondal, J.S. Rugolo, and M.J. Aziz, *Mater. Res. Soc. Symp. Proc.* **1311**, GG10.9 (2010)). The electrode may be a metal mesh (e.g., Ti mesh, Cu mesh, Ni Mesh, Mo mesh, or a mesh made of any appropriate metal material described herein). The

electrode may be a porous electrode (e.g., porous graphene, Ti foam, Cu foam, Ni foam, Mo foam, or a porous electrode made of any appropriate metal material described herein). Electrodes of the present invention may include or be composed of a material resistant to degradation by acid or base. In some embodiments, the electrode may be coated by a material resistant to degradation by acid or base.

- 5 Chemical vapor deposition can be used for conformal coatings of complex 3D electrode geometries by ultra-thin electrocatalyst or protective films. Electrodes suitable for other redox active species are known in the art.

pH Rebalancing Means

- 10 A pH rebalancing means allows for the pH difference between the posolyte and the negolyte of the ARFB to be maintained during operation of the battery. This in turn, allows for an open circuit voltage (e.g., an open circuit voltage provided by a pH difference between the posolyte and the negolyte, e.g., an open circuit voltage greater than the voltage required for water splitting) to be maintained throughout operation. pH rebalancing means of the present invention may use a proton or hydroxide ion producing reaction of the solvent (e.g., water, e.g., hydrogen evolution reactions, oxygen evolution reactions, oxygen reduction reactions, or hydrogen oxidation reactions), allowing for perpetual operation of the pH rebalancing means without requiring the ARFB to be resupplied with external protons or hydroxide ions (e.g., from an external stock solution of acid or base).

- 20 During operation, the concentration of hydroxide in the negolyte and/or the concentration of acidic proton in the posolyte may vary by less than 0.1 M (e.g., less than 0.05 M, less than 0.01 M, less than 0.005 M, less than 0.001, less than 0.0005 M, or less than 0.0001 M).

- In some embodiments, the pH rebalancing means may include a secondary electrochemical cell, referred to as a sub-cell. In some embodiments, the sub cell includes the negolyte of the ARFB; the posolyte of the ARFB; and a membrane therebetween. In some embodiments, the pH rebalancing means may be included within the posolyte and the negolyte half-cells of the ARFB. In some embodiments, the pH rebalancing means may include a means of promoting a proton forming or hydroxide forming reaction (e.g., a hydrogen evolution reaction, an oxygen evolution reaction, a hydrogen oxidation reaction, or an oxygen reduction reaction) in the negolyte or the posolyte.

- 30 The sub-cell may be smaller than the ARFB (e.g., less than 50%, less than 40%, less than 30%, less than 20%, less than 10%, less than 5%, less than 4%, less than 3%, less than 2%, or less than 1% the volume of the half-cells of the ARFB). The sub-cell may operate continuously or periodically. For example, the sub-cell may be operated periodically, only when the pH of the posolyte and/or the pH of the negolyte have drifted significantly away from a desired value. The sub-cell may be controlled independently from the ARFB as a whole.

Bipolar Membrane (BPM) Sub-Cell

- 35 In some embodiments, the pH rebalancing means may utilize the bipolar membrane of a sub-cell. When a DC current is applied to the sub-cell (e.g., by applying a voltage across the sub-cell via the electrode in contact with the negolyte and the electrode in contact with the posolyte), water dissociates within the bipolar membrane, producing protons and hydroxide ions. The bipolar membrane may be oriented such

that hydroxide ions are provided to the negolyte and protons are provided to the posolyte. In some embodiments, voltage across the bipolar membrane to dissociate water may be provided by a second battery.

Proton Coupled Electron Transfer (PCET)

5 In some embodiments, the pH rebalancing means may include a cell with a single membrane to perform a proton or hydroxide ion producing reaction (e.g., a hydrogen evolution reaction, an oxygen evolution reaction, a hydrogen oxidation reaction, or an oxygen reduction reaction).

In some embodiments, the reaction may be performed within a sub-cell. When the reaction is performed within the sub-cell, the reaction is performed by applying a voltage to the sub-cell e.g., via the electrode in
10 contact with the negolyte and the electrode in contact with the posolyte, thereby driving the proton or hydroxide producing reaction. In some embodiments, voltage across the membrane to split water may be provided by a second battery. In some embodiments, the reaction may be performed in the battery cell, either with the battery electrodes or secondary electrodes. The voltage is oriented such that hydroxide ions are produced at the negolyte, thereby raising the pH of the negolyte, and protons are produced at
15 the posolyte, thereby lowering the pH of the posolyte.

