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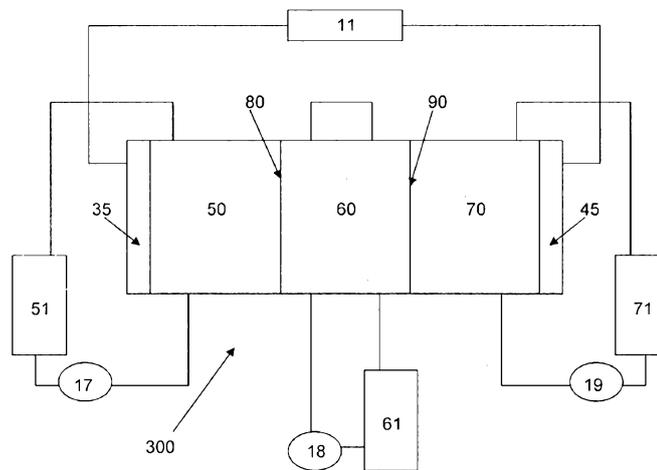
(57) Abstract: A novel design has been invented for redox flow batteries. Different from the single-membrane, double-electrolyte redox flow battery as a basic structure, the design of the present invention involves multiple-membrane (at least one cation exchange membrane and at least one anion exchange membrane), multiple-electrolyte (one electrolyte in contact with the negative electrode, one electrolyte in contact with the positive electrode, and at least one electrolyte disposed between the two membranes) as the basic characteristic, such as a double-membrane, triple electrolyte (DMTE) configuration or a triple-membrane, quadruple electrolyte (TMQE) configuration. The cation exchange membrane is used to separate the negative or positive electrolyte and the middle electrolyte, and the anion exchange membrane is used to separate the middle electrolyte and the positive or negative electrolyte. This particular design physically isolates, but ionically connects, the negative electrolyte and positive electrolyte. The physical isolation offers a great freedom in choosing redox pairs, including anion-cation hybrid redox pairs, in the negative electrolyte and positive electrolyte, making high voltage of redox flow batteries possible. The ionic conduction not only makes the design functional, but also drastically reduces the overall ionic crossover between negative electrolyte and positive one, leading to high columbic efficiency.

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MULTIPLE-MEMBRANE MULTIPLE-ELECTROLYTE
REDOX FLOW BATTERY DESIGN

GOVERNMENT SUPPORT

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority from United States Provisional Application No. 61/660,182, filed June 15, 2012 and incorporated herein by reference in its entirety for all purposes.

FIELD OF THE INVENTION

The invention pertains to redox flow batteries (RFB) that have multiple-membranes (for example, at least two membranes, such as one cation exchange membrane and one anion exchange membrane) and a multiple-electrolyte (for example, at least three electrolytes, such as one electrolyte in contact with a negative electrode, one electrolyte in contact with a positive electrode, and at least one electrolyte disposed between the two membranes) as the basic characteristic.

BACKGROUND

As an electrochemical cell, a redox flow battery (RFB) is a type of rechargeable battery that stores electrical energy, typically in two soluble redox pairs contained in external electrolyte tanks. An ion-selective membrane (either cation exchange membrane, CEM, or anion exchange membrane, AEM) is used to physically separate, but ionically connect, the two electrolytes that dissolve the two redox pairs. The scale of external electrolyte stored can be sized in accordance with application requirements. When n eeded, liquid electrolytes are pumped from storage tanks to flow-through electrodes where chemical energy is converted to electrical energy (discharge) or *vice versa* (charge). Different from other conventional battery systems, RFBs store electrical energy in the flowing electrolytes. Therefore, the energy capacity and the power rating are fundamentally decoupled: The energy capacity is determined by concentration and volume of electrolytes, while the power rating is determined by the size and number of cells in stack. This unique feature, combined with its long cycle-life, low capital-cost, scalability, and independence from geographical/geological limitations that are faced by pumped hydro and compressed air technologies, makes RFB one of the most intrinsically attractive technologies in electrical energy storage, especially in the field of renewable (e.g., wind or solar) electricity generation where the intrinsic intermittency has to be dealt with.

Since the first concept of RFB was put forward about 40 years ago (in 1974), significant progress has been made and some RFB systems, e.g., the all vanadium RFB (AV-RFB), have already been commercialized. However, RFBs have not reached broad market penetration yet because many challenging problems remain unsolved. For example, the generally low energy and power density of RFB have been identified to be main drawbacks when compared with other battery systems, which means more electrolyte/electrode materials are needed when certain energy capacity/power rating is required, negatively impacting their cost-effectiveness. Attempts have been made to increase the solubility of active species by choosing alternative redox pairs or using different electrolytes, which can theoretically increase the energy density, but these efforts do not improve the power density. On the other hand, efforts have been made to improve electrode performance by using better electrode designs or utilizing more active catalysts, which can increase the power density, but not the energy density. The ideal and simple solution would be the increase of RFB's cell voltage, which could increase the energy density and power density simultaneously.

A prior art RFB system 100 is shown in Figure 1. Negative electrolyte 30 flows through negative electrode (anode) 31 from negative electrolyte source 20 via pump 15. Positive electrolyte 40 flows through positive electrode (cathode) 41 from positive electrolyte source 25 via pump 16. Positive electrode 40 and negative electrode 30 are separated by a single ion selective membrane 28. The RFB 100 may be connected to a grid input/output processor 10.

The cell voltage is simply determined by the two redox pairs used, and often the cation-based redox pairs (e.g., Co^{3+}/Co^{2+} redox pair with +1.953 V standard electrode potential and Ce^{4+}/Ce^{3+} one with +1.743 V, all the quoted potential values here and hereinafter calculated based on standard thermodynamic conditions) have more positive electrode potentials (ideally for the positive electrode of RFB) and the anion-based ones (e.g., $Al(OH)_4^-/Al$ with −2.337 V and $Zn(OH)_4^{2-}/Zn$ with −1.216 V) have more negative electrode potentials (ideally for the negative electrode). The use of a single ion-selective membrane, either a cation exchange membrane (CEM) or anion exchange membrane (AEM), in current RFB systems theoretically requires the same ionic type of redox pairs in both positive and negative sides: either all cation-based redox pairs (when AEM used) or all anion-based ones (when CEM used), fundamentally limiting their cell voltages. For example, the earliest RFB system, i.e., the iron-chromium RFB system (Fe/Cr-RFB, $[(Fe^{3+}/Fe^{2+})/(Cr^{3+}/Cr^{2+})]$ with +1.18 V standard cell voltage) and the currently most popular RFB, i.e., the AV-RFB system ($[(VO_2^+/VO^{2+})/(V^{3+}/V^{2+})]$ with +1.26 V) both belong to the all-cation-based RFB

systems. The polysulphide-bromine RFB system (S/Br-RFB, $[(S_4^{2-}/S_2^{2-})/(Br_3^-/Br^-)]$ with +1.36 V) is a typical all-anion-based RFB. Besides, the single ion-selective membrane also requires the same or similar (e.g., having the same cation but different anions when an AEM used, or having the same anion but different cations when a CEM used) supporting (or background) electrolyte in positive side and negative one, which sometimes limits the choices of redox pairs and further narrows the available range of cell voltages. For example, although the zinc-cerium RFB system (Zn/Ce-RFB, $[(Zn^{2+}/Zn)/(Ce^{4+}/Ce^{3+})]$) can offer as high as 2.50 V standard cell voltage (the highest number reported among all known aqueous RFB systems), it suffers a great hydrogen evolution problem in negative side (Zn^{2+}/Zn). The reason is that the acidic supporting electrolyte used (in both sides) creates a huge over-potential (760 mV) for hydrogen evolution reaction (0 V standard electrode potential of H^+/H_2 at pH 0 vs. and -0.760 V standard electrode potential of Zn^{2+}/Zn).

