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(54) Benævnelse: **Vandige redox-flow-batterier omfattende metal-ligand-koordinationsforbindelser**

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DESCRIPTION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part of U.S. Patent Application No. 13/795,878, filed March 12, 2013, which itself claims priority to U.S. Application No. 61/739,145, filed December 19, 2012, U.S. Application No. 61/738,546, filed December 18, 2012, U.S. Application No 61/683,260, filed August 15, 2012, and U.S. Application No. 61/676,473, filed July 27, 2012.

TECHNICAL FIELD

[0002] This disclosure relates to the field of energy storage systems, including electrochemical energy storage systems, batteries, and flow battery systems and methods of operating the same.

BACKGROUND

[0003] There exists a long-felt need for safe, inexpensive, easy-to-use, and reliable technologies for energy storage. Large-scale energy storage enables diversification of energy supply and optimization of the energy grid, including increased penetration and utilization of renewable energies. Existing renewable-energy systems (e.g., solar- and wind-based systems) enjoy increasing prominence as energy producers explore non-fossil fuel energy sources. However, storage is required to ensure a reliable, high quality energy supply when sunlight is not available and when wind does not blow.

[0004] Electrochemical energy storage systems have been proposed for large-scale energy storage. To be effective, these systems must be safe, reliable, low-cost, and highly efficient at storing and producing electrical power. Flow batteries, compared to other electrochemical energy storage devices, offer an advantage for large-scale energy storage applications owing to their unique ability to decouple the functions of power density and energy density. Existing flow batteries, however, have suffered from the reliance on battery chemistries that result in high costs of active materials and system engineering, low cell and system performance (e.g. round trip energy efficiency), poor cycle life, and others.

[0005] Despite significant development effort, no flow battery technology has yet achieved widespread commercial adoption. Accordingly, there is a need in the art for improved flow battery chemistries and systems.
WO 95/12219 A1 relates to a method for stabilising an electrolyte for use in a redox cell, in particular for stabilising an electrolyte for use in an all-vanadium redox cell, a stabilised electrolyte, in particular an all-vanadium stabilised electrolyte, a redox cell, in particular an all-

vanadium redox cell, comprising the stabilised electrolyte, a redox battery, in particular an all-vanadium redox battery, comprising the stabilised electrolyte, a process for recharging a discharged or partially discharged redox battery, in particular an all-vanadium redox battery, comprising the stabilised electrolyte, a process for the production of electricity from a charged redox battery, and in particular a charged all-vanadium redox battery, comprising the stabilised electrolyte, a redox battery/fuel cell and a process for the production of electricity from a redox battery/fuel cell.

US 4362791 A relates to a redox battery using a titanium redox system or chromium redox system as an active material for the negative electrode or a manganese redox system as an active material for the positive electrode, wherein the electromotive force of the battery and the stability of electrolyte solutions are enhanced by addition of a chelating agent such as citric acid or a complexing agent such as phosphoric acid to the redox system used therein.

WO 2007/101284 A1 relates to a redox battery with at least one cell, in which a flow of electrolyte or electrolyte solution surrounds or flows through two electrodes, said electrodes being separated by a membrane. Each electrode is provided with a separate electrolyte circuit and both electrolyte solutions contain the same metal for the redox reaction which has at least two oxidation levels. Preferably, all the metal used for the redox reaction present in the system is in only two oxidation levels and approximately half thereof is in a complex compound with a ligand and half in a complex compound with another substance. The electrolyte solution is characterised in that half of the metal used for the redox reaction is in a complex compound with a ligand and half in a complex compound with another substance.

US 5472807 A relates to a battery which includes an aluminum anode, a ferricyanide electrolyte and a second electrode capable of reducing ferricyanide electrolyte which is either dissolved in an alkaline solution or alkaline seawater solution.

SUMMARY

[0006] The present invention addresses these challenges through the discovery and implementation of a novel class of flow battery active materials. Traditional flow battery active materials comprise simple transition metal salts and/or halogen ions as positive|negative active materials in acidic or caustic electrolyte (e.g., iron-chrome: $Fe^{3+/2+}$ $|Cr^{3+/2+}$; vanadium: $VO_2^+/VO^{2+}|V^{3+/2+}$; zinc-bromine: $Zn(OH)_4^{2-}/Zn|Br_2/Br^-$; hydrogen-bromine: $H^+/H_2|Br_2/Br^-$). In this configuration, the overall battery properties (energy density, cell voltage, charge/ discharge rate, etc) are limited by the inherent chemical properties of the base metal/halogen ions. In particular, the negative couples taught by the prior art may each exhibit adequate electromotive force but with poor electrode kinetics (e.g., $Cr^{3+/2+}$), exhibit modest electromotive force with modest electrode kinetics (e.g., $V^{3+/2+}$), plate metal onto the negative electrode precluding the decoupling of stack size and discharge time and presenting dendrite growth throughout cycling (e.g., $Zn^{2+/0}$), or exhibit modest electromotive force and require the management of flammable gas (e.g., H^+/H_2). Considerable attention has been paid to overcoming these deficiencies, but to date, to little avail.-Instead, the recent art in energy storage has largely taught new ways of arranging and operating cell stacks and modifications to electrolytes and electrodes that address minor deficiencies rather than the broad requirements of effectively storing energy.

[0007] This disclosure describes a novel class of compounds that unexpectedly overcome the deficiencies presented by the prior art. The redox active metal-ligand coordination compounds described herein provide active materials comprising low-cost, earth abundant elements at useful battery half-cell potentials. Unexpectedly, the materials were discovered to exhibit high solubility (allowing for high energy storage density) and high electromotive forces (e.g., including highly negative potentials) and suitably rapid electrode kinetics that enable operation of energy storage devices at high current densities. Through various choices of certain of these electrolyte, active material, and electrode compositions, flow battery cells are enabled that operate at high cell voltages and with high efficiency. Active materials that include a composition of matter described by this invention may be used in energy storage systems in such a way that they are paired with other active materials to form positive couples and negative couples wherein said other active materials are described by the present invention or are previously known in the art or a combination thereof, including those comprising soluble, semisolid, intercalation, capacitive or pseudo-capacitive, or plating-type active materials. That is, the present invention may be used in both half-cells of an energy storage system or as one half-cell in a system where the other half-cell is, for example, $Fe^{2+/3+}$, Br_2/Br^-, H^+/H_2, VO^{2+}/VO_2^+, or another half-cell.

[0008] According to the present invention, a flow battery according to claim 1, a system according to claim 7, a method according to claim 9, and an alternative method according to claim 10 are provided. Preferred embodiments are set forth in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The present application is further understood when read in conjunction with the appended drawings. For the purpose of illustrating the subject matter, there are shown in the drawings exemplary embodiments of the subject matter; however, the presently disclosed subject matter is not limited to the specific methods, devices, and systems disclosed. In addition, the drawings are not necessarily drawn to scale. In the drawings:

FIG. 1 depicts a schematic of an exemplary flow battery.

FIG. 2 provides stability performance data obtained during 250 charge/discharge cycles for a 5 cm^2 system based on $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$, as described in Example 2.

FIG. 3 provides a charge/discharge trace for a flow battery of the present invention as described in Example 2. This example contains $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$as first and second electrolytes, respectively. The battery was charged from 0 % SOC to 60 % SOC and then discharged to 40% SOC at a current density of 200 mA/cm^2 and a RT Voltage efficiency of ~ 76%.

FIG. 4 provides current efficiency data obtained for a system based on $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$, as described in Example 3.

FIG. 5 provides voltage efficiency data, as a function of current density, for a system based on $Ti^{4+/3+}(cat)_2(pyrogallate)^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$, as described in Example 4.

FIG. 6 provides voltage efficiency data, as a function of current density, for a system based on $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$, as described in Example 4.

FIG. 7 provides a charge/discharge trace for a flow battery of the present invention. This example contains $Fe^{3+/2+}(cat)_3^{3-/4-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$ as first and second electrolytes, respectively. The battery was charged from 0 % SOC to 60 % SOC and then discharged to 40% SOC at a current density of 100 mA/cm^2 and a RT voltage efficiency of ca. 82%.

FIG. 8 provides cyclic votammogram, CV traces for $Al(cit)_2(cat)^{2-/3-}$ in pH 11.5 Na_2SO_4 electrolyte recorded at a glassy carbon electrode.

FIG. 9 provides CV traces for titanium tris-pyrogallate over a range of operating potentials. The data were generated using solutions of 75 mM $NaK[Ti(pyrogallate)_3]$ at a pH of 9.8 and 1 M Na_2SO_4, recorded at a glassy carbon electrode.

FIG. 10 provides CV traces for iron tris-catecholate over a range of operating potentials. The data were generated using solutions of 1M $NaK[Fe(catecholate)_3]$ at a pH of 11, and 3 M Na/KCl, recorded at a glassy carbon electrode.

FIG. 11 provides a CV trace for titanium bis-catecholate mono-pyrogallate over a range of operating potentials. The data were generated using solutions of 1.6 M $NaK[Ti(catecholate)_2(pyrogallate)]$ at a pH of 11, recorded at a glassy carbon electrode.

FIG. 12 provides a CV trace for titanium bis-catecholate monolactate over a range of operating potentials. The data were generated using solutions of 0.75 M $NaK[Ti(catecholate)_2(lactate)]$ at a pH of 9, recorded at a glassy carbon electrode.

FIG. 13 provides a CV trace for titanium bis-catecholate mono-gluconate over a range of operating potentials. The data were generated using solutions of 1.5 M $NaK[Ti(catecholate)_2(gluconate)]$ at a pH of 9, recorded at a glassy carbon electrode.

FIG. 14 provides a CV trace for titanium bis-catecholate mono-ascorbate over a range of operating potentials. The data were generated using solutions of 1.5 M $NaK[Ti(catecholate)_2(ascorbate)]$ at a pH of 10, recorded at a glassy carbon electrode.

FIG. 15 provides a CV trace for titanium tris-catecholate over a range of operating potentials. The data were generated using solutions of 1.5 M $Na_2[Ti(catecholate)_3]$ at a pH of 11, recorded at a glassy carbon electrode.

FIG. 16 provides a CV trace for titanium mono-catecholate mono-pyrogallate mono-lactate over a range of operating potentials. The data were generated using solutions of 1.5 M NaK[Ti(catecholate)(pyrogallate)(lactate)] at a pH of 8.5, recorded at a glassy carbon electrode.

FIG. 17 provides a CV trace for titanium tris-citrate over a range of operating potentials. The data were generated using solutions of 0.5 M $Na_4[Ti(citrate)_3]$ at a pH of 5, recorded at a platinum disk electrode.

FIG. 18 provides a CV trace from a solution of 1.5 M $[Fe(CN)_6]^{4-}$ obtained at a glassy carbon disk working electrode at several scan rates using 0.1 M sodium potassium hydrogen phosphate as the supporting electrolyte, as described in Example 5.11. The ratio of Na^+/K^+ counterions in this example was ca. 1:1.

FIG. 19 provides a CV trace for chromium hexacyanide over a range of operating potentials. The data were generated using solutions of 0.05 M $K_3[Cr(CN)_6]$ at a pH of 9, recorded at a glassy carbon electrode.

FIG. 20 provides a CV trace for manganese hexacyanide over a range of operating potentials. The data were generated using solutions of 0.1 M $K_3[Mn(CN)_6]$ at a pH of 9, recorded at a glassy carbon electrode.

FIG. 21 provides data for cell voltage during charge-discharge cycling for 1 M $Fe(CN)_6$ as positive couple and 1 M $Ti(lactate)_2(salicylate)$ as negative couple, both at pH 11, in a 5 cm^2 active area flow battery at a current density of 150 mA/cm^2 except for the area noted as 100 mA/cm^2.

FIG. 22 provides cell voltage in volts plotted versus test time in hours during charge-discharge cycling and iV traces between each cycle for 1 M $Fe(CN)_6$ as positive couple and 1 M $Ti(lactate)_2$(α-hydroxyacetate) as negative couple, both at pH 11, in a 5 cm^2 active area flow battery at a current density of 150 mA/cm^2.

FIG. 23 provides CV traces for 10 mM titanium tris-salicylate at pH 8.6 over a range of operating potentials at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 24 provides CV traces for 1 M iron tris-salicylate at pH 9.3 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte

FIG. 25 provides CV traces for 10 mM titanium mono-lactate at pH 5.6 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 26 provides CV traces for 1 M titanium mono-lactate at pH 9 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 27 provides CV traces for 1 M titanium bis-lactate at pH 2 over a range of operating potentials, recorded at a glassy carbon electrode with Na_2SO_4 supporting electrolyte.

FIG. 28 provides CV traces for 1 M titanium bis-lactate at pH 3.6 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 29 provides CV traces for 0.75 M titanium bis-lactate at pH 9 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 30 provides CV traces for 100 mM titanium-bis-malate-mono-lactate at pH 9.9 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 31 provides CV traces for 200 mM titanium-bis-malate-mono-salicylate at pH 10 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 32 provides CV traces for 0.5 M titanium bis-lactate mono-glycinate at pH 9.9 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 33 provides CV traces for 0.5 M titanium bis-lactate mono-salicylate at pH 10 over a range of operating potentials, recorded at a pH of 9.3 at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 34 provides CV traces for 0.5 M titanium bis-salicylate mono-lactate at pH 9.8 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 35 provides CV traces for 200 mM titanium bis-(α-hydroxyacetate) mono-salicylate over a range of operating potentials, recorded at a pH of 10 at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 36 provides CV traces for 0.5 M titanium bis-(α-hydroxyacetate) mono-lactate at pH 10 over a range of operating potentials at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 37 provides CV traces for 1 M iron tris-malate at pH 9.2 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 38 provides CV traces for 1.5 M iron tris-(α-hydroxyacetate) at pH 8.1 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 39 provides CV traces for 1 M iron mono-lactate at pH 3.1 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 40 provides CV traces for 1.5 M iron bis-lactate at pH 2.6 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

FIG. 41 provides CV traces for 1 M iron mono-lactate bis-glycinate at pH 6.7 over a range of operating potentials, recorded at a glassy carbon electrode with $NaKSO_4$ supporting electrolyte.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0010] The present disclosure may be understood more readily by reference to the following description taken in connection with the accompanying Figures and Examples, all of which form a part of this disclosure. It is to be understood that this disclosure is not limited to the specific products, methods, conditions or parameters described and / or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of any claimed disclosure. Similarly, unless specifically otherwise stated, any description as to a possible mechanism or mode of action or reason for improvement is meant to be illustrative only, and the invention herein is not to be constrained by the correctness or incorrectness of any such suggested mechanism or mode of action or reason for improvement. Throughout this text, it is recognized that the descriptions refer both to methods of operating a device and systems and to the devices and systems providing said methods. That is, where the disclosure describes and/or claims a method or methods for operating a flow battery, it is appreciated that these descriptions and/or claims also describe and/or claim the devices, equipment, or systems for accomplishing these methods.

[0011] In the present disclosure the singular forms "a," "an," and "the" include the plural reference, and reference to a particular numerical value includes at least that particular value, unless the context clearly indicates otherwise. Thus, for example, a reference to "a material" is a reference to at least one of such materials and equivalents thereof known to those skilled in the art, and so forth.

[0012] When a value is expressed as an approximation by use of the descriptor "about," it will be understood that the particular value forms another embodiment. In general, use of the term "about" indicates approximations that can vary depending on the desired properties sought to be obtained by the disclosed subject matter and is to be interpreted in the specific context in which it is used, based on its function. The person skilled in the art will be able to interpret this as a matter of routine. In some cases, the number of significant figures used for a particular value may be one non-limiting method of determining the extent of the word "about." In other cases, the gradations used in a series of values may be used to determine the intended range available to the term "about" for each value. Where present, all ranges are inclusive and combinable. That is, references to values stated in ranges include every value within that range.

[0013] When a list is presented, unless stated otherwise, it is to be understood that each individual element of that list and every combination of that list is to be interpreted as a separate embodiment. For example, a list of embodiments presented as "A, B, or C" is to be interpreted as including the embodiments, "A," "B," "C," "A or B," "A or C," "B or C," or "A, B, or C."

[0014] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. That is, unless obviously incompatible or specifically excluded, each individual embodiment is deemed to be combinable with any other embodiment(s) and such a combination is considered to be another embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Further, while an embodiment may be described as part of a series of steps or part of a more general structure, each said step or part may also be considered an independent embodiment in itself. Additionally, while the chemistries described in the present disclosure are described in terms of flow batteries, it should be appreciated that each of the chemical structures or compositions described or exemplified herein, either by themselves or as electrolytes, are considered independent embodiments of the present invention (including the specific mixed ligand genera and structures described in terms of $M(L1)_x(L2)_y(L3)_z{}^m$ as described below).

[0015] Electrochemical energy storage systems typically operate through the interconversion of electrical and chemical energy. Various embodiments of electrochemical energy storage systems include batteries, capacitors, reversible fuel cells and the like, and the present invention may comprise any one or combination of these systems.

[0016] Unlike typical battery technologies (e.g., Li-ion, Ni-metal hydride, lead-acid, etc.), where energy storage materials and membrane/current collector energy conversion elements are unitized in a single assembly, flow batteries transport (e.g., via pumping) redox active energy storage materials from storage tanks through an electrochemical stack, as in exemplary **FIG. 1,** which is described elsewhere herein in further detail. This design feature decouples the electrical energy storage system power (kW) from the energy storage capacity (kWh), allowing for considerable design flexibility and cost optimization.

[0017] In some embodiments, flow batteries according to the present disclosure may also be described in terms of a first chamber comprising a first or negative electrode contacting a first aqueous electrolyte; a second chamber comprising a second or positive electrode contacting a second aqueous electrolyte; and a separator disposed between the first and second electrolytes. The electrolyte chambers provide separate reservoirs within the cell, through which the first and/or second electrolyte flow so as to contact the respective electrodes and the separator. Each chamber and its associated electrode and electrolyte defines its corresponding half-cell. The separator provides several functions which include, e.g., (1) serving as a barrier to mixing of first and second electrolytes; (2) electronically insulating to reduce or prevent short circuits between the positive and negative electrodes; and (3) to provide for ion transport between the positive and negative electrolyte chambers, thereby balancing electron transport during charge and discharge cycles. The negative and positive electrodes provide a surface for electrochemical reactions during charge and discharge. During a charge or discharge cycle, electrolytes may be transported from separate storage tanks through the corresponding electrolyte chambers. In a charging cycle, electrical power is applied to the system wherein the active material contained in the second electrolyte undergoes a one-or-more electron oxidation and the active material in the first electrolyte undergoes a one-or-more electron reduction. Similarly, in a discharge cycle the second electrolyte is reduced and the first electrolyte is oxidized producing electrical power.

[0018] Certain embodiments of the current invention provide flow batteries, each flow battery comprising:

a first aqueous electrolyte comprising a first redox active material;

a second aqueous electrolyte comprising a second redox active material;

a first electrode in contact with said first aqueous electrolyte;

a second electrode in contact with said second aqueous electrolyte and

a separator disposed between said first aqueous electrolyte and said second aqueous electrolyte;

wherein each of the first and second redox active materials comprise a metal ligand coordination compound that independently exhibits substantially reversible electrochemical kinetics. Either or both of the electrodes that carry out the electrochemical reactions may comprise carbon. The term "metal ligand coordination compound is described below, both in broad and more specific terms and each comprises separate embodiments.

[0019] As used herein, unless otherwise specified, the term "substantially reversible electrochemical kinetics" refers to the condition wherein the voltage difference between the anodic and cathodic peaks is less than about 0.3 V, as measured by cyclic voltammetry, using an ex-situ apparatus comprising a flat glassy carbon disc electrode and recording at 100 mV/s. However, additional embodiments provide that the voltage difference between the anodic and cathodic peaks is less than about 0.2 V, less than about 0.1 V, less than about 0.075 V, or less than about 0.059 V, under these same testing conditions..

[0020] The present invention provides flow batteries as defined in claim 1.
Throughout this disclosure, the phrase "a salts thereof' includes base salts such as, those formed with cations such as sodium, potassium, lithium, calcium, magnesium, ammonium and alkylammonium. Other salts that do not negatively impact the operation of the cell can also be utilized.

[0021] In those embodiments where the first and second aqueous electrolytes each comprises a first and second metal ligand coordination compound, respectively, the first and second metal ligand coordination compounds may either be the same or different.

[0022] In various embodiments, either each or both of the first or second metal ligand coordination compound may also comprise at least one ascorbate, catecholate, citrate, glycolate or polyol (including a ligand derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, phthalate, pyrogallate, sarcosinate, salicylate, or lactate ligand.

[0023] According to the present invention, the metal coordination compounds may include non-zero valent Al, Ca, Ce, Co, Cr, Fe, Mg, Mn, Mo, Si, Sn, Ti, W, Zn, or Zr, for example Al^{3+}, Ca^{2+} , Ce^{4+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Mg^{2+}, Mn^{3+}, Mo^{6+}, Si^{4+}, Sn^{4+}, Ti^{4+}, W^{6+}, Zn^{2+}, or Zr^{4+} as metals. As described above, the first and second metal coordination compound may comprise the same or different non-zero valent metal or metalloid, or the same element having a redox couple of differing oxidation states. Metal ligand coordination compounds comprising Al, Cr, Ti, Mn, or Fe are preferred, in either or both of the first or second compounds. In certain embodiments, the second metal ligand coordination compound comprises an iron hexacyanide compound, for example as a ferro- /ferricyanide couple.

[0024] As is discussed further below, the present invention also provides that either or both of the first or the second metal ligand coordination compound are present in the first or second electrolyte, respectively, at elevated concentrations, for example at least about 0.5 M, at least about 0.6 M, at least about 0.75 M, or at least about 1 M. Higher concentrations are preferred for yielding higher system energy densities. In separate independent embodiments, the energy density of the electrolytes is at least about 10 Wh/L, at least about 20 Wh/L, or at least about 30 Wh/L.

[0025] It is also important to reiterate that the individual embodiments described herein also include those where either or both, preferably both, of the first and second metal ligand coordination compounds each exhibit substantially reversible electrochemical kinetics. Similarly, the flow batteries described herein, whether or not dependent on the specific metal ligand combinations described are capable of providing (and do provide when operating) high round trip voltage and current efficiencies, each of at least 70%, when measured at 200 mA/cm^2 and such performance features are considered individual embodiments of the present invention. Similarly, the present invention provides flow batteries capable of operating, or operating, with a current density of at least about 100 mA/cm^2 and a round trip voltage efficiency of at least about about 70%, at least about 80%, or at least about 90%. These features can be realized even when the separator has a thickness of about 100 micron or less, about 50 micron or less, or about 25 microns or less.

[0026] In other independent embodiments, flow batteries each comprise:

a first aqueous electrolyte comprising a metal ligand coordination compound;

a second aqueous electrolyte comprising a second metal ligand coordination compound;

a first electrode in contact with said first aqueous electrolyte;

a second electrode in contact with said second aqueous electrolyte and

a separator disposed between said first aqueous electrolyte and said second aqueous electrolyte;

wherein at least one metal ligand coordination compound has a formula comprising $M(L1)_x(L2)_y(L3)_z{}^m$, where x, y, and z are selected from the group consisting of (a) x = 3, y = z = 0; (b) x = 2, y = 1, z = 0; (c) x = 1, y = 1, z = 1;

m is -5, -4, -3, -2, -1, 0;

M is Al, Cr, Fe, Mn, or Ti;

and L1, L2, and L3 are each independently ascorbate, a catecholate, citrate, a glycolate or polyol (including a ligand derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, a phthalate, a pyrogallate, sarcosinate, salicylate, or lactate. The terms "a catecholate" and "a pyrogallolate" reflect the fact that these ligands may be optionally substituted with at least one R_1 group, as defined above - i.e., in independent embodiments, the catecholate or pyrogallate are substituted and unsubstituted The catechol- or pyrogallol-type ligands may also be optionally substituted with C_{1-6} alkoxy (e.g., $-O-C_{1-6}$ alkyl), C_{1-6} alkyl, C_{1-6} alkenyl, C_{1-6} alkynyl, 5-6 membered aryl or heteroaryl, a boric acid or a salt thereof, a carboxy acid or a salt thereof, C_{2-6} carboxylate, cyano, halo, hydroxyl, nitro, sulfonate, sulfonic acid or a salt thereof, phosphonate, phosphonic acid or a salt thereof, or a polyglycol (preferably polyethylene glycol, $-[CH_2CH_2-O]_{2-20}-OH$, preferably $-[CH_2CH_2-O]_{2-6}-OH$).