Methods

The present invention provides methods of improving the lifetime, efficiency, or open circuit voltage of an ARFB by including a negolyte and/or a posolyte at a mild pH with only a single membrane separating the negolyte and posolyte, and optionally a pH rebalancing means.

20 The methods of the invention may be employed to improve the lifetime of an ARFB. For example, the methods of the present invention may increase the time for which an ARFB (e.g., an ARFB including an acidic posolyte and a basic negolyte) may be operated without loss of energy efficiency or open circuit voltage. In some embodiments, a method of the present invention may allow an ARFB to be operated (e.g., continuously or periodically) for at least 1 day (e.g., at least 2 days, at least 3 days, at least 4 days,
25 at least 5 days, at least 6 days, at least 7 days, at least 8 days, at least 9 days, at least 10 days, at least 11 days, at least 12 days, at least 13 days, at least 14 days, at least 15 days, at least 16 days, at least 17 days, or at least 18 days).

The battery may be operated to store or discharge energy as is known in the art. pH rebalancing may occur as described herein in either a batch or continuous manner.

EXAMPLES

The invention will be further described by the following non-limiting examples.

Example 1: A Single-Membrane, pH-Decoupling, Aqueous Redox Flow Battery

A single-membrane, pH-decoupling, ARFB including an acidic posolyte and a basic negolyte can be constructed with either a CEM (see, e.g., **FIG. 1A**) or AEM (see, e.g., **FIG. 1B**) separating the posolyte
35 and the negolyte. A charge carrier supplied by, e.g., a salt dissolved in the negolyte or posolyte, is used to transport charge across the membrane. When using a CEM, the major charge carrier is a positively

charged carrier (M^+). When using an AEM, the major charge carrier is a negatively charged carrier (X^-). To reduce membrane traversal by acidic protons or hydroxide ions, the concentration of acidic protons in the posolyte (when using a CEM) or hydroxide ions (when using an AEM) is low compared to the concentration of the major charge carrier. For example, when using a CEM, the proton concentration in the acidic posolyte may be at least 10 times (e.g., 20 times, 50 times, 100 times, 500 times, or 1000 times) lower than the concentration of M^+ . As a further example, when using an AEM, the hydroxide concentration in the basic negolyte should be at least 10 times (e.g., 20 times, 50 times, 100 times, 500 times, or 1000 times) lower than the concentration of X^- .

Example 2: pH-Rebalancing Means in Combination with Single Membrane ARFBs

The present example is directed towards ARFBs utilizing a pH rebalancing means. The pH rebalancing means allows for a pH difference to be maintained across the posolyte and the negolyte during operation, allowing for an open circuit voltage (e.g., an open circuit voltage provided by a pH difference between the posolyte and the negolyte) greater than the voltage for water splitting to be maintained for an increased duration.

Bipolar Membrane (BPM) pH Rebalancing Sub-Cell

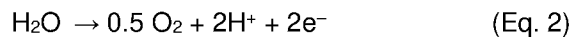
As shown in **FIG. 2**, electrolytes in the single-membrane, pH-decoupling, ARFB can be pumped into a sub-cell that uses a BPM that dissociates water into protons and hydroxides to recover the initial electrolyte pH. The electrolyte recovery operation may be performed in a periodic or continuous manner within the sub-cell. After recovery, the electrolyte can be pumped back to the single-membrane, pH-decoupling, ARFB. **FIG. 3** shows a schematic of the ARFB in fluid communication with a BPM pH rebalancing means sub-cell.

pH Recovery Using PCET

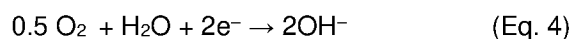
Proton coupled electron transfer (PCET) reactions can generate protons or hydroxides during the electrochemical reaction. These reactions can be used to recover the pH difference in the single-membrane pH-decoupling ARFB as shown in **FIG. 4**. For example, hydrogen oxidation reactions and oxygen evolution reactions can be used to generate protons. An exemplary hydrogen oxidation reaction is represented by Eq. 1.



