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- (71) Applicants: **INTERNATIONAL BUSINESS MACHINES CORPORATION** [US/US]; New Orchard Road, Armonk, NY 10504 (US). **VOLKSWAGEN AG** [DE/DE]; 38436 Wolfsburg (DE).
- (72) Inventors: **KIM, Ho-Cheol**; 650 Harry Road, San Jose, CA 95120 (US). **MCCLOSKEY, Bryan, D.**; 650 Harry Road, San Jose, CA 95120 (US). **SCHEFFLER, Rouven**; 500 Clipper Drive, Belmont, CA 94002 (US). **SPEIDEL, Angela-Kristina**; 500 Clipper Drive, Belmont, CA 94002 (US). **SWANSON, Sally, A.**; 6042 Crossmont Court, San Jose, CA 95120 (US). **WALLRAFF, Gregory, M.**; 650 Harry Road, San Jose, CA 95120 (US).
- (74) Agent: **KALAITZIS, Parashos**; IBM Corporation, 2070 Route 52 / Bldg.321 / Zip 482, Hopewell Junction, NY 12533 (US).
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(54) Title: CATHODE MATERIAL FOR LITHIUM-OXYGEN BATTERY

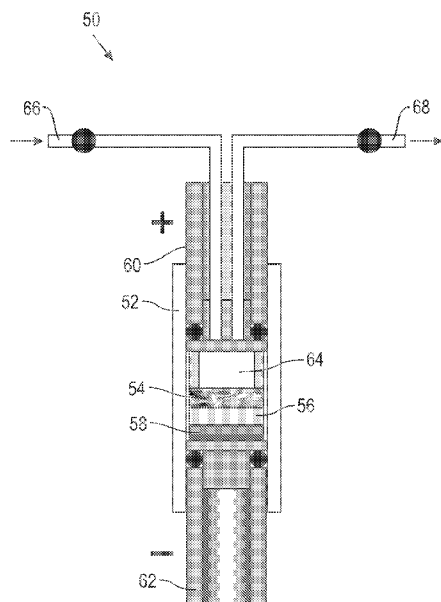


FIG. 6

(57) Abstract: A lithium-oxygen battery may include an anode, a cathode, and an electrolyte between, and in contact with, the anode and the cathode. The anode may include lithium and/or a lithium alloy. In some examples, the cathode defines a surface that is predominantly metal oxide with an electron conductivity of at least 10^{-1} Siemens per centimeter. In some examples, the cathode defines a surface in contact with oxygen, and includes ruthenium oxide. In some examples, the cathode defines a surface that is substantially covered by ruthenium oxide and is in contact with oxygen.



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CATHODE MATERIAL FOR LITHIUM-OXYGEN BATTERY

Technical Field

001 The disclosure relates to lithium-oxygen batteries.

Background

002 Battery technology is continually being developed to enable higher energy density and greater efficiency, thereby permitting use of batteries as power sources for more applications. For example, there is currently a great drive toward the use of batteries for electric vehicle propulsion. Current battery technologies, such as lead-acid or lithium ion batteries, have a lower gravimetric energy density (e.g., expressed as watt-hours per kilogram; Wh/kg) than is desired for use in extended range electric vehicles. Other applications for battery technology may also benefit from battery technologies that provide a higher energy density.

003 A rechargeable lithium-oxygen (Li-O₂) battery can store, theoretically, about 5–10 times more energy than current lithium ion batteries. The high energy density makes the Li-O₂ battery very attractive as an emerging energy storage system for a wide range of applications, including propulsion of electric vehicles. A Li-O₂ battery is composed of a Li metal anode, an air cathode, where oxygen is accessed from the external environment, and an electrolyte containing Li salts, which is in contact with both the anode and cathode. In some examples, oxygen may be provided from air, in which case, the battery may be referred to as a Li-air battery.

Disclosure of the Invention

004 Li-O₂ and Li-air batteries operate by reduction of O₂ to form lithium peroxide (Li₂O₂) on the cathode during discharge, with the process being reversed on charge. Because the chemistry during battery operation is related to generation of superoxides and peroxides (e.g., Li₂O₂), which are highly reactive, the chemical stability of materials used for the cathode affects whether the Li-O₂ battery is stable over repeated charges and discharges.

005 This disclosure describes a new material for a cathode of a Li-O₂ battery. In some examples, the cathode material may include an electrically conductive metal oxide that includes an electron conductivity of at least about 10⁻¹ Siemens per centimeter (S/cm; about 10 S/m). In some examples, the electrically conductive metal oxide may be active to the electrochemistry of the Li-O₂ battery, e.g., to the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that occur at the cathode during discharging and charging of the Li-O₂ battery, respectively. Additionally, in some examples, the electrically conductive metal oxide may be substantially stable in the presence of intermediates and products of the electrochemistry, such as Li₂O₂ and superoxides.

006 In some examples, the cathode material may include ruthenium oxide (RuO₂). RuO₂ is substantially chemically stable in the presence of superoxide and Li₂O₂, is active for the electrochemistry of a Li-O₂ battery, and is electrically conductive. RuO₂ may be present in the cathode at a concentration of greater than, for example, 10 molar percent (mol. %). RuO₂ may be present at a surface of the cathode. In some examples, the surface of the cathode may be substantially covered by RuO₂.

007 In one aspect, the disclosure describes a lithium-oxygen battery including an anode comprising lithium; a cathode defining a surface in contact with oxygen, wherein the cathode comprises ruthenium oxide; and a non-aqueous electrolyte between, and in contact with, both the anode and the cathode.

008 In a further aspect, the disclosure describes a lithium-oxygen battery including a negative electrode comprising lithium; a positive electrode defining a surface, wherein the surface is predominantly metal oxide with an electron conductivity of at least 10⁻¹ S/cm; and an aprotic electrolyte between, and in contact with, both the negative electrode and the positive electrode.

009 In another aspect, the disclosure describes a method including forming a cathode comprising ruthenium oxide, forming an electrode comprising lithium, and assembling the

cathode and anode with a non-aqueous electrolyte to form a lithium-oxygen battery, wherein the non-aqueous electrolyte is between, and in contact with, both the anode and the cathode.

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

Brief Description of the Drawings

0011 FIG. 1 is a conceptual and schematic diagram illustrating an example of an aprotic lithium-oxygen battery.

0012 FIG. 2 is a conceptual and schematic diagram illustrating an example of a bulk electrochemical cell utilizing lithium-oxygen electrochemistry.

0013 FIG. 3 is a cyclic voltammogram of examples of electrochemical cells with either stainless steel or ruthenium oxide-coated stainless steel electrodes.

0014 FIG. 4 is a cyclic voltammogram illustrating an example of cycle stability of a ruthenium oxide electrode.

0015 FIG. 5 is an image of an example of a porous cathode prepared by spreading ruthenium oxide paste on a stainless steel mesh.

0016 FIG. 6 is a conceptual and schematic diagram illustrating an example of a lithium-oxygen battery with a Swagelok® type geometry.

0017 FIG. 7 is a plot of discharge and recharge behavior of an example of a lithium-oxygen battery with a cathode including ruthenium oxide.

0018 FIG. 8 is a plot of discharge and recharge behavior of an example of a lithium-oxygen battery with a cathode including carbon.

0019 FIG. 9 is a plot of gas evolution during discharge of an example of a lithium-oxygen battery with a cathode including ruthenium oxide.

0020 FIG. 10 is an image showing an example of a RuO₂-based cathode when heated to a temperature close to a decomposition temperature of lithium peroxide.