In addition, the use of single ion-selective membrane makes the RFB systems suffer from an irreversible counter-ion crossover that is another challenging problem, because all ion-selective membranes are not perfect. They allow a very low, but measurable, rate of permeation of counter-ions through them (typically, 1% anion crossover for CEMs and 1%−5% cation crossover for AEMs). When the counter-ions cross over the membrane, they will immediately react with the redox pairs in the other side of electrolyte (so-called self-discharging) and never come back, resulting a loss in Coulombic efficiency, permanently reduction of energy capacity, and contamination of two electrolytes which will greatly influence the performance of either side.

Thus, a suitable alternative to a single ion-selective membrane RFB system is needed.

BRIEF SUMMARY OF THE INVENTION

In an aspect, the invention provides a novel redox flow battery design, e.g., a multiple-membrane, multiple-electrolyte (MMME) redox flow based battery design, comprising a first membrane; a second membrane; a first electrolyte disposed between the first membrane and the second membrane; a second electrolyte in contact with the first membrane and a first electrode; and a third electrolyte in contact with the second membrane and a second electrode; and wherein the first electrolyte and second electrolyte are different in terms of at least one species of anion, and the first electrolyte and third electrolyte are different in terms of at least one species of cation; and wherein the first electrode is a negative (or a positive) electrode and the second electrode is a positive (or a negative) electrode; and wherein the first membrane

and/or the second membrane is selected from the group consisting of a cation exchange membrane and an anion exchange membrane.

In an aspect, the invention provides a novel redox flow battery design, e.g., a multiple-membrane, multiple-electrolyte (MMME) based battery design, comprising a first membrane; a second membrane; a first electrolyte disposed between the first membrane and the second membrane; a second electrolyte in contact with the first membrane and a first electrode; a third electrolyte in contact with the second membrane and a second electrode; wherein the battery further comprises a third membrane disposed between the first membrane and the second membrane and a fourth electrolyte disposed between the first membrane and the second membrane; wherein the third membrane separates the fourth electrolyte from the first electrolyte; and wherein the first electrolyte and second electrolyte are different in terms of at least one species of anion, and the first electrolyte and third or fourth electrolyte are different in terms of at least one species of cation; and wherein the first electrode is a negative electrode and the second electrode is a positive electrode; and wherein the first and second membranes are anion-exchange membranes and the third membrane is a cation exchange membrane or wherein the first and second membranes are cation-exchange membranes and the third membrane is an anion-exchange membrane.

In another aspect, the second electrolyte comprises an anion-based redox pair, such as an anion-redox pair selected from the group consisting of an $Al(OH)_4^-/Al$ redox pair, a $Zn(OH)_4^{2-}/Zn$ redox pair, an S_4^{2-}/S_2^{2-} redox pair and a $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ redox pair. In another aspect, the third electrolyte comprises a cation-based redox pair, such as a cation-based redox pair selected from the group consisting of a Co^{3+}/Co^{2+} redox pair, a Fe^{3+}/Fe^{2+} redox pair and a Ce^{4+}/Ce^{3+} redox pair. In another aspect, at least one of the second electrolyte and third electrolyte comprises an anion-based redox pair, a cation-based redox pair or a cation-anion hybrid redox pair. In another aspect, one of the first, second, third and/or fourth electrolytes comprises at least one of: cations based on hydronium, sodium, magnesium, potassium or calcium; or anions based on hydroxide, perchlorate, sulfate, phosphate, acetate, chloride, bromide or carbonate.

In yet another aspect, the invention provides a method of making a redox flow battery comprising: partially surrounding a first electrolyte with a first membrane and a second membrane; b) partially surrounding a second electrolyte with the first membrane and a first electrode; and partially surrounding a third electrolyte with the second membrane and a second electrode; wherein the first membrane and/or the second membrane is selected from the group consisting of a cation exchange membrane and an anion exchange membrane.

In yet another aspect, the invention provides a method of making a redox flow battery comprising: partially surrounding a first electrolyte with a first membrane and a third membrane; partially surrounding a fourth electrolyte with the third membrane and a second membrane; partially surrounding a second electrolyte with the first membrane and a first electrode; and partially surrounding a third electrolyte with the second membrane and a second electrode; wherein the first and second membranes are anion-exchange membranes and the third membrane is a cation exchange membrane or the first and second membranes are cation-exchange membranes and the third membrane is an anion exchange membrane.

In yet a further aspect, the invention provides a redox flow battery made by these methods.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a conventional single-membrane double-electrolyte RFB.

Figure 2 shows an illustration of a multiple-membrane multiple-electrolyte concept.

Figure 3 shows a version of a multiple-membrane multiple-electrolyte RFB.

Figure 4 shows an illustration of another multiple-membrane multiple-electrolyte concept.

Figure 5 shows a version of another multiple-membrane multiple-electrolyte RFB.

Figure 6 shows a standard electrode potential for select redox pairs and cell voltage for different RFBs.

Figure 7 shows the open circuit voltage of an Al/Co-MMME-RFB.

Figure 8 shows the charge and discharge curves of an Al/Co-MMME-RFB.

Figure 9 shows the open circuit voltage of a Zn/Ce-MMME-RFB.

Figure 10 shows the charge and discharge curves of a Zn/Ce-MMME-RFB.

Figure 11 shows a continuous charge-discharge test of a Zn/Ce-DMTE-RFB for 10 cycles.

Figure 12 shows the efficiency calculation of a Zn/Ce-DMTE-RFB for each cycle.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described in detail with reference to a few preferred embodiments thereof. In the following description, numerous specific details

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are set forth in order to provide a thorough understanding of the present invention. It will be apparent, however, to one skilled in the art, that the present invention may be practiced without some or all of these specific details. In other instances, well known process steps and/or structures have not been described in detail in order to not 5 unnecessarily obscure the present invention.

The multiple-membrane, multiple-electrolyte (MMME) RFB systems described herein can dramatically increase cell voltages and decrease ionic crossover simultaneously by involvement of a multiple-membrane arrangement (at least one piece of CEM and at least one piece of AEM) that divides the redox flow battery cell into 10 multiple compartments filled with multiple-electrolyte (one in contact with a negative electrode, one in contact with a positive electrode, and at least one in between the two membranes). By introducing more than one ion-selective membrane, the two electrolytes in the negative side and the positive side can be substantially separated but still remain ionically conductive by the electrolyte(s) positioned between the 15 membranes. This particular design favorably brings great freedom in selecting redox pairs as well as their supporting electrolytes for both the negative side and the positive side, making high cell voltage RFBs possible. Besides providing the function of ionic conduction, the middle electrolyte(s) in between also serves as a great "buffer" that can significantly reduce the overall counter-ion crossover between the negative side 20 and the positive side, fundamentally solving the electrolyte contamination problem and providing great convenience for electrolyte separation and rebalance.

Specifically, the multiple-membrane multiple-electrolyte RFB design described herein allows for a strongly basic negative electrolyte (high pH, e.g. at least 8, at least 9, at least 10 or higher) and a strongly acidic positive electrolyte (low pH, e.g., not 25 more than 6, not more than 5, not more than 4 or lower) to be used at the same time in the same redox flow battery, where a neutral middle electrolyte is in between. As a result, very negative redox pairs that are usually only stable in basic electrolytes and very positive ones that are usually only stable in acidic electrolytes can be simultaneously incorporated into the MMME-RFB, providing very high cell voltage and 30 very low ionic crossover at the same time. Not only can the cell voltage be increased, the side reaction of hydrogen evolution in negative electrode can also be suppressed, as the standard electrode potential for hydrogen evolution reaction is very negatively shifted in a basic electrolyte in comparison with an acidic electrolyte (e.g., from 0 V at pH = 0 to −0.828 V at pH = 14), thermodynamically extending the operational window 35 of cell voltage. Such a low counter-ionic crossover design overcomes the very

challenging electrolyte contamination problems that hamper the commercial use of most of the current batteries.