[0027] Throughout this disclosure, where L1, L2, and L3 are said to be independently ascorbate, a catecholate, citrate, a glycolate or polyol (including ligands derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, phthalate, sarcosinate, salicylate, or lactate, it should be appreciated that these ligands are reflective of a broader class of ligands - i.e., those including aliphatic polyhydroxy, carboxylic, polycarboxylic, or mixed hydroxy-carboxylic species capable of binding, preferably as bi-, tri-, or polydentate chelants, including C_2-C_{10} α-, β-, and γ-hydroxy- or polyhydroxycarboxylic acids (e.g., glycolic acid, sugars such as fructose, glucose) or C_3-C_{10} hydroxy- or polyhydroxydi-, tri-, or poly-carboxylic acids such as EDTA or DTPA. Coordination compounds containing this broader class of ligands are also considered within the scope of the present invention, especially when those coordination compounds also contain at least one catecholate or pyrogallate ligand, at least one polyhydroxy or polycarboxylate, α- and/or β-hydroxycarboxylic acid ligand.

[0028] In certain independent embodiments, flow batteries each comprise:

a first aqueous electrolyte comprising a first redox active material;

a second aqueous electrolyte comprising a second redox active material;

a first electrode in contact with said first aqueous electrolyte;

a second electrode in contact with said second aqueous electrolyte and

a separator disposed between said first aqueous electrolyte and said second aqueous electrolyte;

wherein the second redox active material comprises a metal ligand coordination complex having a formula comprising $M(L1)_x(L2)_y(L3)_z{}^m$,

M is Al, Ca , Ce, Co, Cr, Fe, Mg, Mn, Mo, S, Sn, Ti, W, Zn, or Zr;

L1, L2, and L3 are each each independently ascorbate, a catecholate, citrate, a glycolate or polyol (including ligands derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, a phthalate, a pyrogallate, sarcosinate, salicylate, or lactate;

x, y, and z are selected from the group consisting of (a) $x = 3$, $y = z = 0$; (b) $x = 2$, $y = 1$, $z=0$; (c) $x = 1$, $y = 1$, $z = 1$;

and m is 0, -1, -2, -3, -4, or -5. In preferred embodiments, M is Al, Cr, Fe, or Ti.

[0029] In other embodiments, flow batteries each comprise:

a first aqueous electrolyte comprising a first redox active material;

a second aqueous electrolyte comprising a second redox active material;

a first electrode in contact with said first aqueous electrolyte;

a second electrode in contact with said second aqueous electrolyte and

a separator disposed between said first aqueous electrolyte and said second aqueous electrolyte;

wherein the first, second, or both redox active materials comprise a metal ligand coordination compound in concentrations of at least about 0.5 M, at least about 0.75 M, or at least about 1 M.

[0030] In other independent embodiments, flow batteries each comprise:

a first aqueous electrolyte comprising a first redox active material;

a second aqueous electrolyte comprising a second redox active material;

a first electrode in contact with said first aqueous electrolyte;

a second electrode in contact with said second aqueous electrolyte and

a separator disposed between said first aqueous electrolyte and said second aqueous electrolyte;

wherein the first and second redox active materials comprise metal ligand coordination compounds; and

wherein the separator has a thickness of about 100 microns or less. The separator may also have a thickness of about 50 micron or less or about 25 micron or less.

[0031] Again, each of the specific features described above may be combinable such that the combined features form additional embodiments.

[0032] The invention also contemplates those embodiments wherein the at least one metal ligand coordination compound comprises (a) at least one catecholate or pyrogallate ligand, (b) at least one ascorbate, citrate, a glycolate or polyol (including ligands derived from ethylene glycol, propylene glycol, or glycerol) , gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, phthalate, sarcosinate, salicylate, or lactate ligand, or (c) both at least one catecholate or pyrogallate ligand, and at least one ascorbate, citrate, a glycolate or polyol (including ligands derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, phthalate, sarcosinate, salicylate, or lactate ligand. Similarly, the second metal ligand coordination compound may comprise (a) at least one catecholate or pyrogallate ligand, (b) at least one ascorbate, citrate, a glycolate or polyol (including a ligand derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, phthalate, sarcosinate, salicylate, or lactate ligand, or (c) both at least one catecholate or pyrogallate ligand, and at least one ascorbate, citrate, a glycolate or polyol (including a ligand derived from ethylene glycol, propylene glycol, or glycerol), gluconate, glycinate, α-hydroxyalkanoate (e.g., α-hydroxyacetate, from glycolic acid), β-hydroxyalkanoate, γ-hydroxyalkanoate, malate, maleate, phthalate, sarcosinate, salicylate, or lactate ligand. In some of these embodiments, at least one metal ligand coordination compound is a chromium, iron, manganese, molybdenum, or ruthenium cyanide compound, preferably a chromium, iron, or manganese hexacyanide, such as ferricyanide or ferrocyanide in combination another metal ligand coordination compound as described herein.

[0033] The invention further contemplates those embodiments within the scope of Groups A-F, wherein the first and second metal ligand coordination compounds each exhibit substantially reversible electrochemical kinetics.

[0034] To this point, the various embodiments have been described mainly in terms of individual flow batteries. It should be appreciated that, where possible, the descriptions should be read as including flow batteries that are operating or capable of operating with the specified characteristics. Similarly, the descriptions should be read as including systems of flow batteries, wherein the system comprises at least two of the flow batteries described herein.

[0035] An exemplary flow battery is shown in **FIG. 1.** As shown in that figure, a flow battery system may include an electrochemical cell that features a separator **20** (*e.g.,* a membrane) that separates the two electrodes of the electrochemical cell. Electrode 10 is suitably a conductive material, such as a metal, carbon, graphite, and the like. Tank **50** may contain first redox material **30,** which material is capable of being cycled between an oxidized and reduced state.

[0036] A pump **60** may affect transport of the first active material **30** from the tank 50 to the electrochemical cell. The flow battery also suitably includes a second tank (not labeled) that contains the second active material 40. The second active material **40** may or may not be the same as active material **30.** A second pump (not labeled) may affect transport of second redox material **40** to the electrochemical cell. Pumps may also be used to affect transport of the active materials from the electrochemical cell to the tanks of the system. Other methods of effecting fluid transport - e.g., siphons - may be used to transport redox material into and out of the electrochemical cell. Also shown is a power source or load **70,** which completes the circuit of the electrochemical cell and allows the user to collect or store electricity during operation of the cell.

[0037] It should be understood that **FIG. 1** depicts a specific, non-limiting embodiment of a flow battery. Accordingly, devices according to the present disclosure may or may not include all of the aspects of the system depicted in **FIG. 1.** As one example, a system according to the present disclosure may include active materials that are solid, liquid, or gas and/or solids, liquids, or gases dissolved in solution or slurries. Active materials may be stored in a tank, in a vessel open to the atmosphere, or simply vented to the atmosphere.

[0038] In some cases, a user may desire to provide higher charge or discharge voltages than available from a single battery. In such cases, and in certain embodiments, then, several batteries are connected in series such that the voltage of each cell is additive. An electrically conductive, but non-porous material (e.g., a bipolar plate) may be employed to connect adjacent battery cells in a bipolar stack, which allows for electron transport but prevents fluid or gas transport between adjacent cells. The positive electrode compartments and negative electrode compartments of individual cells are suitably fluidically connected via common positive and negative fluid manifolds in the stack. In this way, individual electrochemical cells can be stacked in series to yield a desired operational voltage.

[0039] In additional embodiments, the cells, cell stacks, or batteries are incorporated into larger energy storage systems, suitably including piping and controls useful for operation of these large units. Piping, control, and other equipment suitable for such systems are known in the art, and include, for example, piping and pumps in fluid communication with the respective electrochemical reaction chambers for moving electrolytes into and out of the respective chambers and storage tanks for holding charged and discharged electrolytes. The energy storage and generation systems described by the present disclosure may also include electrolyte circulation loops, which may comprise one or more valves, one or more pumps, and optionally a pressure equalizing line. The energy storage and generation systems of this disclosure can also include an operation management system. The operation management system may be any suitable controller device, such as a computer or microprocessor, and may contain logic circuitry that sets operation of any of the various valves, pumps, circulation loops, and the like.

[0040] In some embodiments, a flow battery system may comprise a flow battery (including a cell or cell stack), a first chamber containing the first aqueous electrolyte and a second chamber containing the second aqueous electrolyte; at least one electrolyte circulation loop in fluidic communication each electrolyte chamber, said at least one electrolyte circulation loop comprising storage tanks and piping for containing and transporting the electrolytes; control hardware and software (which may include safety systems); and an optional power conditioning unit. The flow battery cell stack accomplishes the conversion of charging and discharging cycles and determines the peak power of energy storage system, which power may in some embodiments be in the kW range. The storage tanks contain the positive and negative active materials; the tank volume determines the quantity of energy stored in the system, which may be measured in kWh. The control software, hardware, and optional safety systems suitably include sensors, mitigation equipment and other electronic/hardware controls and safeguards to ensure safe, autonomous, and efficient operation of the flow battery energy storage system. Such systems are known to those of ordinary skill in the art. A power conditioning unit may be used at the front end of the energy storage system to convert incoming and outgoing power to a voltage and current that is optimal for the energy storage system or the application. For the example of an energy storage system connected to an electrical grid, in a charging cycle the power conditioning unit would convert incoming AC electricity into DC electricity at an appropriate voltage and current for the electrochemical stack. In a discharging cycle, the stack produces DC electrical power and the power conditioning unit converts to AC electrical power at the appropriate voltage and frequency for grid applications.

[0041] The energy storage systems of the present disclosure are, in some embodiments, suited to sustained charge or discharge cycles of several hour durations. For example, in some embodiments, the flow batteries of the present invention are capable of retaining at least about 70% efficiency when subjected to 10 charge / discharge cycles. As such, the systems of the present disclosure may be used to smooth energy supply/demand profiles and provide a mechanism for stabilizing intermittent power generation assets (e.g., from renewable energy sources). It should be appreciated, then, that various embodiments of the present disclosure include those electrical energy storage applications where such long charge or discharge durations are valuable. For example, non-limiting examples of such applications include those where systems of the present disclosure are connected to an electrical grid include, so as to allow renewables integration, peak load shifting, grid firming, baseload power generation consumption, energy arbitrage, transmission and distribution asset deferral, weak grid support, and/or frequency regulation. Cells, stacks, or systems according to the present disclosure may be used to provide stable power for applications that are not connected to a grid, or a micro-grid, for example as power sources for remote camps, forward operating bases, off-grid telecommunications, or remote sensors.

[0042] Flow battery energy storage efficacy is determined by both the round trip DC-DC energy efficiency (RT_{EFF}) and the energy density of the active materials (measured in Wh/L). The RT_{EFF} is a composite of voltage and current efficiencies for both the battery charge and discharge cycles. In electrochemical devices, voltage and current efficiencies are functions of the current density, and while voltage and current efficiency typically decrease as current density (mA/cm^2) increases, high current densities are often desirable to reduce electrochemical stack size/cost required to achieve a given power rating. Active material energy density is directly proportional to the cell OCV (OCV = open circuit voltage), the concentration of active species, and the number of electrons transferred per mole of active species. High energy densities are desirable to reduce the volume of active materials required for a given quantity of stored energy.

[0043] It should be appreciated that, while the various embodiments described herein are described in terms of flow battery systems, the same strategies and design / chemical embodiments may also be employed with stationary (non-flow) electrochemical cells, batteries, or systems, including those where one or both half cells employ stationary electrolytes. Each of these embodiments is considered within the scope of the present invention.

Terms

[0044] Throughout this specification, words are to be afforded their normal meaning, as would be understood by those skilled in the relevant art. However, so as to avoid misunderstanding, the meanings of certain terms will be specifically defined or clarified.

[0045] The term "active material" is well known to those skilled in the art of electrochemistry and electrochemical energy storage and is meant to refer to materials which undergo a change in oxidation state during operation of the system. Active materials may comprise a solid, liquid, or gas and/or solids, liquids, or gasses dissolved in solution. In certain embodiments, active materials comprise molecules and/or supramolecules dissolved in solution. Active materials with a composition of matter described by this invention may be used in energy storage systems in such a way that they are paired with other active materials to form a positive couple and a negative couple wherein said other active materials are described by the present invention or are previously known in the art or a combination thereof, inclusive of soluble, semisolid, intercalation, capacitive or pseudo-capacitive, and plating-type active materials. The concentration of the molecules may be at least about 2 M, between about 1 M and about 2 M, about 1.5 M, between 0.5 M and 1M, or 0.5 M or less.

[0046] In certain embodiments, the active material may comprise a "metal ligand coordination compound," which are known to those skilled in the art of electrochemistry and inorganic chemistry. A metal ligand coordination compound may comprise a metal ion bonded to an atom or molecule. The bonded atom or molecule is referred to as a "ligand". In certain non-limiting embodiments, the ligand may comprise a molecule comprising C, H, N, and/or O atoms. In other words, the ligand may comprise an organic molecule. The metal ligand coordination compounds of the present disclosure are understood to comprise at least one ligand that is not water, hydroxide, or a halide (F , Cl^-, Br^-, I^-). Where presented here as being represented by "$M(L1)_x(L2)_y(L3)_z{}^m$, x, y, and z are independently 0, 1, 2, or 3, such that $1 \leq x + y + z \leq 3$" it should be appreciated that this reflects independent embodiments where "M" contains 1, 2, or 3 ligands of L1, L2, and L3 within its inner coordination sphere, where L1, L2, and L3 are different from one another.

[0047] Metal ligand coordination compounds may comprise a "redox active metal ion" and/or a "redox inert metal ion". The term "redox active metal ion" is intended to connote that the metal undergoes a change in oxidation state under the conditions of use. As used herein, the term "redox inert" metal ion is intended to connote that the metal does not undergo a change in oxidation state under the conditions of use. Metal ions may comprise non-zero valence salts of, *e.g.,* Al, Ca, Co, Cr, Sr, Cu, Fe, Mg, Mn, Mo, Ni, Pd, Pt, Ru, Sn, Ti, Zn, Zr, V, or a combination thereof. The skilled artisan would be able to recognize the circumstances where a given non-zero valence metal would be redox active or inactive under the prescribed electrolyte environments.

[0048] In other embodiments, the active material may comprise an "organic active material". An organic active material may comprise a molecule or supramolecule that does not contain a transition metal ion. It is further understood that organic active materials are meant to comprise molecules or supramolecules that are dissolved in aqueous solution. And organic active material is capable of undergoing a change in oxidation state during operation of the electrochemical energy storage system. In this case, the molecule or supramolecule may accept or donate an electron during operation of the system.

[0049] Unless otherwise specified, the term "aqueous" refers to a solvent system comprising at least about 98% by weight of water, relative to total weight of the solvent. In some applications, soluble, miscible, or partially miscible (emulsified with surfactants or otherwise) co-solvents may also be usefully present which, for example, extend the range of water's liquidity (e.g., alcohols / glycols). When specified, additional independent embodiments include those where the "aqueous" solvent system comprises at least about 55%, at least about 60 wt%, at least about 70 wt%, at least about 75 wt%, at least about 80%, at least about 85 wt%, at least about 90 wt%, at least about 95 wt%, or at least about 98 wt% water, relative to the total solvent. It some situations, the aqueous solvent may consist essentially of water, and be substantially free or entirely free of co-solvents or other species. The solvent system may be at least about 90 wt%, at least about 95 wt%, or at least about 98 wt% water, and, in some embodiments, be free of co-solvents or other species.

[0050] In addition to the redox active materials described below, the aqueous electrolytes may contain additional buffering agents, supporting electrolytes, viscosity modifiers, wetting agents, and the like.

[0051] The term "bipolar plate" refers to an electrically conductive, substantially nonporous material that may serve to separate electrochemical cells in a cell stack such that the cells are connected in series and the cell voltage is additive across the cell stack. The bipolar plate has two surfaces such that one surface of the bipolar plate serves as a substrate for the positive electrode in one cell and the negative electrode in an adjacent cell. The bipolar plate typically comprises carbon and carbon containing composite materials.

[0052] The term "cell potential" is readily understood by those skilled in the art of electrochemistry and is defined to be the voltage of the electrochemical cell during operation. The cell potential may be further defined by Equation 1:

$$\text{Cell Potential} = \text{OCV} - \eta_{pos} - \eta_{neg} - iR \qquad (1)$$

where OCV is the "open circuit potential" ,

η_{pos}

and

η_{neg}

are the overpotentials for the positive and negative electrodes at a given current density, respectively, and iR is the voltage loss associated with all cell resistances combined. The "open circuit potential" or OCV may be readily understood according to Equation 2:

$$\text{OCV} = E^{+} - E^{-} \qquad (2)$$

where E^+ and E are the "half-cell potentials" for the redox reactions taking place at the positive and negative electrodes, respectively. The half-cell potentials may be further described by the well-known Nemst Equation 3:

$$E = E^{o} - RT/nF \ln (X_{red} / X_{ox}) \qquad (3)$$

wherein E^0 is the standard reduction potential for redox couple of interest (e.g., either the positive or negative electrode), the R is the universal gas constant, T is temperature, n is the number of electrons transferred in the redox couple of interest, F is Faraday's constant, and X_{red} / X_{ox} is the ratio of reduced to oxidized species at the electrode.

[0053] The OCV of a battery system may be measured by using standard techniques when the current flow between the first and second electrode is equal to zero. In this condition, the voltage difference between the first and second electrodes corresponds to the OCV. The OCV of a battery system depends on the state of charge (SOC) of said system. Without being bound to the correctness of any theory, the OCV of an ideal battery, will change with state of charge according to the Nemst equation (equation 4 above). For simplicity in this application all OCVs will be referenced to their values at 50% SOC. Those of ordinary skill in the art will recognize that at higher SOCs the OCV of a battery will increase, and at lower SOCs the OCV will decrease from the value at 50% SOC.

[0054] The term "current density" refers to the total current passed in an electrochemical cell divided by the geometric area of the electrodes of the cell and is commonly reported in units of mA/cm^2. In certain embodiments of the present invention, current densities may be in a range of from about 50 mA/cm^2, from about 100 mA/cm^2 or from about 200 mA/cm^2, to about 200 mA/cm^2, to about 300 mA/cm^2, to about 400 mA/cm^2, or to about 500 mA/cm^2, and these ranges may also apply to those embodiments referred to as providing "at least 100 mA/cm^2."

[0055] The term "current efficiency" (I_{EFF}) may be described as the ratio of the total charge produced upon discharge of the system to the total charge passed upon charge. In some embodiments, the charge produced on discharge or passed on charge can be measured using standard electrochemical coulomb counting techniques well known to those of ordinary skill in the art. Without being bound by the limits of any theory, the current efficiency may be a function of the state of charge of the flow battery. In some non-limiting embodiments the current efficiency can be evaluated over an SOC range of about 35% to about 60%.

[0056] The term "energy density" refers to the amount of energy that may be stored, per unit volume, in the active materials. Energy density, as used herein, refers to the theoretical energy density of energy storage and may be calculated by Equation 4:

$$\text{Energy density} = (26.8 \text{ A-h/mol}) \times \text{OCV} \times [e^-] \qquad (4)$$

where OCV is the open circuit potential at 50% state of charge, as defined above, (26.8 A-h/mol) is Faraday's constant, and $[e^-]$ is the concentration of electrons stored in the active material at 99% state of charge. In the case that the active materials largely comprise an atomic or molecular species for both the positive and negative electrolyte, $[e^-]$ may be calculated as:

$$[e^-] = [\text{active materials}] \times n / 2 \qquad (5)$$

where [active materials] is the concentration (mol/L or M) of the active material in either the negative or positive electrolyte, whichever is lower, and n is the number of electrons transferred per molecule of active material. The related term "charge density" refers to the total amount of charge that each electrolyte may contain. For a given electrolyte:

$$\text{Charge density} = (26.8\ \text{A-h/mol}) \times [\text{active material}] \times n \qquad (6)$$

where [active material] and n are as defined above.

[0057] The term "energy efficiency" may be described as the ratio of the total energy produced upon discharge of the system to the total energy consumed upon charge. The energy efficiency (RT_{EFF}) may be computed by Equation 7:

$$RT_{EFF} = V_{EFF,RT} \times I_{EFF} \qquad (7)$$

[0058] As used herein, the term "evolution current" describes the portion of the electrical current applied in an energized flow battery configuration which is associated with the evolution (generation) of a particular chemical species. In the current context, then, when a sufficient overpotential *vide infra*) is applied in a flow battery such that either or both oxygen evolves at the positive electrode or hydrogen evolves at the negative electrode, that portion of the current associated with the evolution of oxygen or hydrogen is the oxygen evolution current or hydrogen evolution current, respectively.

[0059] In certain preferred embodiments, there is no current associated with hydrogen evolution, oxygen evolution, or both hydrogen and oxygen evolution. This may occur when the positive half-cell is operating at a potential less than the thermodynamic threshold potential or the threshold overpotential of the positive electrode (i.e., no oxygen produced; see explanation of terms below) or the negative half-cell cell is operating at a potential more positive than the thermodynamic threshold potential or the threshold overpotential of the negative electrode (i.e., no hydrogen produced), or both. In separate embodiments, the batteries operates within 0.3 V, within 0.25 V, within 0.2 V, within 0.15 V, or within 0.1 V of either the thermodynamic threshold potential or the threshold overpotential of the respective positive or negative electrodes.

[0060] In embodiments wherein gas is evolved, the portion of current associated with gas evolution (either hydrogen or oxygen or both) is suitably less than about 20%, less than about 15%, less than about 10%, less than about 5%, less than about 2%, or less than about 1% of the total applied current. Lower gas evolution currents are considered particularly suitable for battery (cell or cell stack) efficiencies.

[0061] The term "excluding" refers to the ability of a separator to not allow certain ions or molecules to flow through the separator and typically is measured as a percent.

[0062] The term "mobile ion" is understood by those skilled in the art of electrochemistry and is meant to comprise the ion which is transferred between the negative and positive electrode during operation of the electrochemical energy storage system. The term "mobile ion" may also refer to as an ion that carries at least at least 80% of the ionic current during charger/discharge.

[0063] As used herein, the terms "negative electrode" and "positive electrode" are electrodes defined with respect to one another, such that the negative electrode operates or is designed or intended to operate at a potential more negative than the positive electrode (and vice versa), independent of the actual potentials at which they operate, in both charging and discharging cycles. The negative electrode may or may not actually operate or be designed or intended to operate at a negative potential relative to the reversible hydrogen electrode. The negative electrode is associated with the first aqueous electrolyte and the positive electrode is associated with the second electrolyte, as described herein.