0021 FIG. 11 is a plot of discharge and recharge behavior over 10 cycles of an example of a lithium-oxygen battery with a cathode including ruthenium oxide.

Detailed Description

0022 The disclosure describes lithium-oxygen (Li-O₂) batteries (including lithium-air batteries) and techniques for forming lithium-oxygen batteries. For example, the disclosure describes cathode materials for Li-O₂ batteries. The cathode materials may include, for example, ruthenium oxide (RuO₂), which is electrically conductive, active for the electrochemistry of the Li-O₂ battery, and is stable in the presence of products of Li-O₂ battery operation.

0023 Li-O₂ batteries may provide a relatively high gravimetric energy density (watt-hours per kg; Wh/kg), e.g., compared to lithium ion or lead-acid batteries. The theoretical gravimetric energy density of a Li-O₂ battery is about 11,680 Wh/kg, which is calculated using the oxidation of 1 kg of lithium metal. This energy density compares favorably to the gravimetric energy density of gasoline, the current fuel of choice for vehicles, which is about 13,000 Wh/kg.

0024 Other considerations also impact the design and function of Li-O₂ batteries. For example, the power density (measured in watt per kilogram; W/kg) is important for propulsion of a vehicle. The power density of Li-O₂ batteries is currently low. While not wishing to be bound by any theory, current research results indicate that the mechanism of energy discharge in a Li-O₂ battery is reduction of oxygen in the presence of lithium ions to form lithium oxides (such as lithium peroxide). Hence, very large surface areas are required to provide high power. For example, a battery with 100 kW power output at a cell voltage of 2.5 volts (V) and a current density of 25 milliamps per square centimeter (mA/cm²) may require an internal surface area of 160 m².

0025 A Li-O₂ battery may include one of four chemistries: aprotic liquid electrolyte, aqueous electrolyte, a mixed system including an aqueous electrolyte immersing the cathode and an aprotic electrolyte immersing the anode, and a solid-state battery including a solid electrolyte. The fundamental chemistry of energy storage and discharge is affected by the electrolyte surrounding the cathode.

0026 The Li-O₂ battery described in this disclosure includes a Li metal and/or alloy anode, a cathode including a conductive, porous material, and a lithium ion (e.g., Li⁺) conducting electrolyte, which is in contact with both the anode and the cathode. Some cathodes for Li-O₂ batteries use carbon as the conductive, porous material, because carbon is relatively stable to electrochemistry of the battery, allows easy preparation of highly porous structures, and is inexpensive. For example, high surface area carbon black powder may be used as a cathode after binding onto metal meshes using polymeric binders. However, carbon may react with lithium peroxide (Li₂O₂), a product of the battery operation, to form lithium carbonate. The reaction between Li₂O₂ and carbon for forming lithium carbonate is strongly exothermic.

0027 The disclosure describes an alternative material for a cathode of a Li-O₂ battery. In some examples, the cathode may include ruthenium oxide (RuO₂). RuO₂ is substantially inert to the intermediates and products of Li-O₂ battery operation, such as Li₂O₂. RuO₂ is also electrically conductive and gives oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) activity. In some examples, the cathode may include RuO₂ alone, or in combination with one or more other metal oxides or other materials. For example, the cathode may include a stainless steel mesh at least partially covered with a RuO₂ paste and/or a RuO₂ film. In some examples, the cathode may include a surface coverage of, e.g., greater than 10%. In some examples, the cathode may include a surface predominantly covered with RuO₂, e.g., at least 50% of the surface of the cathode may be covered with RuO₂.

0028 In other examples, a cathode for a Li-O₂ battery may include a surface predominantly covered with a metal oxide that has an electron conductivity of at least about 10⁻¹ Siemens per centimeter (S/cm; about 10 S/m). The metal oxide may cover more than 10% of the surface of the cathode, or may cover at least about 50% of the surface (i.e., may predominantly cover the surface). In some examples, the cathode may include at least two different metal oxides. The metal oxide or one of the at least two metal oxides may include RuO₂.

0029 FIG. 1 is a conceptual and schematic diagram that illustrates an example of a Li-O₂ battery 10. In some examples, Li-O₂ battery 10 may utilize an aprotic electrolyte, and may be referred to as an aprotic Li-O₂ battery. In other examples, Li-O₂ battery 10 may utilize another type of electrolyte, such as an aqueous electrolyte, a mixed system including an aqueous electrolyte immersing the cathode and an aprotic electrolyte immersing the anode, or a solid electrolyte.

0030 Li-O₂ battery 10 includes an anode 12. In some examples, anode 12 consists essentially of lithium. In other examples, anode 12 may include lithium alloyed with one or more additional elements. In some implementations, anode 12 may include a thin film formed on a surface of anode 12. The thin film may be a lithium-ion conductive film, such as a lithium-ion-conducting polymer, a lithium-ion-conducting block co-polymer, a lithium-ion-conducting ceramic, or a lithium-ion-conducting polymer-ceramic composite. In some examples, a thin film of lithium-stable conductive material may be present between the lithium anode and the thin film.

0031 Anode 12 is in contact with (e.g., at least partially surrounded by) electrolyte 14. Electrolyte 14 may include a non-aqueous medium, including, but not limited to, an aprotic liquid, such as, for example, an organic solvent. The organic solvent may include, for example, an ether, including alkyl ethers or cyclic ethers (e.g., tetrahydrofuran (THF) or dioxolane); an ester, including γ -butyrolactone; N-methyl-2-pyrrolidone (NMP); dimethyl sulfoxide (DMSO); or another solvent suitable for use in a metal-air and/or metal-oxygen battery. Electrolyte 14 may solvate lithium salts, such as LiPF₆, LiClO₄, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), LiBF₆, LiAsF₆, LiN(SO₂CF₃)₂, LiSO₃CF₃, and/or other salts suitable for use in a metal-air and/or metal-oxygen battery, to form ions, including Li⁺ ions 18. Electrolyte 14 also may have a relatively high oxidative stability. In other examples, electrolyte 14 may include an aqueous electrolyte, a mixed system including an aqueous electrolyte immersing cathode 16 and an aprotic electrolyte immersing lithium anode 12, or a solid electrolyte.

0032 Li-O₂ battery 10 also includes a cathode 16. In some examples, cathode 16 may include an electrically conductive metal oxide that gives OER and ORR activity. In some examples, cathode 16 may be chemically stable in the presence of OER and/or ORR products, such as superoxides and/or Li₂O₂.

0033 In some examples, cathode 16 includes a conductive metal oxide. In some implementations, the conductive metal oxide may possess an electron conductivity of at least 10⁻¹ S/cm. Metal oxides that can be used, which possess an electron conductivity of at least 10⁻¹ S/cm, include, for example, ruthenium oxide (RuO₂), titania suboxides (TiO_{2-x}), tungsten oxide (WO₂), strontium-ruthenium oxide (SrRuO₃), chromium oxide (CrO₂), molybdenum oxide (MoO₂), rhodium oxide (RhO₂), technetium oxide (TcO₂), rhenium oxide (ReO₂), and/or iridium oxide (IrO₂). For example, RuO₂ possesses an electron conductivity of greater than 10⁻⁴ S/cm.

0034 Additionally, RuO₂ may be present at a surface of cathode 16, such that RuO₂ can be in contact with gaseous oxygen molecules 20 that are provided from a back side of cathode 16. In some examples, cathode 16 may include a surface coverage of greater than about 10% of RuO₂. In some examples, the surface of cathode 16 may be predominantly covered (e.g., at least about 50 percent covered) with RuO₂.

