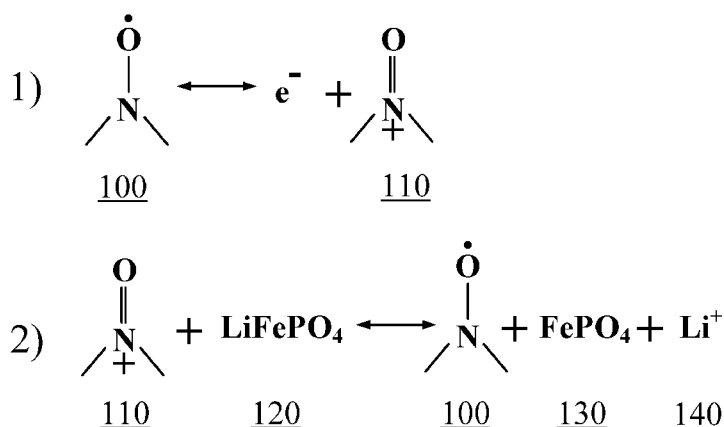




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[Continued on next page]

(54) Title: MATERIALS FOR FLOW BATTERY ENERGY STORAGE AND METHODS OF USING



(57) Abstract: The present disclosure relates to a mixture that includes a mediator having a first redox potential, a non-liquid active material having a second redox potential that is less than the first redox potential, and a cation. In addition, the non-liquid active material has a first condition that includes a first oxidation state, where the cation is intercalated within the non-liquid active material, and the non-liquid active material has a second condition that includes a second oxidation state that is higher than the first oxidation state, where the non-liquid active material is substantially free of the cation. In addition, the mediator has a first condition that includes a third oxidation state and a second condition that includes a fourth oxidation state that is higher than the third oxidation state.

Figure 1



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MATERIALS FOR FLOW BATTERY ENERGY STORAGE AND METHODS OF USING

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application No. 62/300,964 filed
5 February 29, 2016, the contents of which are incorporated herein by reference in its entirety.

CONTRACTUAL ORIGIN

The United States Government has rights in this disclosure under Contract No. DE-
AC36-08GO28308 between the United States Department of Energy and the Alliance for
Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy
10 Laboratory.

BACKGROUND

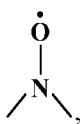
Redox flow battery technology is promising for large-scale, grid energy storage
because of several attractive features including long calendar life, simple design, wide
operating temperature ranges, and a capability to withstand fluctuating power supply. A
15 redox flow battery stores its energy in the form of redox-active materials dissolved/suspended
in liquid electrolytes circulating between external reservoirs and electrochemical cells. This
decoupling of energy and power offers excellent scalability as compared to traditional static
batteries and gives flow batteries a significant advantage for grid applications.

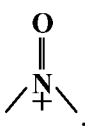
An example of a flow battery system is the vanadium redox flow battery, an aqueous
20 system that relies upon reduction and oxidation of soluble vanadates. Even though this
technology has seen good cycle life (>10,000 cycles) and calendar life (10-20 years), it is not
widely implemented for grid energy storage. This is attributed to the drawbacks of this
technology, which includes limited energy density (~25 Wh/L due to the low cell voltage
<1.8 V) and slow charge transfer kinetics. Low energy densities are a common deficiency
25 present in current flow battery systems with energy densities typically falling below about 10
Wh/L. Thus, there is clearly a need for new solutions that improve the voltage, volumetric
capacity, energy density, kinetics, and/or lifetime of redox flow batteries and systems.

SUMMARY

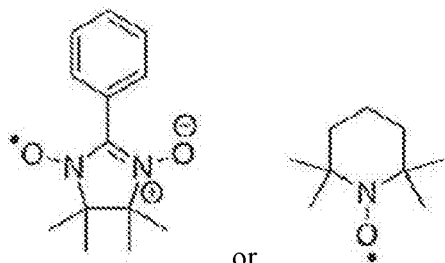
An aspect of the present disclosure is a mixture that includes a mediator having a first redox potential, a non-liquid active material having a second redox potential that is less than the first redox potential, and a cation. In addition, the non-liquid active material has a first condition that includes a first oxidation state, where the cation is intercalated within the non-liquid active material, and the non-liquid active material has a second condition that includes a second oxidation state that is higher than the first oxidation state, where the non-liquid active material is substantially free of the cation. In addition, the mediator has a first condition that includes a third oxidation state and a second condition that includes a fourth oxidation state that is higher than the third oxidation state. In addition, the non-liquid active material is capable of being reversibly cycled between its first condition and its second condition, and the mediator is capable of being reversibly cycled between its first condition and its second condition. In some embodiments of the present disclosure, the mediator may include an organic radical group. In some embodiments of the present disclosure, the organic radical group may include a nitroxide group. In some embodiments of the present disclosure, the mediator may have a molecular weight less than about 10,000 g/mol. In some embodiments of the present disclosure, the mediator may include at least one of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, (1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine), a nitronyl nitroxide, a azephenylenyl, a perchlorophenylmethyl radical, tris(2,4,6-trichlorophenyl)methyl radical, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate), and/or poly[4-(nitronyl nitroxyl)styrene].

In some embodiments of the present disclosure, when in the first condition of the

mediator, the mediator may include , and when in the second condition of the mediator,

the mediator may include .

In some embodiments of the present disclosure, the mediator may include a structure



that includes at least one of

, or

In some embodiments of the present disclosure, the non-liquid active material may include at least one of a solid and/or a gel. In some embodiments of the present disclosure, the non-liquid active material may include a solid particulate. In some embodiments of the present disclosure, the solid particulate may have a particle size between 1 nanometer and 1000 micrometers. In some embodiments of the present disclosure, the non-liquid active material may include at least one of cobalt, nickel, manganese, aluminum, titanium, vanadium, and/or iron. In some embodiments of the present disclosure, the non-liquid active material may include at least one of an oxide and/or a phosphate. In some embodiments of the present disclosure, the non-liquid active material may include at least one of a cobalt oxide, a nickel cobalt oxide, a manganese cobalt oxide, and/or an iron phosphate. In some embodiments of the present disclosure, the non-liquid active material may include at least one of CoO_2 , FePO_4 , and/or $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$.

In some embodiments of the present disclosure, the cation may include at least one of a Group 1, a Group 2, and/or a Group 13 element. In some embodiments of the present disclosure, the cation may include at least one of lithium, magnesium, aluminum, and/or beryllium. In some embodiments of the present disclosure, the mixture may further include a salt, where the salt provides at least a portion of the cation. In some embodiments of the present disclosure, the salt may include at least one of LiPF_6 , LiBF_4 , and/or LiClO_4 . In some embodiments of the present disclosure, the mixture may further include a solvent, where the mediator and the salt are substantially soluble in the solvent. In some embodiments of the present disclosure, the mixture may have an energy storage density greater than or equal to 300 Wh/L, when the non-liquid active material is in its second condition, and the mediator is in its second condition.

An aspect of the present disclosure is a method that includes transferring energy to a mixture by applying a voltage to the mixture, where the mixture includes a mediator, an active material, and a salt mixed within a solvent, the voltage transforms the mediator from

a neutral condition to an oxidized condition, and the mediator in the oxidized condition oxidizes the active material, thereby transforming the active material from a low energy condition to a high energy condition, and regenerating the mediator to its neutral condition. In some embodiments of the present disclosure, the method may further include applying a
5 load to the mixture, wherein the load transforms the active material from its high energy condition to its low energy condition.

An aspect of the present disclosure is a system that includes a first flow battery positioned on a vehicle and a second flow battery positioned external of the vehicle, where the first flow battery is only operated in a charging mode, and the second flow battery is only
10 operated in a discharging mode. In some embodiments of the present disclosure, the first flow battery may include a solid active cathode material. In some embodiments of the present disclosure, the first flow battery and the second flow battery may exchange a cathode mixture that includes an electrolyte and a mediator. In some embodiments of the present disclosure, the first flow battery and the second flow battery may exchange an anode mixture
15 that includes an electrolyte and a solid active anode material such that the anode mixture is a slurry.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates cathode charging half-reactions, according to some embodiments of the present disclosure.

20 Figure 2 illustrates cathode discharging half-reactions, according to some embodiments of the present disclosure.

Figure 3 illustrates a redox flow battery system (energy storage system), according to some embodiments of the present disclosure.

25 Figure 4 illustrates a system that substantially segregates the active cathode material from the mediator (solution-based catholyte) in a separate reactor, according to some embodiments of the present disclosure.

Figure 5 illustrates an energy storage system, according to some embodiments of the present disclosure.

30 Figure 6 illustrates experimental data collected from an energy storage system, according to some embodiments of the present disclosure.

Figure 7 illustrates experimental data collected from an energy storage system, according to some embodiments of the present disclosure.

Figure 8 illustrates compares the experimental data illustrated in Figures 6 and 7.

REFERENCE NUMBERS

5	100.....neutral mediator
	110.....oxidized mediator
	120.....reduced active cathode material
	130.....oxidized active cathode material
	140.....cation
10	300.....energy storage system
	305.....catholyte reservoir
	310.....catholyte
	315.....anolyte reservoir
	320.....anolyte
15	325.....electrochemical cell
	330.....separator
	335.....first half-cell
	340.....second half-cell
	345.....first current collector
20	350.....second current collector
	355.....electrical circuit
	360.....catholyte pump
	365.....first catholyte supply line
	370.....second catholyte supply line
25	375.....catholyte return line
	380.....anolyte pump

	385.....	first anolyte supply line
	390.....	second anolyte supply line
	395.....	anolyte return line
	400.....	catholyte loop
5	410.....	reactor
	500.....	energy storage system
	510.....	liquid mediator
	515.....	mediator reservoir
	520.....	solid active cathode material
10	530.....	anode
	540.....	discharge circuit
	550.....	charge circuit
	560.....	supply line
	570.....	return line

15 DETAILED DESCRIPTION

The present disclosure describes hybrid materials, e.g. matrices, for catholyte mixtures that are suitable for large-scale energy storage flow and/or flow-like batteries, and methods and systems utilizing such catholyte mixtures. The catholyte mixtures described herein have demonstrated improved upper voltage limits, faster kinetics, and higher solution concentrations, resulting in, among other things, energy densities up to an order of magnitude greater than existing catholyte mixtures for flow battery systems. In some embodiments of the present disclosure, energy densities exceed those of current technologies by factors greater than 10 because of their improved voltage levels.

A “catholyte” typically refers to a mixture that includes a cathode material and other additives mixed with an electrolyte. For redox flow battery systems, an “electrolyte” is typically a salt dissolved in a liquid, where the salt provides the ions necessary for the battery’s redox reactions to occur. The present disclosure describes catholyte mixtures that include an active cathode material and a mediator. In some embodiments of the present

disclosure, a catholyte mixture may include an active cathode material, a mediator, and an electrolyte. In some embodiments of the present disclosure, a catholyte mixture may include an active cathode material, a mediator, an electrolyte, and at least one additive. The active cathode material may be in the liquid phase and/or in a non-liquid phase, and may include at least one of a solid, a gel, a dissolved solution, and/or a suspension. In addition, the mediator must have a redox potential, E_m^0 , that is equal to or more positive than the redox potential, E_a^0 , of the active cathode material. Thus, the mediator may define the charge/discharge rates of a flow battery using a catholyte mixture that includes the mediator and an active cathode material, while also limiting the over-potential limits of the active cathode material due to the more positive working voltage of the mediator. This may provide faster “homogeneous or heterogeneous chemical” charging of the cathode and limit over voltage of the active cathode material. The mediator may be in the liquid phase and/or in a non-liquid phase, such as a solid and/or gel, and/or a slurry. The mediator may be dissolved in a solution and/or suspended in a solution. In some embodiments of the present disclosure, the mediator may be a surface modifier of the active cathode material, e.g. resulting in core-shell-like structures as described below.