[0064] The term "overpotential" is well understood by those skilled in the art of electrochemistry and is defined by the difference in voltage between an electrode during operation of an electrochemical cell and the normal half-cell potential of that electrode, as defined by the Nernst equation. Without being bound by theory, the term overpotential is meant to describe the energy, in excess of that required by thermodynamics, to carry out a reaction at a given rate or current density. The term "overpotential" also describes a potential more positive than the thermodynamic onset voltage for oxygen evolution from water at the positive electrode and more negative than the thermodynamic onset voltage for hydrogen evolution from water at the negative electrode.

[0065] Similarly, as used herein, the term "threshold overpotential" refers to the overpotential at which either hydrogen or oxygen gas begins to evolve at the respective electrode. Note that an electrochemical system comprising "imperfect" (i.e., less than ideal catalytically) electrodes can be operated in three regions: (a) at a potential "below" the thermodynamic onset potential (i.e., more positive than the thermodynamic onset potential of the negative electrode and more negative than the thermodynamic onset potential of the positive electrode; no gas evolving so no gas evolution current); (b) at a potential between the thermodynamic threshold potential and threshold overpotential (no gas evolving and still no evolution current); and (c) beyond the threshold overpotential (gas evolving and exhibiting a gas evolution current). Such threshold overpotentials can be identified by those skilled in the art for a given system, for example, by measuring gas evolution as a function of applied half-cell potential (using e.g., a mass spectrometer), in the presence or absence of an electroactive material. See also below.

[0066] The gas evolution threshold potentials are also affected by the nature of the electrolytes. Certain chemicals are known to inhibit the evolution of hydrogen and oxygen in electrolytic cells, either because of some activity in the bulk electrolyte or because of their ability to coat or otherwise deactivate their respective electrodes; for example, macromolecules or oligomers or salts, such as chloride or phosphate, on Pt surfaces. Accordingly, in certain embodiments, then, either the first or second or both first and second electrolytes comprise at least one compound increases the hydrogen or oxygen threshold overpotential of the system, respectively.

[0067] As used herein, the terms "regenerative fuel cell" or "reversible fuel cell" or "flow battery" or "flow energy device" connote the same or similar type of device, which utilizes the same battery configuration (including cell or cell stack) for both energy storage and energy generation.

[0068] The term "reversible hydrogen electrode," or RHE, is used in its conventional meaning. That is, a reversible hydrogen electrode (RHE) is a reference electrode. The potential of the RHE, E(RHE) corresponds to the potential for Equation 8:

$$2H^{-} + 2e^{-} \leftrightarrow H_2 \qquad (8)$$

[0069] When the reaction of Equation 8 is carried out at equilibrium at a given pH and 1 atm H_2. This potential can be reference to a normal hydrogen electrode, E(NHE), by the following relation:

$$E(RHE) = E(NHE) - 0.059 \text{ x } pH = 0.0\ V - 0.059 \text{ x } pH \qquad (9)$$

where *E(NHE)* is the potential for the normal hydrogen electrode (NHE = 0.0 V), defined as the potential for the reaction of Equation 8 at standard state (1M H^+, 1 atm H_2). Thus a potential of 0 V vs. RHE corresponds to a voltage of 0 V vs. NHE at pH 0 and -0.413 V vs. NHE at pH 7.

[0070] The term "selectivity" is well known to those of ordinary skill in the art of electrochemistry and refers to the ability of a membrane to allow a ratio of the movement of mobile ions to active materials through a membrane. For example, a membrane that allows a 50:1 ratio of mobile ions to active materials to pass through would have a selectivity of 50.

[0071] The terms "separator" and "membrane" refer to an ionically conductive, electrically insulating material disposed between the positive and negative electrode of an electrochemical cell.

[0072] The polymer electrolytes useful in the present disclosure may be anion or cation conducting electrolytes. Where described as an "ionomer," the term refers to a polymer comprising both electrically neutral and a fraction of ionized repeating units, wherein the ionized units are pendant and covalently bonded to the polymer backbone. The fraction of ionized units may range from about 1 mole percent to about 90 mole percent, but may be further categorized according to their ionized unit content. For example, in certain cases, the content of ionized units are less than about 15 mole percent; in other cases, the ionic content is higher, typically at least about 80 mole percent. In still other cases, the ionic content is defined by an intermediate range, for example in a range of about 15 to about 80 mole percent. Ionized ionomer units may comprise anionic functional groups comprising carboxylates, sulfonates, phosphonates, salts of a carboxy acid, sulfonic acid, phosphonic acid, and the like. These functional groups can be charge balanced by, mono-, di-, or higher-valent cations, such as alkali or alkaline earth metals. Ionomers may also include polymer compositions containing attached or embedded quaternary ammonium, sulfonium, phosphazenium, and guanidinium residues or salts. The polymers useful in the present disclosure may comprise highly fluorinated or perfluorinated polymer backbones. Certain polymer electrolytes useful in the present disclosure include copolymers of tetrafluoroethylene and one or more fluorinated, acid-functional co-monomers, which are commercially available as NAFION™ perfluorinated polymer electrolytes from E. I. du Pont de Nemours and Company, Wilmington Del.. Other useful perfluorinated electrolytes comprise copolymers of tetrafluoroethylene (TFE) and FSO_2-$CF_2CF_2CF_2CF_2$-O-CF=CF_2.

[0073] The term "stack" or "cell stack" or "electrochemical cell stack" refers to a collection of individual electrochemical cells that are in electrically connected. The cells may be electrically connected in series or in parallel. The cells may or may not be fluidly connected.

[0074] The term "state of charge" (SOC) is well understood by those skilled in the art of electrochemistry, energy storage, and batteries. The SOC is determined from the concentration ratio of reduced to oxidized species at an electrode (X_{red} / X_{ox}). For example, in the case of an individual half-cell, when X_{red} = X_{ox} such that X_{red} / X_{ox} = 1, the half-cell is at 50% SOC, and the half-cell potential equals the standard Nernstian value, E^o. When the concentration ratio at the electrode surface corresponds to X_{red} / X_{ox} = 0.25 or X_{red} / X_{ox} = 0.75, the half-cell is at 25% and 75% SOC respectively. The SOC for a full cell depends on the SOCs of the individual half-cells and in certain embodiments the SOC is the same for both positive and negative electrodes. Measurement of the cell potential for a battery at OCV, and using Equations 2 and 3 the ratio of X_{red} / X_{ox} at each electrode can be determined, and therefore the SOC for the battery system.

[0075] The term "supporting electrolyte" is well-known in the arts of electrochemistry and energy storage, and is intended to refer to any species which is redox inactive in the window of electric potential of interest and aids in supporting charge and ionic conductivity. In the present case, a supporting electrolyte does not substantially compromise the solubility of the coordination compound or complex. Non-limiting examples include salts comprising an alkali metal, ammonium ion including an ammonium ion partially or wholly substituted by alkyl or aryl groups, halide (e.g., Cl^-, Br^-, I^-), chalcogenide, phosphate, hydrogen phosphate, phosphonate, nitrate, sulfate, nitrite, sulfite, perchlorate, tetrafluoroborate, hexafluorophosphate, or a mixture thereof, and others known in the art.

[0076] The term "voltage efficiency" may be described as the ratio of the observed electrode potential, at a given current density, to the half-cell potential for that electrode (x 100%), wherein the half-cell potential is calculated as described above. Voltage efficiencies can be described for a battery charging step, a discharging step, or a "round trip voltage efficiency". The round trip voltage efficiency ($V_{EFF,RT}$) at a given current density can be calculated from the cell voltage at discharge ($V_{Discharge}$) and the voltage at charge (V_{Charge}) using Equation 10:

$$V_{EFF,RT} = V_{Discharge} / V_{Charge} \times 100\% \qquad (10)$$

Exemplary Operating Characteristics

[0077] The present disclosure provides a variety of technical features of the disclosed systems and methods. It should be understood that any one of these features may be combined with any one or more other features. For example, a user might operate a system featuring an electrolyte that includes an organic active material (e.g., a quinone), wherein that electrode has a pH of about 3. Such a system might also feature a membrane separator having a thickness of about 35 microns. It should be further understood that the present disclosure is not limited to any particular combination or combinations of the following features.

[0078] The present invention also provides methods of operating the flow batteries described herein, each method comprising charging said battery by the input of electrical energy or discharging said battery by the removal of electrical energy. Further embodiments provide applying a potential difference across the first and second electrode, with an associated flow of electrons, so as to: (a) reduce the first redox active material while oxidizing the second redox active material; or (b) oxidize the first redox active material while reducing the second redox active material; or (c) both (a) and (b). Complementary methods provide those where each method comprises applying a potential difference across the first and second electrode so as to: (a) oxidize the first redox active metal-ligand coordination compound; or (b) reduce the second redox active metal-ligand coordination compound; or (c) both (a) and (b).

[0079] In traditional flow battery operation, mobile ions comprise proton, hydronium, or hydroxide. In various embodiments of the present disclosure, one may transport ions other than proton, hydronium, or hydroxide (e.g., when these ions are present in comparatively low concentration, such as below 1 M). Separate embodiments of these methods of operating a flow battery include those wherein the mobile ion does not consist essentially of protons, hydronium, or hydroxide. In these embodiments, less than 50% of the mobile ions comprise protons, hydronium, or hydroxide. In other embodiments, less than about 40%, less than about 30%, less than about 20%, less than about 10%, less than about 5%, or less than about 2% of the mobile ions comprise protons, hydronium, or hydroxide. Exemplary mobile ions in these embodiments include alkali metal or alkaline earth metal cations (especially Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+} or Sr^{2+}).

[0080] In some embodiments of the present disclosure, it is advantageous to operate between pH 1 and 13 (e.g., to enable active material solubility and/or low system cost). In this case one or both electrolytes is characterized as having a pH of between about 1 and about 13, or between about 2 and about 12, or between about 4 and about 10, or even between about 6 and about 8. In other embodiments, at least one of the electrolytes has a pH in a range of from about 9 to about 13, from about 8 to about 12, from about 10 to about 12, or from about 10.5 to about 11.5. For the most part, the compounds described herein comprising catecholate or pyrogallate are stable and operable at pH's within each of the ranges described herein. In some embodiments, the pH of the electrolyte may be maintained by a buffer. Typical buffers include salts of phosphate, borate, carbonate, silicate, trisaminomethane (Tris), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), piperazine-N,N'-bis(ethanesulfonic acid) (PIPES), and combinations thereof. A user may add an acid (e.g., HCl, HNO_3, H_2SO_4 and the like), a base (NaOH, KOH, and the like), or both to adjust the pH of a given electrolyte as desired.

[0081] In some embodiments, the pH of the first and second electrolytes are equal or substantially similar; in other embodiments, the pH of the two electrolytes differ by a value in the range of about 0.1 to about 2 pH units, about 1 to about 10 pH units, about 5 to about 12 pH units, about 1 to about 5 pH units, about 0.1 to about 1.5 pH units, about 0.1 to about 1 pH units, or about 0.1 to about 0.5 pH units. In this context, the term "substantially similar," without further qualification, is intended to connote that the difference in pH between the two electrolytes is about 1 pH unit or less. Additional optional embodiments provide that the pH difference is about 0.4 or less, about 0.3 or less, about 0.2 or less, or about 0.1 pH units or less.

[0082] The disclosed systems and methods may also comprise active materials and membrane ionomers which are charged. The term "charge" in refers to the "net charge" or total charge associated with an active material or ionomer moiety. The charged species may be anionic or cationic. In certain desired embodiments of the present disclosure it is advantageous for the active materials and membrane ionomers to comprise charges of the same sign (e.g. to prevent transfer of the active material across the membrane).

[0083] In specific embodiments, both the first and second ionically charged redox active materials and their respective oxidized or reduced forms are negatively charged, and the ion selective membrane having a stationary phase that also has a net negative charge, so as to be selectively permeable to cations to the substantial exclusion of the negatively charged redox active materials. The first and second redox active materials and their respective oxidized or reduced forms may independently exhibit charges in a range of -2 to -5. The term "substantial exclusion" refers to the ability of the membrane to limit the molar flux of ions passing through the membrane attributable to the first or second ionically charged redox active material to less than about 3% of the total ion flux during the operation of the flow battery. In related independent embodiments, the flux of ions attributable to the first or second ionically charged redox active material is about 5% or less, about 2% or less, about 1% or less, about 0.5% or less, about 0.2% or less, about 0.1% of less, about 0.01% or less, or about 0.001% or less of the total ion flux during the operation of the flow battery.

[0084] In other embodiments, both the first and second ionically charged redox active materials and their respective oxidized or reduced forms are positively charged, the ion selective membrane having a stationary phase that also has a net positive charge, so as to be selectively permeable to anions to the substantial exclusion of the positively charged redox active materials. The first and second redox active materials and their respective oxidized or reduced forms may independently exhibit charges in a range of +2 to +5 over the respective potential ranges. The term "substantial exclusion" is as described above.

[0085] The ability to measure the molar flux of the charged redox active material through the membrane during the operation of the flow battery may be conveniently measured for those systems in which each electrolyte comprises a redox active material based on a different metal such as provided in some embodiments described here (e.g., iron in the positive electrolyte and titanium in the negative electrolyte). This may be done by (a) operating such a cell at a fixed temperature (typically ambient room, but also super-ambient, temperatures) for a prescribed period of time (depending on the rate of flux, for example, 1 hour),(b) measuring and quantifying the amount of metal which has passed through the membrane from the source to second electrolyte (using, for example, atomic absorption spectroscopy, inductively coupled plasma, ion chromatography, or other suitable method), and (c) comparing that amount of metal ions with the amount of mobile ion which has passed through the membrane, corresponding to the total electrons which have passed over that period of time. By measuring the flux as a function of time and temperature, and membrane thicknesses, it is also possible to calculate the thermodynamic parameters associated with this particular system, and predict longevity of the system.

[0086] Systems and methods according to the present disclosure also feature active materials comprising metal-ligand coordination compounds. Metal-ligand coordination compounds may be present at, e.g., a concentration of at least about 0.25 M, at least about 0.35 M, at least about 0.5 M, at least about 0.75 M, at least about 1 M, at least about 1.25 M, at least about 1.5 M, at least about 2 M, for example as high as 3 M, 4 M, or 5M.

[0087] The metal ligand coordination compound may be further characterized with respect to the nature of the oxidizable or reducible species. For example, in some cases, the redox potential of the metal ligand coordination compound may be defined by transitions entirely within the metal center - i.e., the redox potential is defined by the accessibility of and energies associated with transitions between various valence states within the metal. In other cases, the oxidation / reduction may be localized within the ligand system. In still other cases, the oxidation / reduction may be distributed throughout the entire redox active complex, such that both the metal and the ligand system sharing in the distribution of charge.

[0088] In particular embodiments of the present disclosure, the metal ligand coordination compound may comprise ligands which are mono-, bi-, tri-, or multidentate. Monodentate ligands bind to metals through one atom, whereas bi-, tri-, or multidentate ligands bind to metals through 2, 3, or more atoms, respectively. Examples of monodentate ligands include halogens (F , Cl^-, Br^-, I^-), cyanide (CN^-), carbonyl or carbon monoxide (CO), nitride (N^{3-}), oxo (O^{2-}), hydroxo (OFF), sulfide (S^{2-}), pyridine, pyrazine, and the like. Other types of ligand bonding moieties include amino groups (NR_3), amido groups (NR_2), imido groups (NR), alkoxy groups ($R\text{-}CO^-$), siloxy ($R\text{-}SiO^-$), thiolate ($R\text{-}S^-$), and the like, which may comprise mono-, bi-, tri-, or multidentate ligands. Examples of bidentate ligands include catechol, bipyridine, bipyrazine, ethylenediamine, diols (including ethylene glycol), and the like. Examples of tridentate ligands include terpyridine, diethylenetriamine, triazacyclononane, trisaminomethane, and the like.

[0089] The disclosed systems and methods may feature electrochemical cell separators and/or membranes that have certain characteristics. In this disclosure, the terms membrane and separator are used interchangeably. The membranes of the present disclosure may, in some embodiments, feature a membrane separator having a thickness of about 500 microns or less, about 300 microns or less, about 250 microns or less, about 200 microns or less, about 100 microns or less, about 75 microns or less, about 50 microns or less, about 30 microns or less, about 25 microns or less, about 20 microns or less, about 15 microns or less, or about 10 microns or less, for example to about 5 microns, and where the phrase "100 microns or less" is used, separate embodiments include those using these ranges.

[0090] Separators are generally categorized as either solid or porous. Solid membranes typically comprise an ion-exchange membrane, wherein an ionomer facilitates mobile ion transport through the body of the polymer. The facility with which ions conduct through the membrane can be characterized by a resistance, typically an area resistance in units of ohm-cm^2. The area resistance is a function of inherent membrane conductivity and the membrane thickness. Thin membranes are desirable to reduce inefficiencies incurred by ion conduction and therefore can serve to increase voltage efficiency of the energy storage device. Active material crossover rates are also a function of membrane thickness, and typically decrease with increasing membrane thickness. Crossover represents a current efficiency loss that must be balanced with the voltage efficiency gains by utilizing a thin membrane.

[0091] Porous membranes are non-conductive membranes that allow charge transfer between two electrodes via open channels filled with conductive electrolyte. Porous membranes are permeable to liquid or gaseous chemicals. This permeability increases the probability of chemicals passing through porous membrane from one electrode to another causing cross-contamination and/or reduction in cell energy efficiency. The degree of this cross-contamination depends on, among other features, the size (the effective diameter and channel length), and character (hydrophobicity / hydrophilicity) of the pores, the nature of the electrolyte, and the degree of wetting between the pores and the electrolyte. Certain embodiments also provide that the first or the second or both the first and second metal ligand coordination compounds are characterized as having a hydrodynamic diameter and separator is characterized as having a mean pore size, wherein the hydrodynamic diameter of the coordination compound is larger than the mean pore size of the separator.

[0092] Such ion-exchange separators may also comprise membranes, which are sometimes referred to as polymer electrolyte membranes (PEMs) or ion conductive membranes (ICMs). The membranes according to the present disclosure may comprise any suitable polymer, typically an ion exchange resin, for example comprising a polymeric anion or cation exchange membrane, or combination thereof. The mobile phase of such a membrane may comprise, and/or is responsible for the primary or preferential transport (during operation of the battery) of at least one mono-, di-, tri-, or higher valent cation and/or mono-, di-, tri-, or higher valent anion, other than protons or hydroxide ions.

[0093] Additionally, substantially non-fluorinated membranes that are modified with sulfonic acid groups (or cation exchanged sulfonate groups) may also be used. Such membranes include those with substantially aromatic backbones, e.g., poly-styrene, polyphenylene, biphenyl sulfone (BPSH), or thermoplastics such as polyetherketones or polyethersulfones. Examples of ion-exchange membranes comprise Nafion.

[0094] Battery-separator style porous membranes, may also be used. Because they contain no inherent ionic conduction capability, such membranes are typically impregnated with additives in order to function. These membranes are typically comprised of a mixture of a polymer, and inorganic filler, and open porosity. Suitable polymers include those chemically compatible with the electrolytes of the presently described systems, including high density polyethylene, polypropylene, polyvinylidene difluoride (PVDF), or polytetrafluoroethylene (PTFE). Suitable inorganic fillers include silicon carbide matrix material, titanium dioxide, silicon dioxide, zinc phosphide, and ceria and the structures may be supported internally with a substantially non-ionomeric structure, including mesh structures such as are known for this purpose in the art.

[0095] The open circuit potential (OCV) of an electrochemical cell is a relevant operating characteristic of electrochemical energy storage systems. In certain embodiments, the OCV may be comparatively large (e.g. at least 1 V, and upwards of 2 V, 3 V, or 4 V). Such comparatively large open circuit potentials are known to enable high cell voltage efficiencies, high AC-AC conversion efficiencies, high energy storage densities, and low system costs. Traditional flow batteries with aqueous electrolytes and soluble active materials may operate with an OCV less than about 1.2 V. An electrochemical cell according to the present disclosure is suitably characterized by an open circuit potential of at least about 1.4 V.

[0096] The present disclosure presents exemplary cyclic voltammetry data for several metal ligand coordination compound couples under a range of conditions (see **Tables** 2 and **3,** and Example 7, *vide infra*). In considering these (or other) sets of half-cell couples, certain embodiments provide that the cells comprise those pairs of metal ligand coordination compounds whose couples provide large open circuit potential, while capable of operating at potentials that are within the potentials associated with the generation of hydrogen and oxygen derived from the electrolysis of water (i.e., so as to operate at potentials where the generation of a hydrogen or oxygen evolution current is minimized or avoided). In certain embodiments, these half-cell couples are chosen to provide large open circuit voltages while operating at or below a half-cell potential of 0 V at the negative electrode and at or above a half-cell potential of 1.23 V at the positive electrode, where the half-cell potentials are with respect to a reversible hydrogen electrode. Through judicious choice of electrode materials which exhibit poor catalytic activity, e.g., an allotrope of carbon or a metal oxide, it is possible to provide systems having large overpotentials, so as to drive the OCV to values higher than the thermodynamic limit of 1.23 V without hydrogen or oxygen evolution. For example, experiments show (and as reflected in **Table 3,** *vide infra*) the $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Al(cit)_2(cat)^{2-/3-}$ pair of couples can exhibit an OCV of 1.70 V using carbon electrodes.

[0097] In some embodiments, the open circuit voltage (OCV) of the flow battery is at least about 1.2 volts, at least about 1.3 V, at least about 1.4 V, at least about 1.5 V, at least about 1.6 V, at least about 1.7 V, at least about 1.8 V, at least about 1.9 V, or at least about 2 V, for example to about 3 V or 4V. As described above, higher open circuit voltages are associated with higher power densities.

[0098] Systems and methods according to the present disclosure may exhibit a particular current density at a given round trip voltage efficiency. Methods for determining current density at a given round trip voltage efficiency are known to those skilled in the art of electrochemistry and electrochemical energy storage.

[0099] To serve as a metric for electrochemical cell performance, a specified current density must be linked to a measured voltage efficiency. Higher current densities for a given round trip voltage efficiency enable lower cost electrochemical cells and cell stacks. In certain embodiments, it is desired to operate a flow battery with a current density of at least about 50 mA/cm^2 at $V_{EFF,RT}$ of at least about 50%. In other embodiments, the current density will be at least about 50 mA/cm^2 at $V_{EFF,RT}$ of at least about 60%, at least about 75%, at least about 85%, or at least about 90%. In other embodiments, the current density will be at least 100 mA/cm^2 at $V_{EFF,RT}$ of at least about 50 %, at least about 60%, at least about 75%, at least about 85%, at least about 90% and the like. In other embodiments, the current density will be at least 200 mA/cm^2 at $V_{EFF,RT}$ of at least about 50 %, at least about 60%, at least about 75%, at least about 85%, at least about 90%, and above.

[0100] Electrolytes that include an organic active material, either in the absence or presence of metal coordination, are considered suitable for one or both half-cells of the disclosed systems and methods. Suitable organic active materials include carbon, aromatic hydrocarbons, including quinones, hydroquinones, viologens, pyridinium, pyridine, acridinium, catechol, other polycyclic aromatic hydrocarbons, and the like. Suitable organic active materials may also include sulfur, including thiol, sulfide, and disulfide moieties. Suitable organic active materials may be soluble in water in concentrations at least about 0.1 M, at least about 0.5 M, at least about 1 M, at least about 1.5 M, at least about 2 M, and above, for example, to about 2M, about 3 M, about 4 M, or about 5 M.

