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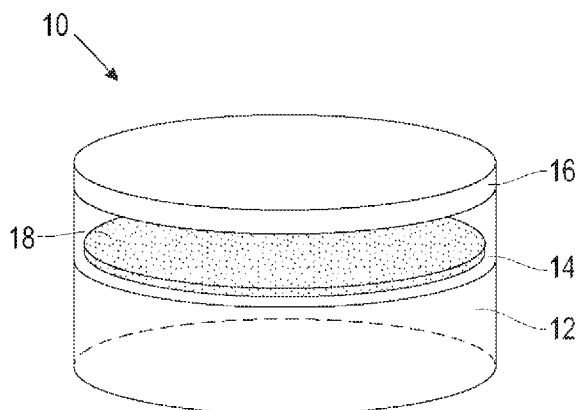


FIG. 1

(57) Abstract: A battery includes: an anode; an electrolyte including: an oxidizing gas; an active cathode material including a metal halide; and a solvent including a heterocyclic compound; and a current collector contacting the active cathode material.



RECHARGEABLE METAL HALIDE BATTERY

BACKGROUND

[0001] Rechargeable batteries are used as a power source in a wide range of applications such as, for example, industrial devices, medical devices, electronic devices, electric vehicles, and grid energy storage systems. Battery technology is continually being developed to enable higher energy density and greater efficiency, thereby permitting the use of batteries as power sources for additional applications.

[0002] The need for high specific capacities and specific energies has led to the study of various metal-element batteries. Lithium intercalation cathode materials, such as lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminum oxide (NCA), lithium cobalt oxide (LCO), lithium iron phosphate (LFP), and the like have relatively low energy densities and may be expensive. To identify new and more efficient cathode materials, conversion cathode materials such as sulfur, oxygen, air, and others have been investigated.

[0003] Batteries made with lithium-oxygen, lithium-air, and lithium with other gas mixtures containing oxygen have excellent performance due at least in part to the low atomic number, low density, and high reducing capability of elemental lithium. Moreover, a lithium-oxygen battery could potentially have a theoretical specific energy three to five times greater than conventional lithium ion batteries.

[0004] Lithium metal has a high energy storage capacity and has been utilized as a primary battery anode material. In some cases lithium metal anodes can form dendrites, which can cause short circuits during cell operation. It has also proven difficult to find reasonably inexpensive cathode materials that can accommodate the large amount of lithium ions and electrons extracted from a lithium metal anode.

SUMMARY

[0005] Some batteries including sulfur, oxygen, air, or other active cathode materials have poor cyclability, low power density, or both. For example, such batteries may be relatively unstable and/or undergo parasitic reactions which may result in electrochemically irreversible carbonate byproducts that reduce the cyclability and/or power density of the battery, e.g., due to electrolyte decomposition or carbon surface oxidation.

[0006] In general, the present invention is directed to a battery with an electrolyte including an oxidizing gas, a metal halide, and a solvent including a heterocyclic compound. In various embodiments of the invention, the battery has one or more of a relatively fast charging rate, high energy efficiency, high power density, and good cyclability. Additionally, in some embodiments of the invention, the electrolyte may be more cost effective and potentially less hazardous than some other battery electrolytes. The electrolyte can provide high power density in metal-based

batteries by forming small and dense nuclei that also have a relatively consistent size, which can powerfully and naturally suppress undesirable dendrite growth on the anode. Additionally, the electrolyte includes no heavy metals such as, for example, cobalt or nickel, and as such is expected to reduce overall battery manufacturing costs.

[0007] In one aspect, the present disclosure is directed to a battery, including: an anode; an electrolyte including: an oxidizing gas; an active cathode material including a metal halide; and a solvent including a heterocyclic compound; and a current collector contacting the active cathode material.

[0008] In another aspect, the present invention is directed to a battery, including: (a) an anode that takes up metal ions from an electrolyte during charging, and releases the ions to the electrolyte during discharging, the electrolyte including: (i) a solvent including a heterocyclic compound, and (ii) a dissolved halide, wherein the halide functions as a cathode for the battery; (b) a solid electrolyte interphase (SEI) layer contacting the anode, the SEI layer including an oxide of the metal; and (c) a current collector including an electrically conductive porous material, wherein the current collector contacts the dissolved halide.

[0009] In another aspect, the present invention is directed to a method of forming a battery, including: dissolving a metal halide in a solvent including a heterocyclic compound to form a solution; soaking a separator with the solution; stacking an anode, the separator soaked with the solution, and a current collector, wherein the stacking includes placing the separator soaked with the solution between the anode and the current collector; and introducing an oxidizing gas to the stacked anode, separator soaked with the solution, and current collector to form the battery, wherein the battery includes: an anode, an electrolyte, including: an oxidizing gas; an active cathode material including a metal halide; and a solvent including a heterocyclic compound; and a current collector contacting the active cathode material.

[0010] The details of one or more examples of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF DRAWINGS

[0011] FIG. 1 is a conceptual diagram illustrating an example battery including an anode, an electrolyte, a current collector, and an optional separator.

[0012] FIG. 2 is a conceptual diagram illustrating the example battery of FIG. 1 within an enclosed cell.

[0013] FIG. 3 is a flow diagram illustrating an example technique for fabricating a battery.

[0014] FIGS. 4A-4B are plots of the discharge and charge galvanostatic cycling behavior of the 1st cycles and areal specific discharge capacity with respect to the cycle number of the cells using 1M LiI-GBL in the presence of oxygen as described in Example 2. The cells were operated at a current density of 5 mA/cm².

[0015] FIGS. 5A-5B are plots of the discharge and charge galvanostatic cycling behavior of the 1st cycles and areal specific discharge capacity with respect to the cycle number of the cells using 1M LiI-ECL in the presence of oxygen as described in Example 3. The cells were operated at a current density of 5 mA/cm².

[0016] FIGS. 6A-6B are plots of the discharge and charge galvanostatic cycling behavior of the 1st cycles and areal specific discharge capacity with respect to the cycle number of the cells using 1M LiI-THF electrolyte in the presence of oxygen as described in Example 4. The cells were operated at a current density of 5 mA/cm².

[0017] FIG. 7 is a plot of the discharge and charge galvanostatic cycling behavior of the 1st cycle using 1 M LiI-GBL in the absence of oxygen in the cell of Comparative Example 1. The cells were operated at a current density of 5 mA/cm².

[0018] FIG. 8 is a plot of the discharge and charge galvanostatic cycling behavior of the 50th cycle using 1 M LiI-TEGDME electrolyte in the presence of oxygen in the cell of Comparative Example 2. The cells were operated at a current density of 5 mA/cm².