Figure 2 shows a MMME-RFB system 200 comprising a double-membrane and triple electrolyte (DMTE), wherein first electrolyte 60 may be partially surrounded by a second electrolyte 50 and a third electrolyte 70, wherein first electrolyte 60 may be separated from second electrolyte 50 by a f irst membrane 80, such as a cation exchange membrane (CEM) 80, and wherein first electrolyte 60 may be separated from third electrolyte 70 by a second membrane 90, such as an anion exchange membrane (AEM) 90. Second electrolyte 50 may be partially surrounded by a first electrode 35, such as a negative electrode (anode) 35. Third electrolyte 70 may be partially surrounded by a second electrode 45, such as a positive electrode (cathode) 45.

Figure 3 shows a DMTE-RFB based battery 300 wherein, and similar to Figure 2, first electrolyte 60 may be partially surrounded by a second electrolyte 50 and a third electrolyte 70, wherein first electrolyte 60 may be separated from second electrolyte 50 by a first membrane 80, such as a cation exchange membrane (CEM) 80, and wherein first electrolyte 60 may be separated from third electrolyte 70 by a second membrane 90, such as an anion exchange membrane (AEM) 90. Second electrolyte 50 may be partially surrounded by a first electrode 35, such as a negative electrode 35. Third electrolyte 70 may be partially surrounded by a second electrode 45, such as a positive electrode 45. Second electrolyte 50 is flowed from second electrolyte source 51 via pump 17. Third electrolyte 70 is flowed from third electrolyte source 71 via pump 19. First electrolyte 60 is flowed from first electrolyte source 61 via pump 18. DMTE based redox flow battery 300 may be connected to a grid input/output processor 11.

It will be understood to those skilled in the art that elements 35 and 45 are referred as electrodes, but they may also include current collectors (not shown). The current collectors may be the same or different material as the electrodes. It will be understood to those skilled in the art that electrodes/current collectors 35, 45 may have high specific surface area (e.g., be highly porous).

Figure 4 shows a MMME-RFB system 400 comprising a triple-membrane and quadruple electrolyte (TMQE), wherein first electrolyte 203 may be partially surrounded by a second electrolyte 201 and a fourth electrolyte 205, wherein fourth electrolyte 205 may be partially surrounded by first electrolyte 203 and a third electrolyte 207, wherein second electrolyte 201 may be partially surrounded by first electrolyte 203 and a first electrode 235, wherein third electrolyte 207 may be partially surrounded by fourth electrolyte 205 and a second electrode 245, wherein first electrolyte 203 may be separated from second electrolyte 201 and fourth electrolyte 205 by a first membrane

220 and a third membrane 230, respectively, wherein fourth electrolyte 205 may be separated from first electrolyte 203 and third electrolyte 207 by a third membrane 230 and a second membrane 240, respectively. Membranes 220, 240 may be anion-exchange membranes and membrane 230 may be a cation exchange membrane or
5   membranes 220, 240 may be cation-exchange membranes and membrane 230 may be an anion-exchange membrane.

Figure 5 shows a TMQE-RFB 500 wherein, and similar to Figure 4, wherein first electrolyte 203 may be partially surrounded by a second electrolyte 201 and a fourth electrolyte 205, wherein fourth electrolyte 205 may be partially surrounded by first
10   electrolyte 203 and a third electrolyte 207, wherein second electrolyte 201 may be partially surrounded by first electrolyte 203 and a first electrode 235, wherein third electrolyte 207 may be partially surrounded by fourth electrolyte 205 and a second electrode 245, wherein first electrolyte 203 may be separated from second electrolyte 201 and fourth electrolyte 205 by a first membrane 220 and a third membrane 230,
15   respectively, wherein fourth electrolyte 205 may be separated from first electrolyte 203 and third electrolyte 207 by a third membrane 230 and a second membrane 240, respectively. Second electrolyte 201 is flowed from second electrolyte source 211 via pump 41. Third electrolyte 207 is flowed from third electrolyte source 217 via pump 44. First electrolyte 203 is flowed from first electrolyte source 213 via pump 42. Fourth
20   electrolyte 205 is flowed from forth electrolyte source 215 via pump 43. TMQE based battery 500 may be connected to a grid input/output processor 12. Similar variations of the electrode and current collector materials and configurations described above with respect to Figure 3 are also applicable to the those of Figure 5.

Adding a third ion exchange membrane can address challenging redox pair
25   isolation problems presented by two anion-cation hybrid pairs. For example, when membranes 220, 240 are anion-exchange membranes and membrane 230 is a cation exchange membrane, the two anion-exchange membranes can block the electro-active cations but not the electro-active anion of the negative and positive hybrid pairs. However, the crossed electro-active anions will be stopped by the cation exchange
30   membrane between the two anion-exchange membranes. A configuration wherein membranes 220, 240 are cation-exchange membranes and membrane 230 is an anion exchange membrane can also isolate two hybrid pairs.

Besides providing the function of electrolyte continuity and serving as an ion cross-over buffer, the middle electrolyte(s) in an MMME-RFB system provides another
35   significant benefit for RFBs based on an anion/anion redox pair vs. a cation/cation redox pair, which is the cleaning of crossed-over ions which may contaminate the

electrolytes. Low level crossed-over ions (e.g., about 100 ppm) may be removed from the contaminated electrolytes by refreshing the middle electrolyte(s) because the crossed-over ions will rapidly diffuse back to the fresh middle electrolyte(s) under the established ion concentration difference. Therefore, the use of middle electrolyte(s)

5   offers an effective to efficiently clean contaminated cells, thereby extending the cell lifetime.

First, second, third and/or fourth electrolytes 50, 60, 70, 201, 203, 205, 207 are not particularly limited and may comprise any suitable electrolyte or salt, such as those based on cations of hydronium, sodium, magnesium, potassium or calcium, or anions

10   based on hydroxide, perchlorate, sulfate, phosphate, acetate, chloride, bromide or carbonate. First and second electrodes 35, 45, 235, 245 are not particularly limited and may comprise any suitable electrode material, such as Al, Zn, Cu, Cd, Pb and C.
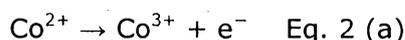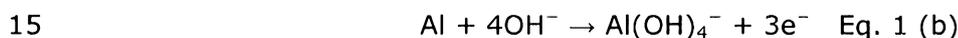
The MMME-RFB systems described herein have great advantages over conventional single-membrane, double-electrolyte batteries and offers high OCV, low

15   ionic crossover, and suppressed hydrogen evolution. The materials used to construct the MMME-RFB systems described herein are not particularly limited and may be a myriad of materials, for example, any materials selected from conventional or otherwise known materials used for similar purposes in the energy arts. Such materials include, but are not limited to, cation exchange membranes, anion exchange

20   membranes, electrolyte solutes and solvents, compounds capable of providing the desired redox pairs, acids, bases, negative electrodes, positive electrodes, and the like. The MMME-RFB systems described herein have a wide range of applications, especially for high voltage and low ionic crossover batteries.

For example, an attractive candidate for a RFB redox flow battery system is an

25   aluminum-cobalt MMME-RFB system (e.g., Al/Co-MMME-RFB), configured as [(Al/Al(OH)$_4^-$)/(Co^{3+}/Co^{2+})]. When compared to Figures 2 or 3, the Al portion of the Al/Co-MMME-RFB is comprised in second electrolyte 50 and the Co portion of the Al/Co-MMME-RFB is comprised in third electrolyte 70. When compared to Figures 4 or 5, the Al portion of the Al/Co-MMME-RFB is comprised in second electrolyte 201 and the Co

30   portion of the Al/Co-MMME-RFB is comprised in third electrolyte 207.