0035 In some examples, cathode 16 may include at least two metal oxides. In some implementations, the at least two metal oxides may include RuO₂ and at least one other metal oxide. The at least one other metal oxide may be electrically conductive (e.g., an electron conductivity of at least about 10⁻¹ S/cm) in some examples. The at least one other metal oxide may provide activity for OER and/or ORR at cathode 16. In other examples, the at least one other metal oxide may not provide activity for OER and/or ORR at cathode 16. In some examples, the at least one other metal oxide may be inert to the intermediates and products of Li-O₂ battery operation, such as Li₂O₂. Hence, in some examples, the at least one other metal oxide may contribute to at least one of electrical conductivity, chemical activity, and/or inertness to intermediates and products of Li-O₂ battery operation. For example, the

at least one other metal oxide may include a titania suboxide (TiO_{2-x}), WO_2 , SrRuO_3 , CrO_2 , MoO_2 , RhO_2 , TcO_2 , ReO_2 , and/or IrO_2 .

0036 As shown in FIG. 1, cathode 16 may be formed as a porous structure. Cathode 16 may include solid portions with pores and/or channels 24 formed between the solid portions. Pores and/or channels 24 allow contact between the oxygen molecules 20 and the Li^+ ions 18 from electrolyte 14 at the surface of cathode 16. In this way, pores and/or channels 24 may facilitate oxidation of Li^+ ions 18 during the ORR and reduction of Li_2O_2 during the OER.

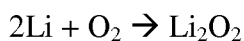
0037 Porosity of cathode 16 may be formed in a variety of ways, such as by forming the electrically conductive metal oxide (e.g., RuO_2) as a monolithic, porous structure using structure-directing materials, such as a surfactant and/or other sacrificial material. For example, precursors of the electrically conductive metal oxide may be deposited simultaneously with a sacrificial material. The sacrificial material and electrically conductive metal oxide may be selected such that the electrically conductive metal oxide forms a continuous matrix phase upon deposition with discontinuous domains of sacrificial material. After deposition is complete, the sacrificial material may be removed, e.g., by heating the structure to burn the sacrificial material or by using a chemical to selectively remove the sacrificial material. Once the sacrificial material is removed, a monolithic, porous structure including the electrically conductive metal oxide remains.

0038 As another example, cathode 16 may be formed using a paste and a structural support. In some examples, the structural support may be conductive and act as a current collector. The paste may include the electrically conductive metal oxide (e.g., RuO_2) powder mixed with a binder. The binder may be, for example, a thermoplastic resin or a thermosetting resin. For example, the binder may include polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene (PE), polyacrylonitrile (PAN), or the like. In some examples, the binder includes at least two thermoplastic resins and/or thermosetting resins.

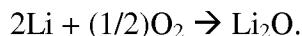
0039 The paste may be applied to structural support 28. In some examples, the structural support may be formed of an electrically non-conductive (e.g., insulating) material. The structural support may be at least partially covered with at least one electrically conductive metal oxide, e.g., RuO₂, a titania suboxide (TiO_{2-x}), WO₂, SrRuO₃, CrO₂, MoO₂, RhO₂, TcO₂, ReO₂, and/or IrO₂. In other examples, the structural support may be formed of an electrically conductive material. Structural support materials include, but are not limited to, 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. Other materials for the structural support may include, for example, stainless steel mesh, aluminum (Al) mesh, nickel (Ni) foam, and carbon paper.

0040 In some examples, an electrically structural support 28 may function as a current collector. Alternatively, cathode 16 may include a separate current collector. A current collector may include a material of suitable electrical conductivity that is electrically connected to cathode 16 and collects electrons generated at the cathode 16 during discharge of Li-O₂ battery 10 and provides a conductive path to an external electrical circuit to which Li-O₂ battery 10 is connected. Similarly, during recharge of Li-O₂ battery 10, the current collector provides an electrical pathway between an external voltage source and cathode 16 to supply voltage for decomposition of Li₂O₂ via the oxygen evolution reaction (OER) (described below). For example, the current collector 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. Materials for the support include, for example, stainless steel mesh, aluminum (Al) mesh, nickel (Ni) foam, and carbon paper. In other examples, the electrically conductive metal oxide (e.g., RuO₂) may function as the current collector and cathode 16 may not include a separate current collector.

0041 In operation of Li-O₂ battery 10, cathode 16 is fed oxygen molecules 20 by an oxygen source 29. The oxygen source may be fluidly connected to a side of cathode 16 away from electrolyte 14. It is currently understood that the fundamental rechargeable cathode discharge reactions in aprotic lithium-oxygen battery 10 are:



and possibly



Hence, insoluble Li_2O_2 22 is formed via the oxygen reduction reaction (ORR) during the discharge reactions. The discharge reactions cause a voltage difference between anode 12 and cathode 16. During recharge of the Li- O_2 battery 10, a voltage is applied to anode 12 and cathode 16 via voltage source 26, and oxygen is evolved by decomposition of Li_2O_2 to Li^+ ions 18 via the oxygen evolution reaction (OER). As described above, the electrically conductive metal oxide (e.g., RuO_2) may provide ORR and OER activity, facilitating these reactions. Additionally, the electrically conductive metal oxide (e.g., RuO_2) may be substantially stable in the presence of Li_2O_2 and other intermediates and products of the OER and ORR.

0042 In some examples, the electrically conductive metal oxide (e.g., RuO_2) may also be thermally stable at temperatures which Li- O_2 battery 10 is likely to experience, along with temperatures within a safety margin above normal operating temperatures of Li- O_2 battery 10. For example, electrically conductive metal oxide (e.g., RuO_2) may exhibit thermal stability up to a temperature of about 220°C.

Example 1

0043 FIG. 2 is a conceptual and schematic diagram illustrating an example of a bulk electrochemical cell utilizing lithium-oxygen electrochemistry. RuO_2 thin films were deposited on a stainless steel disc (0.5" diameter) by sputtering. A bulk electrochemical cell 30 was prepared by placing two electrodes, i.e., a metallic lithium anode 32 and a RuO_2 coated stainless steel disc 34, in electrolyte 36. A solution of 0.25 molar (M) LiTFSI in DME was used as electrolyte 36. Lithium was used as a reference electrode 38. Cell 30 was bubbled with oxygen (O_2) or argon (Ar) 40 from O_2 or Ar source 42 during the measurement. Excess O_2 or Ar was removed from cell 30 using an outlet 44.

0044 Cyclic voltammetry (CV) was used to investigate ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) activities of the RuO_2 surface. FIG. 3 presents a cyclic voltammogram of a stainless steel cathode and a cathode including RuO_2 coated stainless

steel disc 34. The stainless steel cathode does not show any redox activities during CV measurement in an O₂ environment. In comparison, the RuO₂ coated stainless steel disc 34 shows clear redox activities in an O₂ environment. When Ar gas was introduced instead of O₂, the redox activity of RuO₂ coated stainless steel disc 34 disappears, suggesting the redox activity is ORR and OER on the RuO₂ surface.

Example 2

0045 The cycling stability of an electrode including RuO₂ was tested with CV. FIG. 4 is a cyclic voltammogram illustrating an example of cycle stability of a ruthenium oxide electrode under the same experimental setup in Example 1. FIG. 4 illustrates stable cycling behavior of the electrode including RuO₂ between potentials of 1.9 volt (V) and 4.2 V. FIG. 4 also illustrates that instability was exhibited when cycling from 1.9 V to 4.0 V. This suggests that the lower voltage of 4.0 V may have been insufficient to fully remove all material deposits on the surface of the electrode during the oxygen evolution reaction. However, considering that stable cycling of a carbon based cathode uses a potential range of 2.0 V to 4.55 V, RuO₂ shows cycling stability for a lower potential range.