Figure 1 illustrates an example of cathode half-reactions that may occur during the charging of a flow cell battery, according to some embodiments of the present disclosure. In this example, as shown in Reaction 1), a neutral mediator 100 having a nitroxide functional group, reversibly transitions from a neutral state to an oxidized state. For this example of a mediator, when in the neutral state, the nitroxide functional group of the neutral mediator 100 is in the form of a stable, neutral radical. In the oxidized state, the nitroxide functional group of the oxidized mediator 110 is in the form of a non-radical, positively-charged ion. During charging (e.g. application of a voltage to the redox flow battery) the neutral mediator 100 contained in the catholyte mixture is oxidized, converting it to the oxidized mediator 110. In some embodiments of the present disclosure, charging converts the neutral mediator 100 from a low energy state corresponding to the neutral state, to the oxidized mediator 110 at a higher energy, oxidized state.

Referring to Reaction 2) of Figure 1, the oxidized mediator 110 “mediates” oxidation of the active cathode material 120, such that the oxidized mediator 110 is reduced, resulting in the regeneration of the neutral mediator 100. In this example, the active cathode material (120 and 130) includes iron phosphate, either intercalated with lithium to form the reduced active cathode material 120, or substantially free of intercalated lithium to form the oxidized

active cathode material 130. Like the mediator (100 and 110), the active cathode material (120 and 130) has two states, a reduced state and an oxidized state. In some embodiments of the present disclosure, the reduced active cathode material 120 corresponds to a low energy state, while the oxidized active cathode material 130 corresponds to a high energy state. For this example, the low energy state corresponds to the reduced active cathode material 120, where iron phosphate having iron in the 2+ oxidation state is intercalated with lithium cations (the combination referred to a lithium iron phosphate). Conversely, the high energy state corresponds to the oxidized active cathode material 130, where the iron phosphate is substantially free of intercalated lithium ions and the iron is in the 3+ oxidation state. Thus, the oxidized mediator 110 oxidizes (e.g. mediates) the reduced active cathode material 120, through a heterogeneous and/or homogeneous charge transfer reaction resulting in the conversion of the oxidized mediator 110 back to its original state, the neutral mediator 100. Substantially simultaneously, oxidation of the reduced active cathode material 120 transforms this species to the substantially lithium-free oxidized active cathode material 130, producing free lithium cations 140, which are released into the catholyte mixture (not shown).

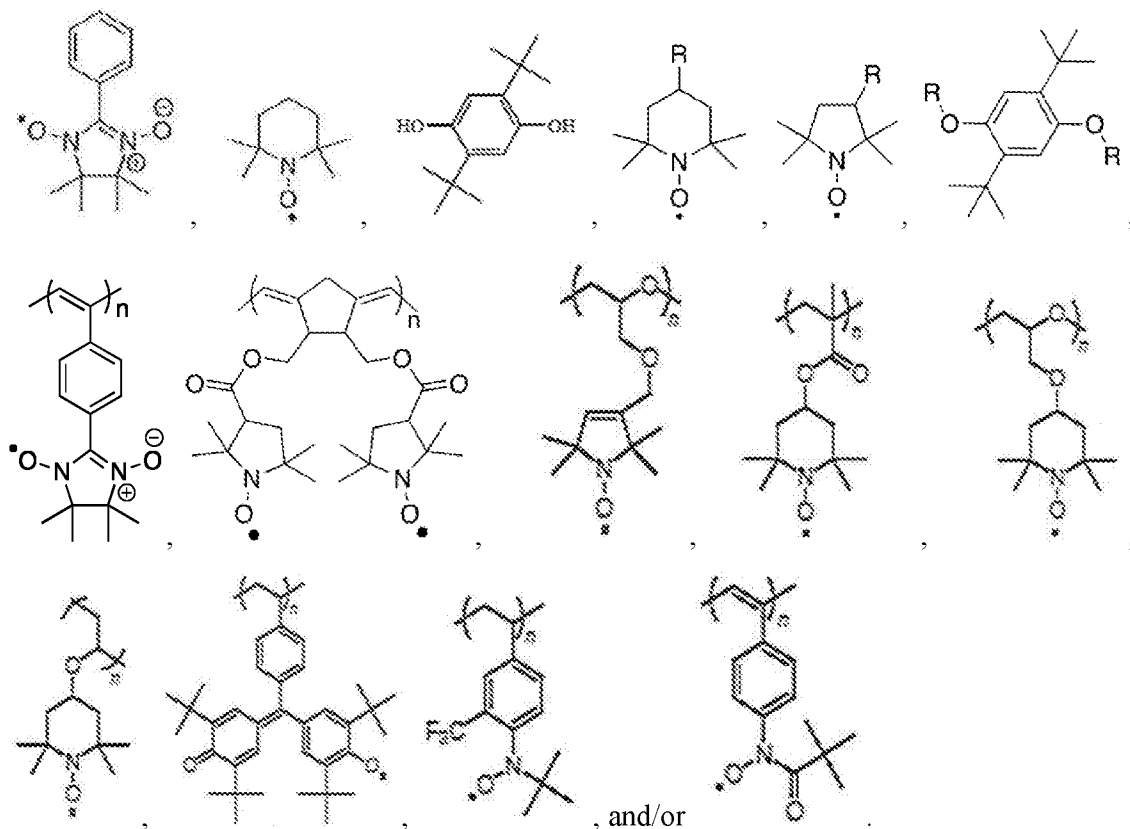
The reactions illustrated in Figure 1 demonstrate that the mediator (100 and 110) acts as an electron and/or energy transfer mediator. Charging the flow battery (e.g. by the application of an appropriate voltage to the flow battery between the flow battery's two electrodes) rapidly oxidizes the neutral mediator 100 to produce the oxidized mediator 110. Thus, Reaction 1) of Figure 1 increases, at least temporarily, the stored energy density of the catholyte mixture during charging. However, the final energy density attainable may be substantially increased by Reaction 2) of Figure 1, by the transfer of the energy stored in the oxidized mediator 110 to the reduced active cathode material 120 converting it to the oxidized active cathode material 130, as described above. Thus, in some embodiments, the active cathode material (120 and 130) is substantially the final energy storage destination and significantly increases the total energy density of the charged catholyte mixture, above the energy storage density of the mediator (100 and 110) alone. In addition, the transfer of energy from the oxidized mediator 110 to the reduced active cathode material 120 results in the regeneration of the neutral mediator 100 to its original uncharged, low energy state, thus making it available for further charging. Thus, the mediator (100 and 110) may function predominantly as an energy and/or charge transfer mediator, as well as a temporary energy storage medium until the primary energy storage medium, the active cathode material (120 and 130), receives the energy and/or charge from the mediator (120 and 130). However, the

mediator (120 and 130) may also include the secondary role of an energy storage material, storing some additional charge/energy above the energy/charge stored by the active cathode material (120 and 130) alone.

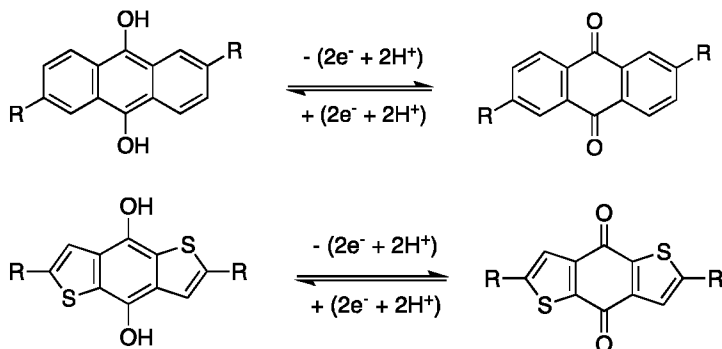
Figure 2 illustrates cathode half-reactions that may occur during discharge of a flow battery, according to some embodiments of the present disclosure. Discharge may occur when a load is applied to the flow battery. Referring to Reaction 1) of Figure 2, during discharge of the flow battery, the oxidized active cathode material 130 is reduced (e.g. in the cathode half-cell of the battery), resulting in the regeneration of the low energy, intercalated reduced active cathode material 120. Thus, application of a load to the battery system results in the transfer of “free” cations 140 (e.g. lithium cations) from the catholyte mixture into the iron phosphate solid of the oxidized active cathode material 130, resulting in the regeneration of FePO_4 having intercalated lithium (the reduced active cathode material 120). In addition, referring to Reaction 2) of Figure 2, application of a load to the flow battery may also result in the reduction of any remaining oxidized mediator 110 to regenerate the neutral mediator 100.

As described above, catholyte mixtures described herein may include at least one of a solvent, a mediator, a non-liquid active cathode material, and/or a cation-containing salt. The solvent (or solvent mixture) used may provide a solubility sufficient to dissolve most or all of the mediator, the active cathode material, and/or the cation-containing salt. In other cases, at least one solvent may be selected where the solvent has a low solubility for one or more of the components of the catholyte mixture, so that the components remain in a second phase, resulting in a heterogeneous mixture such as a solid-liquid slurry. It is often desirable to select a solvent that will not degrade during the charging/discharging of the flow battery, for example due to the system operating conditions (e.g. temperatures and/or voltages). However, in general, suitable solvents may include at least one of an aqueous solvent, a non-aqueous solvent, a protic solvent and/or an aprotic solvent. Examples of aprotic solvents that may be used in catholyte mixtures described herein include carbonates, ethers, acetates, and/or ketones. Further examples of aprotic solvents include tetrahydrofuran, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, and/or propylene carbonate. Examples of protic solvents that may be used in catholyte mixtures described herein include water, alcohols, and/or glycerin. Examples of suitable alcohols include methanol, ethanol, propanol, butanol, and/or other alcohols with molecular weights larger than butanol. Suitable alcohols include both straight-chained and branched alcohols.