[0101] The disclosed systems and methods may also be characterized in terms of their half-cell potentials. Both the negative and positive electrode may exhibit a half-cell potential. An electrochemical cell according to the present disclosure may, in some embodiments, have a half-cell potential for the negative electrode less than about 0.5 V vs. RHE, less than about 0.2 V vs. RHE, less than about 0.1 V vs. RHE, less than about 0.0 V vs. RHE, less than about -0.1 V vs. RHE, less than about -0.2 V vs. RHE, less than about -0.3 V vs. RHE, less than about -0.5 V vs. RHE, for example, to about - 2 V vs. RHE. An electrochemical cell according to the present disclosure may, in some embodiments, have a half-cell potential for the positive electrode at least about 0.5 V vs. RHE, at least about 0.7 V vs. RHE, at least about 0.85 V vs. RHE, at least about 1.0 V vs. RHE, at least about 1.1 V vs. RHE, at least about 1.2 V vs. RHE, at least about 1.3 V vs. RHE, at least about 1.4 V vs. RHE and the like, for example, to about 2 V vs. RHE.

EXAMPLE 1 - GENERAL

[0102] The following Examples are provided to illustrate some of the concepts described within this disclosure. While each Example is considered to provide specific individual embodiments of composition, methods of preparation and use, none of the Examples should be considered to limit the more general embodiments described herein.

Example 1.1 - Materials

[0103] Sodium hexacyanoferrate(II) decahydrate 99%, $Na_4Fe(CN)_6{\bullet}10H_2O$; potassium hexacyanoferrate(II) trihydrate 98+%, $K_4Fe(CN)_6{\bullet}3H_2O$; potassium hexacyanoferrate(III) ACS 99.0% min; $K_3Fe(CN)_6$; ethylene glycol, propylene glycol, glycerol, lactic acid (80-85 aqueous solution); glycine, glycolic acid (67% aqueous solution); maleic acid; malic acid; phthalic acid; salicylic acid; gluconic acid; citric acid; sarcosine; iron (III) sulfate; iron (III) chloride; titanium oxysulfate; manganese (II) sulfate; and chromium (III) sulfate were purchased from Alfa Aesar (Ward Hill, MA) as ACS grade or better unless specified above and were used without additional purification. Ammonium bislactatobishydroxytitanium (IV) was purchased from Sigma Aldrich (St. Louis, MO) as a 50% aq. solution and was used without further purification. Potassium hexacyanochromate(III), $K_3[Cr(CN)_6]$ and potassium hexacyanomanganate(III), $K_3[Mn(CN)_6]$ were purchased from Sigma-Aldrich (St. Louis, MO) and used without additional purification.

[0104] Complexes could be synthesized by several methods. Homoleptic tris-ligated complexes were most easily synthesized by stirring a 3:1 aqueous mixture of ligand and metal salt while slowly adding an alkali metal hydroxide solution until the pH was between 8 and 13, the typical window of stability for the complexes of interest. Certain mixed ligand species, for example $Ti(lactate)_2(salicylate)$, could also be synthesized by this method.

[0105] Mono and bis α-hydroxy acid complexes of iron and titanium were synthesized by the portion-wise addition of 2 equivalents of sodium bicarbonate to stirred solutions of the metal sulfates (2-3 M) and the appropriate proportion of the appropriate ligand. For example, 6 mmol of $TiOSO_4$ and 6 mmol of glycolic acid were stirred, and 12 mmol of $NaHCO_3$ was added slowly, allowing gas evolution to subside between additions. The pH of the resulting solutions was about 3.5 for the solutions of ML_1 and about 2 for the solutions of ML_2. The solubility of these complexes relative to aquated metals is evidenced by the stability with respect to precipitation of metal oxides of TiL_1 and TiL_2 solutions at such high pHs. In a control experiment where no ligand was added, wholesale and irreversible precipitation of TiO_2 was observed when more than 1 equivalent of $NaHCO_3$ was added, corresponding to a pH of about 1.

[0106] Complexes with additional ligands could be synthesized by adding an appropriate amount of ML_1 or ML_2 solution synthesized as described in the previous paragraph to a solution of the desired additional ligand mixed with a suitable base, such as potassium carbonate or potassium hydroxide. Mixed ligand analogs of the Mn, Cr, Ti, and Fe compounds may be prepared by similar reaction schemes.

[0107] Titanium bis-lactate L' complexes could also be synthesized using $(NH_4)_2Ti(lactate)_2(OH)_2$ (available from Sigma Aldrich as a 50% solution) as a synthon. In this case, L' (e.g., salicylic acid) was added, and after about an hour of stirring, an aqueous solution of 2 eq. alkali metal hydroxide was added to deprotonate ammonium, drive off ammonia over the course of about 24 hours of stirring uncapped in a fume hood, and provide the desired metal complex as a sodium/potassium salt, e.g., $NaKTi(lactate)_2(salicylate)$.

[0108] Disodium titanium(IV) triscatecholate, $Na_2Ti(catecholate)_3$ was synthesized by a modification of a procedure described by Davies, see Davies , J. A.; Dutramez, S. J. Am. Ceram. Soc. 1990, 73. 2570-2572, from titanium(IV) oxysulfate and pyrocatechol. Sodium hydroxide was used in place of ammonium hydroxide to obtain the sodium salt. Sodium potassium titanium(IV) trispyrogallate, $NaKTi(pyrogallate)_3$ was made analogously, first as the ammonium salt, $(NH_4)Ti(pyrogallate)_3$, and subsequently converted to the sodium potassium salt by heating in a mixture of aqueous sodium hydroxide and aqueous potassium hydroxide.

[0109] The mixed ligand titanium complexes sodium potassium titanium(IV) biscatecholate monopyrogallate, sodium potassium titanium(IV) biscatecholate-monolactate, sodium potassium titanium (IV) biscatecholate monogluconate, sodium potassium titanium(IV) biscatecholate monoascorbate, and sodium potassium titanium(IV) bis catecholate monocitrate were made from a titanium catecholate dimer, $Na_2K_2[TiO(catecholate)]_2$. For the synthesis of the tetrapotassium salt see Borgias, B. A.; Cooper, S. R.; Koh, Y. B.; Raymond, K. N. Inorg. Chem. 1984, 23, 1009-1016. A one-to-one mixture of titanium dimer with the desired chelate (pyrogallol, lactic acid, gluconic acid, ascorbic acid, or citric acid) gave the mixed ligand species. Sodium potassium titanium(IV) monocatecholate monopyrogallate monolactate was made in a similar fashion by addition of both pyrogallol and lactic acid to the catecholate containing dimer. Mixed ligand analogs of the Al, Cr, Fe, and Mn compounds may be prepared by similar reaction schemes. The structures of several of the titanium compounds were confirmed by mass spectroscopy (see **Table 1**). Mixed ligand analogs of the Al, Cr, Fe, and Mn compounds may be prepared by similar reaction schemes.

Table 1. Mass spectroscopy data for selected compound*

	Mass (m/z) Calc'd / Obs'd
$Ti(catecholate)_3^{2-}$	186.0080 / 186.0
$Ti(pyrogallate)_3^{2-}$	210.0038 / 210.0
$Ti(catecholate)_2(pyrogallate)^{2-}$	194.0055 / 194.0

Table 1. Mass spectroscopy data for selected compound*	
	Mass (m/z) Calc'd / Obs'd
Ti(catecholate)$_2$(ascorbate)$^{2-}$	219.0057 / 219.0
Ti(catecholate)$_2$(gluconate)$^{2-}$	229.0188 / 229.0
Ti(catecholate)$_2$(lactate)$^{2-}$	176.0055 / 176.0
* Mass spectrometry data were obtained on an Agilent 6150B single quadrupole LC/MS in the negative ion mode with electrospray ionization (ESI). Aqueous solution samples of the metal ligand complex were diluted in methanol and introduced to the mass spectrometer ionizer by direct injection using a syringe pump. The reported *m*/*z* peaks in each case are for the dianions, *z* = -2.	

[0110] Sodium potassium iron(III) triscatecholate, $Na_{1.5}K_{1.5}Fe(catecholate)_3$ was prepared according to the procedure outline by Raymond et. al., see Raymond, K. N.; Isied, S.S., Brown, L. D.; Fronczek, F. R.; Nibert, J. H. J. Am. Chem. Soc. 1976, 98, 1767-1774. The only modification was the use of a mixture of sodium hydroxide and potassium hydroxide as the excess base in place of potassium hydroxide.

[0111] Sodium titanium(IV) triscitrate, $Na_4Ti(citrate)_3$, was synthesized by analogy to the method used for sodium titanium(IV) tricatecholate described above except using citric acid in place of catechol. These starting materials were obtained from Alfa Aesar (Ward Hill, MA), were of reagent grade or better, and were used as received.

[0112] Sodium aluminum(III) biscitrate monocatecholate, Al(citrate)$_2$(catecholate), was synthesized in analogy to the method used for sodium titanium(IV) tricatecholate described above except using two equivalents of citric acid and one equivalent of catechol to a solution of aluminum(III) sulfate. These starting materials were obtained from Alfa Aesar (Ward Hill, MA), were of reagent grade or better, and were used as received.

Example 1.2- Cyclic Voltammetry

[0113] Cyclic voltammetry data was recorded using a 760c potentiostat (CH Instruments, Austin, TX) with iR correction. Tests were conducted using glassy carbon working electrodes (Bioanalytical Systems, Inc., West Lafayette, IN), Ag/AgCl reference electrodes (Bioanalytical Systems, Inc. West Lafayette, IN) and platinum wire counter electrodes (Alfa Aesar, Ward Hill, MA). Working electrodes were polished according to the supplier's instructions before each experiment. Reference electrodes were calibrated against a "master" Ag/AgCl electrode known to have a potential of +0.210 V vs. NHE as known by those skilled in the art of electrochemistry. Solutions were sparged with argon for at least 5 minutes before each experiment. All experiments were performed at ambient temperatures (17-22 °C). No supporting electrolytes were added unless otherwise specified. All data were collected at a scan rate of 100 mV/s unless otherwise specified. Under these conditions, hydrogen evolution became significant at potentials more negative than -0.80 V vs. RHE and oxygen evolution became significant at potentials more positive than +2.20 V vs. RHE.

Example 1.3 Experimental procedure for a 5 cm^2 active area flow battery

[0114] Cell hardware designed for 5 cm^2 active area and modified for acid flow was obtained from Fuel Cell Technologies (Albuquerque, NM). Carbon felt, nominally 3 mm thick, was obtained from Alfa Aesar (Ward Hill, MA) and MGL 370 carbon paper was obtained from Fuel Cell Earth (Stoneham, MA). Felts were dip-coated with a suspension of Vulcan XC-72 carbon (Cabot Corp., Boston, MA) and NAFION™ (Ion-Power, New Castle, DE) and air-dried before use and carbon papers were used as received. NAFION™ HP, XL, or NR-212 cation exchange membranes were obtained from Ion-Power in the H+ form and were used as received. Viton™ gaskets were obtained from McMaster Carr (Robinsville, NJ) and were cut to allow for a 5 cm^2 active area with ~1 cm^2 areas left above and below the felts for electrolyte ingress and egress from the positive and negative compartments of the cell. The cell was assembled using gaskets that provided a compression of ~25% of the measured thickness of the felts or papers. The membranes and electrodes were not pretreated before assembly. The electrolyte reservoirs were fashioned from Schedule 80 PVC piping with PVDF tubing and compression fittings. Masterflex™ L/S peristaltic pumps (Cole Parmer, Vernon Hills, IL) were used with Tygon™ tubing. Electrolytes were sparged with UHP argon through an oil-filled bubbler outlet before electrochemical testing and a head pressure of argon was maintained during the testing. An Arbin Instruments BT2000 (College Station, TX) was used to test the electrochemical performance, and a Hioki 3561 Battery HiTESTER (Cranbury, NJ) was used to measure the AC resistance across the cell.

[0115] In a typical experiment, 50 mL each of electrolyte containing active material for the positive and negative electrode were loaded into separate reservoirs and sparged with argon for 20 minutes while circulating the electrolytes through the cell. The electrolytes were charged to 40% SOC (calculated from the concentrations of the active materials and the volumes of the electrolyte), the iV response of the cell was obtained, and then the electrolytes were cycled between 40 and 60% SOC. An analog output from the Hioki battery tester was recorded to monitor changes in the membrane and contact resistances.

EXAMPLE 2

[0116] A redox flow battery cell was assembled according to the methods described in Example 1.3 using titanium *tris*-catecholate ($Ti^{4+/3+}(cat)_3^{2-/3-}$) and ferri/ferro-cyanide ($Fe^{3+/2+}$

$(CN)_6^{3-/4-}$) metal ligand coordination compounds as active materials for the negative and positive electrolytes, respectively. The active materials were prepared at concentrations of 0.5 M in 0.5 M pH 11 Na_2SO_4 supporting electrolyte (negative electrolye, or negolyte) or no supporting electrolyte (positive electrolyte, or posolyte) and were flowed at 100 mL/min through the flow battery cell assembled using 5 cm^2 carbon felt electrodes and a NAFION™ cation selective membrane (50 μm thick) in Na form. The cell was initially charged from 0 to 50% state of charge before several charge/discharge cycles was collected by sweeping the cell current from open circuit to ~150 mA/cm^2 and monitoring the resulting cell potential, **FIG. 2.** At open circuit, a cell potential of 1.63 V was observed as expected for equilibrium cell potential at 50% SOC based on the externally measured $E_{1/2}$ values for $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$. Charge/discharge cycling revealed well behaved, reproducible voltage/current vs. time traces, demonstrating promising durability, **FIG. 2.** An RT voltage efficiency of 69% was measured for this system at 150 mA/cm^2. Typical resistances measured by the Hioki Battery Tester for the membrane and contact resistance component of cells built with NR212, XL, and HP membranes were 0.77, 0.60, and 0.5 ohm-cm^2, respectively.

[0117] FIG. 3 displays the charge / discharge characteristics for a flow battery of the present invention wherein the negative and positive active materials comprise $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$, respectively. The cell potential increases as the battery is charged and decreases as the battery is discharged.

EXAMPLE 3

[0118] A redox flow battery cell was assembled according to the methods described in Example 1.3 using titanium *tris*-catecholate ($Ti^{4+/3+}(cat)_3^{2-/3-}$) and ferri/ferro-cyanide ($Fe^{3+/2+}(CN)_6^{3-/4-}$) metal ligand coordination compounds as active materials for the negative and positive electrolytes, respectively. In a typical cell, stable voltages were observed upon repeatedly charging to 60% SOC and discharging to 40% SOC (see **FIG. 4**) when the discharge energy for each cycle was 99.8% of the charge energy, indicative of 99.8% roundtrip current efficiency. This was achieved by using a constant current density (e.g., 150 mA/cm^2) for both charge and discharge but with a discharge time that was slightly shorter than (i.e., 99.8% of) the charge time. Under these conditions, the open circuit voltages at 40 and 60% SOC were stable for extended periods of time.

[0119] Crossover flux data were obtained by measuring the concentrations of Fe and Ti in each electrolyte at the beginning and end of a suitably lengthy battery test, typically one to two weeks in duration for a membrane area of 7 cm^2. The concentrations were determined by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) experiments performed by Evans Analytical Group, Syracuse, NY. The moles of Fe in the Ti-containing electrolyte before the test were subtracted from the number of moles in the same electrolyte at the end of the test. This was converted to a flux by dividing the moles by the membrane area and the test duration.

[0120] Typical fluxes for boiled DuPont Nafion™ NR212 (50 micron thick) were 5.0×10^{-8} mol cm^{-2} day^{-1} for ferri/ferrocyanide and 6.5×10^{-8} mol cm^{-2} day^{-1} for titanium triscatecholate. For unboiled DuPont Nafion™ HP (20 micron thick), the measured fluxes were 1.1×10^{-5} and 3.3×10^{-6} mol cm^{-2} day^{-1} for the above iron and titanium complexes, respectively. It should be noted that these fluxes are substantially lower than 1% of the total current (and thus the total moles of ions passed across the membrane) during this time. For example, in the NR212 test above, 6.4×10^{-2} mol of total ions were passed over 6.8 days of operation at 100 mA/cm^2, approximately 6 orders of magnitude larger than the amount of active material ion crossover. These results are believed to be representative / typical for the compounds described herein.

EXAMPLE 4

[0121] A redox flow battery cell was assembled according to the general methods described in Example 1.3, again using titanium *bis*-catecholate *mono*-pyrogallate ($Ti^{4+/3+}(cat)_2(gal)^{2-/3-}$) and ferri/ferro-cyanide ($Fe^{3+/2+}(CN)_6^{3-/4-}$) metal ligand coordination compounds as active materials for the negative and positive electrolytes, respectively. In this example the carbon felt electrodes were replaced with TORAY carbon paper electrodes that were catalyzed with Vulcan carbon and NAFION™ in a manner similar to that of Example 2. Additionally, flow fields of the "interdigitated" type were employed. The active material solution concentrations were increased to 1.5 M and the cell performance was evaluated by monitoring the cell potential on both charge and discharge cycles as a function of current density. As can be seen in **FIG. 5,** the cell maintains round trip voltage efficiencies of 84%, 79%, and 73% at current densities of 150, 200, and 250 mA/cm^2, respectively. In this configuration the flow battery active materials exhibited an energy density of 32.79 Wh/L.

[0122] The results of analogous experiments using $Ti^{4+/3+}(cat)_3^{2-/3-}$ and $Fe^{3+/2+}(CN)_6^{3-/4-}$are shown in **FIG. 6** and **FIG. 7.**

EXAMPLE 5

[0123] A redox flow battery cell was assembled according to the methods described in Example 1.3 using titanium *bis*-lactate *mono*-salicylate ($[Ti^{4+/3+}(lactate)_2(salicylate)]^{2-/3-}$) and ferri/ferro-cyanide ($[Fe^{3+/2+}(CN)_6]^{3-/4-}$) metal ligand coordination compounds as active materials for the negative and positive electrolytes, respectively. The active material solutions were prepared at concentrations of 1 M with no additional supporting electrolyte and were flowed at 100 mL/min through the flow battery cell assembled using 5 cm^2 carbon paper electrodes and a NAFION™ cation selective membrane (25 μm thick) in Na form. The cell was initially charged from 0 to 25% state of charge before charge/discharge cycles were collected by charging and discharging the cell at 150 or 100 mA/cm^2 and monitoring the resulting cell potential, **FIG. 21**

[0124] (where visually wider cycles were taken at 100 instead of 150 mA/cm^2). At open circuit, a cell potential of 1.60 V was observed as expected for equilibrium cell potential at 50% SOC based on the externally measured $E_{1/2}$ values for $[Ti^{4+/3+}(lactate)_2(salicylate)]^{2-/3-}$ and $[Fe^{3+/2+}(CN)_6]^{3-/4-}$. Charge/discharge cycling revealed well behaved, reproducible voltage/current vs. time traces, demonstrating promising durability, **FIG. 21.** An encouraging RT voltage efficiency of 67% was measured for this system at 150 mA/cm^2. Typical resistances measured by the Hioki Battery Tester for the membrane and contact resistance component of cells built with NR212, XL, and HP membranes were 0.77, 0.60, and 0.5 ohm-cm^2, respectively.

EXAMPLE 6

[0125] A redox flow battery cell was assembled according to the methods described in Example 1.3 using titanium bis-lactate mono-glycolic acid ($[Ti^{4+/3+}(lactate)_2(\alpha\text{-hydroxyacctatc})]^{2-/3-}$) and ferri/ferro-cyanide ($[Fe^{3+/2+}(CN)_6]^{3-/4-}$) metal ligand coordination compounds as active materials for the negative and positive electrolytes, respectively. In a typical cell, stable voltages were observed upon repeatedly charging to 75% SOC and discharging to 25% SOC (see **FIG. 22**) when the discharge energy for each cycle was 99.8% of the charge energy, indicative of 99.8% roundtrip current efficiency. This was achieved by using a constant current density (e.g., 150 mA/cm^2) for both charge and discharge but with a discharge time that was slightly shorter than (i.e., 99.8% of) the charge time. Under these conditions, the open circuit voltages at 25 and 75% SOC were stable for extended periods of time.

EXAMPLE 7 - Cyclic Voltammetry Data

[0126] The following experiments provide information as to the nature of the half-cell performance for the indicated materials. As described above, certain embodiments of the present invention include those flow batteries comprising these, or analogous, materials which would provide full cell performance reflective of the reported half-cell performance, and such embodiments are considered within the scope of the present invention.

Table 2A. Exemplary electrochemical couples described herein

Couple	$E_{1/2}$, V vs. RHE	pH	FIG.	Solubility (Molar), 25°C	Charge Density (Ah/L)
Al(citrate)$_2$(catecholate)$^{2-/3-}$	1.25	11.5	8	0.5	13.4
Fe(catecholate)$_3{}^{2-/3-}$	-0.50	11	10	1.5	40.2
Ti(catecholate)$_3{}^{2-/3-}$	-0.45	11	15	1.0	26.8
Ti(pyrogallate)$_3{}^{2-/3-}$	-0.55	9.8	9	1.6	42.9
Ti(catecholate)$_2$(pyrogailate)$^{2-/3-}$	-0.50	11	11	1.5	40.2
Ti(catecholate)$_2$(ascorbate)$^{2-/3-}$	-0.55	10	14	1.5	40.2
Ti(catecholate)$_2$(gluconate)$^{2-/3-}$	-0.60	9	13	1.5	40.2
Ti(catecholate)$_2$(lactate)$^{2-/3-}$	-0.49	9	12	1.5	40.2
Ti(catecholate)(pyrogallate)(lactate)$^{2-/3-}$	-0.70	8.5	16	1.5	40.2
Ti(citrate)$_3$	-0.04	5	17	2.0	53.6
Fe(CN)$_6{}^{3-/4-}$	1.18	11	18	1.5	40.2
Cr(CN)$_6{}^{3-/4-}$	-0.60	9	19	1.5	40.2
Mn(CN)$_6{}^{3-/4-}$	-0.60	9	20	1.5	40.2

Table 2B. Exemplary electrochemical couples described herein

Couple	$E_{1/2}$, V vs. RHE	pH	FIG. *	Solubility (Molar), 25°C	Charge Density (Ah/L)
Ti$^{IV/III}$(lactate)$_1$	-0.34	3.6	N/S	1.75	46.9
Ti$^{IV/III}$(lactate)$_1$	-0.40	5.6	25	1.75	46.9
Ti$^{IV/III}$(lactate)$_1$	-0.54	9	26	1.75	46.9
Ti$^{IV/III}$(lactate)$_2$	-0.03	2	27	1.75	46.9
Ti$^{IV/III}$(lactate)$_2$	-0.40	3.6	28	1.75	46.9
Ti$^{IV/III}$(lactate)$_2$	-0.40	9	29	1.75	46.9
Ti$^{IV/III}$(lactate)$_1$(malate)$_2$	-0.40	9.9	30	1.5	40.2
Ti$^{IV/III}$(malate)$_2$(salicylate)	-0.48	10	31	1.5	40.2
Ti$^{IV/III}$(lactate)$_2$(glycinate)	-0.50	9.9	32	1.5	40.2

Table 2B. Exemplary electrochemical couples described herein

Couple	**$E_{1/2}$, V vs. RHE**	**pH**	**FIG. ***	**Solubility (Molar), 25°C**	**Charge Density (Ah/L)**
Ti$^{IV/III}$(lactate)$_2$(salicylate)	-0.48	10	33	1.5	40.2
Ti$^{IV/III}$(salicylate)$_2$(lactate)	-0.50	9.8	34	1.5	40.2
Ti$^{IV/III}$(α-hydroxyacetate)$_2$(salicylate)	-0.48	10	35	1.5	40.2
Ti$^{IV/III}$(malate)$_2$(salicylate)	-0.50	10	N/S	1.5	40.2
Ti$^{IV/III}$(α-hydroxyacetate)$_2$(lactate)	-0.50	10	36	1.5	40.2
Ti$^{IV/III}$(lactate)$_2$(α-hydroxyacetate)	-0.50	10	N/S	1.5	40.2
Ti$^{IV/III}$(lactate)$_3$	-0.45	10	N/S	1.75	46.9
Ti$^{IV/III}$(salicylate)$_3$	-0.25	8.6	23	0.5	13.4
Fe$^{III/II}$(salicylate)$_3$	-0.10	9.3	24	0.5	13.4
Fe$^{III/II}$(malate)$_3$	-0.30	9.2	37	1.0	26.8
Fe$^{III/II}$(α-hydroxyacetate)$_3$	-0.50	8.1	38	1.0	26.8
Fe$^{III/II}$(lactate)$_2$(salicylate)$_1$	-0.39	8.7	N/S	1.0	26.8
Fe$^{III/II}$(lactate)$_2$(glycinate)$_1$	+0.30	6.7	N/S	1.0	26.8
Fe$^{III/II}$(lactate)$_2$	+0.45	2.6	40	1.5	40.2
Fe$^{III/II}$(lactate)$_1$	+0.11	3.1	39	1.5	40.2
Fe(CN)$_6^{3-/4-}$	+1.18	11	18	1.5	40.2
Al(citrate)$_2$(catecholate)$^{2-/3-}$	+1.25	11.5	8	0.5	13.4
Fe$^{III/II}$(H$_2$O)$_6$	+0.77	0	N/S	2	53.6
Ce$^{IV/III}$(H$_2$O)$_x$	+1.75	0	N/S	0.5	13.4

* N/S = Not Shown

Table 3A. Calculated OCVs and theoretical energy density (Wh/L) for various other electrolyte couple pairs calculated from data in Table 2.