[0019] Like symbols in the figures indicate like elements.

DETAILED DESCRIPTION

[0020] FIG. 1 is a conceptual diagram illustrating an example battery 10 including an anode 12, an electrolyte 14, a current collector 16, and an optional separator 18. The battery 10 operates via reduction-oxidation (redox) reactions, and utilizes different oxidation states and redox reactions of one or more components or elements for charge and discharge.

[0021] The anode 12 may be made from any metal, and suitable examples include, but are not limited to, lithium, magnesium, sodium, and mixtures and combinations thereof. In some examples, the anode 12 consists essentially of elemental lithium, magnesium, or sodium, or lithium, or magnesium, or sodium alloyed with one or more additional elements. In some embodiments, the anode 12 consists of elemental lithium, magnesium, sodium, or lithium.

[0022] The anode 12 may take up metal ions from the electrolyte 14 during charging, and release the metal ions

to electrolyte 14 during discharging. In some embodiments, the anode 12 may be an intercalation host material capable of taking up metal ions. In some examples, a solid electrolyte interphase (SEI) layer may be in contact with the anode 12. For example, the SEI layer may include an oxide of a metal from the electrolyte 14.

[0023] The electrolyte 14, which may be aqueous or non-aqueous, includes a solvent including a heterocyclic compound, a metal halide, and an oxidizing gas. In this application the term heterocyclic compound refers to an aromatic or non-aromatic cyclic compound having as ring members atoms of at least two different elements. A cyclic compound (ring compound) as used in the present application refers to a compound in which one or more series of atoms in the compound is connected to form a ring. In various embodiments, suitable cyclic compounds for the electrolyte 14 include 5-membered rings such as pyrrolidines, oxolanes, thiolanes, pyrroles, furans and thiophenes; 6-membered rings such as piperadines, oxanes, thianes, pyridines, pyrans and thiopyrans; and 7-membered rings such as azepanes, oxepanes, thiepanes, azepines, oxepines, and thiepenes. Examples of suitable heterocyclic compounds include, but are not limited to, tetrahydrofuran, tetrahydropyran, tetrahydrothiophene, oxathiolane, succinimide, oxazolidone, γ -butyrolactone, γ -caprolactone, ϵ -caprolactone, γ -valerolactone, pyrrolidine, imidazolidine, sulfolane, thiane and mixtures and combinations thereof. In some embodiments, suitable heterocyclic compounds include, but are not limited to, cyclic ethers, cyclic esters, and mixtures and combinations thereof.

[0024] In some examples, the electrolyte 14 may include one or more additional solvents. In some embodiments, the one or more additional solvents may be chosen from non-aqueous, organic solvents such as an ether, a glyme, a carbonate, a nitrile, an amide, an amine, an organosulfur solvent, an organophosphorus solvent, an organosilicon solvent, a fluorinated solvent, adiponitrile (ADN), propylene carbonate (PC), dimethoxyethane (DME), and mixtures and combinations thereof. In some examples, the electrolyte 14 includes equal parts of the solvent including the heterocyclic compound and the one or more additional solvents. In some examples, the one or more additional solvents in the electrolyte 14 may be selected to further improve the electrochemical performance of battery 10, such as, for example, by enhancing rechargeability, cyclability, or the like.

[0025] The electrolyte 14 includes an oxidizing gas. In some examples, electrolyte 14 may be in the presence of an oxidizing gas, and the phrase "includes an oxidizing gas" is intended to include such a configuration. In some examples, the oxidizing gas may be dissolved in the solvent including the heterocyclic compound of electrolyte 14. In some examples, which are not intended to be limiting, the oxidizing gas includes at least one of oxygen, air, nitric oxide, or nitrogen dioxide. The oxidizing gas helps induce the redox reactions of battery 10 as described above, and helps achieve highly reversible redox reactions, which may contribute to enhanced electrochemical performance of battery 10. The oxidizing gas may help induce such redox reactions, but is not consumed or evolved during use of battery 10 (e.g., the oxidizing gas does not participate in the redox reactions of battery 10). In some examples, an electrolyte including a metal halide and a solvent including a heterocyclic compounds, but not including an oxidizing gas, may exhibit little or no rechargeability.

[0026] The electrolyte 14 also includes a metal halide (e.g., MX, where M is a metal element and X is a halogen element). In some examples, the metal halide includes an electrolyte salt that dissociates into a respective halide ion and a respective metal ion. For example, the metal halide may dissolve in the solvent including the heterocyclic compound, and dissociate into the respective metal and halide ions. In some examples, the halide ion may include an ion of at least one of I, Br, Cl, or F (e.g., X may be I, Br, Cl, or F), and the metal ion may include an ion of at least one of Li, Mg, or Na (e.g., M may be Li, Mg, or Na). In other examples, the metal halide may include elements other than I, Br, Cl, F, Li, Mg, and/or Na. The metal halide may provide the electrolyte 14 with ionic conductivity.

[0027] In some embodiments, the electrolyte 14 includes an optional additional salt that dissociates into a respective metal ion and a respective counter anion. In some examples, which are not intended to be limiting, the metal ion includes at least one of Li, Mg, and Na, and the counter anion includes one or more of nitrate (NO_3^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bisoxalato borate (BOB^-), difluorooxalato borate (DFOB^-), trifluoromethanesulfonate (TF^-), and trifluorosulfonylimide (TFSI^-).

[0028] Additionally, or alternatively, the metal halide of electrolyte 14 may function as an active cathode material. For example, the metal halide may receive, store, and release the metal ions during charging and discharging of battery 10. In this way, the battery 10 may not include a dedicated cathode material. Instead, battery 10 may include the active cathode material of the metal halide of electrolyte 14 and a current collector 16. In turn, the battery 10 may be cheaper to make, more lightweight, have a higher power density, or combinations thereof. In some cases, the high power density of the electrolyte including the metal halide that functions as an active cathode material may enable the battery 10 to be charged significantly faster than some other batteries that do not include the electrolyte described herein. In some examples, an electrolyte comprising a solvent including a heterocyclic compound and an oxidizing gas, but not including a metal halide, may have reduced electrochemical performance (e.g., reversibility, rechargeability, and/or cyclability), produce irreversible carbonate byproducts, have reduced power density, or combinations thereof in comparison to electrolyte 14.