The Al/Co-MMME-RFB system offers a very high cell voltage (4.29 V standard cell voltage), as it successfully combines the very negative redox pair of Al/Al(OH)$_4^-$ (−2.337 V standard electrode potential) in base and the very positive redox pair of Co^{3+}/Co^{2+} (+1.953 V standard electrode potential) in acid. Such a high standard cell

35   voltage (4.29 V) is believed to be the highest one reported among all known RFB systems, which value is 1.7 times that of Zn/Ce-RFB systems (2.50 V), 3.2 times that

of Polysulfide-bromide S/Br-RFB systems (1.36 V), 3.4 times that of All-Vanadium RFB systems (1.26 V), and 3.6 times that of Iron-Chromium Fe/Cr-RFB systems (1.18 V), as shown in Figure 6. The very high standard cell voltage of the Al/Co-MMME-RFB system is even higher than that of lithium ion batteries (around 3.5 V), suggesting a

5   great potential of the design to rival other redox flow battery technologies.

    The test of open circuit voltage (OCV) for the Al/Co-MMME-RFB system is shown in Figure 7. As can be seen, a high initial OCV (3.54 V) and a stable OCV (3.28 V) after 20 min is realized. Considering the very sluggish kinetics observed for the Co^{3+}/Co^{2+} redox pair previously and the completely non-optimized electrodes used, these OCV

10   data are believed to be fairly consistent with the standard cell voltage (4.29 V). Additionally, the Al/Co-MMME-RFB system is functional, as shown by the charge/discharge curves of Figure 8. The expected discharge reactions and charge reactions are shown in Eq. 1 and Eq. 2, respectively.

$$Co^{3+} + e^- \rightarrow Co^{2+} \quad \text{Eq. 1 (a)}$$

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$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^- \quad \text{Eq. 1 (b)}$$

$$Co^{2+} \rightarrow Co^{3+} + e^- \quad \text{Eq. 2 (a)}$$

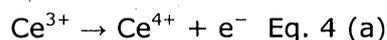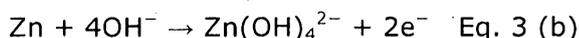$$Al(OH)_4^- + 3e^- \rightarrow Al + 4OH^- \quad \text{Eq. 2 (b)}$$

    For the discharge process (lower curve of Figure 8), the cell voltage slightly and smoothly decreases from the initial 3.11 V to 2.84 V for 10 min of discharge. An even

20   longer time of discharge is also possible although only 10 min of discharge operation is shown here as a preliminary experiment. The charge process has also been tried, and the cell voltage increases from the initial 3.25 V to 3.59 V for 10 min of charge (upper curve of Figure 8). Clearly, the experimental demonstration of the Al/Co-MMME-RFB system confirms that such a design is feasible and successful.

25   For example, another attractive candidate for a RFB system is a zinc-cerium MMME-RFB system (Zn/Ce-MMME-RFB), configured as $[(Zn/Zn(OH)_4^{2-})/(Ce^{4+}/Ce^{3+})]$. When compared to Figures 2 or 3, the Zn portion of the Zn/Ce-MMME-RFB is comprised in second electrolyte 50 and the Ce portion of the Zn/Ce-MMME-RFB is comprised in third electrolyte 70. When compared to Figures 4 or 5, the Zn portion of the Zn/Ce-

30   MMME-RFB is comprised in second electrolyte 201 and the Ce portion of the Zn/Ce-MMME-RFB is comprised in third electrolyte 207.

    The Zn/Ce-MMME-RFB system offers a standard cell voltage of 2.96 V, as it combines the negative electrode potential (−1.216 V) from the $Zn/Zn(OH)_4^{2-}$ redox pair and the positive one (+1.743 V) from the Ce^{4+}/Ce^{3+} redox pair. Such a high

standard cell voltage is also higher than those of all conventional aqueous RFB systems, e.g., higher than that of AV-RFB system (1.26 V) and that of Zn/Ce-RFB system (2.50 V, in spite of the strong concern of hydrogen evolution in negative electrode for Zn/Ce-RFB system). The discharge and charge reactions are represented
5   in Eq. 3 and Eq. 4, respectively.

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \quad Eq. \ 3 \ (a)$$

$$Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^- \quad Eq. \ 3 \ (b)$$

$$Ce^{3+} \rightarrow Ce^{4+} + e^- \quad Eq. \ 4 \ (a)$$

$$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^- \quad Eq. \ 4 \ (b)$$

10   During charge process, the zincate anions are reduced to zinc metal and the sodium cations are balanced from the middle compartment to the negative compartment. In the meanwhile, cerium(III) cations are oxidized into cerium(IV) and the perchlorate anions are balanced from the middle compartment to the positive compartment. During the discharge process, the opposite reactions and ion transfer
15   directions will apply.

After being charged to reach a state of charge of 90%, the OCV is monitored for 15 minutes. As seen in Figure 9, it shows an initial OCV of 3.14 V and quickly stabilizes to 3.10 V. These OCVs are higher than the standard one (2.96 V), which is reasonable since the cell is in charged state (90% of state of charge). Clearly, such a high
20   observed OCV again confirms and verifies that the MMME-RFB system is feasible and successful.

Equally important, both a discharge operation and a charge operation have been successfully achieved with a constant current (60 mA current or 5 mA/cm^2 current density). As seen in Figure 10, the cell voltage, in the charge operation (upper curve of
25   Figure 10), slightly and very smoothly increases from initial 3.08 V to 3.17 V after 30 min of charge, indicating very high voltage efficiency (93%−96%). Different from the conventional Zn/Ce-RFB system where hydrogen evolution was found to be a strong concern (760 mV over-potential when acidic electrolyte used), the hydrogen evolution reaction is greatly suppressed in the Zn/Ce-MMME-RFB system of the present invention
30   as its over-potential drops from 760 mV in Zn/Ce-RFB to 388 mV in the inventive Zn/Ce-MMME-RFB system (−1.216 V of Zn/Zn(OH)$_4^{2-}$ redox pair vs. −0.828 V of OH$^-$/H$_2$ at pH = 14). Indeed, the hydrogen evolution phenomenon has not been found during the whole discharge operation as well as during the charge operation. In the discharge operation (lower curve of Figure 10), the cell voltage decreases from the
35   initial 2.88 V to 2.72 V after nearly 4 hours of discharge, showing a very steady voltage

region, and then drops sharply after available species being mostly consumed. The voltage efficiency for discharge ranges from 92%−97%, almost equivalent to this number for charge.

The discharge duration lasts for 3 hours and 56 minutes, very close to the charge duration 4 hours, indicating high Coulombic efficiency. The overall Coulombic efficiency, voltage efficiency and energy efficiency are calculated in Table 1. Combining the increased cell voltage, decreased ionic crossover, and suppressed hydrogen evolution, the Zn/Ce-MMME-RFB system of the present invention is clearly superior to the conventional Zn/Ce-RFB system.

Discharge time (s)	Charge time (s)	Average discharge Voltage (V)	Average charge voltage (V)	Columbic efficiency	Voltage efficiency	Energy efficiency
13777	14400	2.82	3.12	96%	90%	86%

Table 1. Efficiency calculation for one charge-discharge cycle

The charge-discharge voltage curve at 5 mA/cm^2 is shown in Figure 11, showing 10 successful continuous cycles without obvious Coulombic efficiency, voltage efficiency and energy efficiency change (as shown in Figure 12 of efficiency for each cycle).