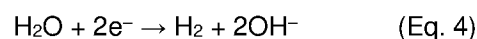
An exemplary oxygen evolution reaction is represented by Eq. 2.



Oxygen reduction reactions and hydrogen evolution reactions can be used to generate hydroxides. An exemplary oxygen reduction reaction is represented by Eq. 3.



An exemplary hydrogen evolution reaction is represented by Eq. 4.



These reactions can be done in a sub-cell in fluid communication with the main cell of the ARFB, or they can be done in the main cell itself. The recovery can be periodic or at constant steady state. When the reaction includes a gaseous reactant (e.g., a hydrogen oxidation reaction or an oxygen evolution reaction) the gas may be stored in a gas reservoir in fluid communication with the ARFB (e.g., in fluid

5 communication with the main cell of the ARFB or in fluid communication with a sub-cell of the ARFB).

When pH recovery is periodic, the gas may be provided from the reservoir periodically. When pH recovery is at a constant steady state, gas may be continuously provided from the reservoir at a rate sufficient to achieve a steady state concentration of gas in the ARFB.

Example 3: pH-Decoupling to suppress a side reaction

10 An example of an aqueous flow battery using an anthraquinone negolyte and a ferrocyanide or ferricyanide posolyte is provided. The anthraquinone negolyte is provided to the ARFB at pH between 12-14 while the posolyte containing ferrocyanide or ferricyanide is provided at a lower pH, e.g. 9-12. The ferricyanide has a slower self-reduction rate at lower pH, than at higher pH, thus maintaining the pH difference between each side of the battery helps maintain the charge capacities of two sides. pH

15 recovery using PCET reactions or BPM sub-cells can be used to recover the cell pH differential after enough hydroxide has crossed over from the negolyte to the posolyte.

CLAIMS

1. A flow battery comprising a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, a single membrane disposed between the negolyte and the posolyte, and a pH rebalancing means, wherein:

the membrane is a cation exchange membrane that allows the passage of one or more cationic charge carriers other than proton or hydronium;

the negolyte comprises a solution of a first redox active species at a first pH, and the posolyte comprises a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH; and

the pH rebalancing means is configured to supply hydroxide ions to the negolyte and protons to the posolyte.

2. The flow battery of claim 1, wherein the negolyte pH is from about 10.5 to about 14.5.

3. A flow battery comprising a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode; a single membrane disposed between the negolyte and the posolyte; and a pH rebalancing means, wherein:

the membrane is an anion exchange membrane that allows the passage of one or more anionic charge carriers other than hydroxide;

the negolyte comprises a solution of a first redox active species at a first pH, and the posolyte comprises a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH; and

the pH rebalancing means is configured to supply hydroxide ions to the negolyte and protons to the posolyte.

4. The flow battery of claim 3, wherein the posolyte pH is from about 0 to 4.

5. The flow battery of any one of claims 1 to 4, further comprising a posolyte storage reservoir and/or a negolyte storage reservoir.

6. The flow battery of any one of claims 1 to 5, wherein the pH rebalancing means comprises a sub-cell comprising:

- (a) the negolyte in contact with a second negolyte electrode;
- (b) the posolyte in contact with a second posolyte electrode; and
- (c) a membrane separating the negolyte and the posolyte.

7. The flow battery of claim 6, wherein the membrane is a bipolar membrane comprising an anion exchange membrane in contact with the negolyte and a cation exchange membrane in contact with the posolyte.

8. The flow battery of claim 7, wherein the sub-cell further comprises a voltage source in electrical contact with the second negolyte electrode and the second posolyte electrode, wherein the voltage source is of sufficient potential to perform a water-dissociation reaction, producing hydroxide ions in the negolyte and producing protons in the posolyte.

9. The flow battery of claim 6, wherein the sub-cell further comprises a voltage source, wherein the voltage source is of sufficient potential to perform a proton coupled electron transfer (PCET) reaction, wherein the proton coupled electron transfer reaction results in the generation of protons from water in the posolyte and/or hydroxide from water in the negolyte.

10. The flow battery of claim 9, wherein PCET reaction comprises a hydrogen evolution reaction, an oxygen evolution reaction, a hydrogen oxidation reaction, or an oxygen reduction reaction.