Example 3

0046 A Li-O₂ battery was prepared to test discharging and charging properties. FIG. 5 is an image of an example of a porous cathode prepared by spraying RuO₂ paste on a stainless steel mesh. Stainless steel mesh (left side of FIG. 5) was cut into ½ inch diameter segments and coated with RuO₂ paste, which was prepared by mixing RuO₂ powder with 20 weight percent (wt. %) of polytetrafluoroethylene (PTFE) in a water dispersion. A battery was assembled using a Swagelok® type geometry. FIG. 6 is a conceptual and schematic diagram illustrating an example of a Li-O₂ battery with a Swagelok® type geometry. Li-O₂ battery 50 includes quartz tubing 52 forming a package for cathode 54, electrolyte/separator 56, and Li anode 58. Li metal anode 58 was about 248 microns thick. Electrolyte/separator 56 included a monolayer polypropylene separator available under the trade designation Celgard® 2400 from Celgard, LLC, Charlotte, North Carolina, soaked in 0.25M LiTFSI in DMF solution. Cathode 54 included a RuO₂-coated stainless steel mesh.

0047 A positive terminal 60 was electrically connected to cathode 54, and a negative terminal 62 was electrically connected to Li anode 58. Above cathode 54 was a head space 64, which provided a manifold for oxygen entering Li-O₂ battery 50 from oxygen inlet 66 and gases exiting Li-O₂ battery 50 via outlet 68.

0048 Battery 50 was discharged/recharged with 200 μ A for 5 hours while monitoring the consumption and generation of O₂. FIG. 7 is a plot of discharge and recharge behavior of an example of a Li-O₂ battery with a cathode including RuO₂. FIG. 8 is a plot of discharge and recharge behavior of an example of a Li-O₂ battery with a cathode including carbon. The Li-O₂ battery with the carbon cathode included a geometry similar to that of the Li-O₂ battery with the RuO₂-coated stainless steel mesh cathode.

0049 FIG. 7 shows that the Li-O₂ battery utilizing the RuO₂-coated stainless steel mesh cathode offers very stable discharge potential. For recharge, the cell with the RuO₂-coated stainless steel mesh cathode shows much lower recharging potential than a carbon cathode. The cell including the carbon cathode shows almost a linear increase of potential during the entire period of recharging. This suggests that a RuO₂-coated stainless steel mesh cathode allows less overpotential during recharging, which may reduce any likelihood of decomposing materials in the cell during recharging.

0050 FIG. 9 is plot of gas evolution during discharge of an example of a Li-O₂ battery with a cathode including RuO₂. The Li-O₂ battery had the Swagelok® geometry described above. Gas evolution was measured using DEMS (differential electrochemical mass spectroscopy). As shown in FIG. 9, O₂ evolves during recharging and some CO₂ evolves at the very end of the recharge, which may be due to another chemical reaction in the cell, such as a reaction in the electrolyte. Also, a very small amount of H₂ evolves, which is believed to be due to possible decomposition of the electrolyte and/or trace amounts of water in the electrolyte.

Example 4:

0051 The reaction of the discharge product of the Li-O₂ battery with cathode materials was tested. A carbon-based cathode (Ketjenblack® with PTFE binder) and RuO₂-based cathode

were prepared using Ni foam as the current collector and discharged with 0.25M LiTFSI in DME electrolyte. The amount of discharge was controlled similarly for the two cells: 280 mAh/g for the carbon cathode and 300 mAh/g for the RuO₂-based cathode. The discharge cathodes were rinsed with solvent in a dry box to remove lithium salt residue and dried. The discharged cathodes were placed on a hot plate with a set temperature close to the decomposition temperature of lithium peroxide (about 195°C) under ambient conditions. FIG. 10 is an image showing the RuO₂-based cathode when heated to a temperature close to a decomposition temperature of lithium peroxide. The RuO₂ cathode does not show any evidence of reaction under these experimental conditions, which indicates that the RuO₂ cathode is stable with the discharge products of the Li-O₂ battery (e.g., Li₂O₂). In contrast, for a carbon-based cathode, a strong exothermic reaction may occur between carbon and the products deposited on the cathode during discharge (e.g., Li₂O₂).

Example 5

0052 The cyclability of the Li-O₂ battery with a RuO₂-based cathode was tested. Material stacks for the battery were: Li metal anode (248 micron thick)/a glass fiber membrane soaked in 0.1M LiClO₄ in DMSO/RuO₂-coated stainless steel mesh cathode. FIG. 11 is a plot of discharge and recharge behavior of the LiO₂ battery over 10 cycles. Similar to the results shown in FIG. 7, the recharge potential is lower than for a carbon-based cathode, which is very likely due to no passivation of the cathode surface with lithium(alkyl)carbonates. As shown in FIG. 11, discharging/recharging behavior is very stable up to 10 cycles, which indicates stable and good cyclability of the Li-O₂ battery with the RuO₂-based cathode.

0053 Various examples have been described. These and other examples are within the scope of the following claims.

0054 Statement of Industrial Applicability: The present invention has a wide array of potential industrial applications, including the manufacture and use of batteries, which themselves have a wide array of industrial application in a range of mechanical and electrical devices.

CLAIMS

What is claimed is:

1. A lithium-oxygen battery comprising:
an anode comprising lithium;
a cathode defining a surface in contact with oxygen, wherein the cathode comprises ruthenium oxide; and
a non-aqueous electrolyte between, and in contact with, both the anode and the cathode.
2. The lithium-oxygen battery of claim 1, wherein the cathode is covered by ruthenium oxide over more than 10% of its surface.
3. The lithium-oxygen battery of claim 1, wherein the cathode is covered by ruthenium oxide over more than 50% of its surface.
4. The lithium-oxygen battery of claim 1, wherein the cathode further comprises at least one additional electrically conductive metal oxide.
5. The lithium-oxygen battery of claim 4, wherein the at least one additional electrically conductive metal oxide comprises at least one of a titania suboxide (TiO_{2-x}), WO_2 , SrRuO_3 , CrO_2 , MoO_2 , RhO_2 , TcO_2 , ReO_2 , and IrO_2 .
6. The lithium-oxygen battery of claim 1, wherein the cathode further comprises an electrically conductive current collector, and wherein the ruthenium oxide is attached to a surface of the conductive current collector.
7. The lithium-oxygen battery of claim 1, wherein the cathode defines a porous structure.

8. A lithium-oxygen battery comprising:
a negative electrode comprising lithium;
a positive electrode defining a surface, wherein the surface is predominantly metal oxide with an electron conductivity of at least 10^{-1} S/cm; and
an aprotic electrolyte between, and in contact with, the negative electrode and the positive electrode.
9. The lithium-oxygen battery of claim 8, wherein the metal oxide comprises ruthenium oxide.
10. The lithium-oxygen battery of claim 8, wherein the positive electrode comprises two different species of metal oxide.
11. The lithium-oxygen battery of claim 10, wherein the two different species of metal oxide comprise ruthenium oxide and at least one of a titania suboxide (TiO_{2-x}), WO_2 , SrRuO_3 , CrO_2 , MoO_2 , RhO_2 , TcO_2 , ReO_2 , and IrO_2 .
12. The battery of claim 8, wherein the positive electrode is covered by ruthenium oxide over more than 10% of its surface.
13. The lithium-oxygen battery of claim 8, wherein the positive electrode defines a porous structure.
14. The battery of claim 8, wherein the metal oxide gives oxygen reduction reaction and oxygen evolution reaction activity.
15. The lithium-oxygen battery of claim 8, wherein the metal oxide functions as a current collector.
16. The lithium-oxygen battery of claim 8, wherein the cathode further comprises a current collector, wherein the metal oxide is attached to the current collector.