[0029] The current collector 16 may include a material of suitable electrical conductivity that collects electrons generated by a redox reaction during discharge of battery 10 and provides a conductive path to an external electrical circuit to which battery 10 is connected. Similarly, during recharge of battery 10, the current collector 16 provides an electrical pathway between an external voltage source and electrolyte 14 to supply voltage for another redox reaction to charge battery 10. In some examples, current collector 16 may include electrically conductive powders such as metal and/or carbon powders, woven or non-woven metal fibers, metal foam, woven or non-woven carbon fibers, or the like. Additionally, or alternatively, current collector 16 may include stainless-steel mesh, aluminum (Al) mesh, nickel (Ni) foam, and/or carbon paper. For example, in one embodiment, the current collector 16 may include a stainless-steel mesh with carbon nanoparticles deposited thereon. As yet another example, current collector may be a porous material that is electrically conductive.

[0030] In other examples, the battery 10 may include a dedicated cathode material in addition to the metal halide functioning as the active cathode material and current collector 16. For example, battery 10 may include a cathode that provides a conductive path to an external electrical circuit to which battery 10 is connected. In some cases, the battery 10 may include a cathode that may be used in a Li-ion battery. For example, the cathode may include at least one of lithium cobalt oxide (LCO, e.g., LiCoO_2), nickel cobalt aluminum (NCA, e.g., $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$), lithium ion manganese oxide (LMO, e.g., LiMn_2O_4), lithium nickel manganese cobalt oxide (NMC, e.g., LiNiMnCoO_2), nickel cobalt manganese (NCM, e.g., $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$) or lithium iron phosphate (LFP, e.g., LiFePO_4). In other examples, battery 10 may include a different or an additional cathode material.

[0031] In some examples, the battery 10 includes an optional separator 18. The separator 18 may force electrons through an external electrical circuit to which battery 10 is connected such that the electrons do not travel through battery 10 (e.g., through electrolyte 14 of battery 10), while still enabling the metal ions to flow through battery 10 during charge and discharge. In some examples, separator 18 may be soaked with electrolyte 14, within electrolyte 14, surrounded by electrolyte 14, or the like. The separator 18 may include an electrically non-conductive material to prevent movement of electrons through battery 10 such that the electrons move through the external circuit instead. For example, separator 18 may include glass, non-woven fibers, polymer films, rubber, or the like.

[0032] In some examples, the battery 10 has a closed or substantially closed volume. For example, anode 12, electrolyte 14, current collector 16, and separator 18 may be within a closed or substantially closed cell or other enclosure. In this way, the oxidizing gas of electrolyte 14 remains within the battery 10 such that the battery 10 has a relatively fast charging rate, high energy efficiency, high power density, high reversibility, high cyclability, or combinations thereof, as described herein.

[0033] The battery 10 may be capable of undergoing many charging and discharging cycles (e.g., exhibits good rechargeability), even at relatively high charging densities. In some examples, battery 10 is capable of completing at least 100 cycles of charging and discharging at a current density of greater than or equal to about 1 mA/cm^2 , about 5 mA/cm^2 , about 10 mA/cm^2 , or about 20 mA/cm^2 . As one example, battery 10 may be capable of completing at least 1000 cycles of charging and discharging at a current density of greater than or equal to about 1 mA/cm^2 , about 5 mA/cm^2 , about 10 mA/cm^2 , or about 20 mA/cm^2 .

[0034] Additionally, or alternatively, the battery 10 may exhibit a relatively high energy efficiency. For example, battery 10 may exhibit an energy efficiency of greater than or equal to 90% at a current density of greater than or equal to about 1 mA/cm^2 , about 5 mA/cm^2 , about 10 mA/cm^2 , or about 20 mA/cm^2 . In some examples, battery 10 may exhibit an energy efficiency of greater than or equal to 99% at a current density of greater than or equal to

about 1 mA/cm², about 5 mA/cm², about 10 mA/cm², or about 20 mA/cm².

[0035] FIG. 2 is a conceptual diagram illustrating the example battery 10 of FIG. 1 within an enclosed cell system 20. The enclosed cell system 20 may include a cell that houses battery 10 during operation of battery 10, a cell used to fabricate battery 10, or both. For example, enclosed cell system 20 may include a cell available from Swagelok of Solon, OH, under the trade designation SWAGELOK, and may be used to fabricate battery 10. In some examples, enclosed cell system 20 may include an inlet tube 22 and/or an outlet tube 24. Inlet tube 22 and outlet tube 24 may be used to introduce and remove air or other gases, such as the oxidizing gas of electrolyte 14, into and out of the enclosed cell.

[0036] FIG. 3 is a flow diagram illustrating an example technique for fabricating battery 10 of FIG. 1. The technique of FIG. 3 will be described with respect to enclosed cell system 20 of FIG. 2. In other examples, however, the technique of FIG. 3 may be used with a system other than enclosed cell system 20 of FIG. 2. Moreover, although the technique of FIG. 3 is described with respect to an enclosed cell system, in some examples, FIG. 3 may be used with a cell that is not fully enclosed (e.g., at least partially open).

[0037] The technique of FIG. 3 includes dissolving a metal halide in a solvent including a heterocyclic compound to form a solution (30). To dissolve the metal halide in the solvent including the heterocyclic compound, the metal halide may be added to the solvent including the heterocyclic compound and lightly stirred, such as lightly stirred overnight. In some examples, the solution of the metal halide dissolved in the solvent including the heterocyclic compound may have a concentration of between about 0.1 M and about 20 M, about 0.5 M and about 10 M, or about 1 M and about 5 M.

[0038] In some examples, the metal halide may be dried prior to being dissolved in the solvent including the heterocyclic compound. The drying temperature and/or drying time may be chosen based on the metal halide to be used in electrolyte 14, and in some non-limiting examples the metal halide may be dried on a hotplate in an argon filled glovebox at about 120°C for greater than 12 hours.

[0039] Additionally, or alternatively to drying the metal halide, in some examples, the solvent including the heterocyclic compound may also be dried prior to dissolving the metal halide therein. For example, the solvent including the heterocyclic compound may be stored overnight with a molecular sieve.

[0040] The technique of FIG. 3 further includes soaking the optional separator 18 with the solution (32). Soaking separator 18 with the solution may include dipping separator 18 into the solution, applying the solution to separator 18, or any other method of soaking separator 18 with the solution. In some examples, soaking separator 18 with the solution may include soaking separator 18 with the solution in a range of about 1 μL/cm² to about 500 μL/cm², about 10 μL/cm² to about 250 μL/cm², or about 50 μL/cm² to about 100 μL/cm².