11. The flow battery of any one of claims 1 to 5, further comprising a second negolyte electrode in contact with the negolyte, a second posolyte electrode in contact with the posolyte, and a voltage source in electrical contact with the second negolyte electrode and the second posolyte electrode, wherein the voltage source is of sufficient potential to perform a PCET reaction, wherein the PCET reaction results in the generation of protons from water in the second posolyte and/or hydroxide from water in the second negolyte.

12. The flow battery of claim 11, wherein the PCET reaction comprises a hydrogen evolution reaction, an oxygen evolution reaction, a hydrogen oxidation reaction, or an oxygen reduction reaction.

13. The flow battery of any one of claims 1 to 12, wherein the pH rebalancing means maintains the concentration of hydroxide ions in the negolyte to within 0.01 M of its original value.
14. The flow battery of any one of claims 1 to 13, wherein the pH rebalancing means maintains the concentration of protons in the posolyte to within 0.01 M of its original value.
15. The flow battery of any one of claims 1 to 14, wherein the flow battery comprises an open circuit voltage of at least 1.3 V.
16. The flow battery of claim 15, wherein the flow battery comprises an open circuit voltage of at least 1.75 V.
17. The flow battery of any one of claims 1 to 16, wherein the flow battery can be continuously operated for at least 7 days with an energy efficiency loss of at most 20%.
18. The flow battery of claim 17, wherein the flow battery can be continuously operated for at least 18 days with an energy efficiency loss of at most 20%.
19. The flow battery of any one of claims 1 to 18, wherein the first redox active species comprises a quinone, an anthraquinone, a naphthoquinone, a phenazine, a phenoxazines, a phenothiazine, a diquaternized bipyridine, a metal chelate, or a reduced form thereof.
20. The flow battery of claim 19, wherein the first redox active species comprises an anthraquinone.
21. The flow battery of any one of claims 1 to 20, wherein the second redox active species comprises aluminum, vanadium, chromium, cobalt, iron, manganese, cobalt, nickel, copper, or lead, or an oxide thereof.
22. The flow battery of any one of claims 1 to 21, wherein the second redox active species comprises bromine, chlorine, iodine, molecular oxygen, ferricyanide or ferrocyanide, a ferrocene derivative, $\text{Fe}(\text{Bhmbpy})_3$ and salts or ions thereof; aluminum(III) biscitrate monocatecholate, or a benzoquinone.

23. The flow battery of claim 22, wherein the second redox active species comprises ferricyanide or ferrocyanide
24. A method of maintaining the pH of a flow battery comprising:
- (a) providing the flow battery of any one of claims 1 to 23;
 - (b) allowing the battery to discharge for a duration; and
 - (c) operating the pH rebalancing system, returning the pH of the negolyte to the first pH and/or returning the pH of the posolyte to the second pH.
25. A method of maintaining the pH of a flow battery comprising:
- (a) providing the flow battery of any one of claims 1 to 23; and
 - (b) allowing the battery to discharge for a duration, wherein the pH of the negolyte is maintained at about the first pH for the duration, and/or the pH of the posolyte is maintained at about the second pH for the duration.
26. The method of claim 24 or 25, wherein the concentration of hydroxide ions in the negolyte varies by less than 0.01 M from its initial value throughout the duration.
27. The method of any one of claims 24 to 26, wherein the concentration of protons in the posolyte varies by less than 0.01 M from its initial value throughout the duration.
28. A pH-rebalancing redox flow battery comprising a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, and a single cation exchange membrane disposed between the negolyte and the posolyte, wherein:
- the negolyte comprises a solution of a first redox active species at a first pH, and the posolyte comprises a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH; and
 - the cation exchange membrane allows the passage of one or more cationic charge carriers other than proton or hydronium.

29. A pH-rebalancing redox flow battery comprising a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, and a single anion exchange membrane disposed between the negolyte and the posolyte, wherein:

the negolyte comprises a solution of a first redox active species at a first pH, and the posolyte comprises a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH; and

the anion exchange membrane allows the passage of one or more anionic charge carriers other than hydroxide.