17. The lithium-oxygen battery of claim 8, wherein the metal oxide exhibits thermal stability up to a temperature of about 220°C.

18. A method comprising:

forming a cathode comprising ruthenium oxide;

forming an electrode comprising lithium; and

assembling the cathode and anode with a non-aqueous electrolyte to form a lithium-oxygen battery, wherein the non-aqueous electrolyte is between, and in contact with, both the anode and the cathode.

19. The method of claim 18, wherein the cathode is covered by ruthenium oxide over more than 10% of its surface.

20. The method of claim 18, wherein forming the cathode comprising ruthenium oxide comprises forming a cathode comprising ruthenium oxide and at least one of a titania suboxide (TiO_{2-x}), WO_2 , SrRuO_3 , CrO_2 , MoO_2 , RhO_2 , TcO_2 , ReO_2 , and IrO_2 .

1/11

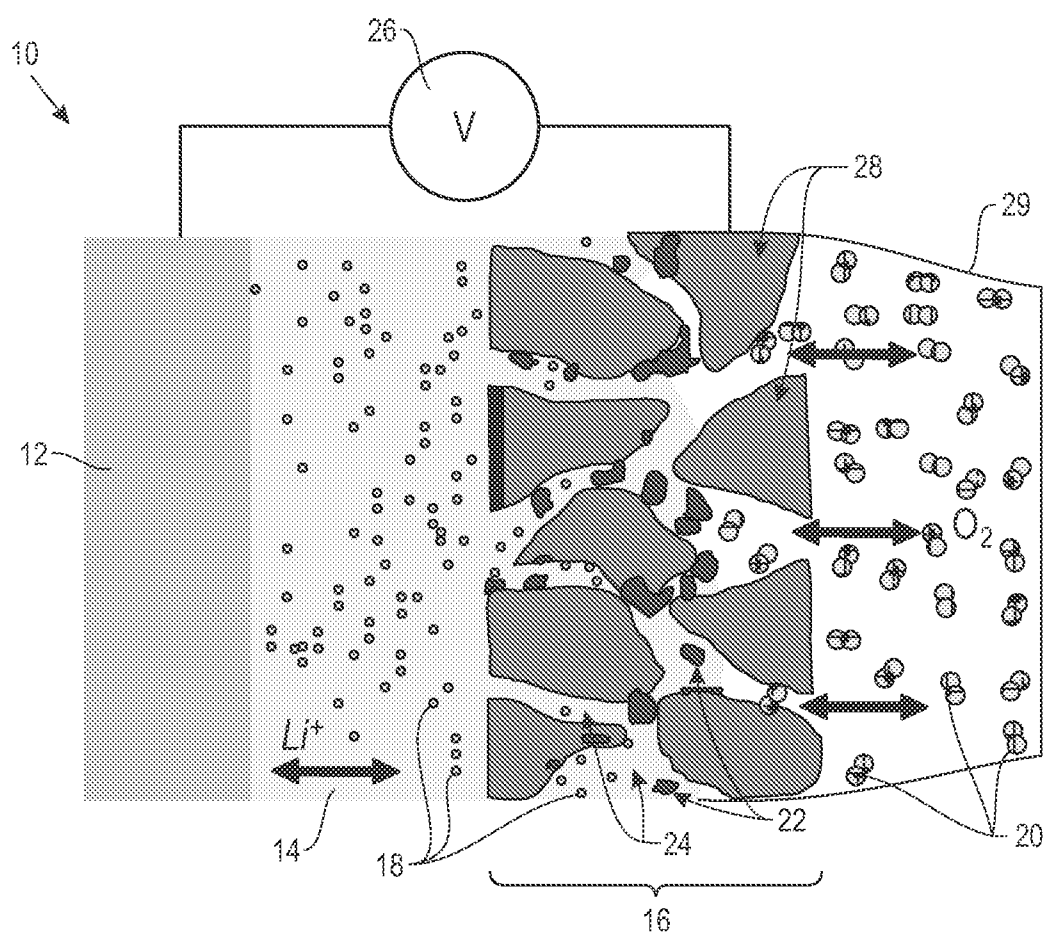


FIG. 1

2/11

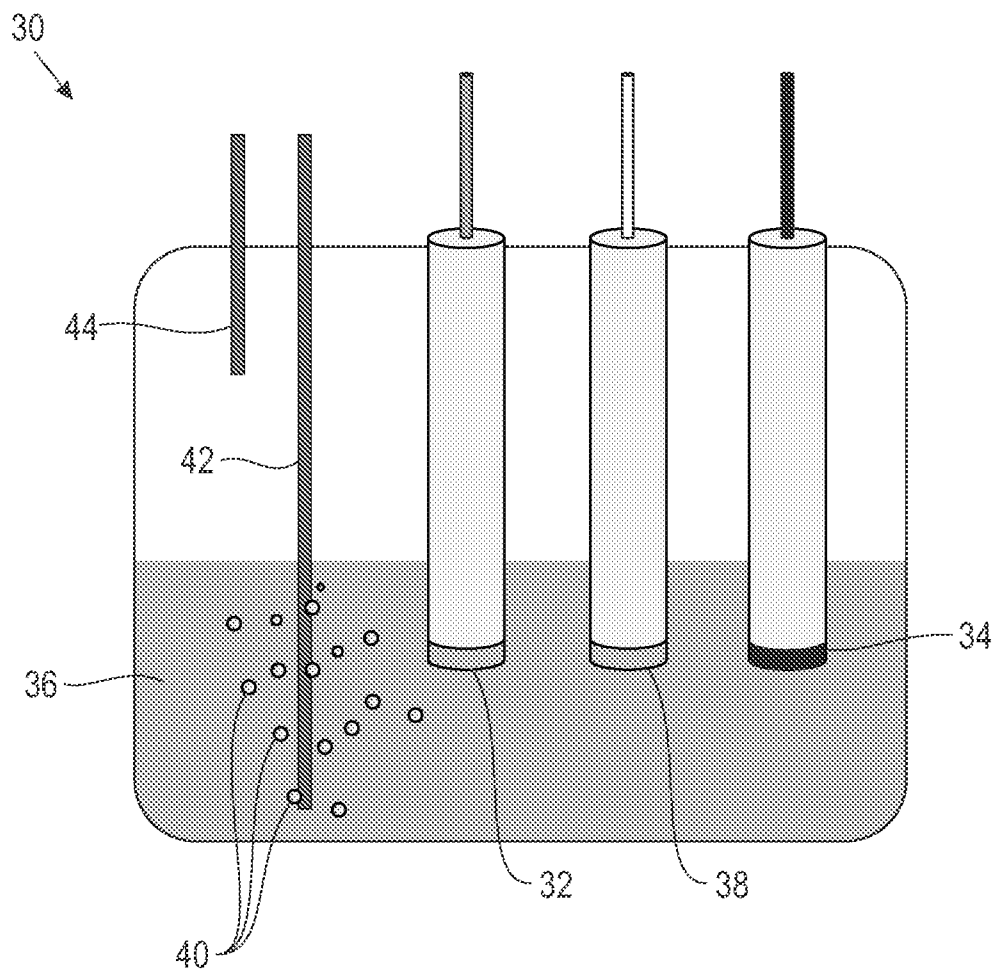
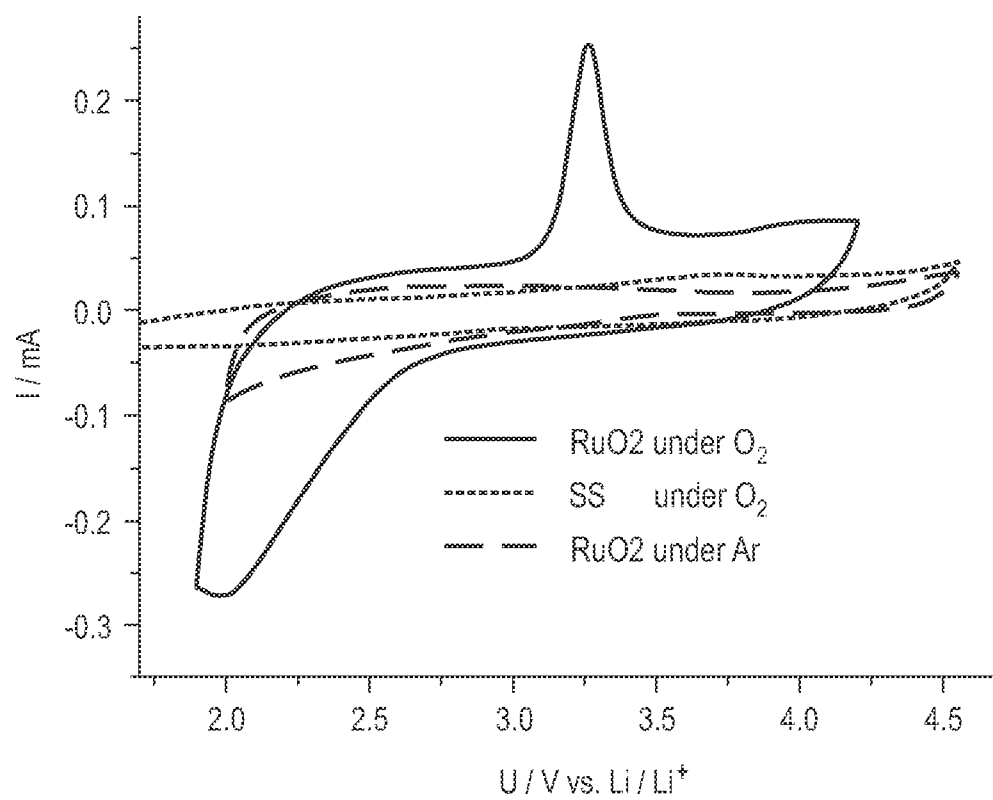