	$Fe(CN)_6^{3-/4-}$		$Al(cit)_2(cat)^{2-/3-}$	
Couple	OCV (V)	Energy Density (Wh/L)	OCV (V)	Energy Density (Wh/L)
$Mn(CN)_6^{3-/4-}$	1.78	35.8	1.85	12.4
$Fe(catecholate)_3^{2-/3-}$	1.68	33.8	1.75	11.7
$Ti(catecholate)_3^{2-/3-}$	1.63	21.8	1.70	11.4
$Ti(pyrogallate)_3^{2-/3-}$	1.73	34.8	1.80	12.1
$Ti(catecholate)_2(pyrogallate)^{2-/3-}$	1.68	33.8	1.75	11.7
$Ti(catecholate)_2(ascorbate)^{2-/3-}$	1.73	34.8	1.80	12.1
$Ti(catecholate)_2(gluconate)^{2-/3-}$	1.78	35.8	1.85	12.4
$Ti(catecholate)_2(lactate)^{2-/3-}$	1.67	33.6	1.74	11.7
$Ti(catecholate)(pyrogallate)(lactate)^{2-/3-}$	1.73	34.8	1.80	12.1
$Ti(citrate)_3$	1.22	24.5	1.29	8.6

Table 3B. Calculated OCVs and theoretical energy density (Wh/L) for various electrolyte couple pairs calculated from data in Table 2.

	$Fe(CN)_6^{3-/4-}$		$Al(cit)_2(cat)^{2-/3-}$	
Couple	OCV (V)	Energy Density (Wh/L)	OCV (V)	Energy Density (Wh/L)
$Ti^{IV/III}(lactate)_1$	1.60	34.9	1.67	25.2
$Ti^{IV/III}(lactate)_2$	1.46	31.8	1.53	23.1
$Ti^{IV/III}(lactate)_3$	1.57	34.2	1.64	24.7
$Ti^{IV/III}(salicylate)_3$	1.29	17.3	1.36	9.1
$Ti^{IV/III}(lactate)_1(malate)_2$	1.51	30.4	1.58	21.2
$Ti^{IV/III}(malate)_2(salicylate)$	1.60	32.2	1.67	22.4
$Ti^{IV/III}(lactate)_2(glycinate)$	1.61	32.4	1.68	22.5
$Ti^{IV/III}(lactate)_2(salicylate)$	1.60	32.2	1.67	22.4
$Ti^{IV/III}(salicylate)_2(lactate)$	1.61	32.3	1.68	22.5

Table 3B. Calculated OCVs and theoretical energy density (Wh/L) for various electrolyte couple pairs calculated from data in Table 2.

	$Fe(CN)_6^{3-/4-}$		$Al(cit)_2(cat)^{2-/3-}$	
Couple	OCV (V)	Energy Density (Wh/L)	OCV (V)	Energy Density (Wh/L)
$Ti^{IV/III}$(α-hydroxyacetate)$_2$(salicylate)	1.60	32.2	1.67	22.4
$Ti^{IV/III}$(malate)$_2$(sal)	1.62	32.6	1.69	22.6
$Ti^{IV/III}$(α-hydroxyacetate)$_2$(lactate)	1.62	32.6	1.69	22.6
$Ti^{IV/III}$(lactate)$_2$(α-hydroxyacetate)	1.62	32.6	1.69	22.6
Fe^{IIVII}(salicylate)$_3$	1.18	15.8	1.25	8.4
$Fe^{III/II}$(malate)$_3$	1.37	23.0	1.44	14.5
$Fe^{III/II}$(α-hydroxyacetate)$_3$	1.51	25.3	1.58	15.9

Table 4. Calculated OCVs and theoretical energy density (Wh/L) for various electrolyte couple pairs calculated from data in Table 2 in mildly acidic solutions.

	2 M $Fe^{III/II}$, pH 2		0.5 M $Ce^{IV/III}$, pH 2	
Couple	OCV (V)	Energy Density (Wh/L)	OCV (V)	Energy Density (Wh/L)
$Ti^{IV/III}$(lactate)$_1$	1.32	33.2	2.30	34.7
$Ti^{IV/III}$(lactate)$_2$	0.92	23.1	1.90	28.6

[0127] Example 7.1: Using an Al(citrate)$_2$(catecholate)$^{2-/3-}$ couple ($E_{1/2}$ = ~1.25 V vs. RHE) as a demonstrative case, a high potential was observed with well-behaved electrochemical signatures at glassy carbon electrodes, **FIG. 8.** When coupled with the Ti^{4+}(catecholate)$_3^{2-}$ complex described above these pairs may give aqueous battery pairs with OCVs of ~1.7 - 1.9 V. When coupled with the Ti and Fe complexes comprising α- and β-hydroxy acid ligands, these pairs may give aqueous battery pairs with OCVs of ~1.3 - 1.6 V.

[0128] Examples 7.2 through 7.5: FIG. 9 (for titanium tris-pyrogallate) and **FIG. 10** (for iron tris-catecholate) illustrate the CV curves resulting from the use of catecholate-like ligands over a range of low and negative operating potentials, under conditions described above, showing the good electrochemical reversibility of these systems under these conditions. **FIG. 23** (for titanium tris-salicylate) and **FIG. 24** (for iron tris-salicylate) illustrate the CV curves resulting from the use of β-hydroxy acid ligands over a range of low and negative operating potentials, under conditions described above, showing the good electrochemical reversibility of these systems under these conditions.

[0129] Examples 7.6 through 7.12: FIG. 11 ($NaK[Ti(catecholate)_2(pyrogallate)]$), **FIG. 12** ($NaK[Ti(catecholate)_2(lactate)]$), **FIG. 13** ($NaK[Ti(catecholate)_2(gluconate)]$), **FIG. 14** ($NaK[Ti(catecholate)_2(ascorbate)]$), **FIG. 15** ($Na_2[Ti(catecholate)_3]$), **FIG. 16** (NaK[Ti(catecholate)(pyrogallate)(lactate)]), and **FIG. 17** ($Na_4[Ti(citrate)_3]$) illustrate the CV curves resulting from the use of several mixed ligand or tris-citrate systems over a range of low and negative operating potentials, under conditions described above, showing the good electrochemical reversibility of these systems under these conditions.

[0130] Examples 7.13 through 7.29: FIG. 25 through **FIG. 41** illustrate the CV curves resulting from the use of several mixed ligand or tris-α-hydroxy acid systems over a range of low and negative operating potentials, under conditions described above, showing the good electrochemical reversibility of these systems under these conditions.

Example 7.30. Ferrocyanide Samples

[0131] Solid $Na_4Fe(CN)_6 \cdot 10H_2O$ (33.89 g, 0.070 mol) and $K_4Fe(CN)_6 \cdot 3H_2O$ (29.57 g, 0.070 mol) were stirred in 80 mL deionized water. To dissolve the solids, sufficient water was then slowly added to provide a sample containing ca. 1.5 M of $Fe(CN)_6{}^{4-}$. This solubility was unexpected given that the solubilities of $Na_4Fe(CN)_6 \cdot 10H_2O$ and $K_4Fe(CN)_6 \cdot 3H_2O$ are each known in the art to be less than 0.7 M at the same ambient temperatures.

[0132] The 1.5 M $[Fe(CN)_6]^{4-}$ solution was interrogated by cyclic voltammetry, using a glassy carbon working electrode. **FIG. 18.** In these experiments, sufficient solid sodium potassium hydrogen phosphate, NaOH, and KOH was added to the 1.4 M $[Fe(CN)_6]^{4-}$ solution to yield a working solution having a pH of 11.1 (ratio $N^+/K^+ \sim 1$) and containing 1.4 M $[Fe(CN)_6]^{4-}$and 0.1 M phosphate.

[0133] Examples 7.31 and 7.32: FIG. 19 ($K_3[Cr(CN)_6]$) and **FIG. 20** ($K_3\ [Mn(CN)_6]$) illustrate the CV curves resulting from the use of two other hexacyanide systems over a range of low and negative operating potentials, under conditions described above, showing the good electrochemical reversibility of these systems under these conditions.

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Patentkrav

1. Flow-batteri, der omfatter:

en første vandig elektrolyt, der omfatter en første redoxaktiv metal-ligand-koordinationsforbindelse;

en anden vandig elektrolyt, der omfatter en anden redoxaktiv metal-ligand-koordinationsforbindelse;

en første elektrode i kontakt med den første vandige elektrolyt;

en anden elektrode i kontakt med den anden vandige elektrolyt og

en separator, der er anbragt mellem den første vandige elektrolyt og den anden vandige elektrolyt;

hvor den første redoxaktive metal-ligand-koordinationsforbindelse har en formel omfattende $M(L1)_x(L2)_y(L3)_z{}^m$, hvor M er valgt fra gruppen bestående af Al, Ce, Co, Cr, Fe, Mn, Mo, Sn, Ti, W eller Zr,

hvor x, y og z er valgt fra gruppen bestående af (a) x = 3, y = z = 0; (b) x = 2, y = 1, z = 0; og (c) x = 1, y = 1, z = 1;

m uafhængigt er -5, -4, -3, -2, -1, 0; og

L1, L2 og L3 hver især uafhængigt er ascorbat, catecholat, citrat, glycolat, gluconat, glycinat, α-hydroxyalkanoat, β-hydroxyalkanoat, γ-hydroxyalkanoat, malat, maleat, phthalat, polyol, sarcosinat, salicylat, lactat, :

hvor den anden redoxaktive metal-ligand-koordinationsforbindelse omfatter en chrom-, jern- eller mangancyanidforbindelse.

2. Flow-batteri ifølge krav 1, hvor:

(a) enhver af den første og anden redoxaktive metal-ligand-koordinationsforbindelse uafhængigt udviser i det væsentlige reversibel elektrokemisk kinetik; eller

(b) den første, anden eller begge redoxaktive metal-ligand-koordinationsforbindelser er til stede i henholdsvis den første eller anden vandige elektrolyt i en koncentration på mindst 0,75 M; eller

(c) separatoren har en tykkelse på 100 mikrometer (mikron) eller mindre; eller

(d) flow-batteriet omfatter enhver kombination af (a) til (c).

3. Flow-batteri ifølge et hvilket som helst af kravene 1 til 2, hvor den første redox-aktive metal-ligand-koordinationsforbindelse omfatter Ce^{4+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Mg^{2+}, Mn^{3+}, Mo^{6+}, Sn^{4+}, Ti^{4+}, W^{6+}, Zn^{2+} eller Zr^{4+}.

4. Flow-batteri ifølge et hvilket som helst af kravene 1 til 3, hvor den anden redoxaktive metal-ligand-koordinationsforbindelse omfatter en chrom-, jern-, mangan- eller rutheniumcyanidforbindelse, fortrinsvis hvor den anden redoxaktive metal-ligand-koordinationsforbindelse omfatter en chrom-, jern- eller manganhexacyanidforbindelse, mere fortrinsvis hvor den anden redoxaktive metal-ligand-koordinationsforbindelse omfatter en jernhexacyanidforbindelse.

5. Flowbatteri ifølge et hvilket som helst af kravene 1 til 4, hvor den første redoxaktive metal-ligand-koordinationsforbindelse omfatter Cr, Ti eller Fe.

6. Flow-batteri ifølge et hvilket som helst af kravene 1 til 5, hvor flow-batteriet:
(a) udviser en returspændingseffektivitet på mindst 70%, målt ved 200 mA/cm^2; eller
(b) bevarer mindst 70% returspændingseffektivitet, når den udsættes for 10 opladnings-/afladningscyklusser; eller
(c) både (a) og (b).

7. System, der omfatter et flowbatteri ifølge et hvilket som helst af kravene 1 til 6, og yderligere omfatter:
(a) et første kammer, der indeholder den første vandige elektrolyt, og et andet kammer, der indeholder den anden vandige elektrolyt;
(b) mindst en elektrolytcirkulationssløjfe i fluidforbindelse i hvert kammer, hvor den mindst ene elektrolytcirkulationssløjfe omfatter lagertanke og rør til at indeholde og transportere de vandige elektrolytter;
(c) kontrolhardware og -software; og

(d) en valgfri strømkonditioneringsenhed.

8. System ifølge krav 7, hvor systemet er:

(a) konfigureret til at tilvejebringe vedvarende energiintegration, spidsbelastningsforskydning, netforstærkning, basislastkraftproduktion/-forbrug, energiarbitrage, energitransmission, understøttelse til svagt net, frekvensregulering eller en kombination heraf ved en forbindelse med et elektrisk net, eller

(b) konfigureret til at levere stabil strøm til fjerntliggende steder, forskudte indsatsbaser, telekommunikation uden tilslutning til det overordnede forsyningsnet eller fjernsensorer.

9. Fremgangsmåde til drift af et flow-batteri ifølge et hvilket som helst af kravene 1 til 6, hvilken fremgangsmåde omfatter opladning af flow-batteriet ved input af elektrisk energi eller afladning af flow-batteriet ved fjernelse af elektrisk energi.

10. Fremgangsmåde til drift af et flow-batteri ifølge et hvilket som helst af kravene 1 til 6 med en tilhørende strøm af elektroner, hvilken fremgangsmåde omfatter:

(a) påføring af en potentialforskel over den første og anden elektrode for at:

(i) reducere den første redoxaktive metal-ligand-koordinationsforbindelse; eller

(ii) oxidere den anden redoxaktive metal-ligand-koordinationsforbindelse; eller

(iii) både (i) og (ii); eller

(b) påføring af en potentialforskel over den første og anden elektrode for at:

(iv) oxidere den første redoxaktive metal-ligand-koordinationsforbindelse; eller

(v) reducere den anden redoxaktive metal-ligand-koordinationsforbindelse; eller

(vi) både (iv) og (v).

DRAWINGS

FIG. 1

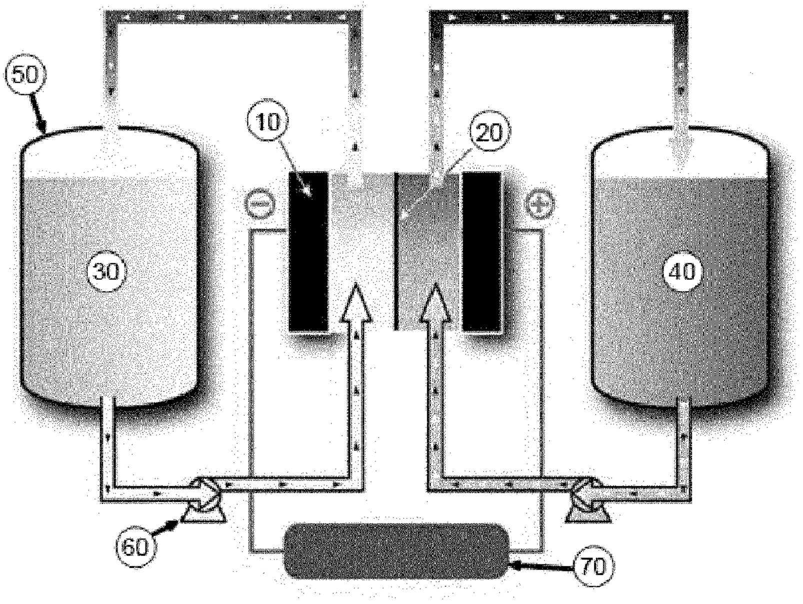


FIG. 2

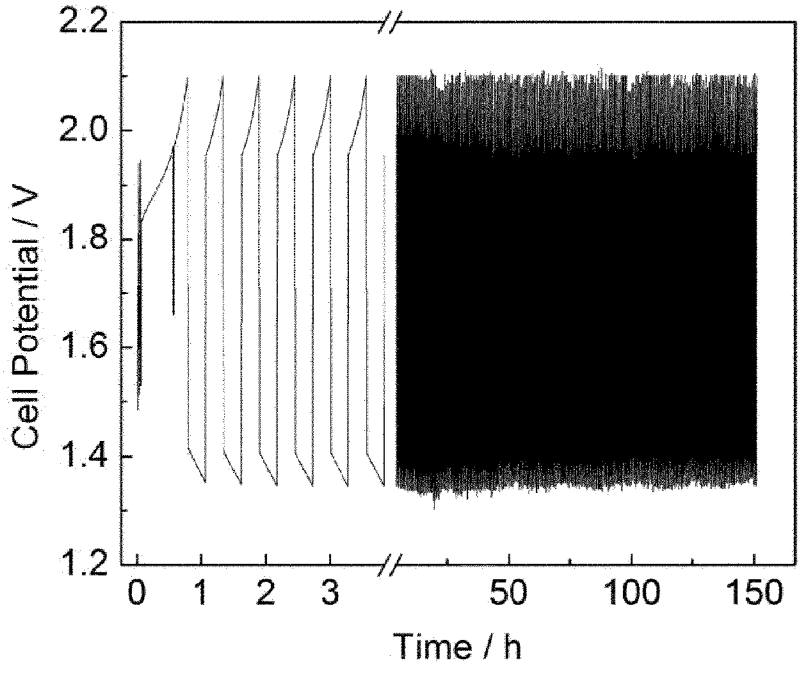


FIG. 3

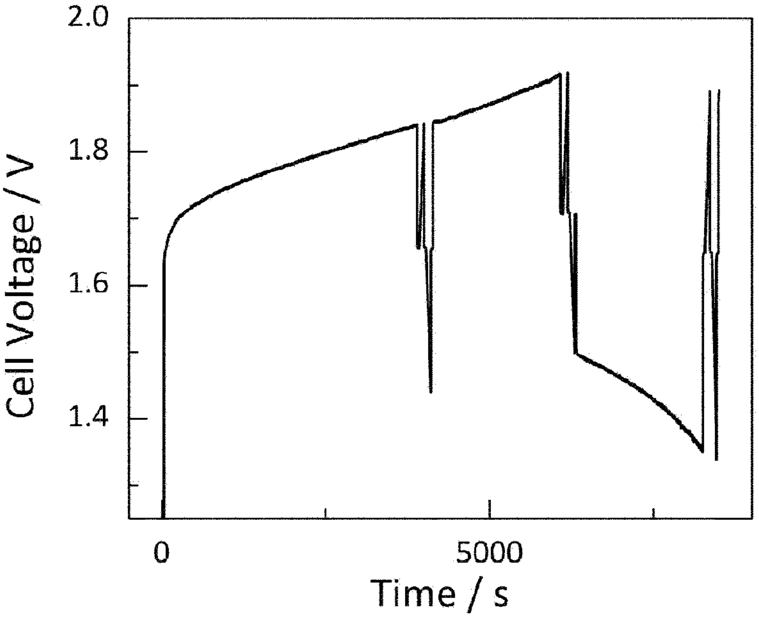

2.0
1.8
1.6
1.4
Cell Voltage / V
0
5000
Time / s

FIG. 4

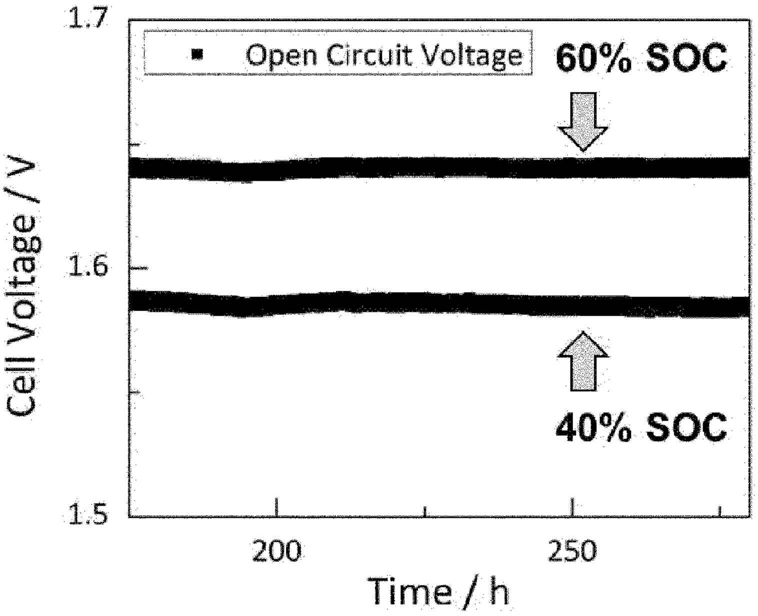

1.7
1.6
1.5
Cell Voltage / V
■ Open Circuit Voltage
60% SOC
40% SOC
200
250
Time / h

FIG. 5

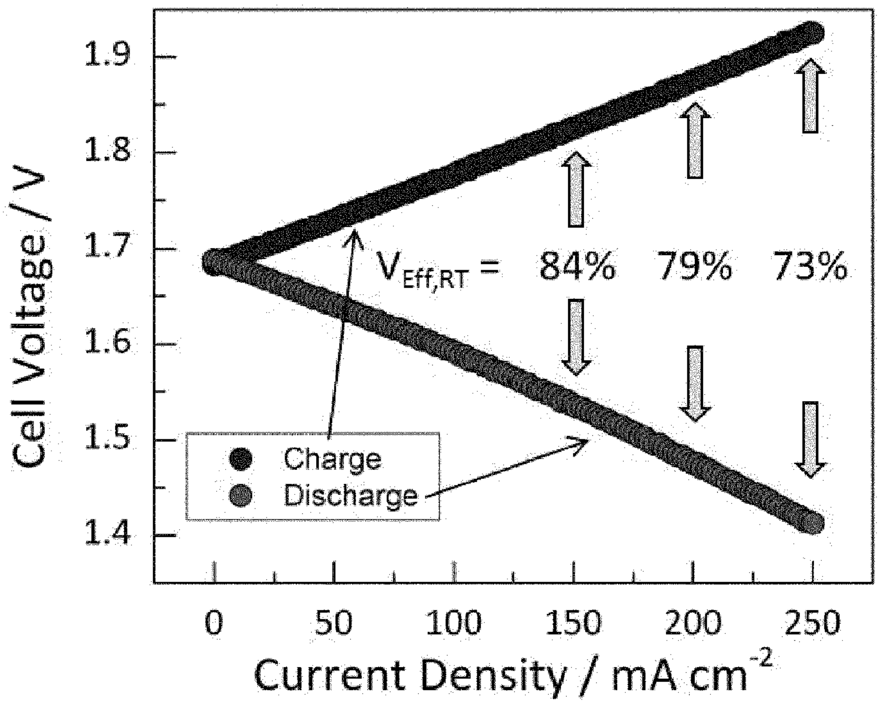

Cell Voltage / V
1.9
1.8
1.7
1.6
1.5
1.4
0
50
100
150
200
250
Current Density / mA cm^{-2}
$V_{Eff,RT}$ = 84% 79% 73%
● Charge
● Discharge