[0041] The technique of FIG. 3 additionally includes stacking anode 12, optional separator 18 soaked with the solution, and current collector 16 within the enclosed cell system 20 (34), e.g., as shown in FIG. 2. In some examples, the stacking may include placing separator 18 between anode 12 and current collector 16. In some examples, one or more of anode 12, separator 18 soaked with the solution, or current collector 16 may be stacked prior to soaking separator 18 with the solution. For example, the separator 18 may be stacked on anode 12 and then soaked with the solution. In some cases, the enclosed cell system 20 may be at least partially open during the stacking procedure, and after anode 12, separator 18 soaked with the solution, and current collector 16 have been stacked, the enclosed cell system 20 may be closed or substantially closed to form a closed or substantially closed volume around anode 12, separator 18 soaked with the solution, and current collector 16.

[0042] In other examples, battery 10 may not include separator 18. In such examples, electrolyte 14 may be introduced to battery 10 in a different manner. For example, battery 10 may include electrolyte 14 between anode 12 and current collector 16 without separator 18. Electrolyte 14 may be introduced into battery 10 in any applicable manner such that electrolyte 14 can function as described herein. In this way, the technique of FIG. 3 may include stacking anode 12 and current collector 16 within enclosed cell system 20.

[0043] The technique of FIG. 3 also includes introducing an oxidizing gas to enclosed cell system 20 to produce electrolyte 14 and fabricate battery 10 (36). In some examples, introducing the oxidizing gas to enclosed cell system 20 to produce electrolyte 14 and fabricate battery 10 includes introducing the oxidizing gas to the enclosed cell 20 via inlet tube 24. In some examples, enclosed cell system 20 may include or be in the presence of an inert gas, such as argon, prior to introducing the oxidizing gas to enclosed cell system 20. In some such examples, introduction of the oxidizing gas may purge and completely replace the inert gas within enclosed cell system 20 with the oxidizing gas. For example, the oxidizing gas may be introduced to the enclosed cell 20 via inlet tube 24, and the inert gas may be purged through outlet tube 26. In some examples, the concentration of the oxidizing gas in enclosed cell system 20 may be between about 5 weight (wt) % and about 100 wt %, about 50 wt % and about 100 wt %, or about 80 wt % and about 100 wt % of the total amount of gases within enclosed cell system 20, such as of the total amount of the oxidizing gas and the inert gas within enclosed cell system 20.

[0044] The present invention will now be described with respect to the following non-limiting examples.

EXAMPLES

Example 1: Preparation of the Electrolyte and Cell Assembly

[0045] Lithium iodide (LiI) was placed in a vial and dried on a hot plate inside an argon filled glovebox (< 0.1 ppm H₂O, O₂) at 120 °C for 1 hour. γ -Butyrolactone (GBL), ϵ -Caprolactone (ECL), and Tetrahydrofuran (THF) were selected as suitable examples of heterocyclic compounds for the battery cell electrolyte, and were purified with a

molecular sieve (3 Å) overnight. 1M of dried LiI powder was added, dissolved into a solution including the selected heterocyclic compound, and lightly stirred overnight.

[0046] 1M LiI in the heterocyclic compound electrolyte solution was used to soak the separator positioned on top of the lithium metal anode, and a carbon coated current collector was placed on the other side of the separator. Thus, the separator wetted by the electrolyte solution was placed between the anode and the cathode and was in contact with both the anode and the cathode. The cell assembly was performed in an argon-filled glovebox.

[0047] All the cell components were placed within a cell available under the trade designation SWAGELOK from Swagelok, Inc., Solon, OH, which included both inlet and outlet tubing for oxygen flow. Oxygen was then introduced through the inlet tubing, purged and completely replaced the argon gas inside the cell.

[0048] As shown below, cells using electrolytes including GBL showed higher energy efficiency, whereas the use of ECL provided a longer cycle life. A mixture of these solvents would likely provide the strength of each solvent and become an ideal electrolyte system for the rechargeable metal halide battery.

[0049] For comparative examples, 1M LiI-GBL in an oxygen-free environment and 1M LiI in tetraethylene glycol dimethyl ether (TEGDME) in an oxygen-containing environment were tested with the same cell configuration.

Example 2: Rechargeable Lithium Iodide Battery with GBL Electrolyte and Oxygen

[0050] FIG. 4A shows 1st discharge and charge cycle of the cell of Example 1 incorporating 1M LiI-GBL electrolyte in the presence of ultrahigh purity oxygen at current density of 5 mA/cm². LiI was chosen as an example of the metal halide salt, GBL was selected as an example of the heterocyclic compound, and oxygen was chosen as an example of the oxidizing gas.

[0051] The cells maintained excellent energy efficiency (> 90%) and produced high output power (> 10 mW/cm²) over 500 cycles as shown in FIG. 4B. The specific capacity was normalized by the area of the electrode.

Example 3: Rechargeable Lithium Iodide Battery with ECL Electrolyte and Oxygen

[0052] FIG. 5A shows 1st discharge and charge cycle of a cell of Example 1 incorporating 1M LiI-ECL electrolyte in the presence of ultrahigh purity oxygen at current density of 5 mA/cm². LiI was chosen as an example of the metal halide salt, ECL was the heterocyclic compound, and oxygen was the oxidizing gas.

[0053] The cells maintained high output power (> 10 mW/cm²) over 500 cycles as shown in FIG. 5B. The specific

capacity was normalized by the area of the electrode.

Example 4: Rechargeable Lithium Iodide Battery with THF Electrolyte and Oxygen

[0054] Figure 6A shows 1st discharge and charge cycle of a cell of Example 1 incorporating 1M LiI-THF electrolyte in the presence of ultrahigh purity oxygen at current density of 5 mA/cm². LiI was chosen as the metal halide salt, THF was chosen as an example of the heterocyclic compound, and oxygen was selected as the oxidizing gas.

[0055] The cells maintained high output power (> 10 mW/cm²) for over 100 cycles as shown in FIG. 6B. The specific capacity was normalized by the area of the electrode.

Comparative Example 1: Lithium Iodide Battery with GBL Electrolyte without Oxygen

[0056] FIG. 7 shows 1st discharge and charge cycle of a cell of Example 1 incorporating 1M LiI-GBL electrolyte in the absence of oxygen at a current density of 5 mA/cm². The cell provides negligible discharge capacity in the 1st cycle with the same electrolyte solution as utilized in the cell of Example 2. The coulombic efficiency was less than 10% in the 1st cycle and did not improve at all in the following cycles. The specific capacity was normalized by the area of the electrode.