In some embodiments of the present disclosure, at least one mediator is dissolved or substantially dissolved within at least one solvent to form a catholyte mixture. In some embodiments of the present disclosure, at least one mediator remains substantially undissolved in at least one solvent, for example in the form of a solid and/or second insoluble liquid. A mediator may contain at least one functional group that may be reversibly oxidized and reduced such as a nitroxide functional group (e.g. R_2NO). In some embodiments of the present disclosure, a mediator may be a nitroxide-containing mediator. In some embodiments of the present disclosure, a mediator may include at least one of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl or (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl), TEMPOL (1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine), nitronyl nitroxides, azephenylenyls, radicals derived from PTM (perchlorophenylmethyl radical), and/or TTM (tris(2,4,6-trichlorophenyl)methyl radical). A mediator may include at least one of poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA), poly[4-(nitronylnitroxyl)styrene] (PNNS and/or PNNS-c), and/or TEMPO. Other examples of mediators include stable and/or persistent radicals such as nitric oxide, thiazyl radicals, and/or triphenylmethyl radical. In some embodiments of the present disclosure, mediators may include at least one of the following chemical structures:

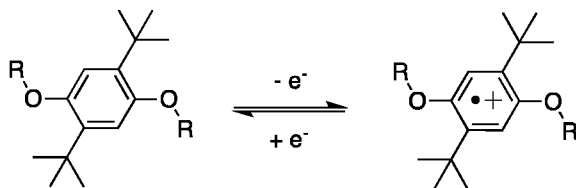


In some embodiments of the present disclosure, quinones may be used as mediators in a catholyte mixture, where the quinones may be reversibly cycled between a high energy oxidized state and a low energy reduced state. Examples of quinones include,



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In some embodiments of the present disclosure 2,5-di-tert-butyl-1,4-bis(2-methoxyethoxy)benzene (DBBB) may be used as a mediator in a catholyte mixture, where the DBB may be reversibly cycled between a higher energy oxidized state and a low energy reduced state, according to,



10

Thus, mediators may include one or more small molecules (e.g. monomers) and/or one or more polymeric molecules. In some examples, a mediator may have a molecular weight of less than about 10,000 g/mol, or less than about 1,000 g/mol. In some examples, a mediator may have a molecular weight of larger than about 1,000 g/mol, or larger than about 10,000 g/mol. The molecular weight of a mediator selected for a specific application will depend on the operating conditions of the application (e.g. temperature, voltages, etc.) and other design criteria (e.g. desired solubility of the mediator within the solvent selected, or choice of cell separator etc.). In the case of polymers, the term “molecular weight” refers to the number average molecular weight, defined as the total weight of the polymer divided by the number of molecules.

15

20

In some embodiments of the present disclosure, one or more of the mediators described above may be modified such that they are not soluble and/or only partially soluble within the electrolyte. This may be accomplished, for example, by increasing the molecular

weight of the polymer backbone supporting the organic radical functional groups (e.g. increasing the length of the polymer chain and/or providing cross-linking). In some embodiments of the present disclosure, when a mediator is no longer soluble in the electrolyte, it may behave as an active cathode material as well as and/or instead of as a mediator.

Active cathode materials may be in liquid form and/or a non-liquid form. Non-liquid active cathode materials may include solids and/or gels. Examples of non-liquid active cathode materials include one or more oxides and/or phosphates, such as the oxides and/or phosphates of cobalt, nickel, manganese, aluminum, titanium, vanadium, and/or iron. Non-liquid active cathode materials may include at least one of a cobalt oxide, a nickel cobalt oxide, a manganese cobalt oxide, an iron phosphate, and/or a manganese iron phosphate. Non-liquid active cathode materials may include anionic matrices that enable the reversible intercalation of cationic counter-ions into the non-liquid matrices to balance the negative charge of the matrices. Cations that may reversibly intercalate into and out of active cathode material matrices include Group 1, Group 2, and/or Group 13 elements. Examples of such elements include lithium, magnesium, aluminum, and/or beryllium. Further, compounds that may be used as non-liquid active cathode materials in catholyte mixtures for flow battery systems include at least one of LiCoO_2 , LiFePO_4 (with a voltage range of about 3.5 volts), and/or $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$. Another example of a non-liquid active cathode material is $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ where $x \geq 0.5$ (voltage range of about 5 volts). Further examples of non-liquid active cathode materials include LiNiO_2 , LiCoO_2 , $\text{LiCo}_{1-x-y}\text{Ni}_x\text{Mn}_y\text{O}_2$, LiMnO_2 , and/or $\text{Li}_{1+y}\text{Mn}_{2-x}\text{M}_x\text{O}_4$ (voltage ranges of about 4 volts). Further examples of non-liquid active cathode materials include $\text{Li}_x\text{Mn}_{1-y}\text{M}_y\text{O}_2$, and/or $\text{Li}[\text{Li}_x\text{M}_y\text{Mn}_{1-x-y}]\text{O}_2$ (voltage ranges of about 3 volts to about 4 volts). Further examples of non-liquid active cathode materials include Mn spinels such as $\text{Li}_4\text{Mn}_5\text{O}_{12}$, Li_xMnO_2 , and/or $\text{Li}_x\text{V}_y\text{O}_z$ (voltage ranges of about 3 volts). Further examples of non-liquid active cathode materials include sulfur and polysulfides (voltage ranges of about 2 volts) and FeS_2 (voltage range of about 1.5 volts).

Non-liquid active cathode materials may be provided in the form of solid particles. Active cathode materials in the form of solid particles may significantly increase the energy density of a catholyte mixture above that attainable by the mediator alone. However, as charging and/or discharging rates may be limited by the mass-transfer rates of the cations at the interface between the solid phase of the non-liquid active cathode material and its surrounding environment (e.g. a liquid solvent mixture) and/or by intra-solid mass-transfer of

the cations (e.g. within the phosphate and/or oxide solid bulk matrix), it may be desirable to minimize the average particle size of active cathode material particles to reduce these potentially rate-limiting mass-transfer steps. Thus, an active cathode material in the form of solid particles may include solid particles that have a characteristic diameter of less than about 1000 micrometers, or less than about 100 micrometers, or less than about 10 micrometers, or less than about 1 micrometer, or less than about 100 nanometers, or less than about 10 nanometers. In some embodiments of the present disclosure, active cathode materials in the form of solid particles may include solid particles that have a characteristic diameter between about 2 nanometers and about 2 micrometers. Particles may be in any suitable shape; e.g. flakes, spheres, rods, whiskers, cylinders, pellets, irregular/non-geometric shapes, and/or any other suitable shape. Particles may be completely solid and/or contain at least some void space; e.g. particles may be hollow. In addition, particles may include one or more layers of different solid materials.

In some embodiments of the present disclosure, mediators may be present substantially in the liquid form, for example dissolved in a solvent or “neat” where the mediator itself is a liquid in the absence of a solvent. For example, a catholyte mixture may include a nitroxide-containing liquid polymer (the mediator) slurried together with LiPF_6 and/or LiFePO_4 (the active cathode material). However, mediators may also be provided in the solid phase and then dispersed within a solvent that has a very low solubility for the solid mediator. In addition, a solid mediator may be combined directly with a solid active cathode material to form a “core-shell” structured hybrid material and/or a core shell at least partially covered by an outside layer. For example, a composite solid particle may be formed by depositing an outside layer of a solid mediator on the outer surface of an internal core of active cathode material. In some embodiments of the present disclosure, a composite solid particle may be formed by depositing an outside layer of solid active cathode material on an internal core of mediator. Such composite particles may then be suspended in a catholyte mixture, including a solvent and/or a cation-providing salt. In some examples, a mediator layer may be coated onto an underlying active cathode material layer; e.g. LiFePO_4 may be nucleated, grown in, and/or grown on a nitroxide polymer.

In some embodiments of the present disclosure, nitroxide functional groups may be grafted onto the surface of an active cathode material, e.g. onto LiFePO_4 particles. In some embodiments of the present disclosure, the mediator may be dissolved in the electrolyte solution and then passed through channels of a solid active cathode material, and/or passed

over one or more surfaces of the solid active cathode material resulting in the oxidation of the active cathode material, such that the resultant reduced mediator may be directed back to the active “charging” half of the cell, and then recycled again across the solid active cathode material. Thus, the circulating flow of a catholyte solution containing the mediator from the charging half-cell to the solid active cathode material may proceed until the active cathode material is fully charged, and/or some other process target is achieved, at which point a load may be applied to the cell and the process reversed to utilize the stored energy as needed. (See Figures 5-8 for details and experimental results of such an embodiment.)

A catholyte mixture may include at least one salt that provides the one or more cations shown in the redox reactions illustrated in Figures 1 and 2, as well as the redox half-reactions that occur in the anolyte mixture in the complimentary half-cell of a flow battery (refer to Figure 3). Examples of such salts for providing lithium cations include LiPF_6 , LiBF_4 , and/or LiClO_4 . Other salts known to one skilled in the art may be used for providing other cations, for example magnesium cations.

As describe above, the mediator may have a redox potential, E^0_m , that is more positive than the redox potential, E^0_a , of an active cathode material. Table 1 below summarizes redox potentials for some materials covered within the scope of the present disclosure. Table 1 illustrates that many different mediator/active cathode material combinations exist where E^0_m is greater than E^0_a .

Table 1: Redox Potentials

mediator		active material	
name	E^0_m [V]	name	E^0_a [V]
TEMPO	> 3.4	LiFePO_4	3.2
TEMPOL	>3.4	LiCoO_2	3.8
PTMA	3.4	$\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$	3.4
PNNS	3.7	LiMn_2O_4	4.1
PNNS-c	3.58		
DBBB	4.1		

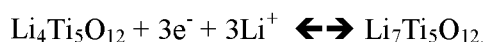
Figure 3 illustrates an exemplary energy storage system 300, according to embodiments of the present disclosure. The energy storage system 300 includes an electrochemical cell 325, which is divided into a first half-cell 335 and a second half-cell 340 by a separator 330. The cathode half-reactions illustrated in Figures 1 and 2, and described above, occur in the first half-cell 335. Corresponding anode half-reactions occur in the

second half-cell 340. The catholyte mixture 310 is stored in a catholyte reservoir 305 and is circulated through the first half-cell 335 as needed by a catholyte pump 360. Thus, during charging, the catholyte pump 360 moves the low energy, reduced catholyte mixture 310 from the catholyte reservoir 305, through a first catholyte supply line 365 and a second catholyte supply line 370 into and/or through the first half-cell 335. An appropriate voltage applied to the electrochemical cell 325, causes the oxidation of the mediator and active cathode material contained within the catholyte mixture, as described above and illustrated in Figure 1, resulting in the conversion of the low energy catholyte mixture to the higher energy, oxidized form of the catholyte mixture. The high energy catholyte mixture is then returned to the catholyte reservoir 305 through a catholyte return line 375, for storage until discharge of the battery. During discharge, the catholyte mixture 310 follows the same path through the first half-cell 335 as during charging (alternatively, the direction of flow could be reversed). The difference is that during discharge a load is applied to the electrochemical cell 325, resulting in the reduction of the active cathode material and the mediator contained within the catholyte mixture, as illustrated in Figure 2.

The second half-cell 340 is configured in a fashion similar to the first half-cell 335. An anolyte mixture 320 is stored in an anolyte reservoir 315 until charging or discharging is needed. For both charging and discharging of the anolyte mixture 320, an anolyte pump 380 circulates the anolyte mixture from the anolyte reservoir 315 through a first anolyte supply line 385 and a second anolyte supply line 390 into and/or through the second half-cell 340 to be charged or discharged. The charging and discharging of the anolyte mixture 320 in the second half-cell 340 are defined by the half-reactions of the components making up the anolyte mixture 320. For example, elemental lithium may be used as the active anode material in an anolyte mixture, whose half-reaction is defined by,



After charging or discharging the anolyte mixture 320 within the second half-cell 340, the anolyte mixture 320 may be returned to the anolyte reservoir 315 for storage until the next charging or discharging cycle is needed. In some embodiments the following reaction may provide the active anode material for an anolyte mixture:



As described above, a catholyte mixture 310 may contain a liquid mediator substantially dissolved within a solvent, and an active species in the form of solid particles.

Thus, a catholyte mixture 310 may be stored in the catholyte reservoir 305, and circulated through the first half-cell 335, in the form of a liquid slurry. In such a scenario, the oxidation and reduction reactions of the mediator may occur mostly within the first half-cell 335, while the oxidation and reduction reactions of the solid active cathode material may occur anywhere within the catholyte loop; e.g. the redox reactions of the active cathode material (as shown in Figures 1 and 2) may occur within the first half-cell 335, within the catholyte reservoir 305, and/or within any of the loop's piping (the first catholyte supply line 365, second catholyte supply line 370, and/or the catholyte return line 375.)