FIG. 6

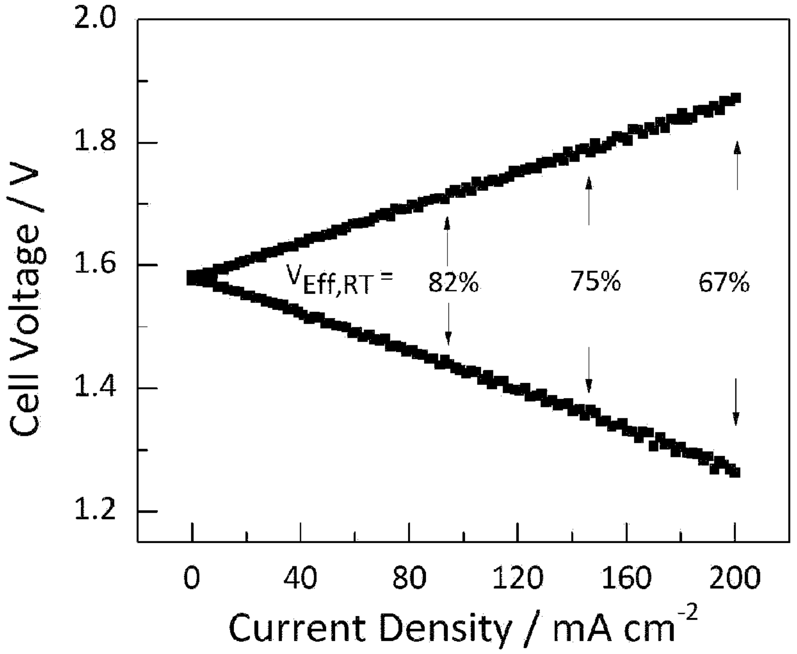

Cell Voltage / V
2.0
1.8
1.6
1.4
1.2
0
40
80
120
160
200
Current Density / mA cm^{-2}
$V_{Eff,RT}$ = 82% 75% 67%

FIG. 7

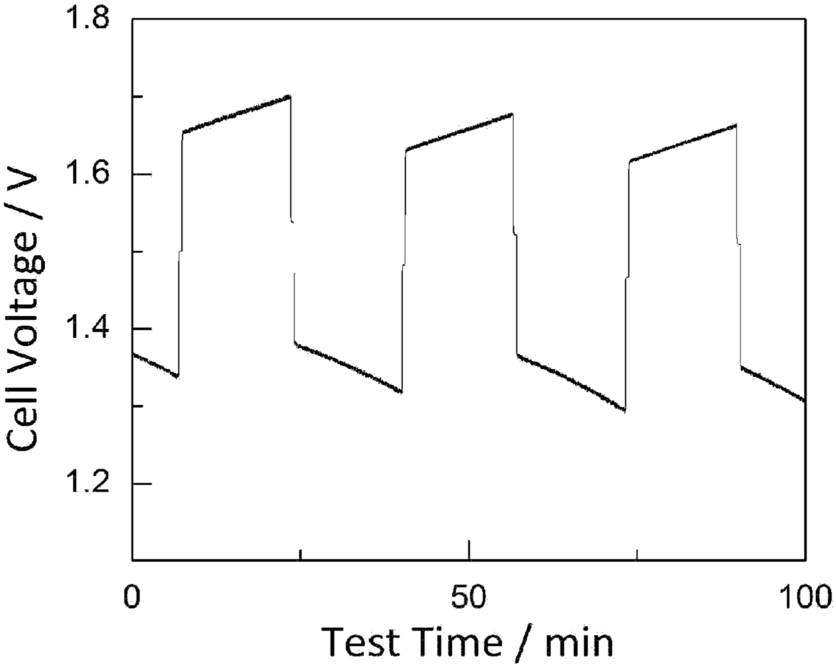

Cell Voltage / V
1.8
1.6
1.4
1.2
0
50
100
Test Time / min

FIG. 8

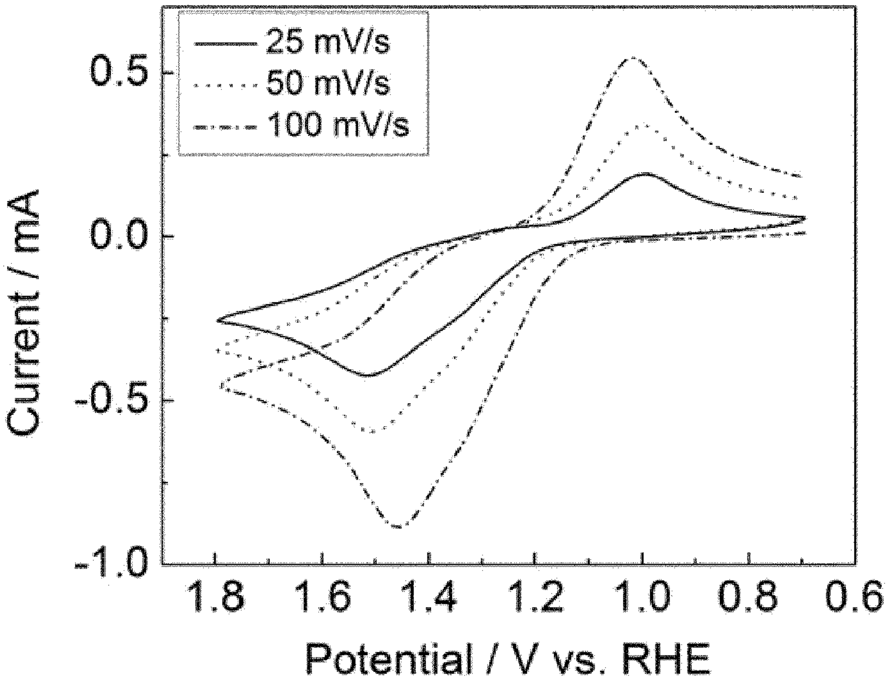

25 mV/s
50 mV/s
100 mV/s
Current / mA
0.5
0.0
-0.5
-1.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
Potential / V vs. RHE

FIG. 9

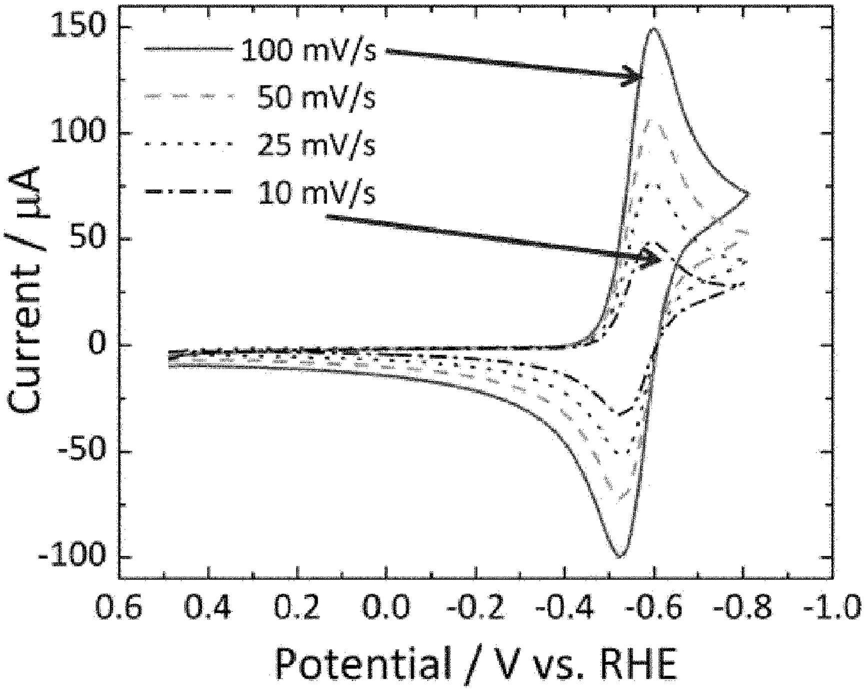

100 mV/s
50 mV/s
25 mV/s
10 mV/s
150
100
50
0
-50
-100
Current / μA
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Potential / V vs. RHE

FIG. 10

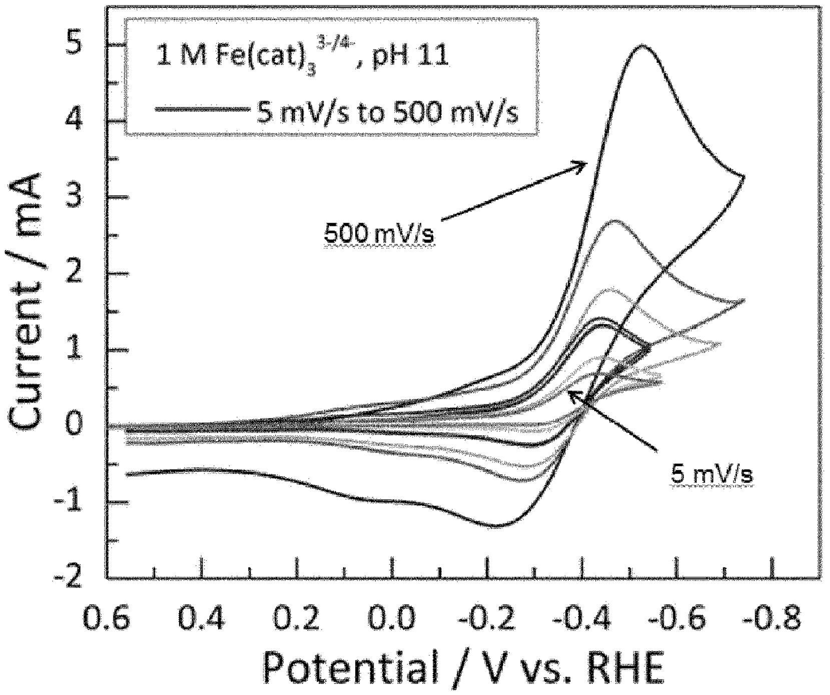

1 M Fe(cat)3 3-/4-, pH 11
5 mV/s to 500 mV/s
500 mV/s
5 mV/s
5
4
3
2
1
0
-1
-2
Current / mA
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Potential / V vs. RHE

FIG. 11

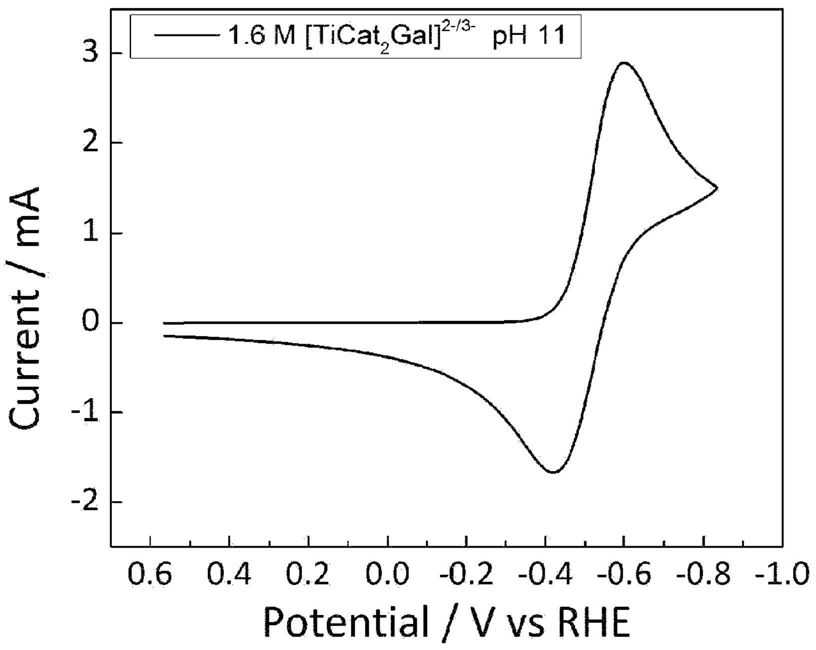

1.6 M [TiCat$_2$Gal]$^{2-/3-}$ pH 11
Current / mA
3
2
1
0
-1
-2
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Potential / V vs RHE

FIG. 12

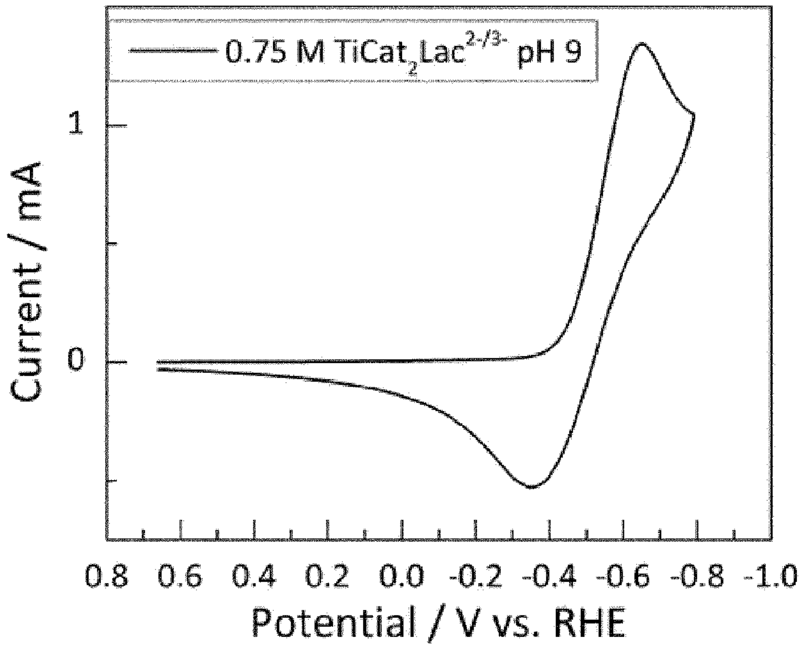

0.75 M TiCat$_2$Lac$^{2-/3-}$ pH 9
Current / mA
1
0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Potential / V vs. RHE

FIG. 13

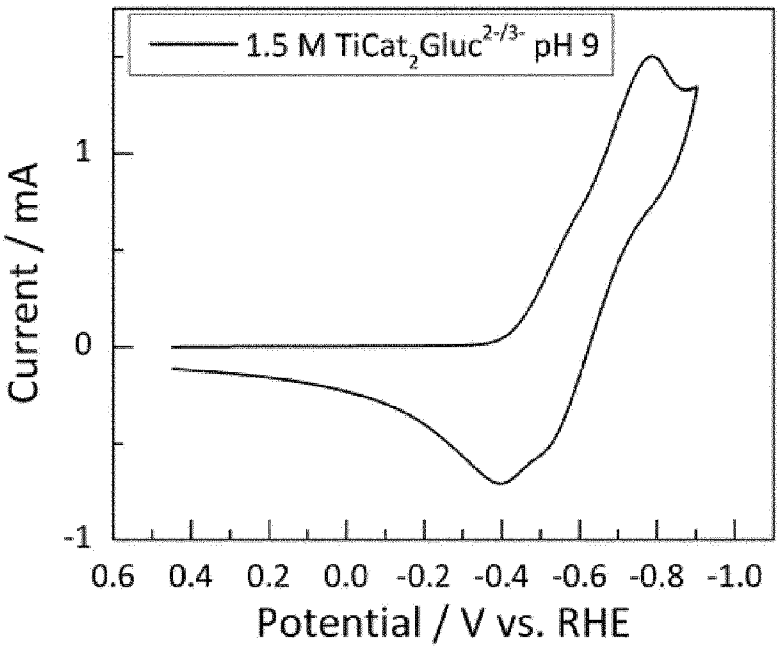

1.5 M TiCat$_2$Gluc$^{2-/3-}$ pH 9
Current / mA
1
0
-1
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Potential / V vs. RHE

FIG. 14

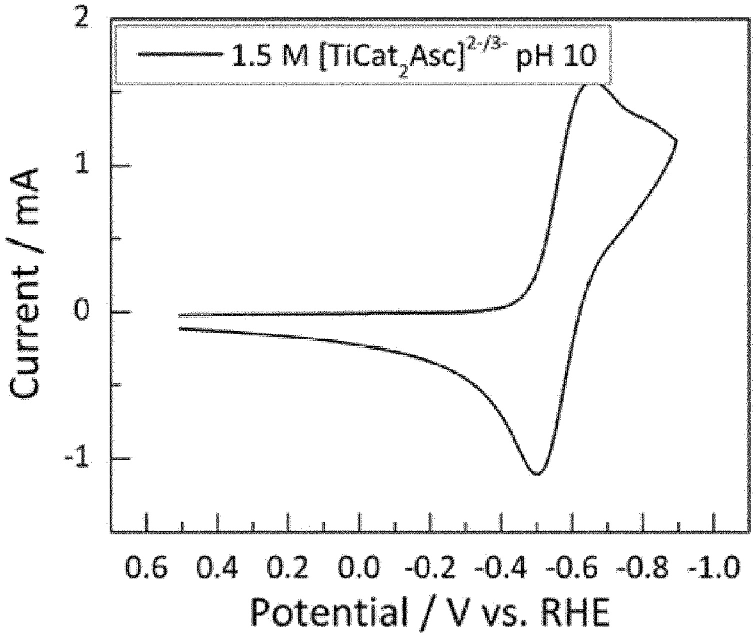

1.5 M [TiCat$_2$Asc]$^{2-/3-}$ pH 10
Current / mA
2
1
0
-1
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Potential / V vs. RHE

FIG. 15

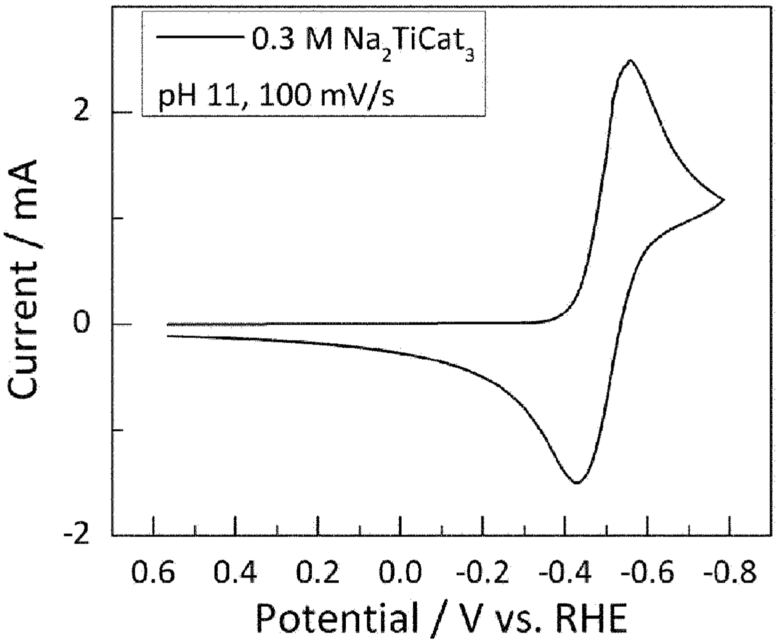

0.3 M Na_2TiCat_3
pH 11, 100 mV/s
Current / mA
2
0
-2
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Potential / V vs. RHE

FIG. 16

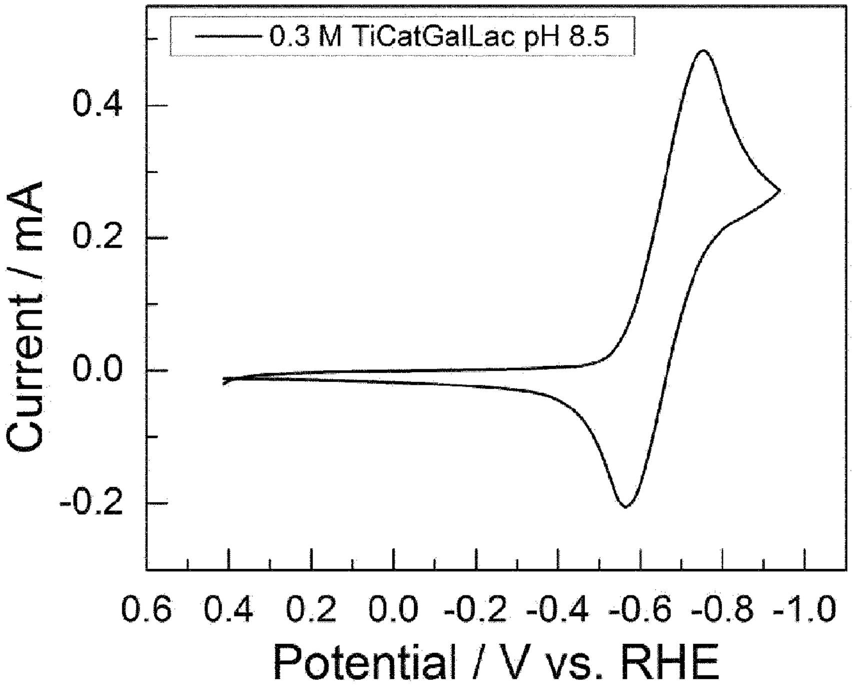

0.3 M TiCatGalLac pH 8.5
Current / mA
0.4
0.2
0.0
-0.2
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
Potential / V vs. RHE

FIG. 17

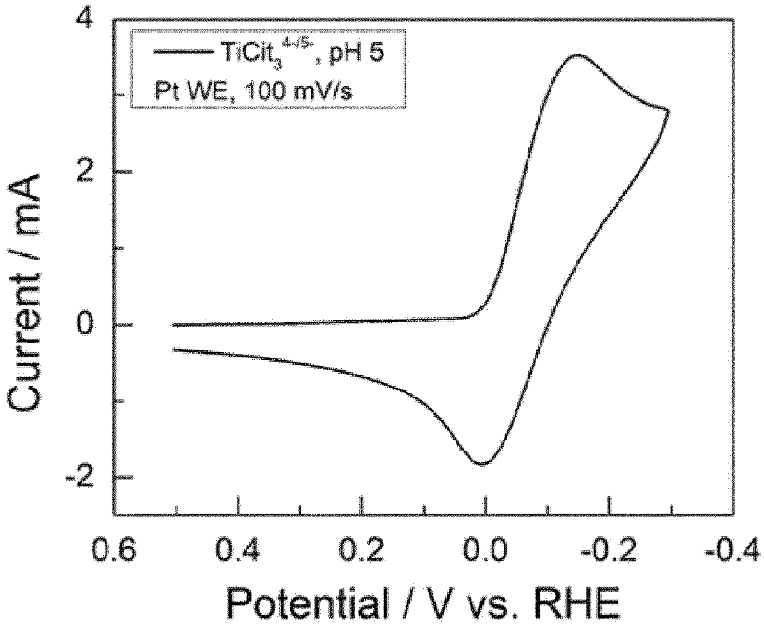

TiCit$_3^{4-/5-}$, pH 5
Pt WE, 100 mV/s
Current / mA
4
2
0
-2
0.6
0.4
0.2
0.0
-0.2
-0.4
Potential / V vs. RHE