FIG. 1A

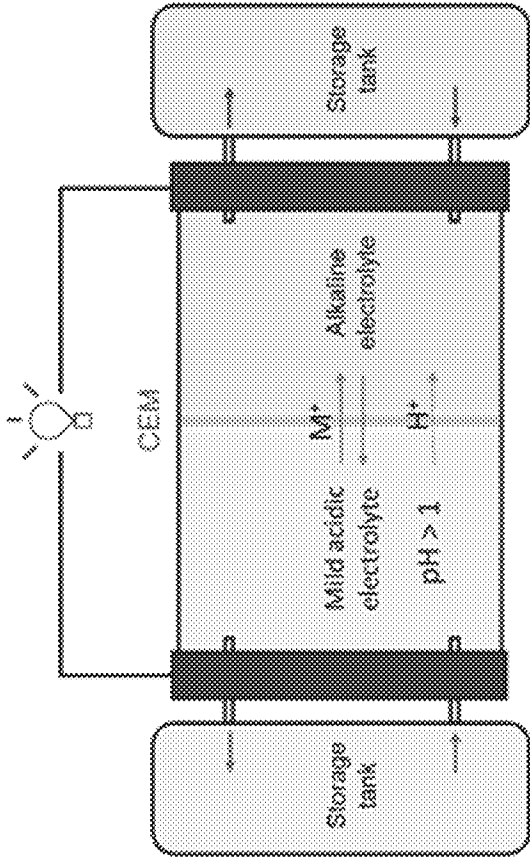


FIG. 1B

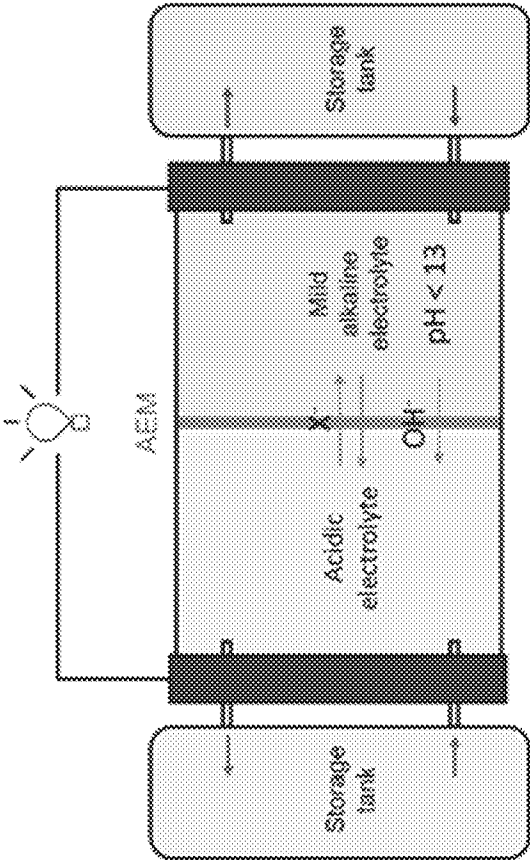