Example 1

An aluminum-cobalt DMTE-RFB system (Al/Co-DMTE-RFB), configured as $[(Al/Al(OH)_4^-)/(Co^{3+}/Co^{2+})]$ was constructed. A three-compartment cell made up of three plastic jars was designed and used as follows. Three 50 ml plastic jars were put in series with a hole (a quarter inch of diameter) opened between adjacent two jars. The three jars, based on half-reaction inside, were assigned as negative, middle and positive compartments. One piece of Nafion® 212 membrane (DuPont, 50 μm thickness) and one piece of Fumasep® FAA membrane (FuMa-Tech, 70 μm thickness) were used as the CEM and AEM, respectively. The CEM is put between the negative compartment and the middle compartment while the AEM is put between the middle compartment and the positive compartment, along with an O-ring to seal the conjunction part. Two clamps were used to compress three jars tightly to avoid electrolyte leakage. A potentiostat/galvanostat (Solartron 1287A) was used in both OCV and discharge-charge cycle tests.

A solution that contained 3.76 M NaOH, 0.24 M NaAlO$_2$ and 0.05 M NaSnO$_2$ was used as the negative electrolyte. A solution that contained 0.1 M Co(ClO$_4$)$_2$ and 2 M HClO$_4$ was used as the positive electrolyte, which was prepared by dissolving CoCO$_3$ into perchloric acid. A 4 M NaClO$_4$ solution was used as the middle supporting

electrolyte. A small piece of Al strip (ESPI Metals, 2 cm by 3 cm, 5N grade) and a small piece of graphite felt (SGL Group, 2 cm by 3 cm, Sigracell® GFA5 EA type) were used as the negative electrode and the positive electrode, respectively. The cell was first charged at 50 mA (or 8.3 mA/cm^2 of current density) for 2.5 hours and the OCV was tested for 20 min. The discharge-charge cycle is then carried out for 20 min by setting current constant at 5 mA (or 0.83 mA/cm^2 of current density).

Example 2

A zinc-cerium DMTE-RFB (Zn/Ce-DMTE-RFB), configured as [(Zn/Zn(OH)$_4^{2-}$)/(Ce^{4+}/Ce^{3+})] was constructed. A three-compartment cell made up of three acrylic flow channels was designed and used as follows. Three 5cm by 6cm rectangular channels were put in series with membranes in between. The three channels, based on half-reaction inside, were assigned as negative, middle and positive compartments. One piece of Nafion® 1135 membrane (DuPont, 87.5 µm thickness) and one piece of Fumasep® FAA membrane (FuMa-Tech, 70 µm thickness) were used as the CEM and AEM, respectively. The CEM is put between the negative compartment and the middle compartment while the AEM is put between the middle compartment and the positive compartment, along with silicone gasket to seal the conjunction part. The positive electrode and negative electrode are each put next to its corresponding compartment, respectively. Two clamps were used to compress the three channels and electrodes tight ly to avoid electrolyte leakage. Electrolytes are stored outside the channel in three tanks and delivered by peristaltic pump (Masterflex® L/S® 100RPM). The working flow battery set-up is a potentiostat/galvanostat (Solartron 1287A) and was used in both OCV and discharge-charge cycle tests.

The negative electrolyte contained 3 M NaOH and 0.5 M Na$_2$[Zn(OH)$_4$)] A solution that contained 0.5 M Ce(ClO$_4$)$_3$, 2 M HClO$_4$ was used as the positive electrolyte, which was prepared by dissolving Ce$_2$(CO$_3$)$_3$ into perchloric acid. The middle electrolyte used was 4 M NaClO$_4$ solution. The volume for each electrolyte used in test is 30 ml. A rectangular copper plate (ESPI Metals, 5cm by 6cm, 3N grade) was used as negative current collector. Before the experiment, the copper was rinsed with acetone and deposited with a layer of cadmium according to the method in reference. Graphite based bipolar plate (SGL group, 5 cm by 6 cm, Sigracet® TF6 type) was used as positive current collector. Graphite felt (SGL Group, 3 cm by 4 cm, Sigracell® GFA5 EA type) was used as positive electrode and compressed by plastic frame to contact bipolar plate. The cut-off voltage for charge and discharge are 3.24 and 1.8 respectively. The discharge-charge cycle was carried out at constant current density at

60 mA (or 5 mA/cm^2 of current density) with flow rate for all three electrolytes at 20 ml/min.

The MMME-RFB systems described above may have other configurations besides those of acid/neutral/base configurations and are not limited thereto. Tables 2-4 list some possible candidates and combinations of MMME-RFB configurations.

Table 2 - Redox pairs examples of MMME-RFB configurations

Anion-based redox pairs			Cation-based redox pairs			Anion-cation hybrid redox pairs		
Name	Standard electrode potential / V	Typical electrolyte	Name	Standard electrode potential / V	Typical electrolyte	Name	Standard electrode potential / V	Typical electrolyte
$ClBr_2^-/Br^-$	1.07	HCl	Co^{3+}/Co^{2+}	1.95	$HClO_4$	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl
Br_3^-/Br^-	1.05	H_2SO_4	Ce_2O^{6+}/Ce^{3+}	1.87	$HClO_4$	$Cr(edta)^+/Cr(edta)^-$	1.14	NaAc
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	0.36	NaOH	Ce^{4+}/Ce^{3+}	1.74	H_2SO_4			
$Fe(C_6H_4O)^-/Fe(C_6H_4O)^{2-}$	0.21	NaAc	Mn^{3+}/Mn^{2+}	1.54	H_2SO_4			
$Fe(edta)^-/Fe(edta)^{2-}$	0.18	NaAc	NpO_2^{2+}/NpO_2^+	1.14	HNO_3			
$Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$	−0.12	NaAc	VO_2^+/VO^{2+}	0.99	H_2SO_4			
S_4^{2-}/S_2^{2-}	−0.45	H_2SO_4	Fe^{3+}/Fe^{2+}	0.77	HCl			
$Cr(edta)^-/Cr(edta)^{2-}$	−0.96	NaBr	Cu^{2+}/Cu	0.34	H_2SO_4			
$Zn(OH)_4^{2-}/Zn$	−1.21	NaAc	Np^{4+}/Np^{3+}	0.15	HNO_3			
$Al(OH)_4^-/Al$	−2.33	NaOH	Sn^{4+}/Sn^{2+}	0.15	H_2SO_4			
		NaOH	Ti^{4+}/Ti^{3+}	−0.06	H_2SO_4			
			V^{3+}/V^{2+}	−0.26	H_2SO_4			
			Cr^{3+}/Cr^{2+}	−0.41	H_2SO_4			
			Fe^{2+}/Fe	−0.45	HCl			
			Zn^{2+}/Zn	−0.76	CH_3SO_3H			

Table 3 - Combination examples of MMME-RFB configurations (DMTE-RFB)