Comparative Example 2: Lithium Iodide Battery with TEGDME Electrolyte and Oxygen

[0057] FIG. 8 shows the 50th discharge and charge cycle of a cell of Example 1 incorporating 1M LiI-TEGDME electrolyte in the presence of ultrahigh purity oxygen at a current density of 5 mA/cm². The cell provides negligible discharge capacity in the 50th cycle under an oxygen environment. Although the coulombic efficiency of the cell was greater than 90% in the 1st cycle, it dropped significantly starting with the next cycle, and eventually dropped to less than 10% in the 50th cycle. The specific capacity was normalized by the area of the electrode. It is noteworthy from the result of this example that battery performance drops when the cyclic compound in the electrolyte does not include an ether group.

[0058] Various embodiments of the invention have been described. These and other embodiments of the invention are within the scope of the following claims.

CLAIMS

1. A battery, comprising:
an anode;
an electrolyte, wherein the electrolyte comprises:
an oxidizing gas;
an active cathode material comprising a metal halide; and
a solvent comprising a heterocyclic compound; and
a current collector contacting the active cathode material.
2. The battery of claim 1, wherein the solvent in the electrolyte comprises a heterocyclic compound selected from the group consisting of cyclic ethers, cyclic esters, and mixtures and combinations thereof.
3. The battery of claim 1, wherein the current collector comprises a porous material that is electrically conductive.
4. The battery of claim 1, further comprising a separator between the anode and the current collector.
5. The battery of claim 1, wherein the anode comprises at least one of Li, Mg, and Na.
6. The battery of claim 1, wherein the oxidizing gas is selected from the group consisting of oxygen, air, nitric oxide, nitrogen dioxide, and mixtures and combinations thereof.
7. The battery of claim 1, wherein the solvent in the electrolyte is selected from the group consisting of tetrahydrofuran, tetrahydropyran, tetrahydrothiophene, oxathiolane, succinimide, oxazolidone, γ -butyrolactone, γ -caprolactone, ϵ -caprolactone, γ -valerolactone, pyrrolidine, imidazolidine, sulfolane, thiane, and mixtures and combinations thereof.
8. The battery of claim 1, wherein the metal halide comprises an electrolyte salt that dissociates into a respective halide ion and a respective metal ion in the solvent, and wherein the halide ion comprises an ion of at least one of I, Br, Cl, and F, and the metal ion comprises an ion of at least one of Li, Mg, and Na.
9. The battery of claim 1, further comprising an additional salt that dissociates into a respective metal ion and a respective counter anion, wherein the metal ion is selected from the group consisting of Li, Mg, and Na, and mixtures and combinations thereof, and the anion is selected from the group consisting of nitrate (NO_3^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), bisoxalato borate (BOB^-), and difluorooxalato borate (DFOB^-), trifluoromethanesulfonate (TF^-), trifluorosulfonylimide (TFSI^-), and mixtures and combinations thereof.

10. The battery of claim 1, wherein the solvent further comprises an organic solvent selected from the group consisting of an ether, a glyme, a carbonate, a nitrile, an amide, an amine, an organosulfur solvent, an organophosphorus solvent, an organosilicon solvent, a fluorinated solvent, and mixtures and combinations thereof.
11. The battery of claim 1, further comprising a dedicated cathode material in addition to the active cathode material comprising the metal halide, wherein the dedicated cathode material provides a conductive path to an external electrical circuit to which the battery is connected.
12. A battery, comprising:
- (a) an anode that takes up metal ions from an electrolyte during charging, and releases the ions to the electrolyte during discharging, the electrolyte comprising:
 - (i) a solvent comprising a heterocyclic compound, and
 - (ii) a dissolved halide, wherein the halide functions as a cathode for the battery;
 - (b) a solid electrolyte interphase (SEI) layer contacting the anode, the SEI layer including an oxide of the metal ions; and
 - (c) a current collector comprising an electrically conductive porous material, wherein the current collector contacts the dissolved halide.
13. The battery of claim 12, wherein the electrolyte is non-aqueous.
14. The battery of claim 12, wherein the halide is selected from the group consisting of I-, Br-, Cl-, F-, and mixtures and combinations thereof.
15. The battery of claim 12, wherein the electrolyte comprises a salt that releases the metal ions.
16. The battery of claim 12, wherein the anode comprises an intercalation host material capable of taking up metal ions.
17. The battery of claim 12, further comprising a second cathode in addition to the metal halide that functions as the active cathode material.
18. A method of forming a battery, comprising:
- dissolving a metal halide in a solvent, the solvent comprising a heterocyclic compound, thereby forming a solution;
 - soaking a separator with the solution;
 - stacking an anode, the separator soaked with the solution, and a current collector, wherein the stacking comprises placing the separator soaked with the solution between the anode and the current collector; and

introducing an oxidizing gas to the stacked anode, the separator soaked with the solution, and the current collector to form the battery, wherein the battery comprises:

an anode,

an electrolyte, comprising:

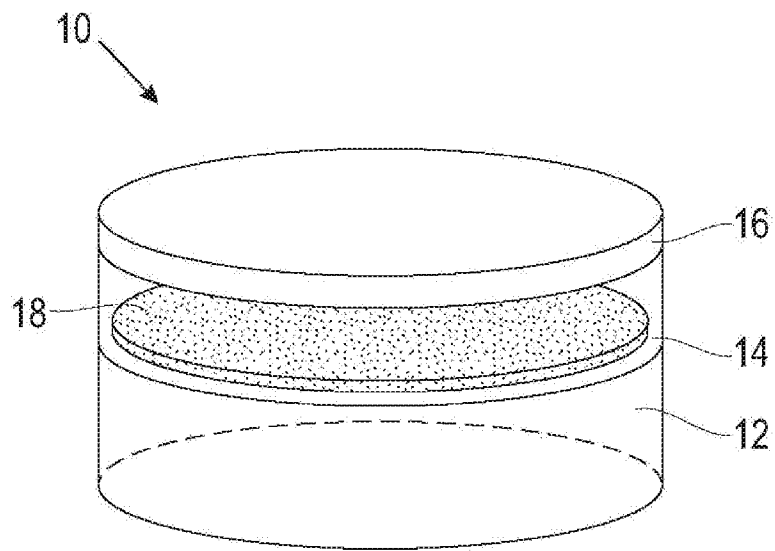
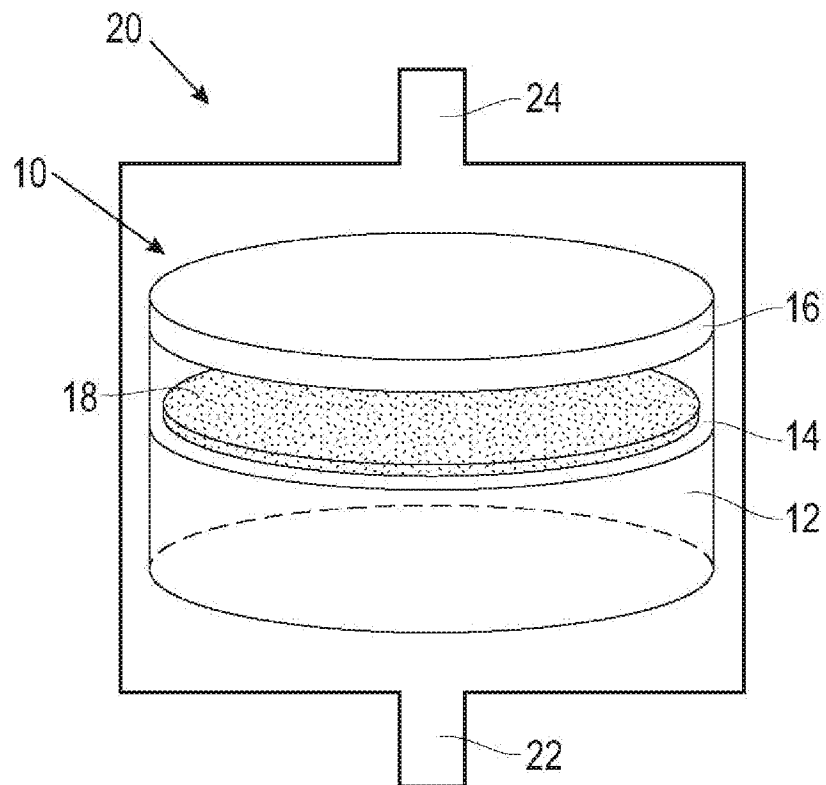
an oxidizing gas;