FIG. 2

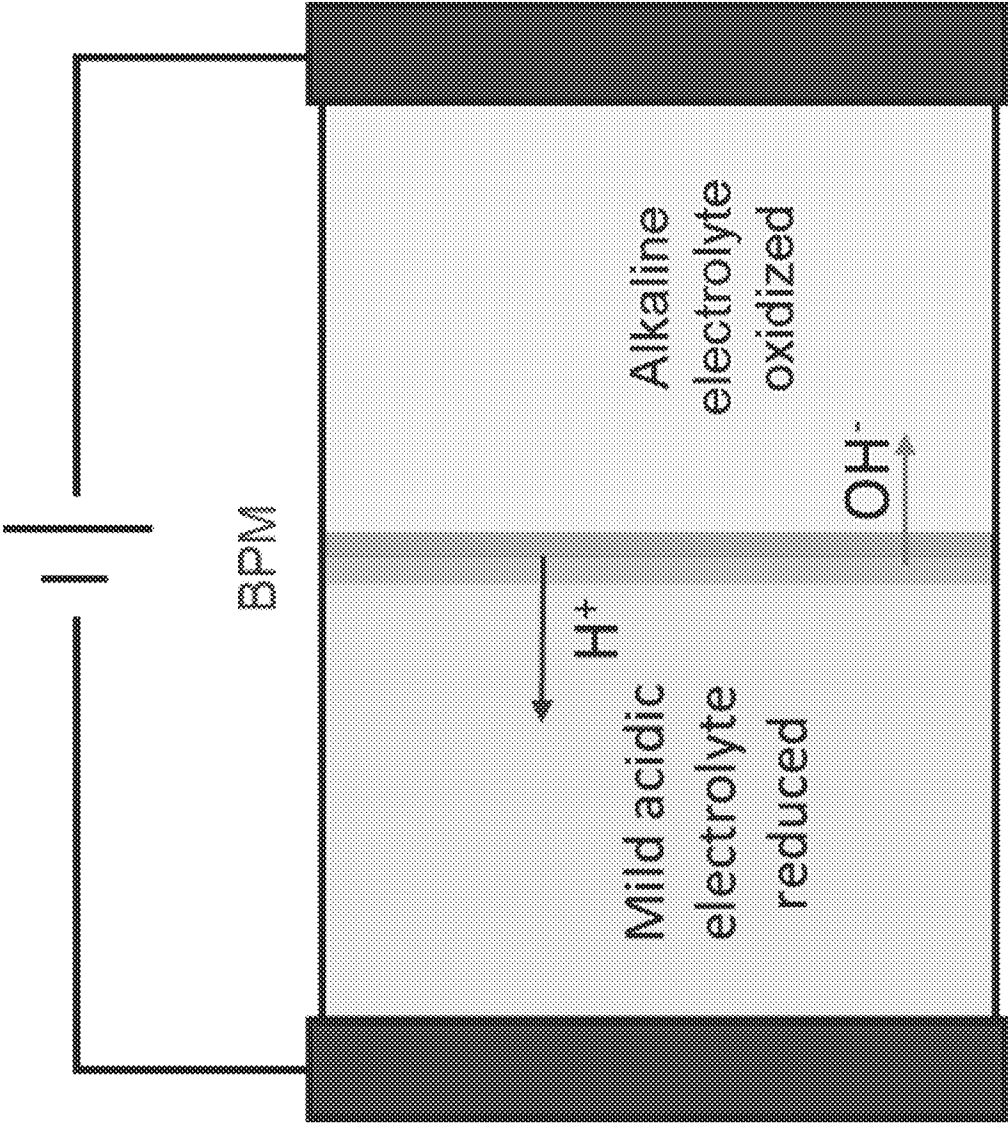


FIG. 3

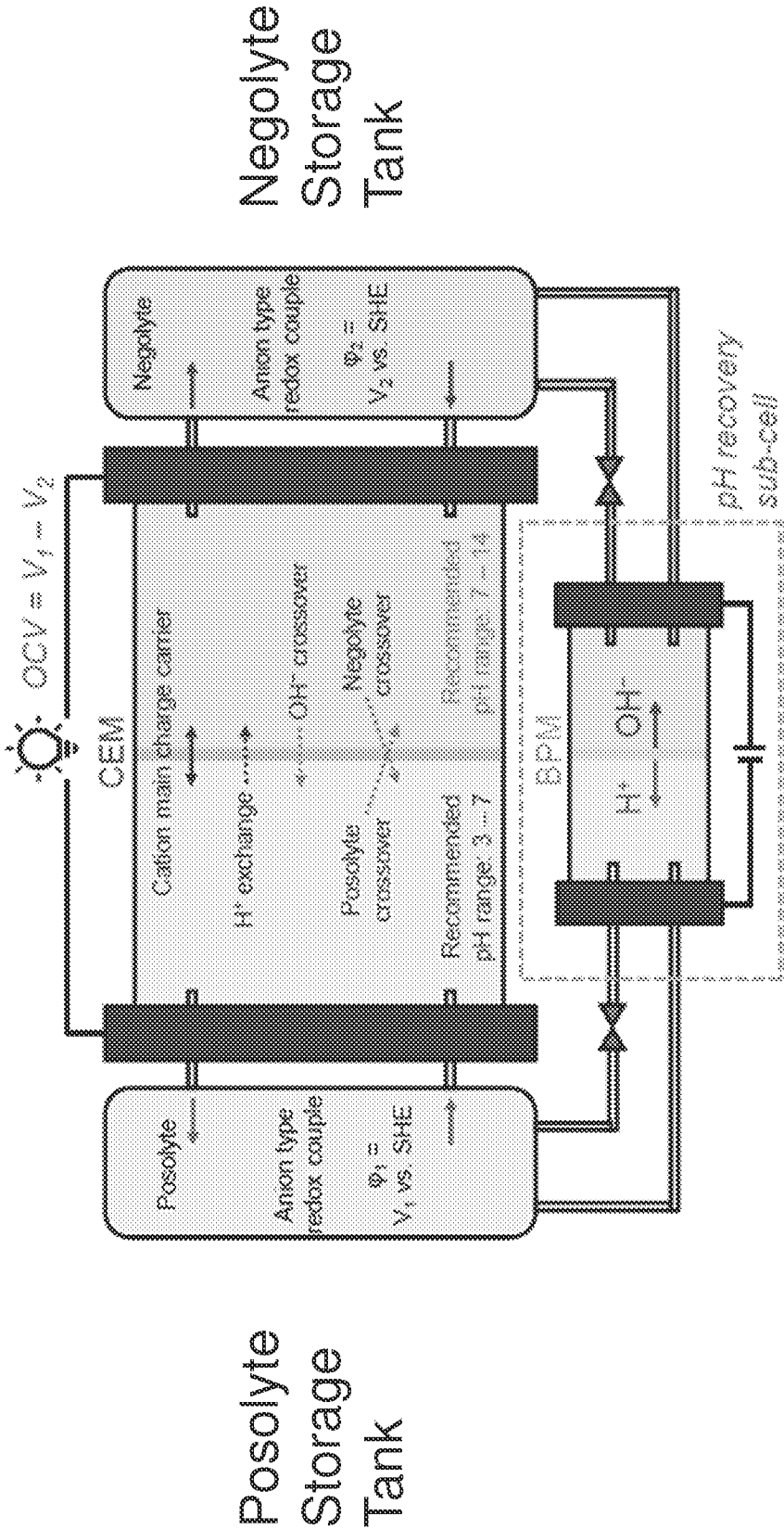