FIG. 18

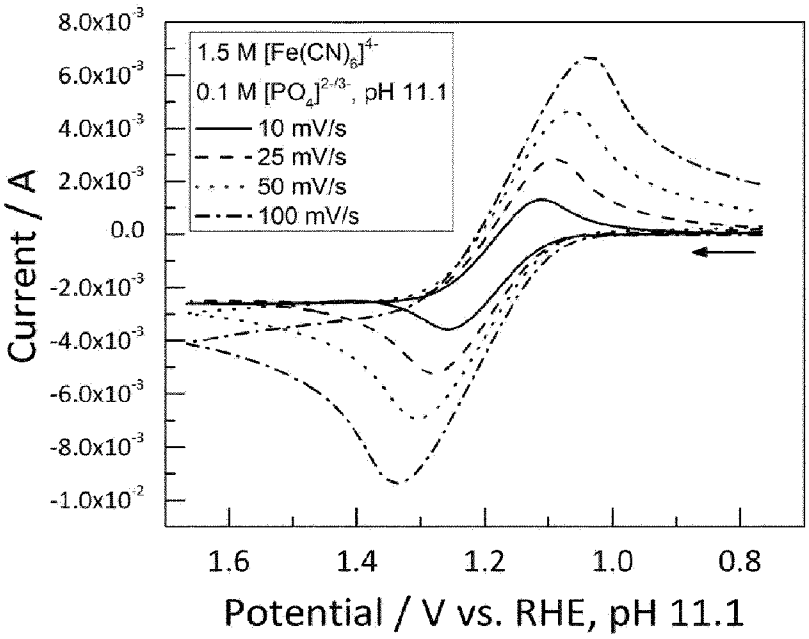

1.5 M [Fe(CN)$_6$]$^{4-}$
0.1 M [PO$_4$]$^{2-/3-}$, pH 11.1
10 mV/s
25 mV/s
50 mV/s
100 mV/s
Current / A
8.0x10^{-3}
6.0x10^{-3}
4.0x10^{-3}
2.0x10^{-3}
0.0
-2.0x10^{-3}
-4.0x10^{-3}
-6.0x10^{-3}
-8.0x10^{-3}
-1.0x10^{-2}
1.6
1.4
1.2
1.0
0.8
Potential / V vs. RHE, pH 11.1

FIG. 19

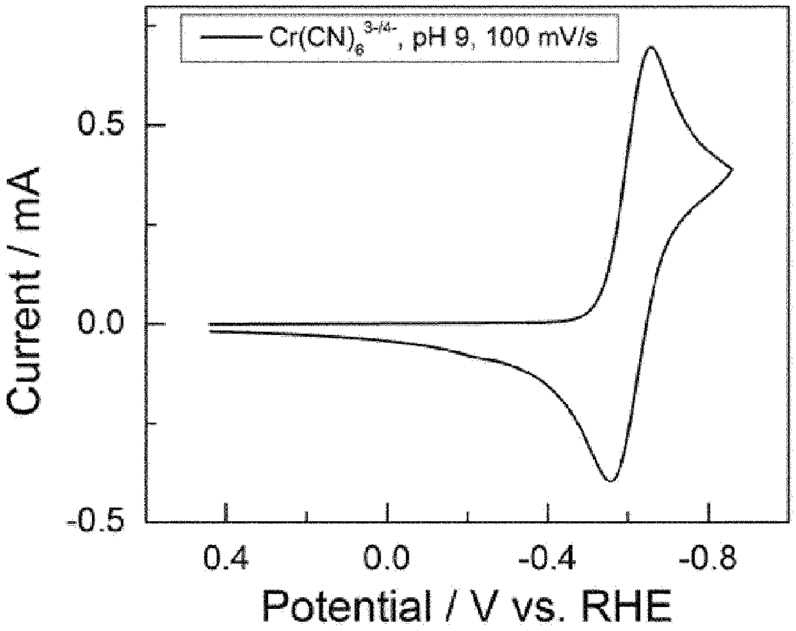

Cr(CN)$_6^{3-/4-}$, pH 9, 100 mV/s
Current / mA
0.5
0.0
-0.5
0.4
0.0
-0.4
-0.8
Potential / V vs. RHE

FIG. 20

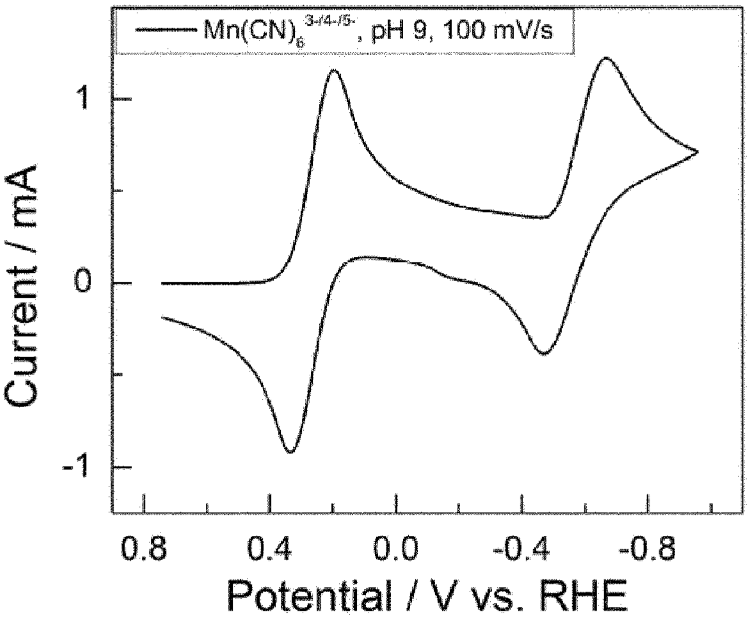

Mn(CN)$_6^{3-/4-/5-}$, pH 9, 100 mV/s
Current / mA
1
0
-1
0.8
0.4
0.0
-0.4
-0.8
Potential / V vs. RHE

FIG. 21

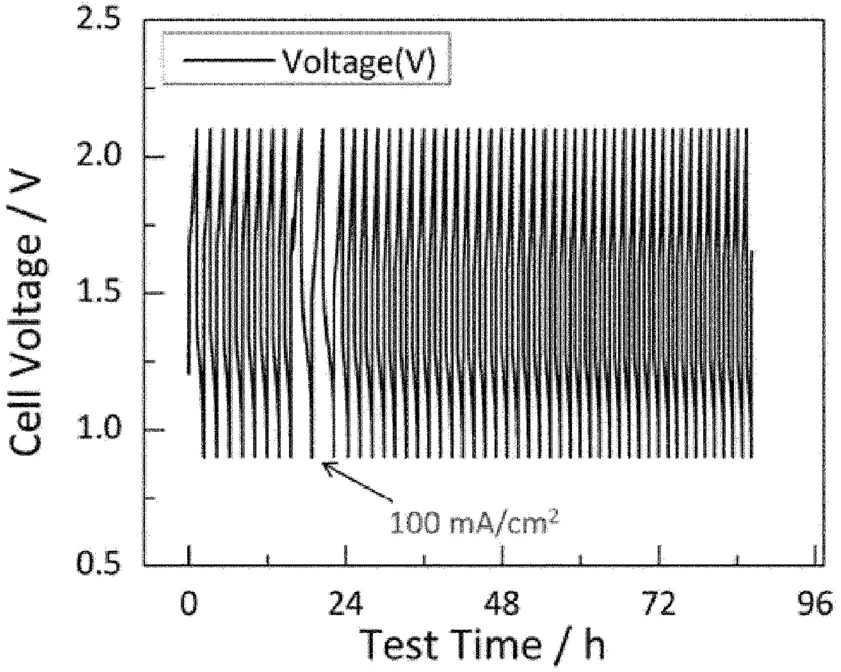

Voltage(V)
Cell Voltage / V
2.5
2.0
1.5
1.0
0.5
100 mA/cm²
0
24
48
72
96
Test Time / h

FIG. 22

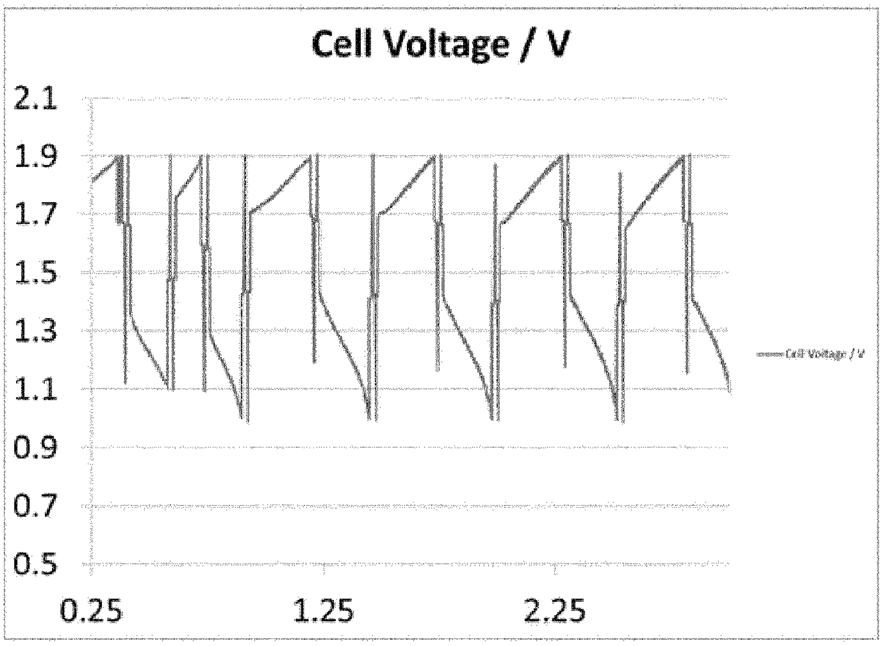

Cell Voltage / V
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
0.25
1.25
2.25
Cell Voltage / V

FIG. 23

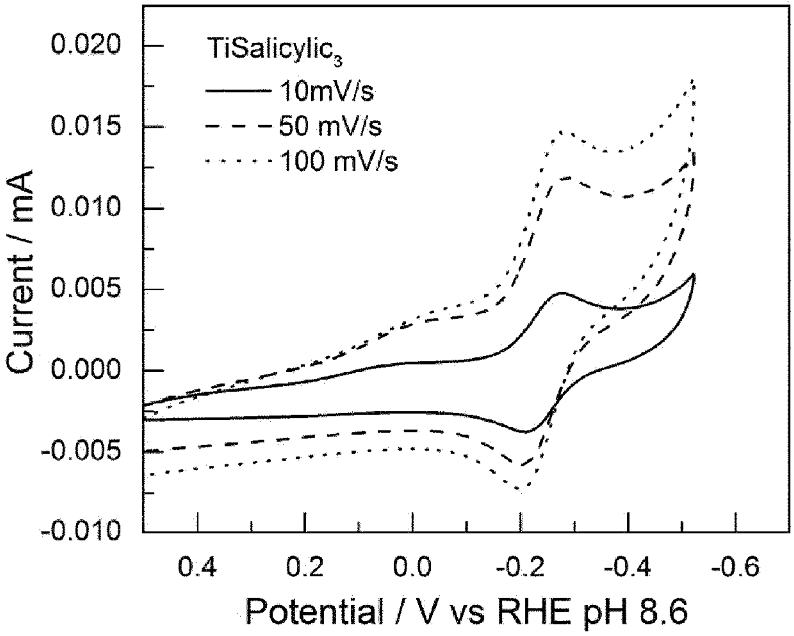

TiSalicylic$_3$
10mV/s
50 mV/s
100 mV/s
Current / mA
0.020
0.015
0.010
0.005
0.000
-0.005
-0.010
0.4
0.2
0.0
-0.2
-0.4
-0.6
Potential / V vs RHE pH 8.6

FIG. 24

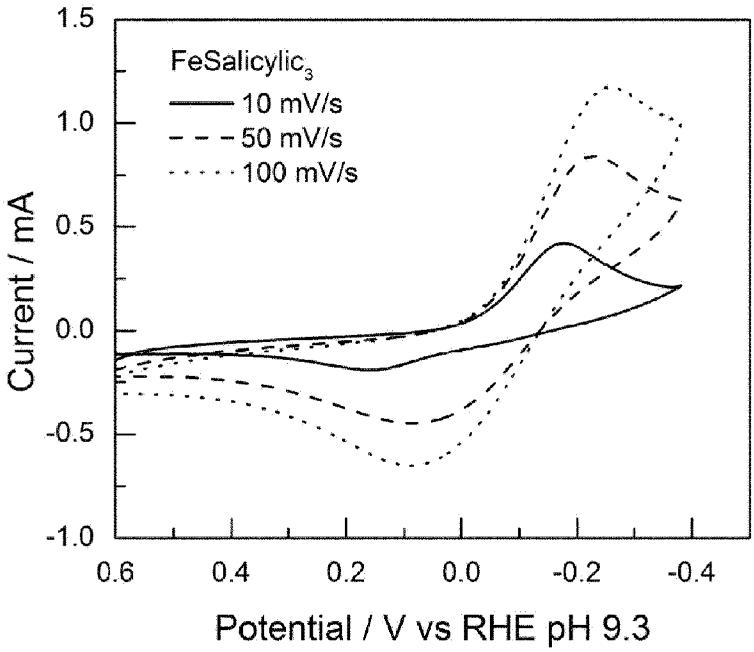

FeSalicylic$_3$
10 mV/s
50 mV/s
100 mV/s
Current / mA
1.5
1.0
0.5
0.0
-0.5
-1.0
0.6
0.4
0.2
0.0
-0.2
-0.4
Potential / V vs RHE pH 9.3

FIG. 25

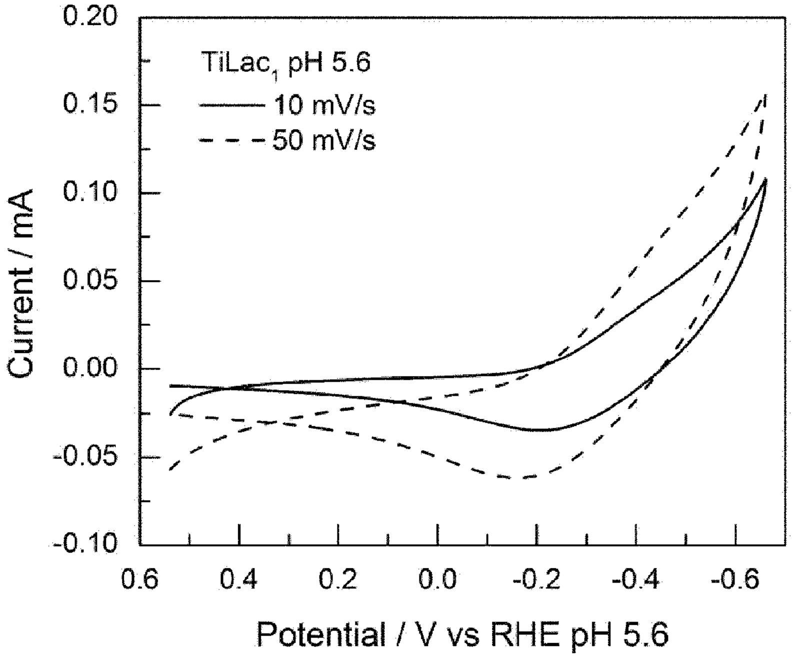

TiLac$_1$ pH 5.6
10 mV/s
50 mV/s
Current / mA
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
Potential / V vs RHE pH 5.6

FIG. 26

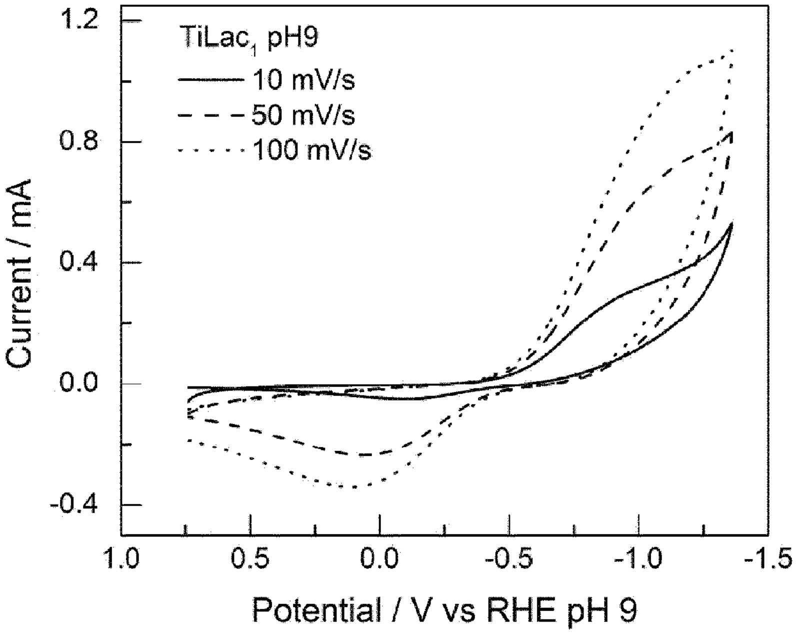

TiLac$_1$ pH9
10 mV/s
50 mV/s
100 mV/s
Current / mA
1.2
0.8
0.4
0.0
-0.4
1.0
0.5
0.0
-0.5
-1.0
-1.5
Potential / V vs RHE pH 9

FIG. 27

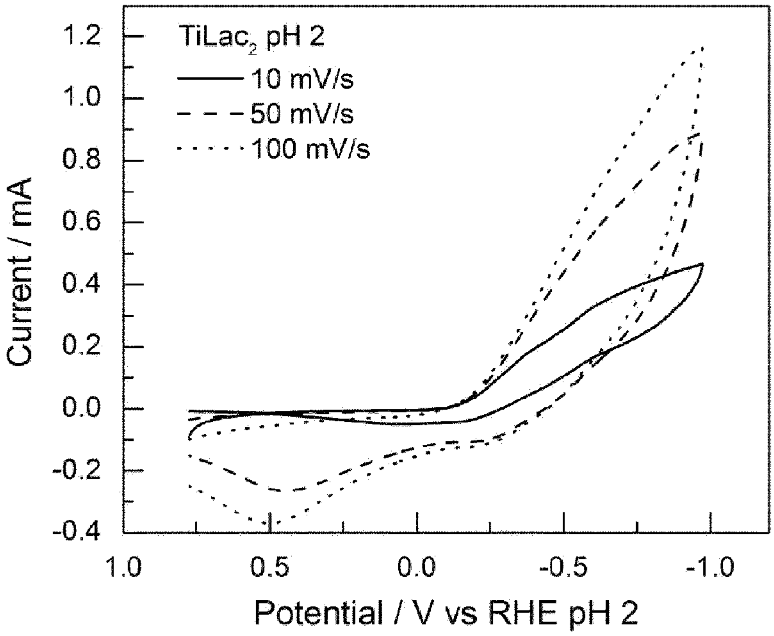

TiLac$_2$ pH 2
10 mV/s
50 mV/s
100 mV/s
Current / mA
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
1.0
0.5
0.0
-0.5
-1.0
Potential / V vs RHE pH 2

FIG. 28

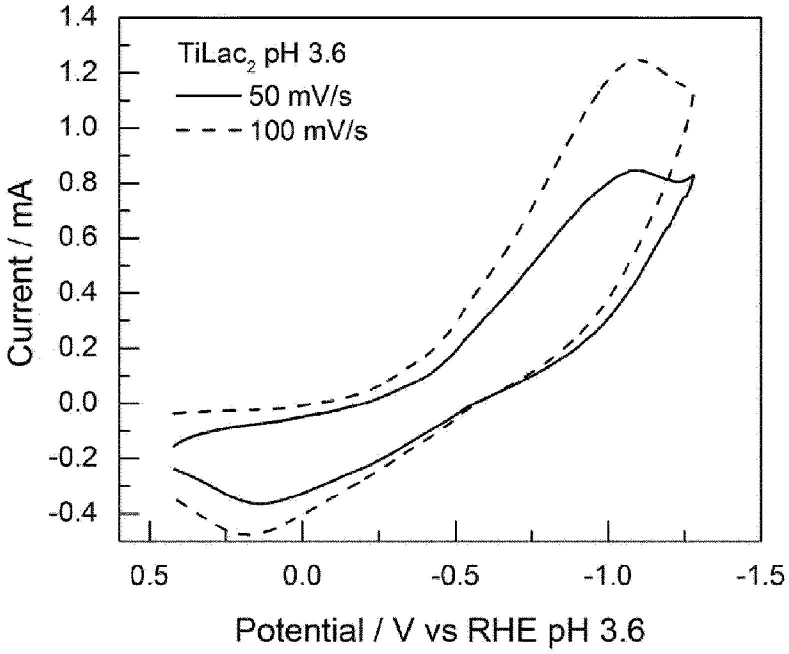

TiLac$_2$ pH 3.6
50 mV/s
100 mV/s
Current / mA
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
0.5
0.0
-0.5
-1.0
-1.5
Potential / V vs RHE pH 3.6

FIG. 29

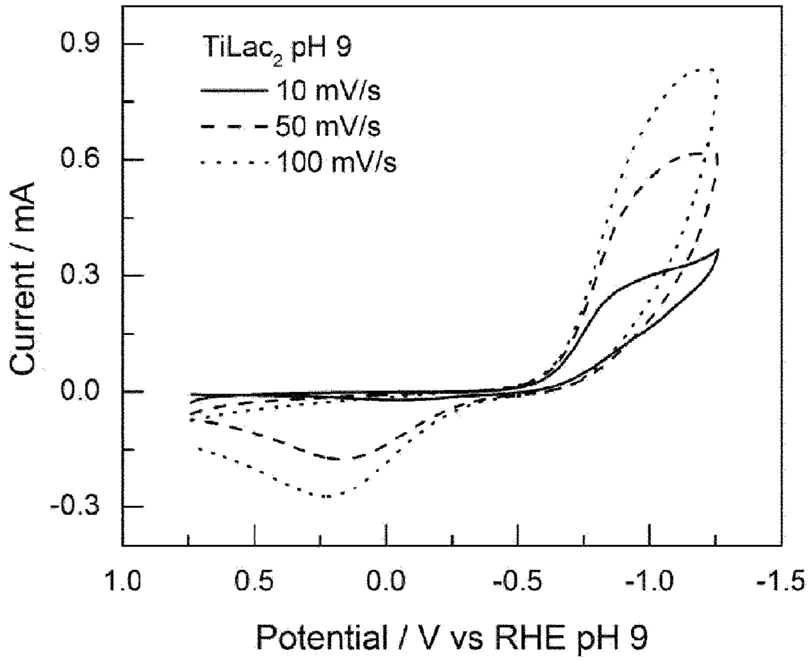

TiLac$_2$ pH 9
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.9
0.6
0.3
0.0
-0.3
1.0
0.5
0.0
-0.5
-1.0
-1.5
Potential / V vs RHE pH 9