Referring to Figure 4, in some embodiments of the present disclosure, a catholyte loop 400 may include at least one reactor 410 containing the active cathode material in a solid phase, where the reactor 410 is positioned outside of the first half-cell and/or reservoir. Two possible reaction positions are shown in Figure 4, although other locations fall within the scope of the present disclosure. First, a reactor may be positioned between the catholyte reservoir 305 and the catholyte pump 360, represented by reactor 410A. Second, a reactor may be positioned between the catholyte pump 360 and the first half-cell 335, as represented by reactor 410B. In either configuration, Reaction 1) of Figure 1 and Reaction 2) of Figure 2 of the mediator may occur substantially within the first half-cell 235, while Reaction 2) of Figure 1 and Reaction 1) of Figure 2 may occur substantially within at least one of the reactors, 410A and/or 410B. The reactor (410A or 410B) may be a fixed bed reactor with active cathode material positioned within the fixed bed reactor. Alternatively, the reactor (410A or 410B) may be continuous stirred-tank reactor, or the active cathode material may be a non-suspended active cathode material in a reservoir. Although Figure 4 illustrates two reactors (410A and 410B), one or more reactors containing the active cathode material may be positioned in any desirable location within the catholyte loop 400. By containing the active cathode material in reactors (e.g. 410A and 410B), movement of the active particles may be minimized or eliminated, which thus may minimize physical degradation of the solid active cathode material particles. Containing the active cathode material in reactors separate from the electrochemical cell may also result in manufacturing benefits such as easier control of the amount of active cathode material relative to the catholyte, easier charging of the active cathode material to the system, easier maintenance and replacement of the active cathode material from the system, and easier scale-up from small systems to larger industrial-scale systems. Thus, by utilizing at least some of the feature described herein, some embodiments of the present disclosure may provide an energy storage system having a specific power

between 160 W/kg and 320 W/kg for a corresponding specific energy between 60 Wh/kg and 160 Wh/kg.

Figure 5 illustrates another example of an energy storage system 500, as described above. In this example, a liquid mediator 510, as described above, is stored in a mediator reservoir 515. The liquid mediator 510 may be charged using a charge circuit 540, while the liquid mediator 510 resides in the mediator reservoir 515, resulting in the oxidation of the liquid mediator 510 as shown in Reaction 1) of Figure 1. The higher energy, oxidized form of the liquid mediator 510 may then pass/flow over and/or through a solid active cathode material 520, for example lithium iron phosphate. The liquid mediator 510 may be directed to the solid active cathode material 520 by a supply line 560, such that after contacting the solid active cathode material 520, the liquid mediator 510 may be recycled to the mediator reservoir 515 by a return line 570. Once the solid active cathode material 520 is sufficiently charged, the solid active cathode material 520 is discharged using a discharge circuit 550. The anode 530 in this example may be any suitable anolyte/anode material, for example lithium metal and/or lithium-carbon and/or other anode materials with appropriate redox potentials. In the example of Figure 5, a first separator 330A and a second separator 330B may be used to limit crossover of the solid active cathode material 520, which can short-circuit the energy storage system 500, where any ion-conductive membrane may be used as the separator (330A and/or 330B).

A system similar to that illustrate in Figure 5 and described above was constructed and tested using TEMPO and PTMA as a liquid mediator 510 and lithium iron phosphate as a solid active cathode material 520. Thus, in this example, lithium ions were reversibly intercalated within the iron phosphate active cathode material. The solvent in this case was either propylene carbonate or a 50:50 mixture of ethyl and dimethyl carbonate electrolytes which contained 1M of the salt LiPF_6 . The anode 530 was constructed of lithium metal. The active cathode material (LFP) was shown first to be oxidized by immersion for less than one minute in the oxidized mediator solution. The LFP was also oxidized by flowing the energized mediator solution over the surface of the LFP solid active cathode material. In this case, two thicknesses of active cathode material were investigated. It was determined that the oxidation of the LFP would be limited by diffusion of the mediator if the active cathode material was “too” thick. Thus, in some embodiments of the present disclosure, an energy storage system may include a solid active cathode material having micro-channels and/or an optimized thickness to minimize such mass-transfer limitations.

Figures 6-8 illustrate experimental results collected from a system similar to that shown in Figure 5 and described above. As described above for Figure 5, a solid active cathode material of lithium iron phosphate (LFP) was used, which was oxidized by a mediator of liquid TEMPO having a 50 millimolar concentration within a carbonate 1M LiPF₆ electrolyte solution. Cycling of the mediator solution across the solid surfaces of the solid active cathode material (LFP) resulted in the charging, e.g. oxidation of the solid state LFP active cathode material. The rate of the LFP oxidation was effectively charged at a temperature of about 40°C; e.g. the solid active cathode material was fully charged in about 1.5 minutes. In typical cases this would cause detrimental effects on the battery, reducing its performance because of the rapid charging of the material. However, as can be seen in Figure 6, the discharge of both materials (of the varying thickness cathode) after liquid catholyte charging were within 10% of theoretical values. Figures 7 and 8 show the recharge cycles for the same system after the initial flow charge of the LFP cathode. In this system, because the cathode was a flat surface, the thickness (mass) of the sample was not optimized to maximize the charging rate. So, in this particular case, the 1mg/cm² sample showed the ability to achieve 98% theoretical charging capacity of the cathode in 1.5 minutes, while the thicker cathode was slightly slower and only charged to 90% of its capacity. For this example of a solution phase mediator and solid active cathode material, the following approximate limits were identified:

1) An effective charge rate at a charging temperature between about 30°C and about 40°C. Therefore, in this particular case, the redox mediator oxidation of the active cathode material will not limit the charge rate.

2) It is important to identify that the high charging rate capability of the organic liquid catholyte mediator, and the high charging rate conversion of the cathode material (LFP) to the energized state enables the use of reduced concentrations of the mediator and volume of the nonaqueous solvent, which in turn, enables a reduced solution impedance enhanced charge/discharge rates. This has the effect of reducing cost and environmental impact.

3) Finally, in this construct of mediator/cathode material, one cannot overcharge the cathode in the chemical oxidation of the LFP. This overvoltage effect for fast charging rates in a typical battery cell has irreversible deleterious effects on the LFP material, leading to catastrophic failure of the battery. These overvoltage losses typically seen with many of the metal-oxide cathodes cannot occur in the systems described herein. Therefore,

according to some embodiments of the present disclosure the active cathode material may discharge at continuous high rates at temperatures greater than 10 °C, with excellent life-cycles, which may be extended even further by utilizing the mediator/active cathode material systems described herein.

5 In some embodiments of the present disclosure, two energy storage systems (e.g. flow batteries) as described above and illustrated in Figure 3 may be combined such that one of the energy storage systems contained within a vehicle may be easily and quickly recharged, and the second energy storage system is external to the vehicle and provides the charged materials needed to power the vehicle. For example, such a two-flow battery system may include a
10 primary energy storage system (flow battery) positioned within the vehicle such that the first primary energy storage system only provides an energy source for discharging (e.g. to propel the vehicle), and a secondary energy storage system provided externally to the vehicle, for example at a charging station, that only provides a charging capacity. In such a system, current will flow in only one direction between the anode and the cathode in the primary
15 energy storage system and/or the secondary energy storage system. Current that is restricted to flow in only one direction (e.g. for discharging or charging), among other things, provides the benefit of preventing the formation of coatings or layers (e.g. of dendrites) and the battery active materials, which may block the desired transfer of cations (e.g. Li^+ and/or Mg^{2+}) to and/or from the anode and/or cathode active materials.

20 Thus, according to some embodiments of the present disclosure, a solid active cathode material for the flow battery located on the vehicle may be recharged using a cathode mixture containing an oxidized mediator as described previously. This “charged” cathode mixture may be formed by the external secondary “charging station” battery, which may also produce the “charged” form of an anode mixture. According to some embodiments of the present
25 disclosure, the anode mixture produced by the secondary “charging station” battery may include a mixture of a soluble active anode material within an electrolyte solution. In some cases, the anode mixture produced by a secondary “charging station” battery may include a mixture of a solid active anode material within an electrolyte solution, such that the anode mixture is in the form of slurry. Thus, the solid active anode material may be provided in
30 particulate form to facilitate easier transfer of the anode mixture from the first flow battery to the second flow battery, and to minimize mass-transfer limitation of the ions being transferred into and out of the solid active anode material.

In other words, a vehicle charging system may include a first flow battery that is positioned within the vehicle and a second flow battery positioned external to the vehicle. The first flow battery system may only operate in discharge mode (see Figure 2) and the second flow battery system may only operate in charging mode (see Figure 1). Thus, the first
5 flow battery may only discharge a cathode mixture and an anode mixture, whereas the second flow battery may only charge the cathode mixture and the anode mixture. Thus, both flow batteries may include storage containers, one each for the charged cathode mixture, discharged cathode mixture, charged anode mixture, and discharged anode mixture. When the first flow battery of the vehicle has spent all of a previous charge, its discharged cathode
10 container and its discharged anode container will contain the discharged cathode mixture and the discharged anode mixture, respectively, and the charged cathode container and the charged anode container will be empty, the charged cathode mixture and charged anode mixture having been consumed. At that point, the user may transfer the discharged cathode mixture from the first flow battery to the discharged cathode container of the second flow
15 battery ("charging station"), as well as transfer the discharged anode mixture from the first flow battery to the discharged anode container of the second flow battery. Similarly, the user may transfer a fresh bolus of charged cathode mixture from the storage container of the second flow battery to the charged cathode container of the first flow battery ("vehicle"), as well as transfer the charged anode mixture from the second flow battery to the charged anode
20 container of the first flow battery. At that point, the first flow battery of the vehicle will have a new charge of stored energy and the vehicle may resume travel, and the second flow battery may proceed with re-charging the received discharged cathode mixture and/or anode mixture, as described above.

In some embodiments of the present disclosure, such a two flow battery system may
25 utilize a cathode mixture as described above and illustrated in Figures 1-4. For example, the cathode mixture may include at least one of an active cathode material, a mediator, and/or an electrolyte. In some embodiments of the present disclosure, the cathode mixture may include an active cathode material, a mediator, an electrolyte, and at least one additive. In some
30 embodiments, the cathode mixture may only contain an electrolyte (e.g. solvent containing ions) and the mediator. In some embodiments of the present disclosure, the active cathode material of the vehicle's flow battery may be provided as a solid that remains in the vehicle (e.g. it is not replaced), such that the cathode mixture only includes an electrolyte and the mediator. Once the charged mediator, contained within the cathode mixture and provided by

the second flow-battery, is provided to the first flow-battery and is contacted with the solid active cathode material, the transfer of charge and/or energy from the mediator to the solid active cathode material will occur quickly.

5 In some embodiments of the present disclosure, the anode mixture of the first flow battery may be the same as the anode mixture of the second flow battery, or the two systems may be different. At a minimum the anode mixture of the second flow battery requires a redox potential (voltage) capable of charging the cathode mixture of the first flow battery cathode. Nor does this second flow battery need to cycle quickly. For a first flow battery utilizing a solid active cathode material placed on the vehicle, as long as the cathode mixture
10 containers and/or anode mixture containers are sufficiently large, the solid active cathode material of the vehicle's flow battery may be charged as fast as required for a specific application. This is because the charged cathode solution (e.g. electrolyte plus mediator) may be cycled over/through the solid active cathode material resulting in the essentially instantaneous transfer of energy/charge from the mediator to the solid active cathode material
15 due to respective redox potentials of the mediator and the solid active cathode material. In addition, and cathode mixture (e.g. electrolyte plus mediator) may be recharged when it is convenient, such as from the grid during off-peak hours or during high wind or solar power production in the second flow battery (charging station). In addition, the cathode mixture (e.g. electrolyte plus mediator) may be charged at the optimal charging for the second flow
20 battery.