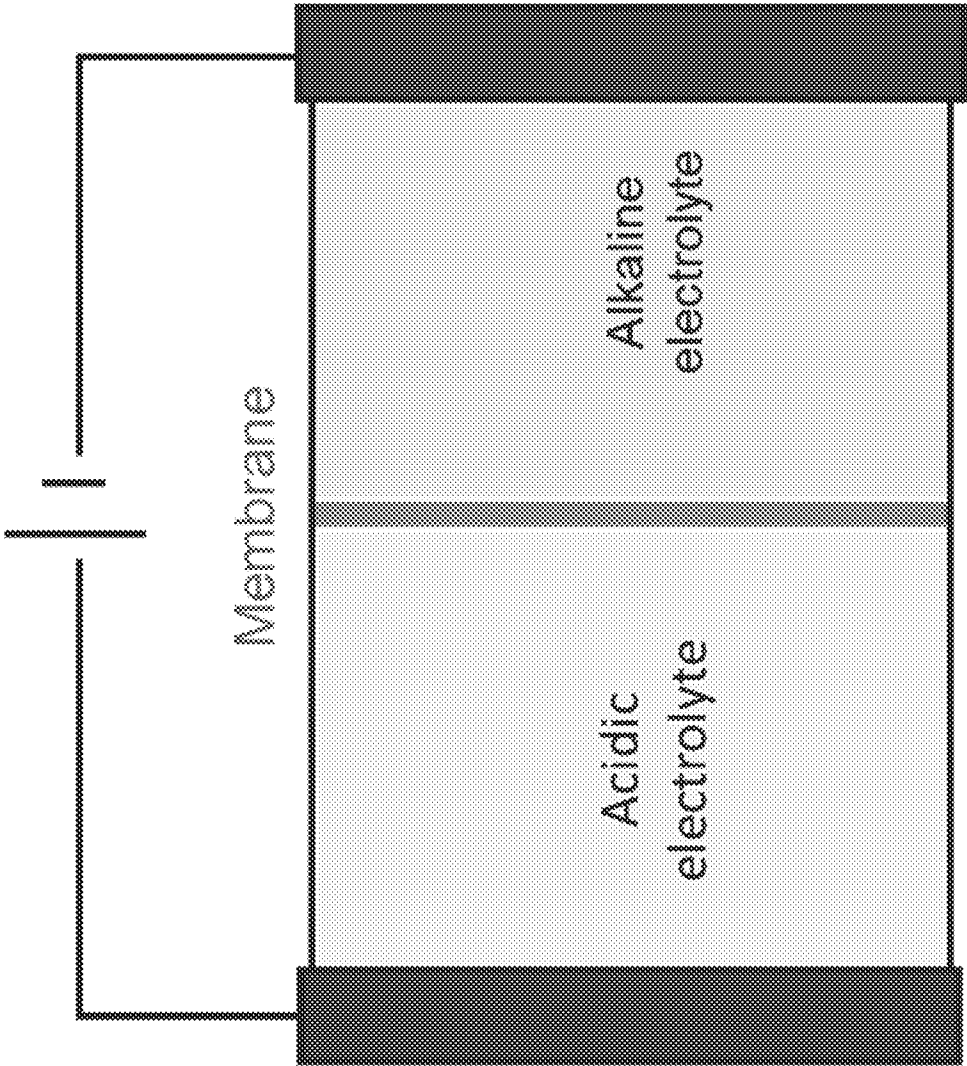
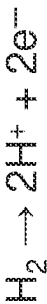