Case 1: negative electrode-CEM-middle electrolyte-AEM-positive electrode

Negative redox pair and electrolyte			Middle electrolyte	Positive redox pair and electrolyte			Standard Cell voltage / V
Name	Standard electrode potential / V	Typical electrolyte		Name	Standard electrode potential / V	Typical electrolyte	
$Al(OH)_4^-/Al$	−2.33	NaOH	$NaClO_4$	Co^{3+}/Co^{2+}	1.95	$HClO_4$	4.28
$Zn(OH)_4^{2-}/Zn$	−1.21	NaOH	$NaClO_4$	Ce_2O^{6+}/Ce^{3+}	1.87	$HClO_4$	3.08
$Zn(OH)_4^{2-}/Zn$	−1.21	NaOH	Na_2SO_4	Mn^{3+}/Mn^{2+}	1.54	H_2SO_4	2.75
$Cr(edta)^-/Cr(edta)^{2-}$	−0.96	NaBr	Na_2SO_4	Mn^{3+}/Mn^{2+}	1.54	H_2SO_4	2.50
S_4^{2-}/S_2^{2-}	−0.45	NaBr	Na_2SO_4	Mn^{3+}/Mn^{2+}	1.54	H_2SO_4	1.99
$Cr(edta)^-/Cr(edta)^{2-}$	−0.96	NaBr	NaCl	Fe^{3+}/Fe^{2+}	0.77	HCl	1.73
$Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$	−0.12	NaAc	Na_2SO_4	Mn^{3+}/Mn^{2+}	1.54	H_2SO_4	1.66
S_4^{2-}/S_2^{2-}	−0.45	NaBr	NaCl	Fe^{3+}/Fe^{2+}	0.77	HCl	1.22
$Fe(C_2O_4)_3^{3-}/Fe(C_2O_4)_3^{4-}$	−0.12	NaAc	NaCl	Fe^{3+}/Fe^{2+}	0.77	HCl	0.89
$Cr(edta)^-/Cr(edta)^{2-}$	−0.96	NaBr	NaCl	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	2.19
S_4^{2-}/S_2^{2-}	−0.45	H_2SO_4	NaCl	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	1.68

Fe(C2O4)3^3-/Fe(C2O4)3^4-	-0.12	NaAc	NaCl	Cr2O7^-/Cr^3+	1.23	HCl	1.35
Cr(edta)^-/Cr(edta)^2-	-0.96	NaBr	NaAc	Cr(edta)^+/Cr(edta)^-	1.14	NaAc	2.10
S4^2-/S2^2-	-0.45	H2SO4	NaAc	Cr(edta)^+/Cr(edta)^-	1.14	NaAc	1.59
Fe(C2O4)3^3-/Fe(C2O4)3^4-	-0.12	NaAc	NaAc	Cr(edta)^+/Cr(edta)^-	1.14	NaAc	1.26

Case 2: negative electrode-AEM-middle electrolyte-CEM-positive electrode

Negative redox pair and electrolyte			Middle electrolyte	Positive redox pair and electrolyte			Standard Cell voltage / V
Name	Standard electrode potential / V	Typical electrolyte		Name	Standard electrode potential / V	Typical electrolyte	
Zn^{2+}/Zn	-0.76	CH_3SO_3H	CH_3SO_3Na	$ClBr_2^-/Br^-$	1.07	HCl	1.83
Zn^{2+}/Zn	-0.76	CH_3SO_3H	CH_3SO_3Na	Br_3^-/Br^-	1.05	H_2SO_4	1.81
Fe^{2+}/Fe	-0.45	HCl	NaCl	$ClBr_2^-/Br^-$	1.07	HCl	1.52
Fe^{2+}/Fe	-0.45	HCl	NaCl	Br_3^-/Br^-	1.05	H_2SO_4	1.50
Cr^{3+}/Cr^{2+}	-0.41	H_2SO_4	$NaSO_4$	$ClBr_2^-/Br^-$	1.07	HCl	1.48
Cr^{3+}/Cr^{2+}	-0.41	H_2SO_4	$NaSO_4$	Br_3^-/Br^-	1.05	H_2SO_4	1.46
V^{3+}/V^{2+}	-0.26	H_2SO_4	$NaSO_4$	$ClBr_2^-/Br^-$	1.07	HCl	1.33
V^{3+}/V^{2+}	-0.26	H_2SO_4	$NaSO_4$	Br_3^-/Br^-	1.05	H_2SO_4	1.31
Zn^{2+}/Zn	-0.76	CH_3SO_3H	CH_3SO_3Na	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	1.99
Fe^{2+}/Fe	-0.45	HCl	NaCl	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	1.68
Cr^{3+}/Cr^{2+}	-0.41	H_2SO_4	$NaSO_4$	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	1.64
Zn^{2+}/Zn	-0.76	CH_3SO_3H	CH_3SO_3Na	Cr(edta)^+/Cr(edta)^-	1.14	NaAc	1.90
Fe^{2+}/Fe	-0.45	HCl	NaCl	Cr(edta)^+/Cr(edta)^-	1.14	NaAc	1.59
Cr^{3+}/Cr^{2+}	-0.41	H_2SO_4	$NaSO_4$	Cr(edta)^+/Cr(edta)^-	1.14	NaAc	1.55

Table 4 - Combination examples of MMME-RFB configurations (TMQE-RFB)

Case 1: negative electrode-CEM-middle electrolyte 1-AEM-middle electrolyte 2-CEM-positive electrode

Negative redox pair and electrolyte			Middle electrolyte 1	Middle electrolyte 2	Positive redox pair and electrolyte			Standard Cell voltage / V
Name	Standard electrode potential / V	Typical electrolyte			Name	Standard electrode potential / V	Typical electrolyte	
Cr(edta)^+/Cr(edta)^-	1.14	NaAc	NaAc	NaCl	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	0.09

Case 2: negative electrode-AEM-middle electrolyte 1-CEM-middle electrolyte 2-AEM-positive electrode

Negative redox pair and electrolyte			Middle electrolyte 1	Middle electrolyte 2	Positive redox pair and electrolyte			Standard Cell voltage / V
Name	Standard electrode potential / V	Typical electrolyte			Name	Standard electrode potential / V	Typical electrolyte	
Cr(edta)^+/Cr(edta)^-	1.14	NaAc	NaAc	NaCl	$Cr_2O_7^-/Cr^{3+}$	1.23	HCl	0.09

Case 3: negative electrode-CEM-middle electrolyte 1-AEM-middle electrolyte 2-CEM-positive electrode or negative electrode-AEM-middle electrolyte 1-CEM-middle electrolyte 2-AEM-positive electrode

Negative redox pair and electrolyte			Middle electrolyte 1	Middle electrolyte 2	Positive redox pair and electrolyte			Standard Cell voltage / V
Name	Standard electrode potential / V	Typical electrolyte			Name	Standard electrode potential / V	Typical electrolyte	
A^-/C^+					A^-/C^+			
A^-/C^+					C^+/A^-			

Other attractive candidates for use in the redox flow battery systems described herein may be those based on non-aqueous mixed ion systems, such as a non-aqueous all-ruthenium RFB ($Ru(acac)_3$/$[Ru(acac)_3]^-$ vs. $[Ru(acac)_3]^+$/$Ru(acac)_3$), a non-aqueous all-vanadium RFB ($V(acac)_3$/$[V(acac)_3]^-$ vs. $[V(acac)_3]^+$/$V(acac)_3$), a non-aqueous all-chromium RFB ($[Cr(acac)_3]^-$/$[Cr(acac)_3]^{2-}$ vs. $[Cr(acac)_3]^+$/$Cr(acac)_3$), and a non-aqueous all-magnesium RFB ($Mn(acac)_3$/$[Mn(acac)_3]^-$ vs. $[Mn(acac)_3]^+$/$Mn(acac)_3$).

While this invention has been described in terms of several preferred embodiments, there are alterations, permutations, and substitute equivalents, which fall within the scope of this invention. It should also be noted that there are many alternative ways of implementing the methods and apparatuses of the present invention. It is therefore intended that the following appended claims be interpreted as including all such alterations, permutations, and substitute equivalents as fall within the true spirit and scope of the present invention.

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What is claimed is:

1.   A redox flow battery comprising:

       a)   a first membrane;

       b)   a second membrane;

5   c)   a first electrolyte disposed between the first membrane and the second membrane;

       d)   a second electrolyte disposed between the first membrane and a first electrode; and

       e)   a third electrolyte disposed between the second membrane and a second

10 electrode.