Examples:

Example 1. A mixture comprising: a mediator having a first redox potential; a non-liquid active material having a second redox potential that is less than the first redox potential; and a cation, wherein: the non-liquid active material has a first condition
25 comprising a first oxidation state, where the cation is intercalated within the non-liquid active material, the non-liquid active material has a second condition comprising a second oxidation state that is higher than the first oxidation state, where the non-liquid active material is substantially free of the cation, the mediator has a first condition comprising a third oxidation state and a second condition comprising a fourth oxidation state that is higher than the third
30 oxidation state, the non-liquid active material is capable of being reversibly cycled between its first condition and its second condition, and the mediator is capable of being reversibly cycled between its first condition and its second condition.

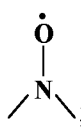
Example 2. The mixture of claim 1, wherein the mediator comprises an organic radical group.

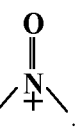
Example 3. The mixture of claim 2, wherein the organic radical group comprises a nitroxide group.

5 Example 4. The mixture of any one of claims 1-3, wherein the mediator has a molecular weight less than about 10,000 g/mol.

Example 5. The mixture of any one of claims 1-4, wherein the mediator comprises at least one of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, (1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine), a nitronyl nitroxide, a azephenylenyl, a perchlorophenylmethyl radical,
10 tris(2,4,6-trichlorophenyl)methyl radical, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate), or poly[4-(nitronylnitroxyl)styrene].

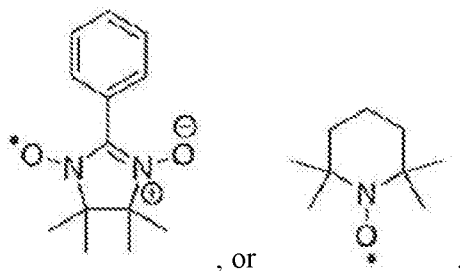
Example 6. The mixture of any one of claims 1-5, wherein, when in the first

condition of the mediator, the mediator comprises ; and when in the second condition

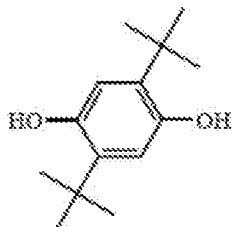
of the mediator, the mediator comprises .

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Example 7. The mixture of any one of claims 1-6, wherein the mediator includes a structure comprising at least one of



Example 8. The mixture of any one of claims 1-7, wherein the mediator includes



Example 9. The mixture of any one of claims 1-8, wherein the non-liquid active material comprises at least one of a solid or a gel.

5 Example 10. The mixture of any one of claims 1-9, wherein the non-liquid active material comprises a solid particulate.

Example 11. The mixture of claim 10, wherein the solid particulate has a particle size between 1 nanometer and 1000 micrometers.

10 Example 12. The mixture of any one of claims 1-11, wherein the non-liquid active material comprises at least one of cobalt, nickel, manganese, aluminum, titanium, vanadium, or iron.

Example 13. The mixture of any one of claims 1-12, wherein the non-liquid active material comprises at least one of an oxide or a phosphate.

15 Example 14. The mixture of any one of claims 1-13, wherein the non-liquid active material comprises at least one of a cobalt oxide, a nickel cobalt oxide, a manganese cobalt oxide, or an iron phosphate.

Example 15. The mixture of any one of claims 1-14, wherein the non-liquid active material comprises at least one of CoO_2 , FePO_4 , or $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$.

20 Example 16. The mixture of any one of claims 1-15, wherein the cation comprises at least one of a Group 1, a Group 2, or a Group 13 element.

Example 17. The mixture of any one of claims 1-16, wherein the cation comprises at least one of lithium, magnesium, aluminum, or beryllium.

Example 18. The mixture of any one of claims 1-17, wherein the cation comprises lithium.

25 Example 19. The mixture of any one of claims 1-18, further comprising a salt, wherein the salt provides at least a portion of the cation.

Example 20. The mixture of claim 19, wherein the salt comprises at least one of LiPF_6 , LiBF_4 , or LiClO_4 .

Example 21. The mixture of claim 19, further comprising a solvent, wherein the mediator and the salt are substantially soluble in the solvent.

5 Example 22. The mixture of claim 21, wherein the solvent comprises at least one aprotic solvent.

Example 23. The mixture of either claim 21 or 22, wherein the aprotic solvent comprises at least one of a carbonate, an ether, an acetate, or a ketone

10 Example 24. The mixture of claim 22, wherein the aprotic solvent comprises at least one of tetrahydrofuran, ethyl acetate, acetone, dimethylformamide, acetonitrile, dimethyl sulfoxide, or propylene carbonate.

Example 25. The mixture of claim 21, wherein the solvent comprises at least one protic solvent.

15 Example 26. The mixture of claim 25, wherein the protic solvent comprises at least one of water, an alcohol, or glycerin.

Example 27. The mixture any one of claims 21-26, wherein the mixture has an energy storage density greater than or equal to 300 Wh/L, when the non-liquid active material is in its second condition, and the mediator is in its second condition.

20 Example 28. The mixture of claim 1, wherein the cation comprises lithium and the first redox potential is greater than 2.8 V.

Example 29. The mixture of claim 1, wherein the cation comprises magnesium and the first redox potential is greater than 1.0 V.

Example 30. The mixture of claim 1, wherein the cation comprises aluminum and the first redox potential is greater than 2.0 V.

25 Example 31. The mixture of claim 1, wherein the cation comprises beryllium and the first redox potential is greater than 1.3 V.

30 Example 32. A method comprising transferring energy to a mixture by applying a voltage to the mixture, wherein: the mixture comprises a mediator, an active material, and a salt mixed within a solvent, the voltage transforms the mediator from a neutral condition to an oxidized condition, and the mediator in the oxidized condition oxidizes the active material,

thereby transforming the active material from a low energy condition to a high energy condition, and regenerating the mediator to its neutral condition.

Example 33. The method of claim 32, further comprising applying a load to the mixture, wherein the load transforms the active material from its high energy condition to its
5 low energy condition.

Example 34. A system comprising: a first flow battery positioned on a vehicle; and a second flow battery positioned external of the vehicle, wherein: the first flow battery is only operated in a charging mode, and the second flow battery is only operated in a discharging mode.

10 Example 35. The system of Example 34, wherein the first flow battery comprises a solid active cathode material.

Example 36. The system of Example 34, wherein the first flow battery and the second flow battery exchange a cathode mixture comprising an electrolyte and a mediator.

15 Example 37. The system of Example 34, wherein the first flow battery and the second flow battery exchange an anode mixture comprising an electrolyte and a solid active anode material such that the anode mixture is a slurry.

The foregoing discussion and examples have been presented for purposes of illustration and description. The foregoing is not intended to limit the aspects, embodiments, or configurations to the form or forms disclosed herein. In the foregoing Detailed
20 Description for example, various features of the aspects, embodiments, or configurations are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure. The features of the aspects, embodiments, or configurations, may be combined in alternate aspects, embodiments, or configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention
25 that the aspects, embodiments, or configurations require more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment, configuration, or aspect. While certain aspects of conventional technology have been discussed to facilitate disclosure of some embodiments of the present invention, the Applicants in no way disclaim these
30 technical aspects, and it is contemplated that the claimed invention may encompass one or more of the conventional technical aspects discussed herein. Thus, the following claims are

hereby incorporated into this Detailed Description, with each claim standing on its own as a separate aspect, embodiment, or configuration.

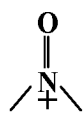
CLAIMS

What is claimed is:

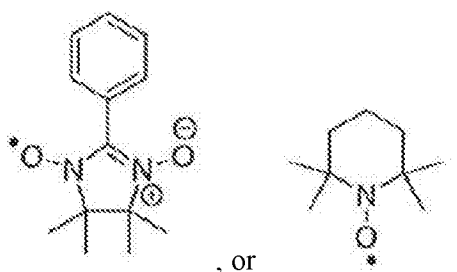
1. A mixture comprising:
 - a mediator having a first redox potential;
 - a non-liquid active material having a second redox potential that is less than the first redox potential; and
 - a cation, wherein:
 - the non-liquid active material has a first condition comprising a first oxidation state, where the cation is intercalated within the non-liquid active material,
 - the non-liquid active material has a second condition comprising a second oxidation state that is higher than the first oxidation state, where the non-liquid active material is substantially free of the cation,
 - the mediator has a first condition comprising a third oxidation state and a second condition comprising a fourth oxidation state that is higher than the third oxidation state,
 - the non-liquid active material is capable of being reversibly cycled between its first condition and its second condition, and
 - the mediator is capable of being reversibly cycled between its first condition and its second condition.
2. The mixture of claim 1, wherein the mediator comprises an organic radical group.
3. The mixture of either claim 1 or 2, wherein the organic radical group comprises a nitroxide group.
4. The mixture of any one of claims 1-3, wherein the mediator has a molecular weight less than about 10,000 g/mol.
5. The mixture of any one of claims 1-4, wherein the mediator comprises at least one of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, (1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine), a nitronyl nitroxide, a azephenylenyl, a perchlorophenylmethyl radical, tris(2,4,6-trichlorophenyl)methyl radical, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate), or poly[4-(nitronylnitroxyl)styrene].

6. The mixture of any one of claims 1-5, wherein, when in the first condition of the

mediator, the mediator comprises ; and

when in the second condition of the mediator, the mediator comprises .

7. The mixture of any one of claims 1-6, wherein the mediator includes a structure comprising at least one of



8. The mixture of any one of claims 1-7, wherein the non-liquid active material comprises at least one of a solid or a gel.
9. The mixture of any one of claims 1-8, wherein the non-liquid active material comprises a solid particulate.
10. The mixture of any one of claims 1-9, wherein the solid particulate has a particle size between 1 nanometer and 1000 micrometers.
11. The mixture of any one of claims 1-10, wherein the non-liquid active material comprises at least one of cobalt, nickel, manganese, aluminum, titanium, vanadium, or iron.
12. The mixture of any one of claims 1-11, wherein the non-liquid active material comprises at least one of an oxide or a phosphate.
13. The mixture of any one of claims 1-12, wherein the non-liquid active material comprises at least one of a cobalt oxide, a nickel cobalt oxide, a manganese cobalt oxide, or an iron phosphate.