FIG. 4



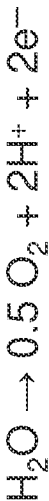
Eq. 1



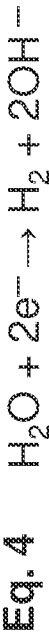
Eq. 3



Eq. 2



Eq. 4



Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: **6-27**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-2, 5/(1-2) and 28 are directed towards a flow battery/pH-rebalancing redox flow battery comprising a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode, a single cation exchange membrane disposed between the negolyte and the posolyte, and a pH rebalancing means, wherein: the membrane is a cation exchange membrane that allows the passage of one or more cationic charge carriers other than proton or hydronium; the negolyte comprises a solution of a first redox active species at a first pH, and the posolyte comprises a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH; and the pH rebalancing means is configured to supply hydroxide ions to the negolyte and protons to the posolyte.

Group II: Claims 3-4, 5/(3-4) and 29 are directed towards a flow battery/pH-rebalancing redox flow battery comprising a negolyte in contact with a negolyte electrode, a posolyte in contact with a posolyte electrode; a single anion exchange membrane disposed between the negolyte and the posolyte; and a pH rebalancing means, wherein: the membrane is an anion exchange membrane that allows the passage of one or more anionic charge carriers other than hydroxide; the negolyte comprises a solution of a first redox active species at a first pH, and the posolyte comprises a solution of a second redox active species at a second pH that is at least 0.5 pH units lower than the first pH; and the pH rebalancing means is configured to supply hydroxide ions to the negolyte and protons to the posolyte.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2025/010436

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-2, 5/(1-2) and 28**

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2025/010436

A. CLASSIFICATION OF SUBJECT MATTERIPC: **H01M 10/052** (2025.01); **H01M 10/05** (2025.01); **H01M 10/056** (2025.01); **H01M 4/02** (2025.01)CPC: **H01M 10/052**; **H01M 10/05**; **H01M 10/056**; **H01M 4/02**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2023/028041 A1 (PRESIDENT AND FELLOWS OF HARVARD COLLEGE) 02 March 2023 (02.03.2023) entire document especially page 25, 2, 17, and 8	28
X	US 2021/0305609 A1 (LOCKHEED MARTIN ENERGY, LLC) 30 September 2021 (30.09.2021) entire document especially para [0203], [0030], [0031], [0032], [0033], [0073], [0046], [0080], [0090], [0074], [0077], [0089], [0042], and abstract	1-2, 5/(1-2)
A	US 2019/0067725 A1 (CASE WESTERN RESERVE UNIVERSITY) 28 February 2019 (28.02.2019) entire document	1-2, 5/(1-2), 28
A	US 2023/0307682 A1 (THE CHINESE UNIVERSITY OF HONG KONG) 28 September 2023 (28.09.2023) entire document	1-2, 5/(1-2), 28
A	WO 2023/091940 A1 (QUINO ENERGY, INC.) 25 May 2023 (25.05.2023) entire document	1-2, 5/(1-2), 28

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“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

26 February 2025 (26.02.2025)

Date of mailing of the international search report

06 May 2025 (06.05.2025)

Name and mailing address of the ISA/US

COMMISSIONER FOR PATENTS
MAIL STOP PCT, ATTN: ISA/US
P.O. Box 1450
Alexandria, VA 22313-1450
UNITED STATES OF AMERICA

Authorized officer

KARI RODRIQUEZ

Facsimile No. 571-273-8300

Telephone No. PCT Help Desk: 571-272-4300