2.   The redox flow battery of Claim 1, further comprising:

       a third membrane disposed between the first membrane and the second membrane and a fourth electrolyte disposed between the first membrane and the

15 second membrane; wherein the third membrane separates the fourth electrolyte from the first electrolyte.

3.   The redox flow battery of Claim 1, wherein the first electrolyte and second electrolyte are different in terms of at least one species of anion, and the first

20 electrolyte and third electrolyte are different in terms of at least one species of cation.

4.   The redox flow battery of Claim 1, wherein at least one of the second electrolyte and third electrolyte comprises an anion-based redox pair, a cation-based redox pair or a cation-anion hybrid redox pair.

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5.   The redox flow battery of Claim 1, wherein the second electrolyte comprises a redox pair selected from the group consisting of an $Al(OH)_4^-/Al$ redox pair, a $Zn(OH)_4^{2-}/Zn$ redox pair, an S_4^{2-}/S_2^{2-} redox pair and a $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ redox pair.

30 6.   The redox flow battery of Claim 1, wherein the third electrolyte comprises a redox pair selected from the group consisting of a Co^{3+}/Co^{2+} redox pair, a Fe^{3+}/Fe^{2+} redox pair and a Ce^{4+}/Ce^{3+} redox pair.

7.   The redox flow battery of Claim 1, wherein the second electrolyte comprises an

35 $Al(OH)_4^-/Al$ redox pair and the third electrolyte comprises a Co^{3+}/Co^{2+} redox pair.

8.   The redox flow battery of Claim 1, wherein the second electrolyte comprises a $Zn(OH)_4^{2-}/Zn$ redox pair and the third electrolyte comprises a Ce^{4+}/Ce^{3+} redox pair.

9.   The redox flow battery of Claim 1, wherein the second electrolyte comprises a $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ redox pair and the third electrolyte comprises a Co^{3+}/Co^{2+} redox pair.

10.   The redox flow battery of Claim 1, wherein the second electrolyte comprises an S_4^{2-}/S_2^{2-} redox pair and the third electrolyte comprises a Fe^{3+}/Fe^{2+} redox pair.

11.   The redox flow battery of Claim 2, wherein the first and second membranes are anion-exchange membranes and the third membrane is a cation exchange membrane; or wherein the first and second membranes are cation-exchange membranes and the third membrane is an anion-exchange membrane.

12.   The redox flow battery of Claim 1, wherein the second electrolyte and the third electrolyte both comprise an anion-cation hybrid redox pair.

13.   The redox flow battery of Claim 1, wherein one of the first, second and third electrolytes comprises at least one of: cations based on hydronium, sodium, magnesium, potassium or calcium; or anions based on hydroxide, perchlorate, sulfate, phosphate, acetate, chloride, bromide or carbonate.

14.   A method of making a redox flow battery comprising:

        a)   partially surrounding a first electrolyte with a first membrane and a second membrane;
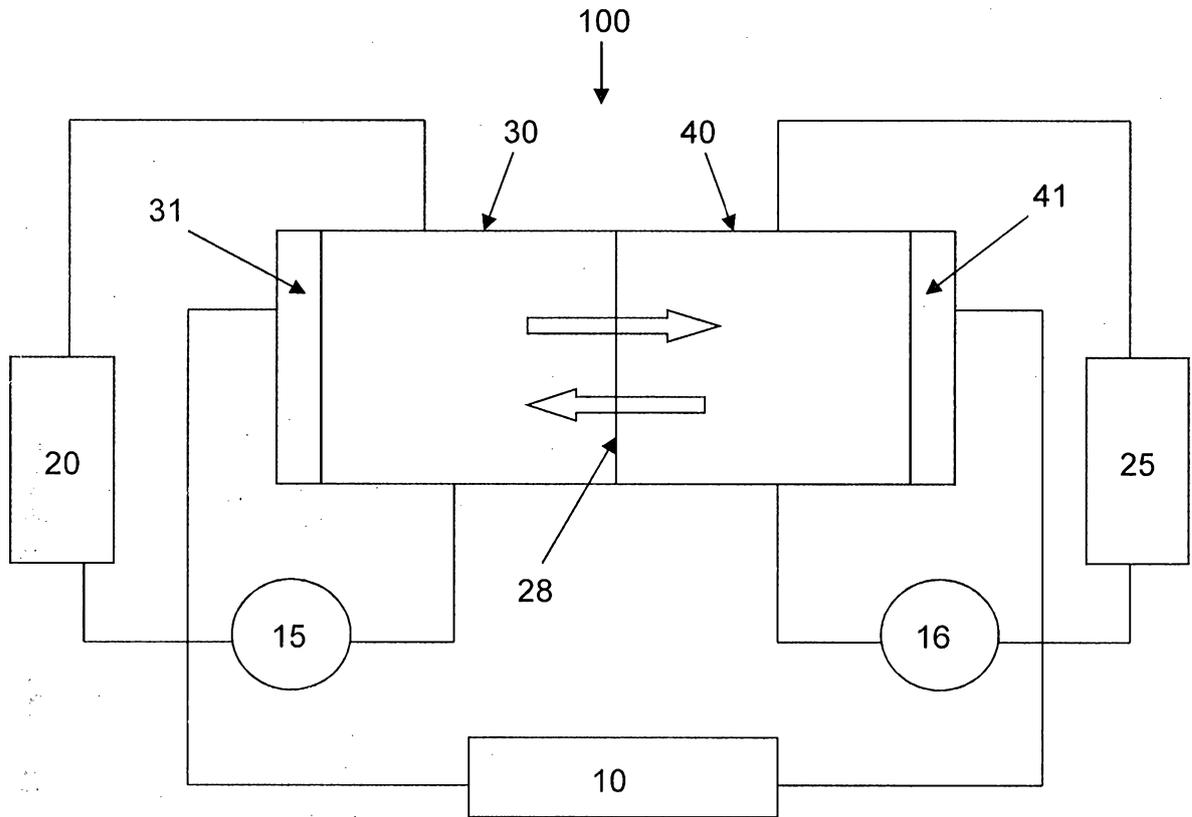
        b)   partially surrounding a second electrolyte with the first membrane and a first electrode; and

        c)   partially surrounding a third electrolyte with the second membrane and a second electrode.

15.   The method of Claim 14, wherein the second electrolyte comprises a redox pair selected from the group consisting of an $Al(OH)_4^-/Al$ redox pair, a $Zn(OH)_4^{2-}/Zn$ redox pair, an S_4^{2-}/S_2^{2-} redox pair and a $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ redox pair.

16.   The method of Claim 14, wherein the third electrolyte comprises a cation-based redox pair selected from the group consisting of a Co^{3+}/Co^{2+} redox pair, a Fe^{3+}/Fe^{2+} redox pair and a Ce^{4+}/Ce^{3+} redox pair.

5   17.   A method of making a redox flow battery comprising:

       a)   partially surrounding a first electrolyte with a first membrane and a third membrane;

       b)   partially surrounding a fourth electrolyte with the third membrane and a second membrane;

10   c)   partially surrounding a second electrolyte with the first membrane and a first electrode;

       d)   partially surrounding a third electrolyte with the second membrane and a second electrode.

15   18.   The method of Claim 17, wherein the first and second membranes are anion-exchange membranes and the third membrane is a cation exchange membrane; or wherein the first and second membranes are cation-exchange membranes and the third membrane is a anion-exchange membrane.

20   19.   The method of Claim 17, wherein the second electrolyte comprises a redox pair selected from the group consisting of an $Al(OH)_4^-/Al$ redox pair, a $Zn(OH)_4^{2-}/Zn$ redox pair, an S_4^{2-}/S_2^{2-} redox pair and a $Co(CN)_6^{3-}/Co(CN)_6^{4-}$ redox pair; or wherein the third electrolyte comprises a cation-based redox pair selected from the group consisting of a Co^{3+}/Co^{2+} redox pair, a Fe^{3+}/Fe^{2+} redox pair and a Ce^{4+}/Ce^{3+} redox pair.