an active cathode material comprising a metal halide; and

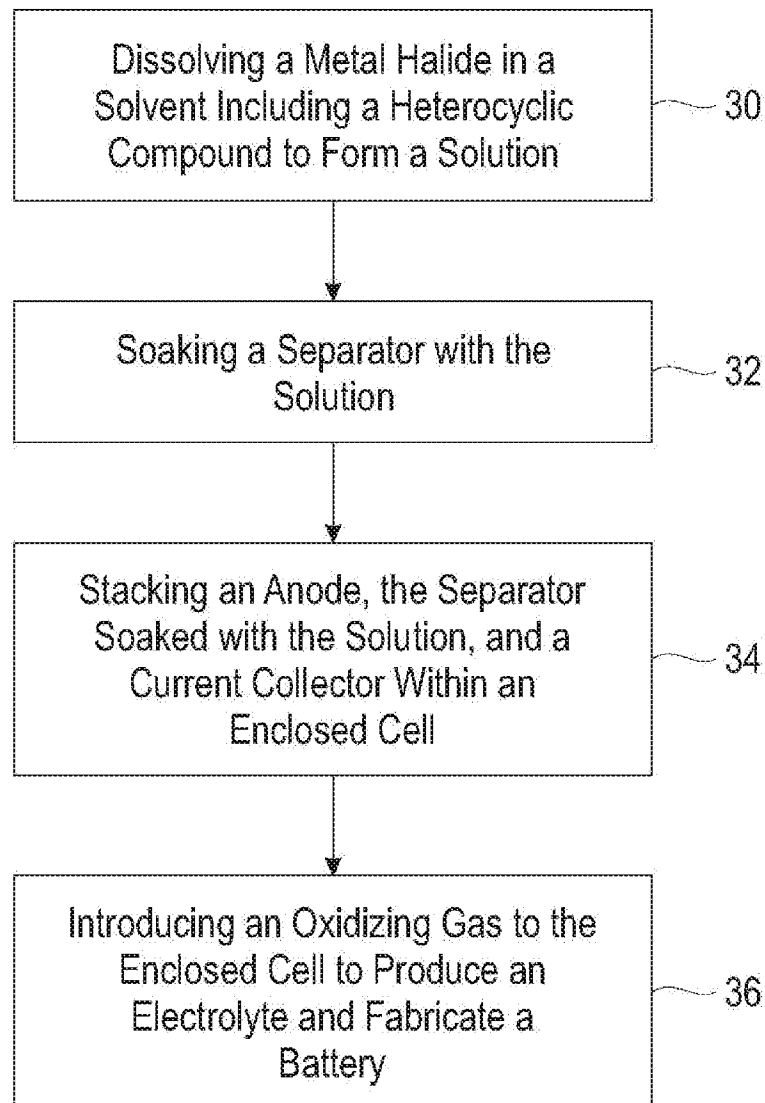
a solvent comprising a heterocyclic compound; and

a current collector contacting the cathode material.

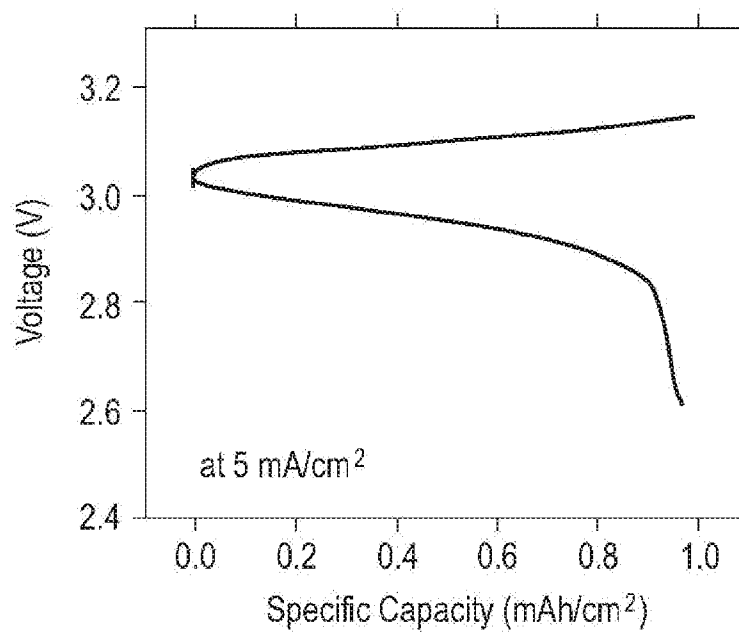
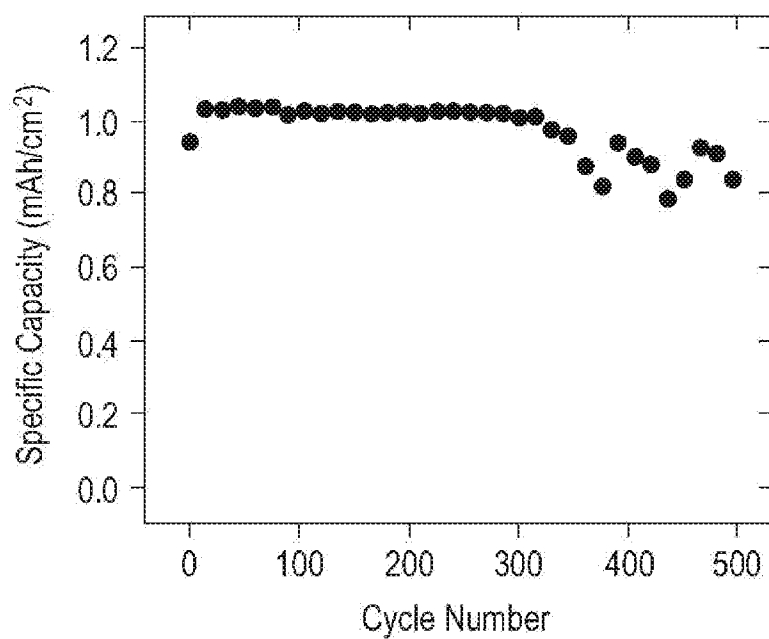
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**FIG. 1****FIG. 2**