14. The mixture of any one of claims 1-13, wherein the non-liquid active material comprises at least one of CoO_2 , FePO_4 , or $\text{Fe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$.
15. The mixture of any one of claims 1-14, wherein the cation comprises at least one of a Group 1, a Group 2, or a Group 13 element.
16. The mixture of any one of claims 1-15, wherein the cation comprises at least one of lithium, magnesium, aluminum, or beryllium.
17. The mixture of any one of claims 1-16, further comprising a salt, wherein the salt provides at least a portion of the cation.
18. The mixture of claim 17, wherein the salt comprises at least one of LiPF_6 , LiBF_4 , or LiClO_4 .
19. The mixture of claim 17, further comprising a solvent, wherein the mediator and the salt are substantially soluble in the solvent.
20. The mixture of claim 19, wherein the mixture has an energy storage density greater than or equal to 300 Wh/L, when the non-liquid active material is in its second condition, and the mediator is in its second condition.
21. A method comprising transferring energy to a mixture by applying a voltage to the mixture, wherein:
 - the mixture comprises a mediator, an active material, and a salt mixed within a solvent,
 - the voltage transforms the mediator from a neutral condition to an oxidized condition, and
 - the mediator in the oxidized condition oxidizes the active material, thereby transforming the active material from a low energy condition to a high energy condition, and regenerating the mediator to its neutral condition.
22. The method of claim 21, further comprising applying a load to the mixture, wherein the load transforms the active material from its high energy condition to its low energy condition.

23. A system comprising:
a first flow battery positioned on a vehicle; and
a second flow battery positioned external of the vehicle, wherein:
the first flow battery is only operated in a charging mode, and
the second flow battery is only operated in a discharging mode.
24. The system of claim 23, wherein the first flow battery comprises a solid active cathode material.
25. The system of claim 23, wherein the first flow battery and the second flow battery exchange a cathode mixture comprising an electrolyte and a mediator.
26. The system of claim 23, wherein the first flow battery and the second flow battery exchange an anode mixture comprising an electrolyte and a solid active anode material such that the anode mixture is a slurry.

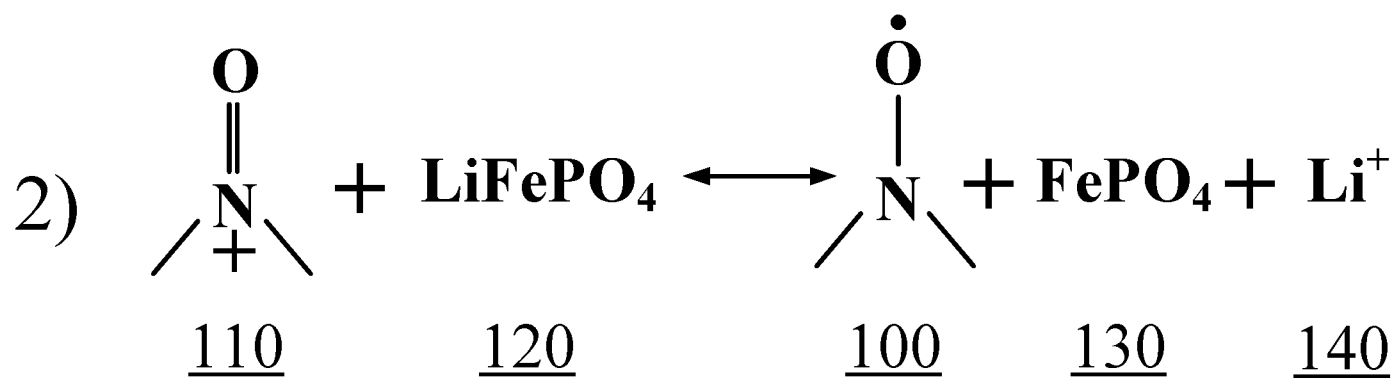
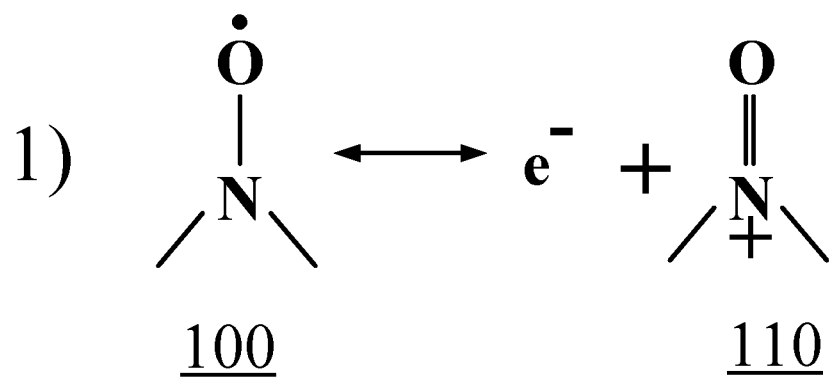


Figure 1

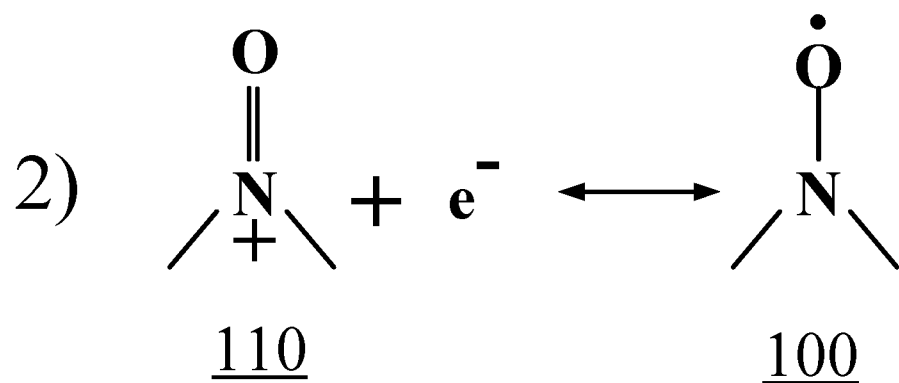
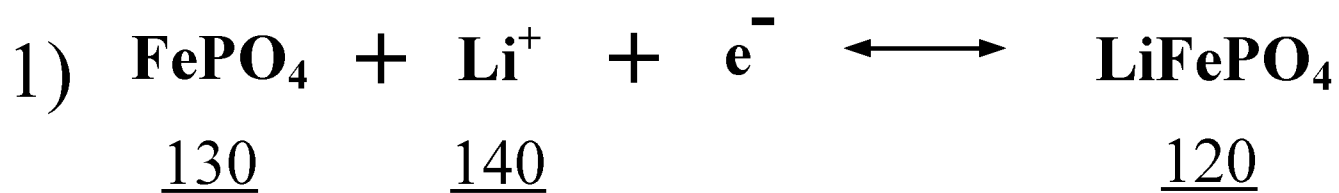