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15   28   16

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PRIOR ART

FIGURE 1

FIGURE 2

FIGURE 3

235   220   230   240   245

| | 201 | 203 | 205 | 207 | |

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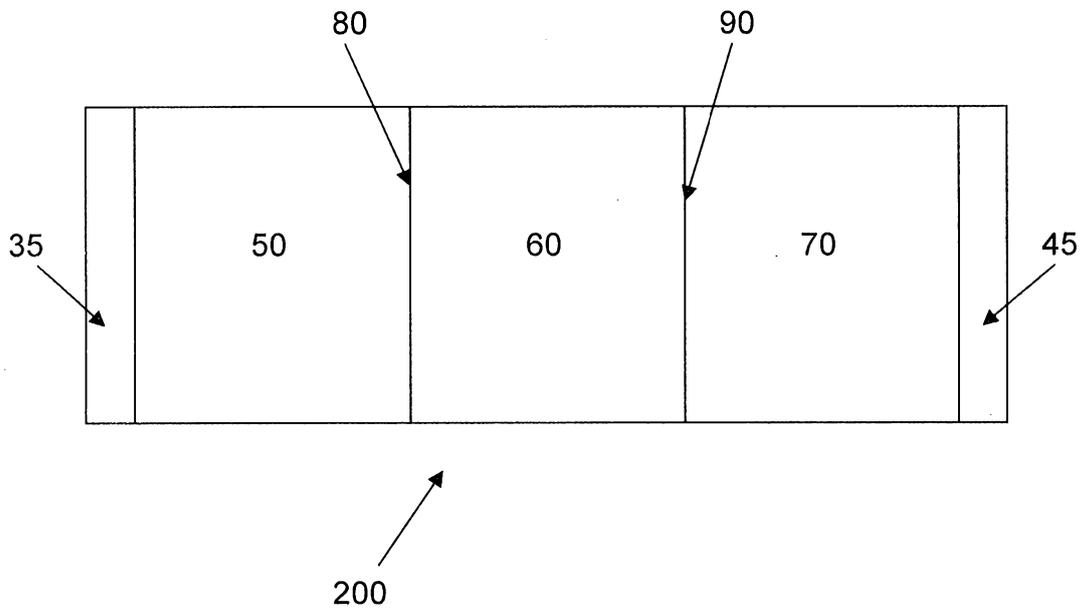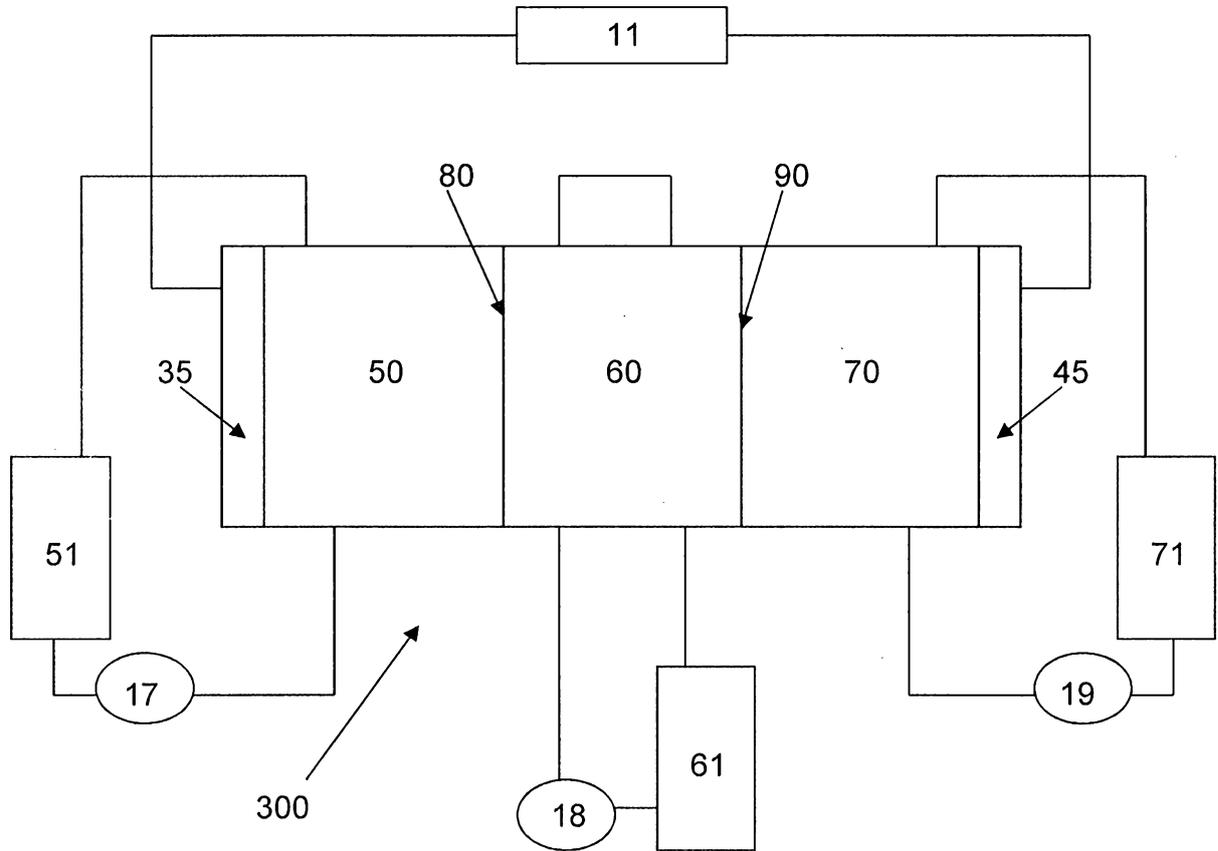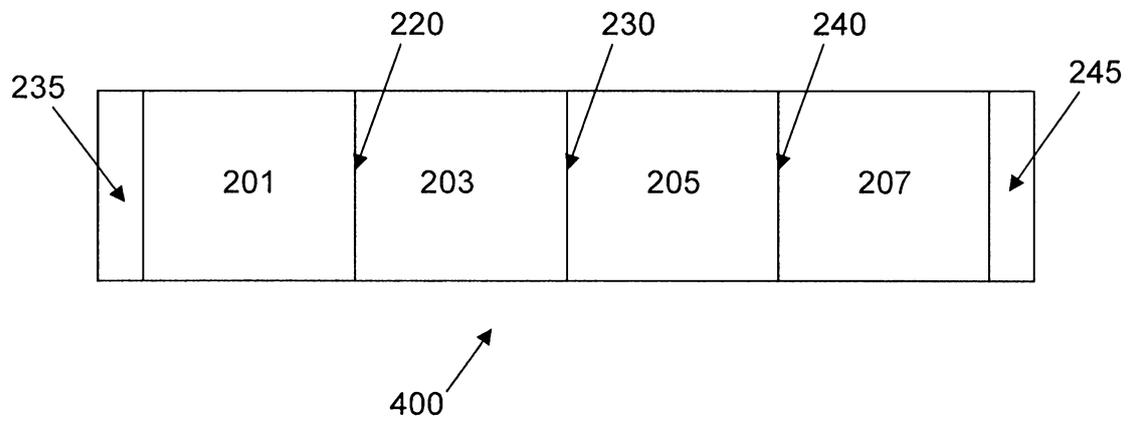
FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

FIGURE 10

FIGURE 11

FIGURE 12