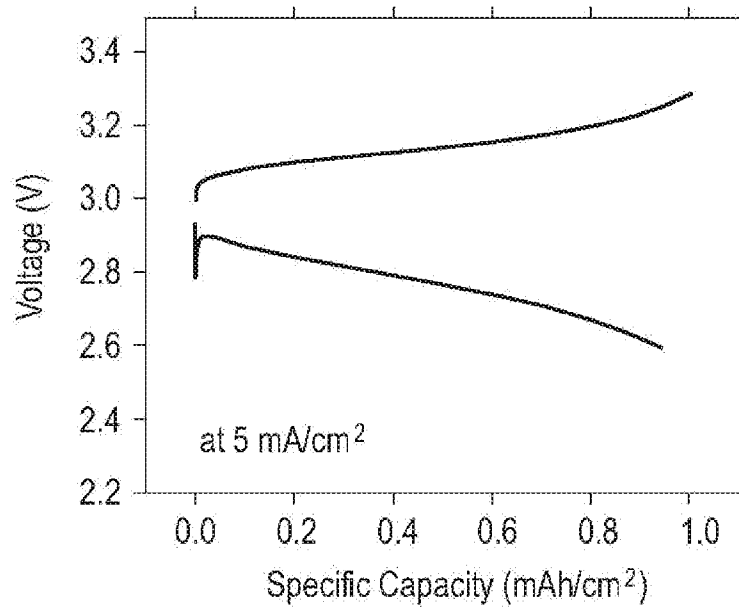
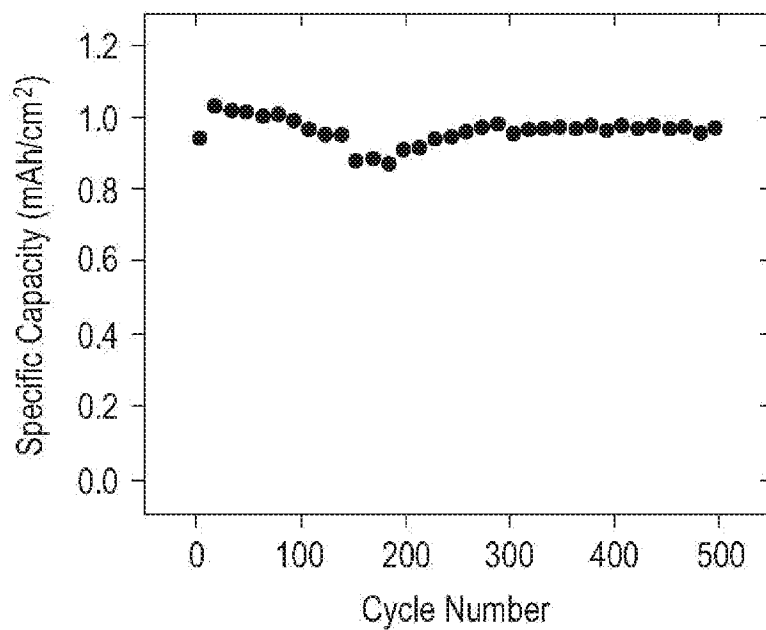
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**FIG. 3**

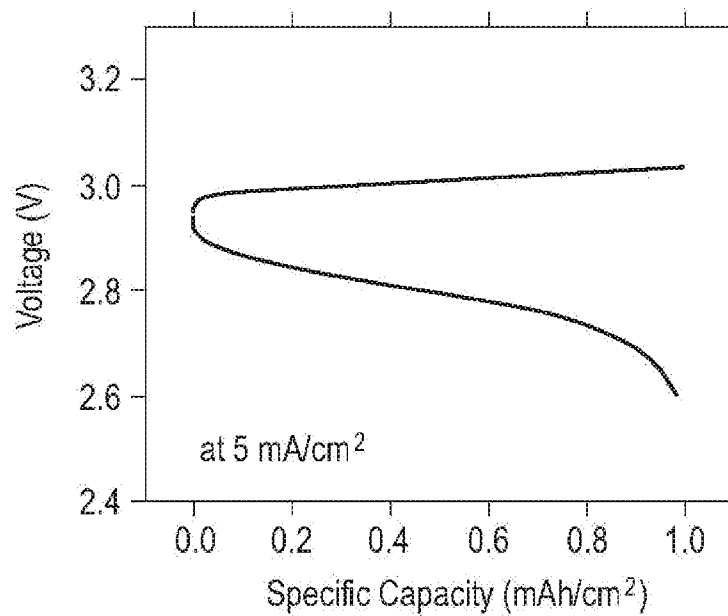
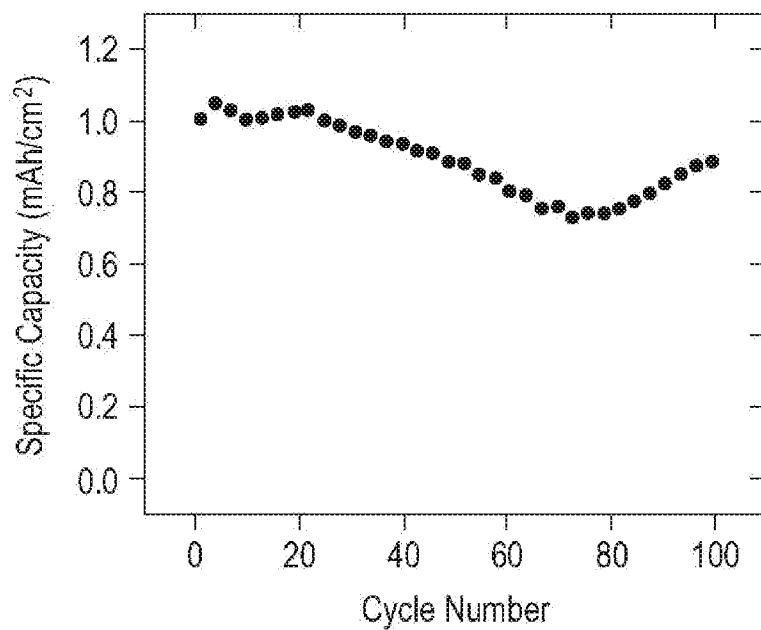
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**FIG. 4A****FIG. 4B**