FIG. 30

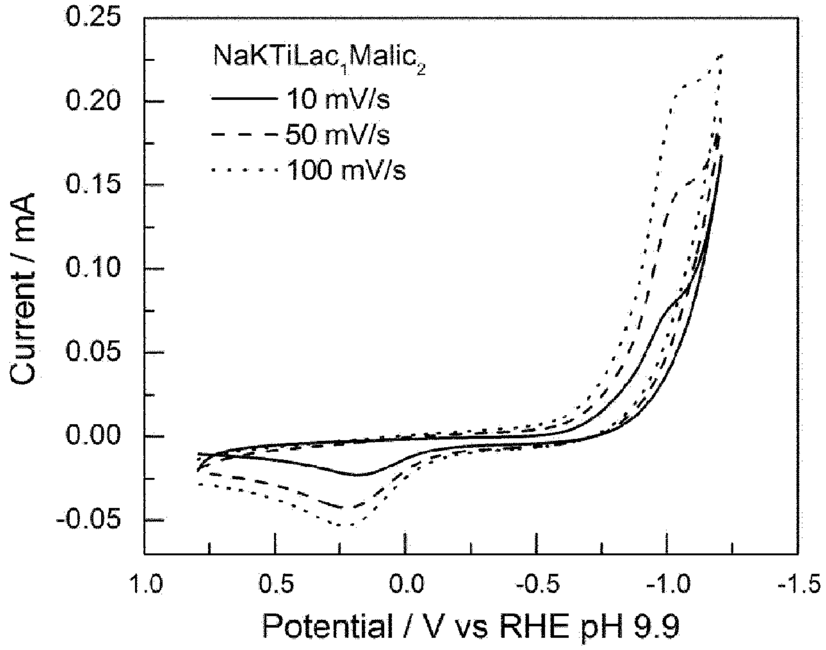

NaKTiLac$_1$Malic$_2$
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
1.0
0.5
0.0
-0.5
-1.0
-1.5
Potential / V vs RHE pH 9.9

FIG. 31

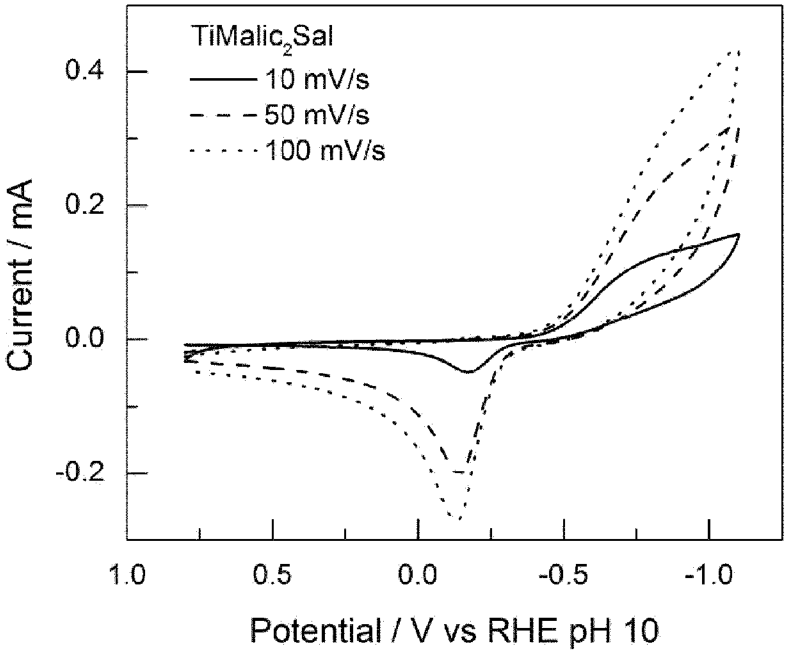

TiMalic$_2$Sal
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.4
0.2
0.0
-0.2
1.0
0.5
0.0
-0.5
-1.0
Potential / V vs RHE pH 10

FIG. 32

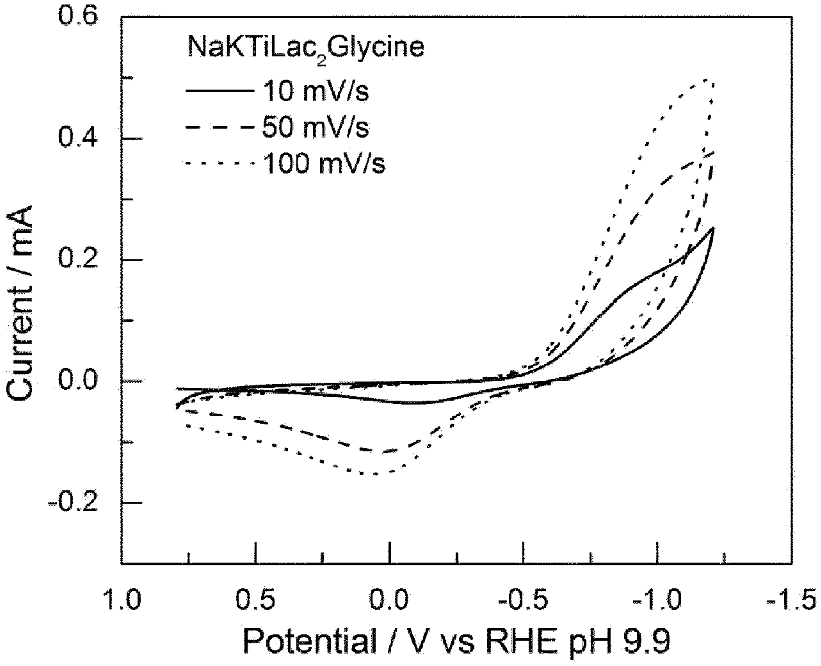

NaKTiLac$_2$Glycine
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.6
0.4
0.2
0.0
-0.2
1.0
0.5
0.0
-0.5
-1.0
-1.5
Potential / V vs RHE pH 9.9

FIG. 33

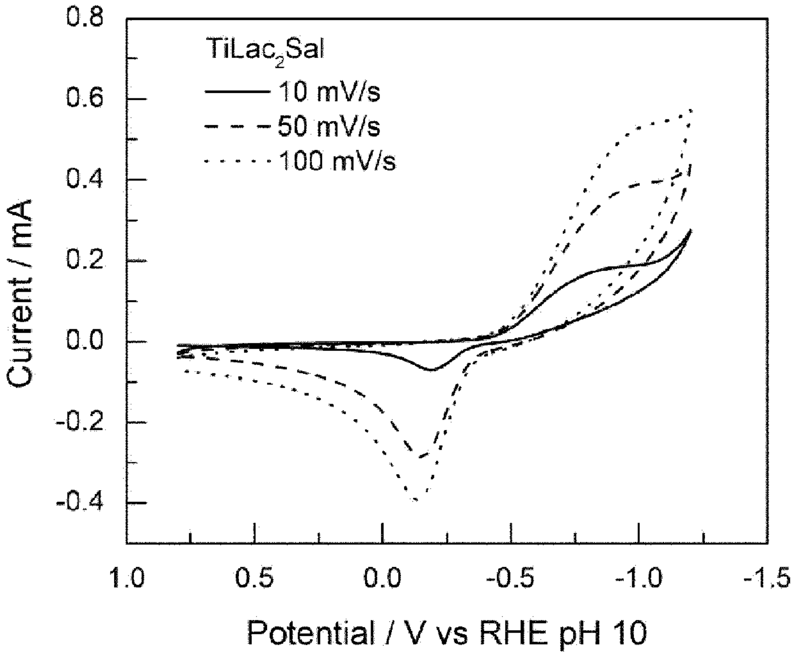

TiLac$_2$Sal
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
1.0
0.5
0.0
-0.5
-1.0
-1.5
Potential / V vs RHE pH 10

FIG. 34

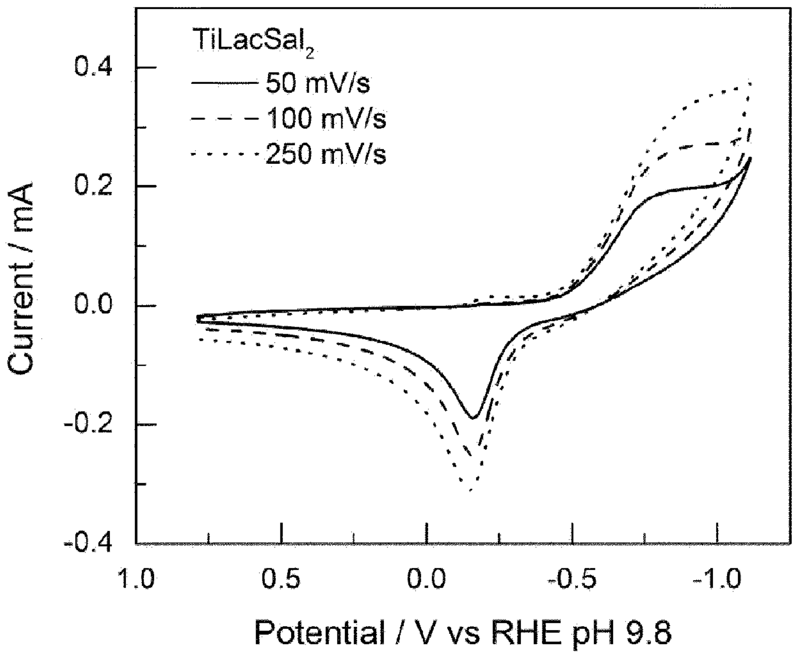

TiLacSal$_2$
50 mV/s
100 mV/s
250 mV/s
Current / mA
0.4
0.2
0.0
-0.2
-0.4
1.0
0.5
0.0
-0.5
-1.0
Potential / V vs RHE pH 9.8

FIG. 35

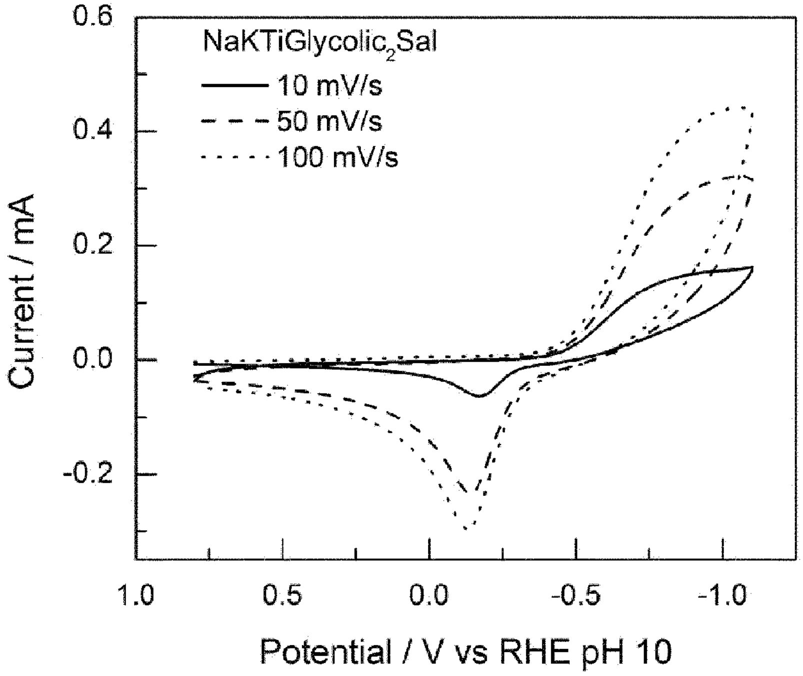

NaKTiGlycolic$_2$Sal
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.6
0.4
0.2
0.0
-0.2
1.0
0.5
0.0
-0.5
-1.0
Potential / V vs RHE pH 10

FIG. 36

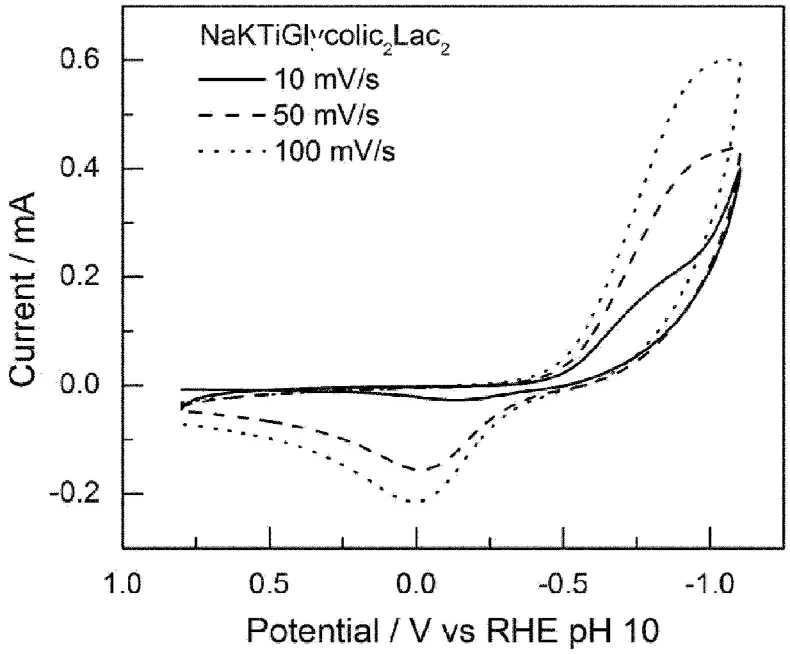

NaKTiGlycolic$_2$Lac$_2$
10 mV/s
50 mV/s
100 mV/s
Current / mA
0.6
0.4
0.2
0.0
-0.2
1.0
0.5
0.0
-0.5
-1.0
Potential / V vs RHE pH 10

FIG. 37

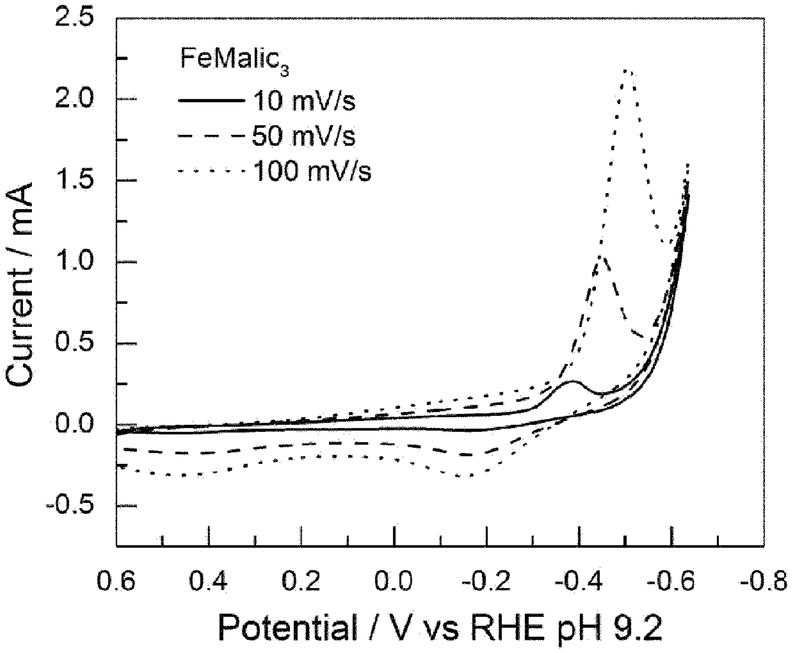

FeMalic$_3$
10 mV/s
50 mV/s
100 mV/s
Current / mA
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Potential / V vs RHE pH 9.2

FIG. 38

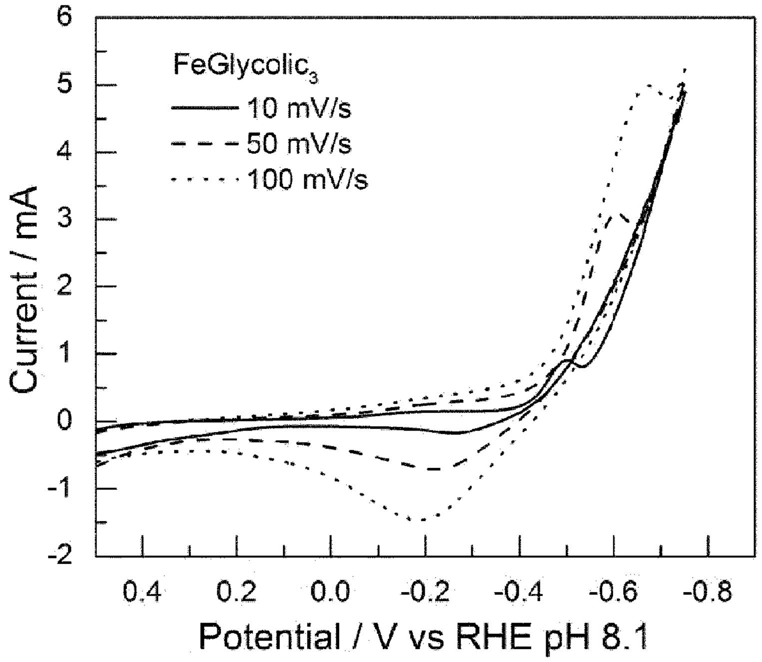

FeGlycolic$_3$
10 mV/s
50 mV/s
100 mV/s
Current / mA
6
5
4
3
2
1
0
-1
-2
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Potential / V vs RHE pH 8.1

FIG. 39

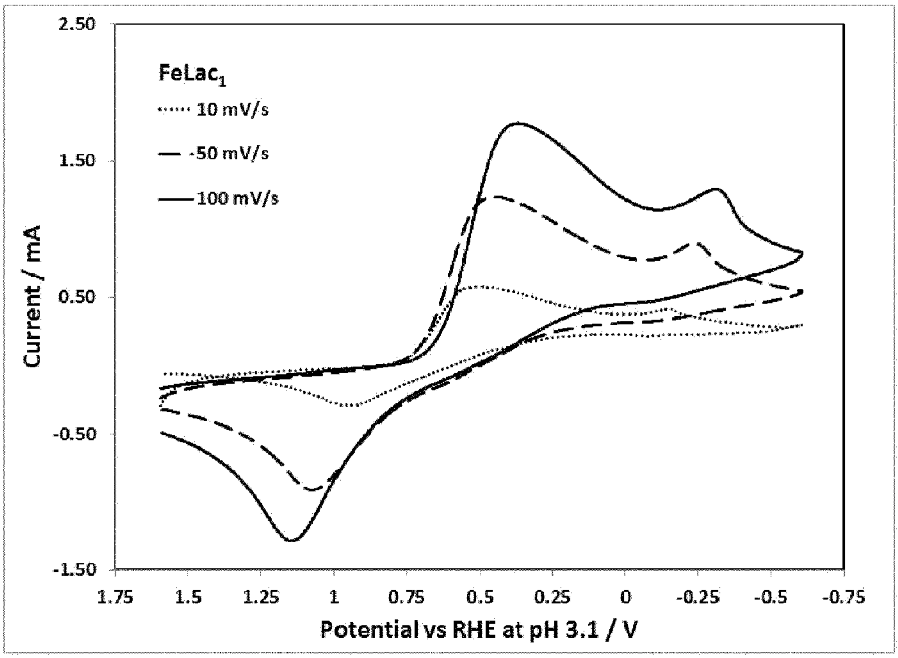

FeLac$_1$
10 mV/s
50 mV/s
100 mV/s
Current / mA
2.50
1.50
0.50
-0.50
-1.50
1.75
1.5
1.25
1
0.75
0.5
0.25
0
-0.25
-0.5
-0.75
Potential vs RHE at pH 3.1 / V

FIG. 40

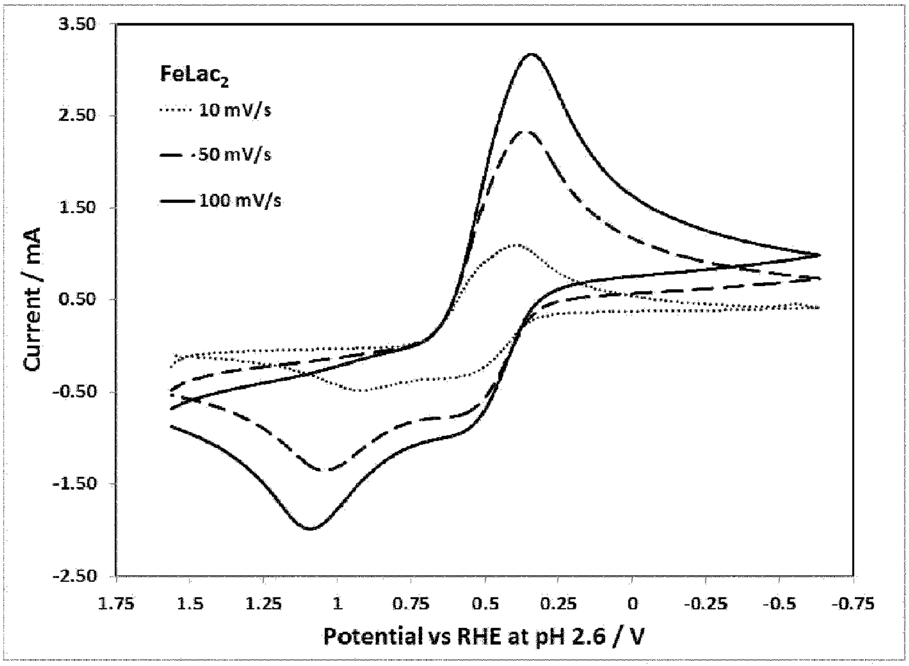
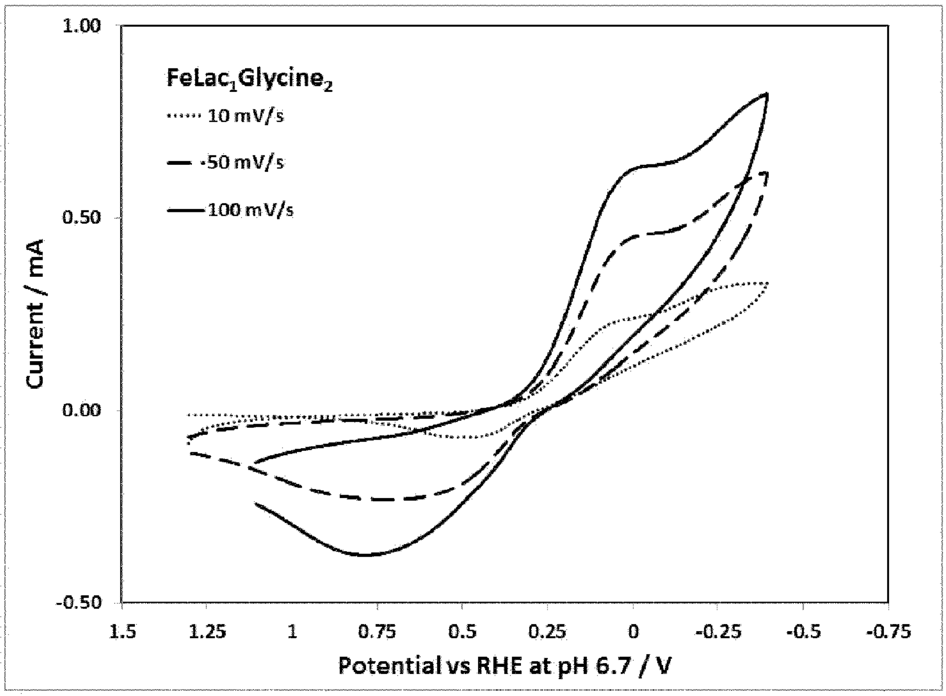

FeLac$_2$
10 mV/s
50 mV/s
100 mV/s
Current / mA
3.50
2.50
1.50
0.50
-0.50
-1.50
-2.50
1.75
1.5
1.25
1
0.75
0.5
0.25
0
-0.25
-0.5
-0.75
Potential vs RHE at pH 2.6 / V

FIG. 41


FeLac$_1$Glycine$_2$
10 mV/s
50 mV/s
100 mV/s
Current / mA
1.00
0.50
0.00
-0.50
1.5
1.25
1
0.75
0.5
0.25
0
-0.25
-0.5
-0.75
Potential vs RHE at pH 6.7 / V