Figure 2

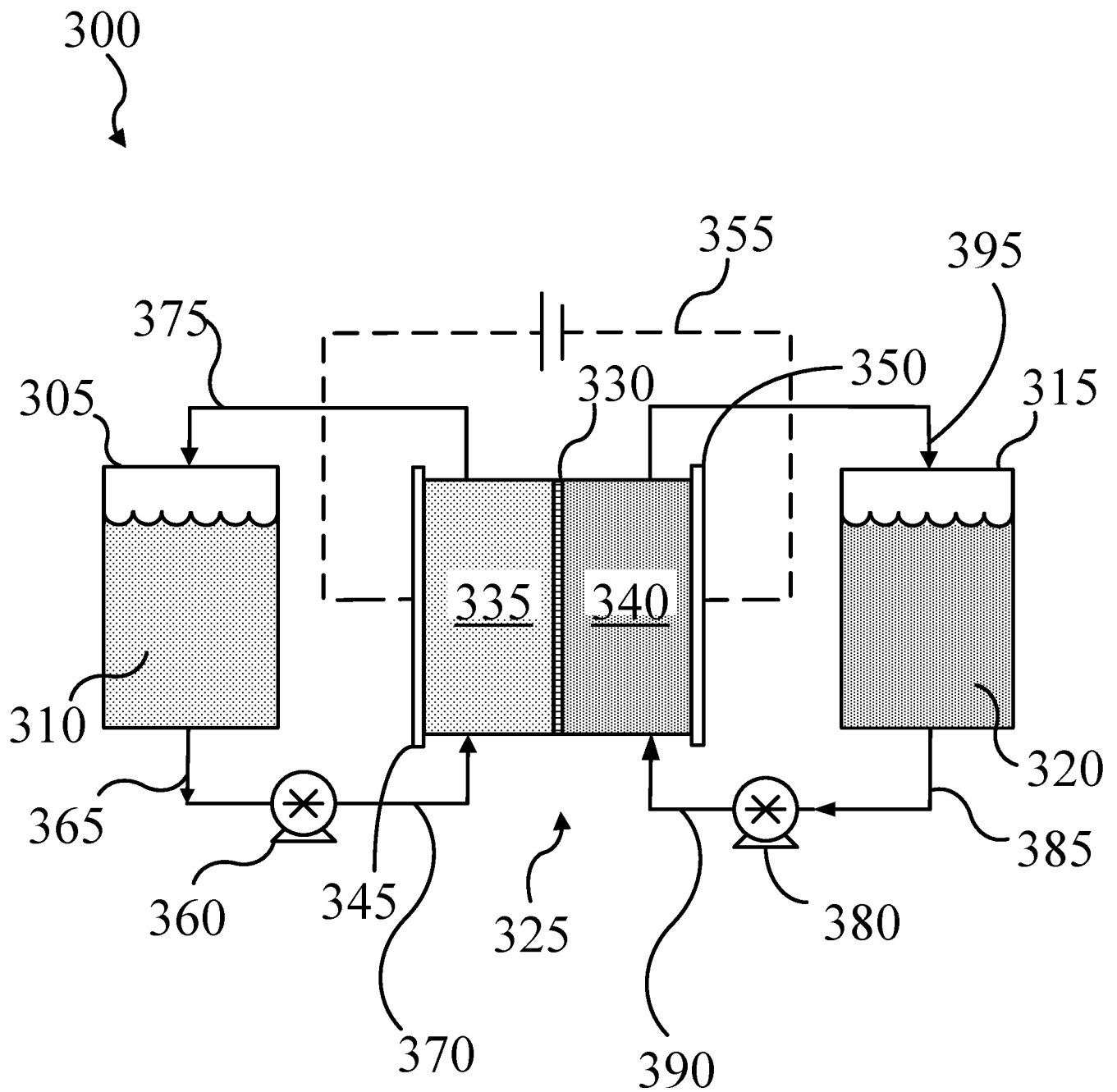


Figure 3

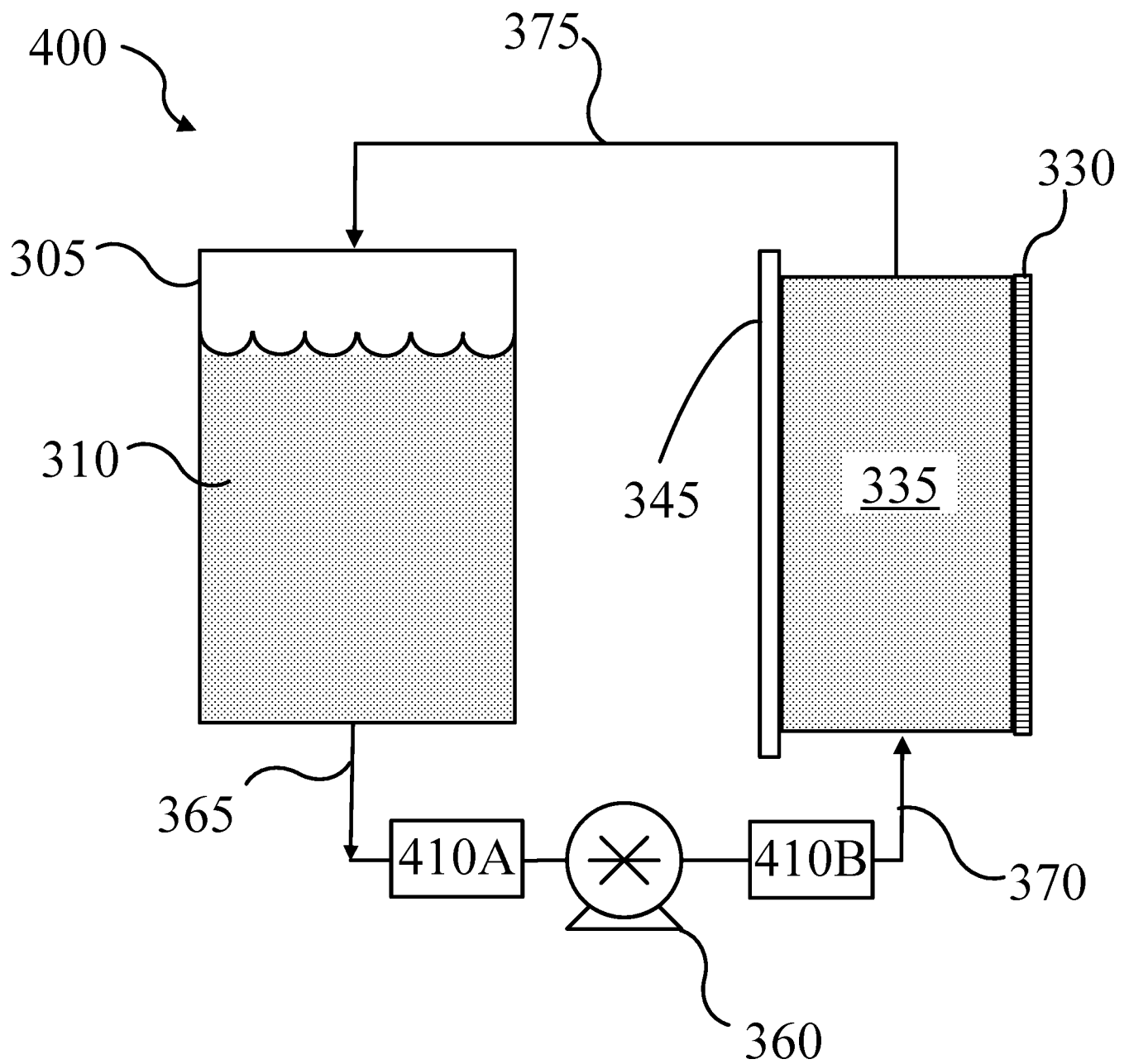


Figure 4

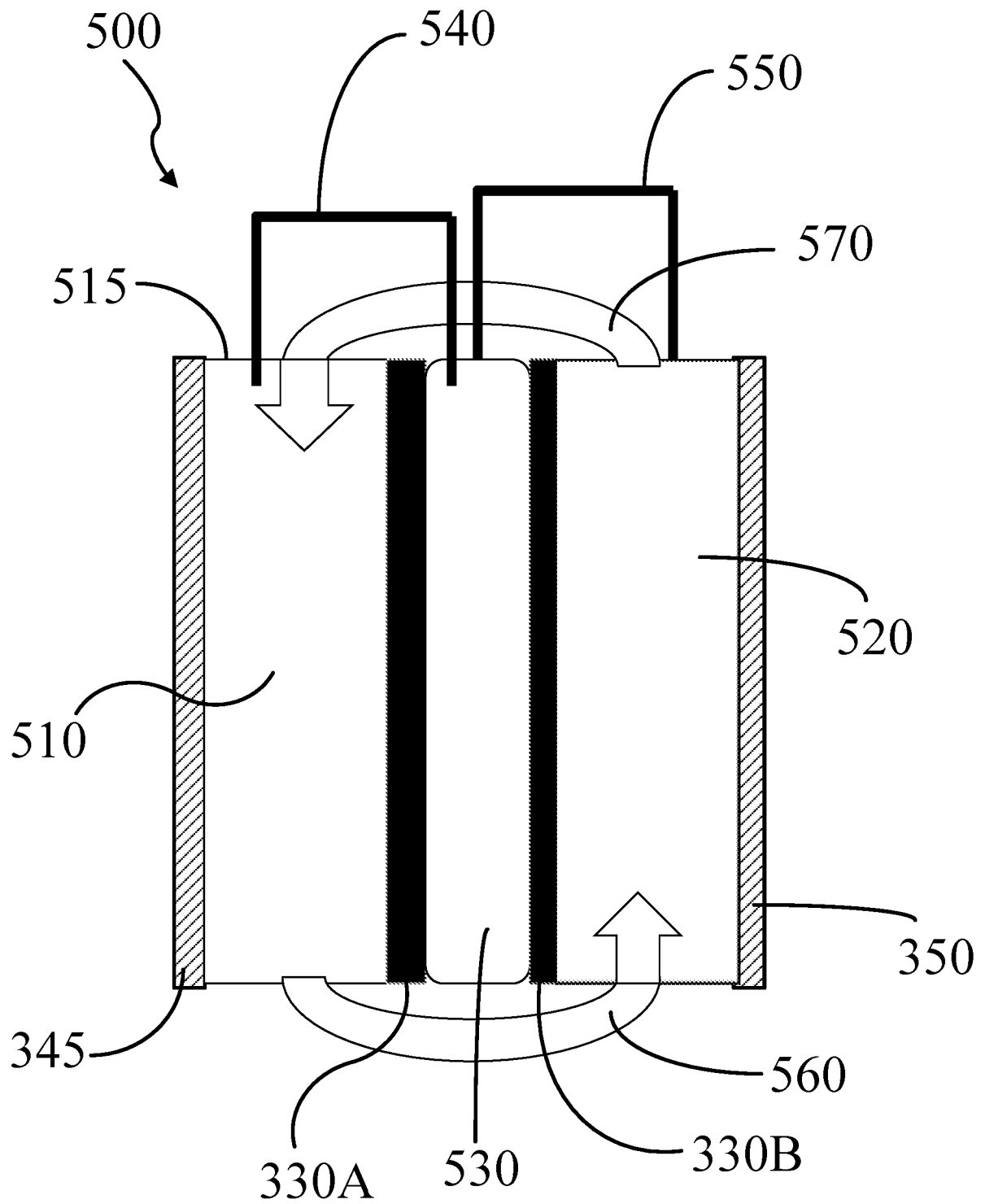


Figure 5

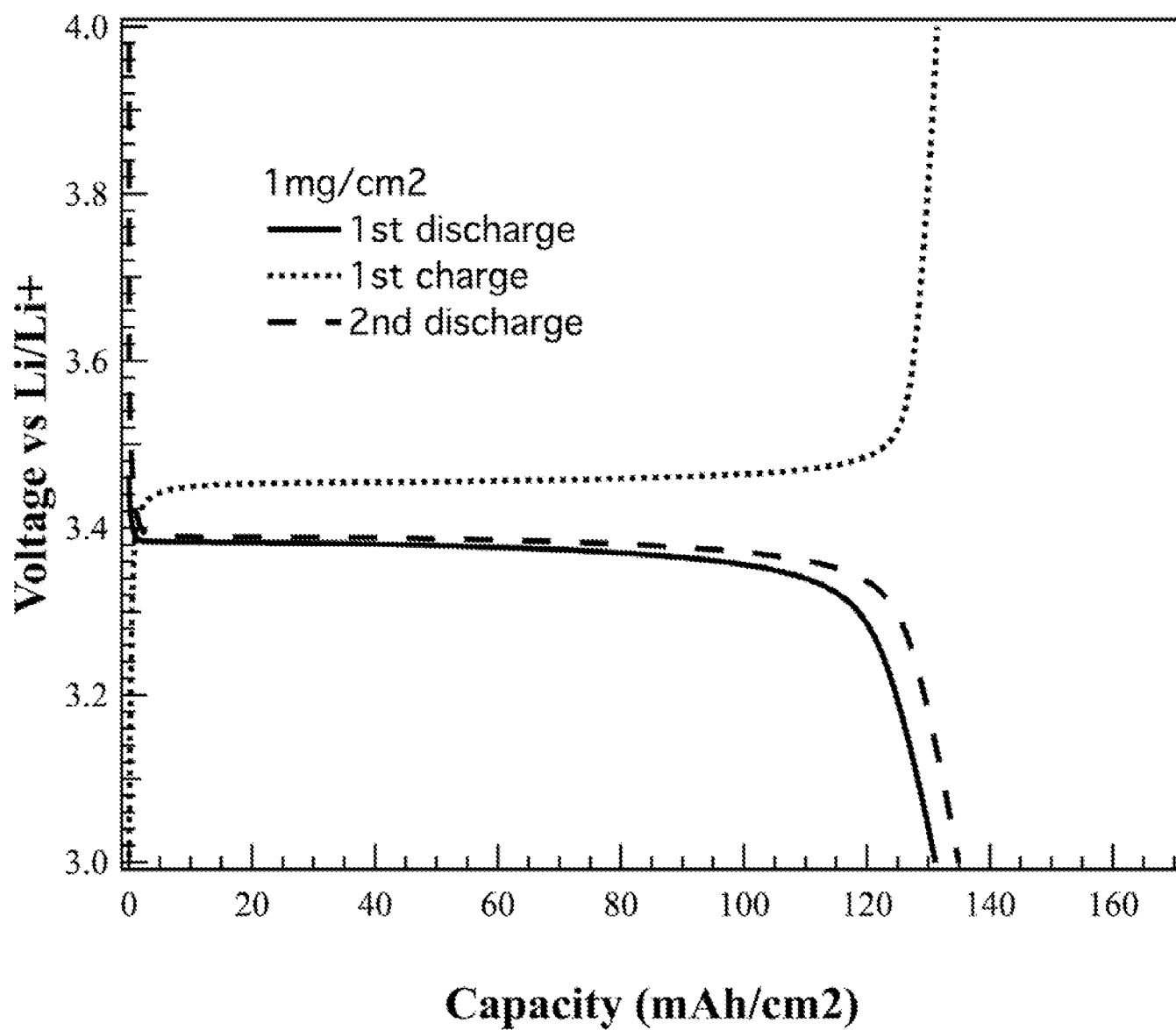


Figure 6

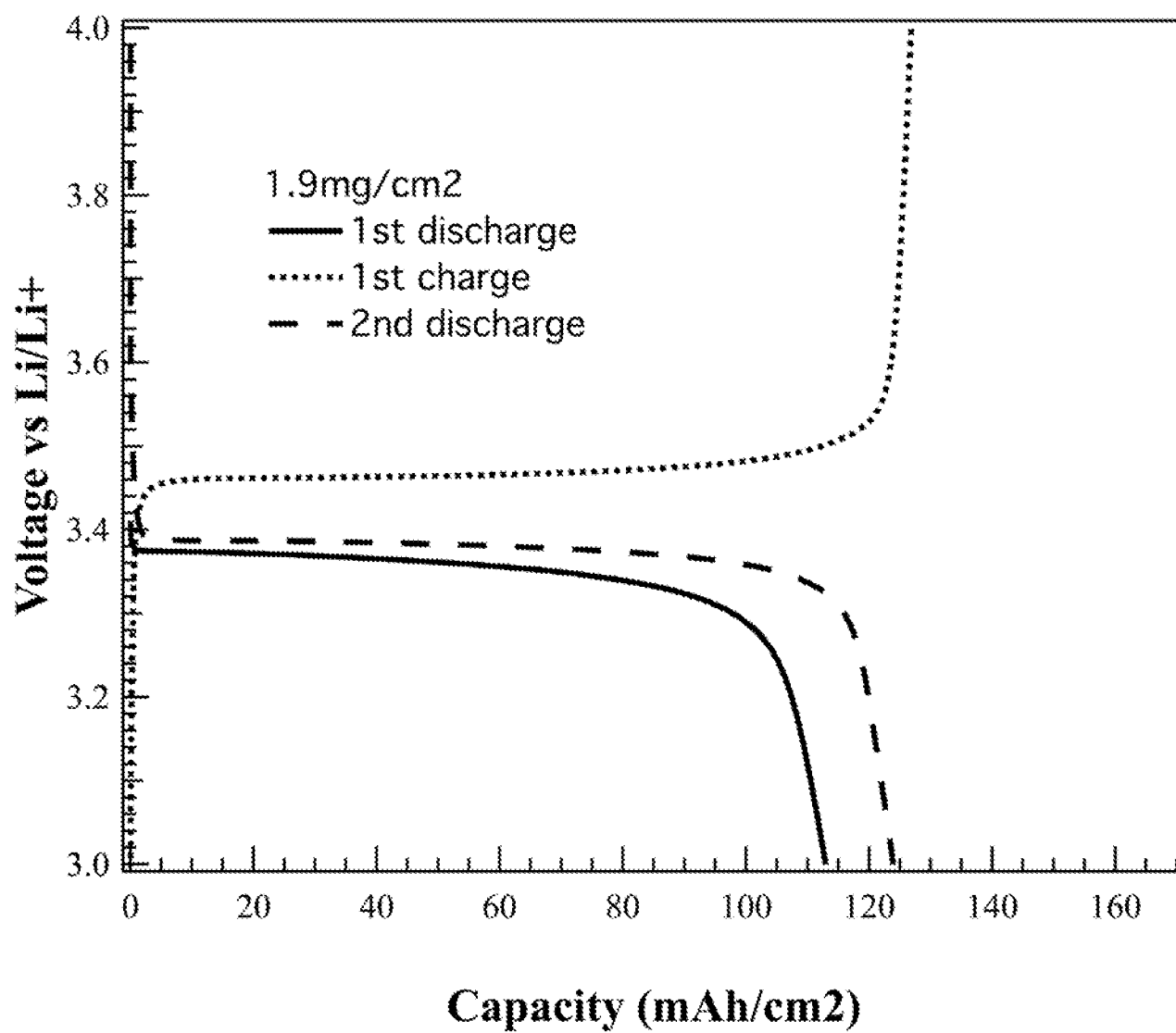


Figure 7

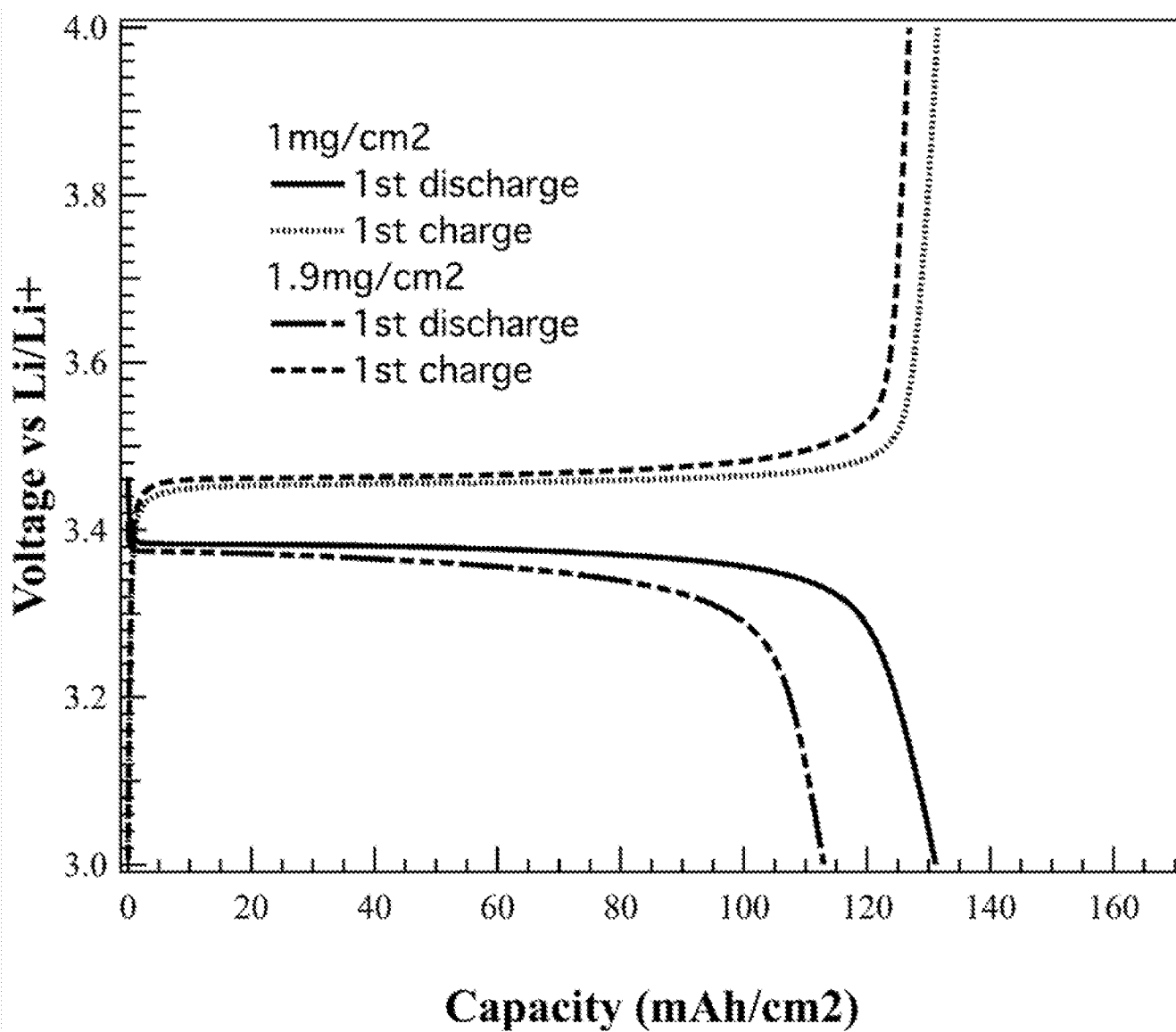


Figure 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/19992

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01G 11/58, H01G 11/26 (2017.01)

CPC - H01G 11/60, H01G 11/62, C07D 333/34, C09K 2211/1007, C09K 2211/1092, C09K 9/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

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

See Search History Document

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

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/0143805 A1 (HINTERMANN et al.) 10 June 2010 (10.06.2010), entire document, especially: para [0014]; para [0015]; para [0016]; para [0017]; para [0018]; para [0019]; para [0029], (I) a lithium salt; para [0031], (iii) formula (d1)-(d6); para [0032], G is nitroxide of indicated formulae; para [0064].	1-3
A	US 7,226,697 B2 (NAKAHARA et al.) 5 Jun 2007 (05.06.1007), entire document.	1-3
A	US 2015/0333551 A1 (ARONOV et al.) 19 November 2015 (19.11.2015), entire document.	1-3

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

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

24 April 2017

Date of mailing of the international search report

28 JUN 2017

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/19992

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-20
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:
--See attached extra sheet--

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

Remark on Protest

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

--Box III--

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-3, drawn mixture comprising: a mediator having a first redox potential; a non-liquid active material having a second redox potential that is less than the first redox potential; and a cation wherein: the non-liquid active material has a first condition comprising a first oxidation state, wherein the cation is intercalated within the non-liquid active material, the non-liquid active material has a second condition comprising a second oxidation state that is higher than the first oxidation state, where the non-liquid active material is substantially free of the cation, the mediator has a first condition comprising a third oxidation state and a second condition comprising a fourth oxidation state that is higher than the third oxidation state, the non-liquid active material is capable of being reversibly cycled between its first condition and its second condition, and the mediator is capable of being reversibly cycled between its first condition and its second condition.

Group II: Claims 21-22, drawn to a method comprising transferring energy to a mixture by applying a voltage to the mixture, wherein: the mixture comprises a mediator, an active material, and a salt mixed within a solvent, the voltage transforms the mediator from a neutral condition to an oxidized condition, And the mediator in the oxidized condition oxidizes the active material, thereby transforming the active material from a low energy condition to a high energy condition, and regenerating the mediator to its neutral condition