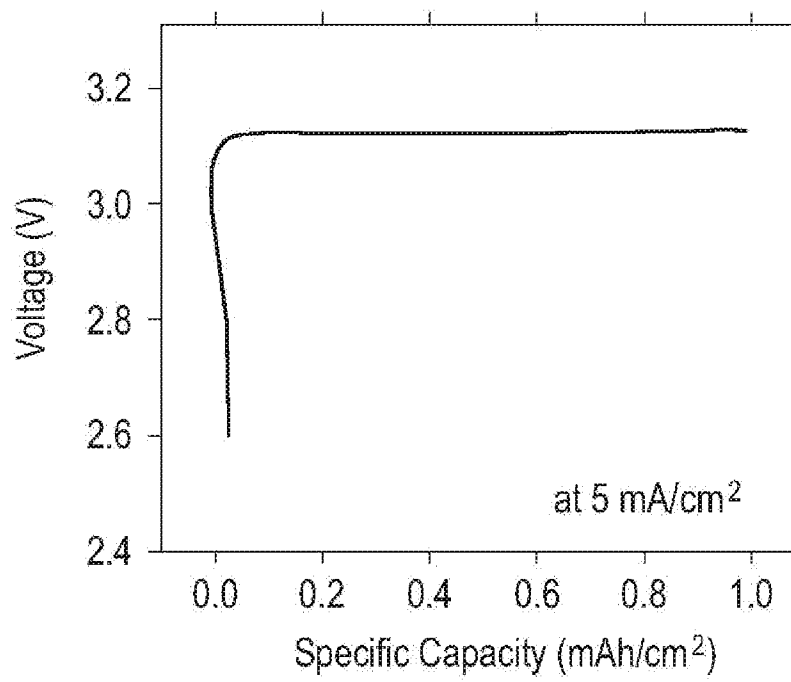
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**FIG. 5A****FIG. 5B**

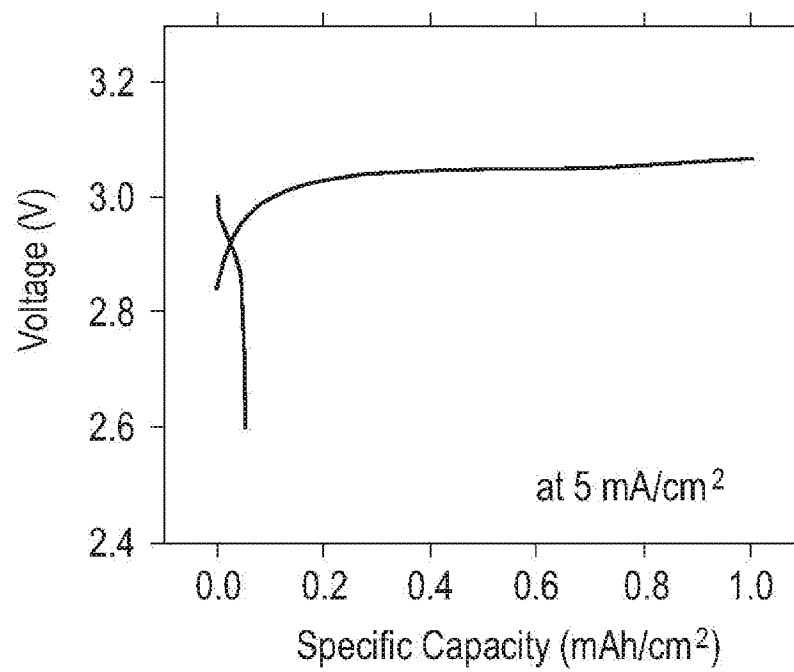
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**FIG. 6A****FIG. 6B**

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**FIG. 7**

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**FIG. 8**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2020/051752

A. CLASSIFICATION OF SUBJECT MATTER

H01M 6/14(2006.01)i; H01M 4/06(2006.01)i

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)

H01M

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

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

CNPAT,EPODOC,WPI,CNKI,IEEE: battery, cell, electrolyte, anode, cathode, collector, separator, oxygen, air, oxid+, +cyclic, redox, inlet, outlet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 104916810 A (GM GLOBAL TECHNOLOGY OPERATIONS LLC.) 16 September 2015 (2015-09-16) (description, paragraphs [0013]-[0054], and figure 1	12-17
Y	US 4296185 A (CATANZARITE, Vincent O.) 20 October 1981 (1981-10-20) claims 1-14, description, column 3 line 14 - column line 68	12-17
A	CN 106207264 A (GM GLOBAL TECHNOLOGY OPERATIONS LLC.) 07 December 2016 (2016-12-07) the whole document	1-18
A	CN 101567472 A (INSTITUTE OF PHYSICS, CHINESE ACADEMY OF SCIENCE) 28 October 2009 (2009-10-28) the whole document	1-18
A	CN 101267046 A (SAMSUNG SDI CO., LTD.) 17 September 2008 (2008-09-17) the whole document	1-18
A	US 2013137001 A1 (U.S GOVERNMENT AS REPRESENTED BY THE SECRETARY OF THE ARMY) 30 May 2013 (2013-05-30) the whole document	1-18

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

* Special categories of cited documents:

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“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

19 May 2020

Date of mailing of the international search report

28 May 2020

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Telephone No. 86-(10)-53961229

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/IB2020/051752

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				US	10593988	B2	17 March 2020
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				EP	1970989	B1	18 November 2009
				US	2008226977	A1	18 September 2008
				DE	602008000271	D1	31 December 2009
				CN	101267046	B	24 November 2010
				EP	1970989	A1	17 September 2008
				KR	100884439	B1	19 February 2009
US	2013137001	A1	30 May 2013	US	2015318590	A1	05 November 2015