FIG. 2

3/11

**FIG. 3**

4/11

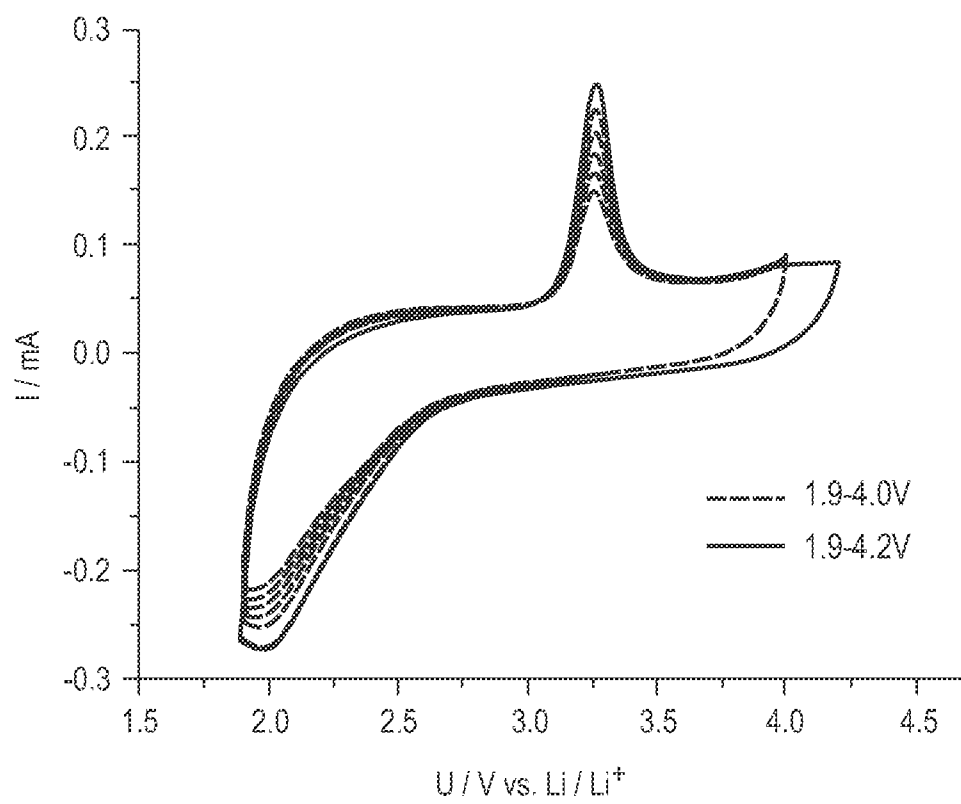


FIG. 4

5/11

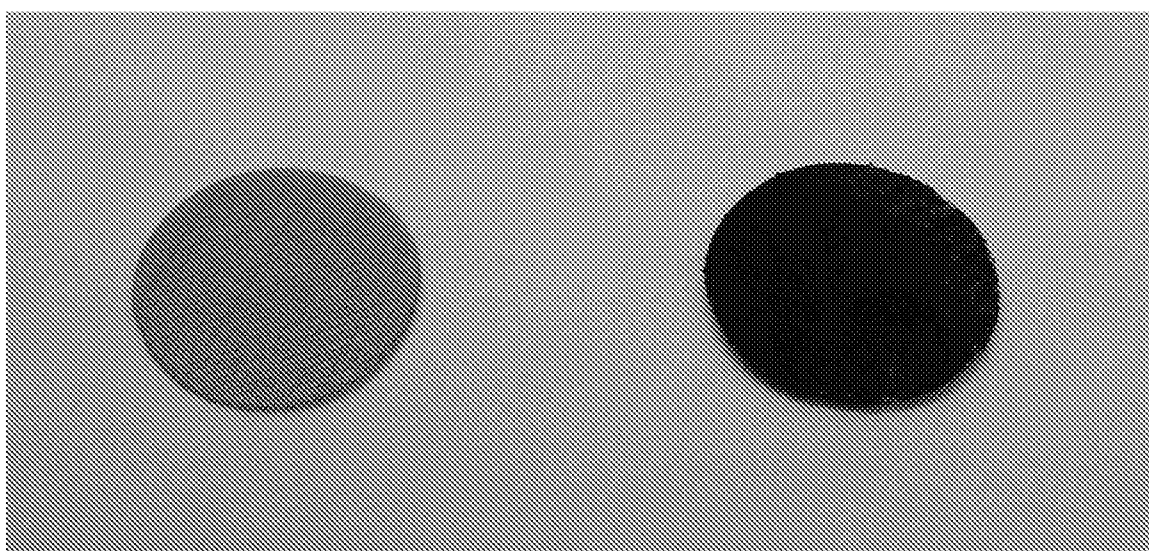


FIG. 5

6/11

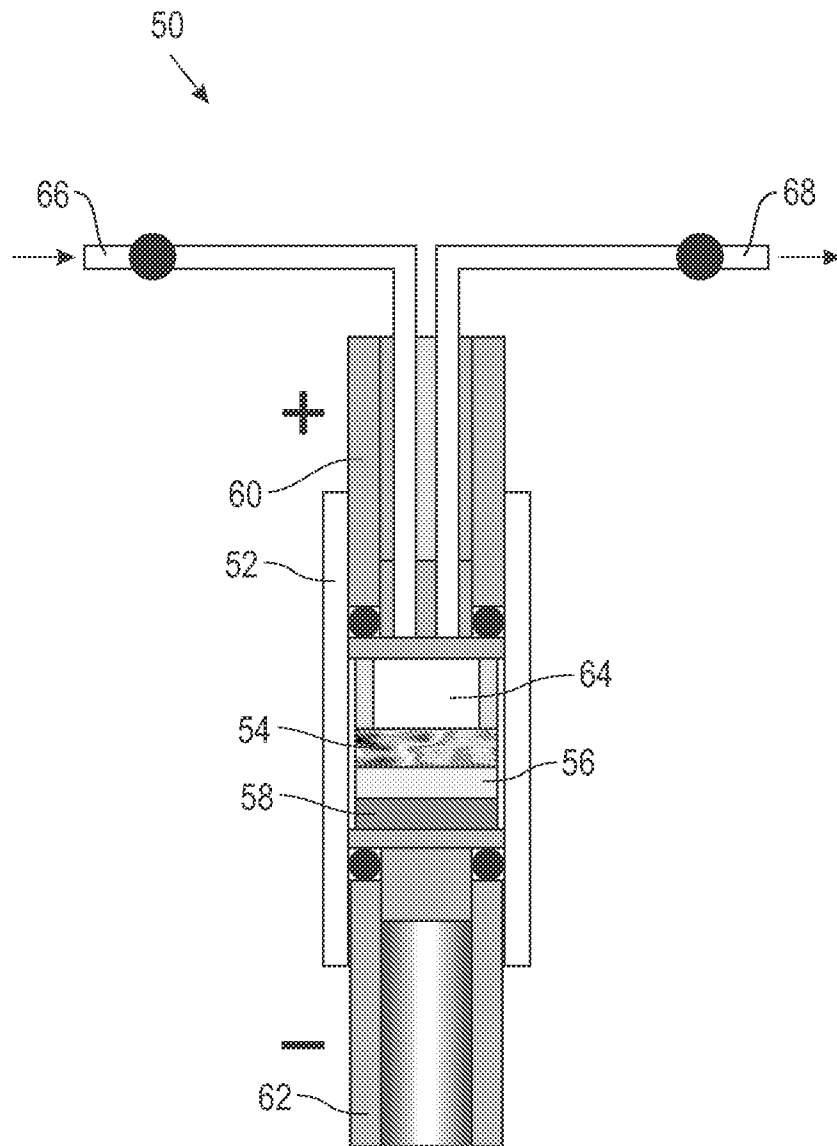


FIG. 6

7/11

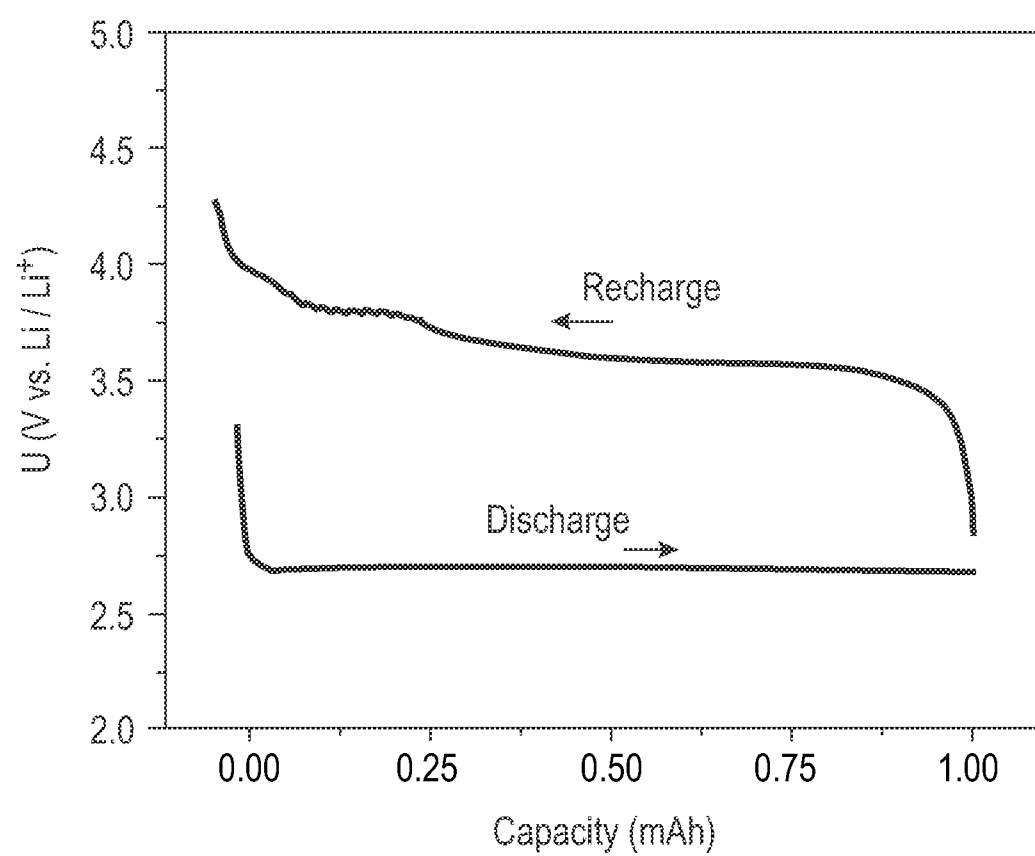


FIG. 7

8/11

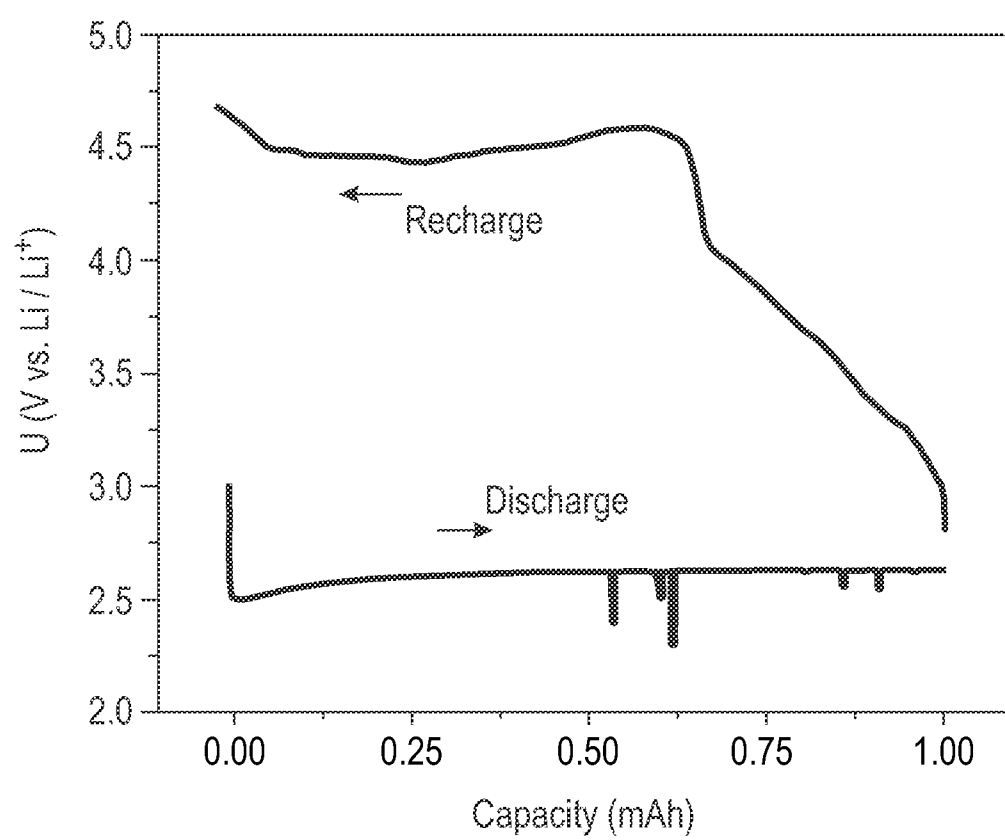


FIG. 8

9/11

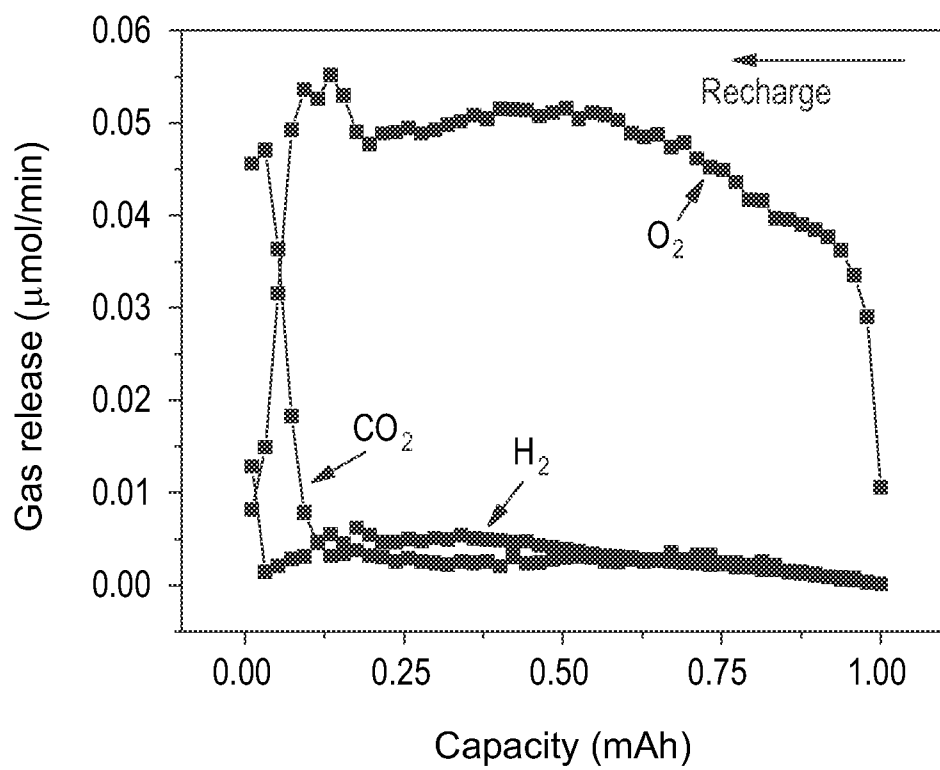


FIG. 9

10/11



FIG. 10

11/11

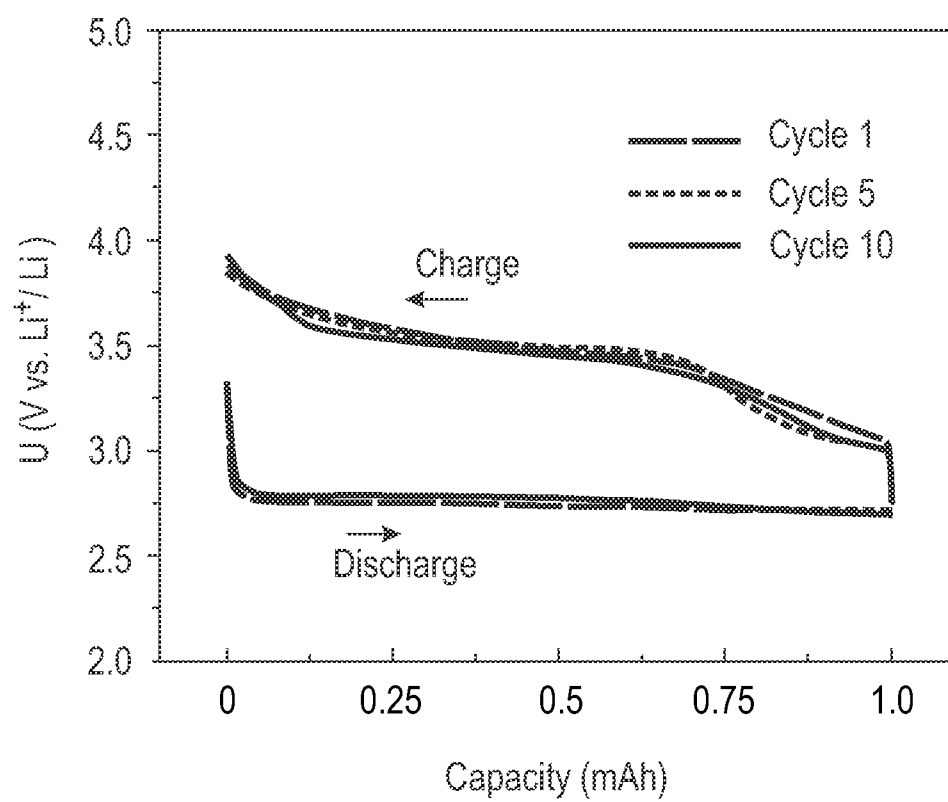


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/076857**A. CLASSIFICATION OF SUBJECT MATTER****H01M 12/08(2006.01)i, H01M 10/04(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 12/08; B60L 11/18; H01M 4/96; H01M 8/02; H01M 8/22; H01M 6/16; H01M 2/02; H01M 10/04

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: lithium-oxygen battery, a cathode comprising metal oxide, ruthenium oxide, titania oxide, non-aqueous electrolyte, aprotic electrolyte, current collector

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010-0273066 A1 (JOHN SCOTT FLANAGAN et al.) 28 October 2010 See paragraphs [0010]-[0056], claim 1 and figure 2.	1-7, 18-20
Y		8-17
Y	US 2009-0053594 A1 (LONNIE G. JOHNSON et al.) 26 February 2009 See abstract, paragraph [0039] and claim 1.	8-17
A	EP 2511972 A2 (LG CHEM, LTD.) 17 October 2012 See abstract, paragraphs [0030]-[0032] and claim 1.	1-20
A	US 2012-0141889 A1 (DONG-JOON LEE et al.) 07 June 2012 See paragraphs [0018]-[0022], claim 1 and figure 1.	1-20
A	US 2012-0107728 A1 (YOUNG-GYOON RYU et al.) 03 May 2012 See abstract, paragraphs [0028]-[0033] and figure 1.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

23 April 2014 (23.04.2014)

Date of mailing of the international search report

24 April 2014 (24.04.2014)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

SHIN, Ju Cheol

Telephone No. +82-42-481-8656



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/076857

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