Group III: Claims 23-26, drawn to a system comprising: a first flow battery positioned on a vehicle; and a second flow battery positioned external of the vehicle, wherein: the first flow battery is only operated in a charging mode, and the second flow battery is only operated in a discharging mode.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group I requires a mixture comprising: a mediator having a first redox potential; a non-liquid active material having a second redox potential that is less than the first redox potential; and a cation wherein: the non-liquid active material has a first condition comprising a first oxidation state, wherein the cation is intercalated within the non-liquid active material, the non-liquid active material has a second condition comprising a second oxidation state that is higher than the first oxidation state, where the non-liquid active material is substantially free of the cation, the mediator has a first condition comprising a third oxidation state and a second condition comprising a fourth oxidation state that is higher than the third oxidation state, the non-liquid active material is capable of being reversibly cycled between its first condition and its second condition, and the mediator is capable of being reversibly cycled between its first condition and its second condition, not required by groups II-III

Group II requires a method comprising transferring energy to a mixture by applying a voltage to the mixture, wherein: the mixture comprises a mediator, an active material, and a salt mixed within a solvent, the voltage transforms the mediator from a neutral condition to an oxidized condition, And the mediator in the oxidized condition oxidizes the active material, thereby transforming the active material from a low energy condition to a high energy condition, and regenerating the mediator to its neutral condition, not required by groups I and III

Group III requires a system comprising: a first flow battery positioned on a vehicle; and a second flow battery positioned external of the vehicle, wherein: the first flow battery is only operated in a charging mode, and the second flow battery is only operated in a discharging mode, not required by groups I-II

Shared Common Features

The only feature shared by Groups I and II that would otherwise unify the groups is a mediator having a redox potential; and mediator in the oxidized condition oxidizes the active material. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is anticipated by US 2010/0143805 A1 to Hintermann (hereinafter 'Hintermann') which discloses a mixture comprising: a mediator (para [0031], (iii) formula (d1)-(d6); see also para [0032], G is nitroxide of indicated formulae) having a first redox potential (para [0015] The term 'molecular redox shuttle for redox targeting' or 'molecular redox shuttle' refers to an electrochemically reversible species. During charging, the molecular redox shuttle (S) for redox targeting is oxidized at the current collector. The oxidized species (S+), delivers the positive charge to the corresponding particles of the active electrode material, for example LiFePO₄, by bulk diffusion and are reduced back to S. By contrast, during the discharging process, S+ is reduced at the current collector to S, Which in turn delivers electrons to the oxidized active electrode material); a non-liquid active material having a second redox potential that is less than the first redox potential (para [0015] The term 'molecular redox shuttle for redox targeting' or 'molecular redox shuttle' refers to an electrochemically reversible species. During charging, the molecular redox shuttle (S) for redox targeting is oxidized at the current collector. The oxidized species (S+), delivers the positive charge to the corresponding particles of the active electrode material, for example LiFePO₄, by bulk diffusion and are reduced back to S. By contrast, during the discharging process, S+ is reduced at the current collector to S, Which in turn delivers electrons to the oxidized active electrode material).

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I-III therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.