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(54) Title: TRANSITION METAL DEPOSITION AND OXIDATION ON SYMMETRIC METAL OXIDE ELECTRODES FOR STORAGE APPLICATION

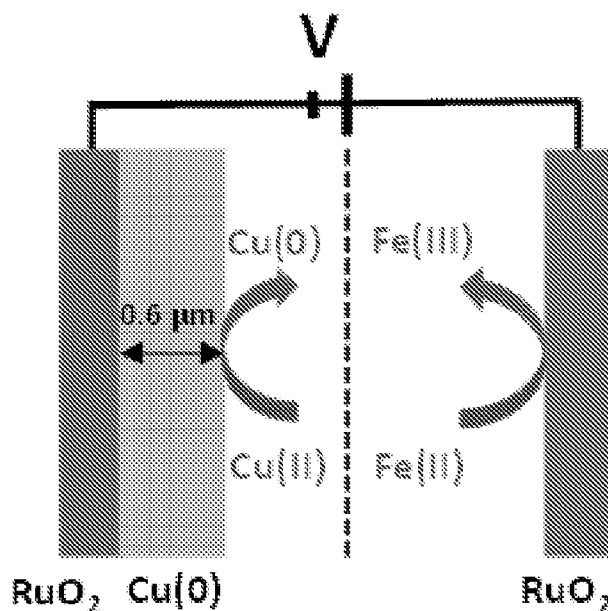


FIG. 1

(57) Abstract: The disclosure provides for an electrochemical cell comprising metal oxide electrodes and an electrolyte solution comprising at least two transition metals capable of forming a redox pair, wherein one of the transition metals is reduced and deposited on one electrode, while another transition metal is solubly oxidized at the other electrode. The disclosure further provides for the use of the electrochemical cell in rechargeable batteries and flow cells.



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TRANSITION METAL DEPOSITION AND OXIDATION ON SYMMETRIC METAL OXIDE ELECTRODES FOR STORAGE APPLICATION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application serial number 62/258,365, filed on November 20, 2015, the disclosures of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The disclosure provides for an electrochemical cell comprising metal oxide electrodes and an electrolyte solution comprising at least two transition metals capable of forming a redox pair, wherein one of the transition metals is reduced and deposited on one electrode, while another transition metal is solubly oxidized at another electrode. The disclosure further provides for the use of the electrochemical cell in rechargeable batteries and flow cells.

BACKGROUND

[0003] Achieving high power densities in the most energy dense battery technologies (e.g. Li-ion) is a challenge due to the reliance on slow solid-state ion diffusion and complex chemical transformations to store high energy densities. Pure Li metal would be used in Li-ion batteries if its growth did not also involve dendrites through a solid electrolyte interface, though progress on this front is being made. An example of such a battery is the Zn-Cerium battery that involves metal ion reduction/deposition on one electrode and soluble metal oxidation on the other. While traditionally either pure transition metal or carbon electrodes are utilized, the facility and reversibility of the faradaic process of metal deposition can vary significantly depending on the compatibility of the metal being deposited and the electrode material.

SUMMARY

[0004] Disclosed herein is an electrochemical cell comprising metal oxide electrodes and an electrolyte solution comprising at least two metals (e.g., transition metals), wherein the reversible and facile deposition and soluble oxidation of the metals on electrodes allow for stable output voltages and generate high average areal power. Accordingly, the electrochemical cells disclosed herein are ideally suited for use in batteries and other energy storage applications. In particular embodiments presented herein, the electrodes can comprise one or more mixed metal oxides. Examples of mixed metal oxides include lanthanum metal oxides; alkali metal oxides; alkaline earth metal oxides; and transition metal oxides, like RuO₂. Ideally, the metal oxide electrode should be strongly adherent to the deposited transition metal but prevent diffusion of metal ions into the electrode, thereby allowing for large capacities that do not impede areal power delivery. In further embodiments, the disclosure provides for rechargeable batteries or flow-cells comprising the electrochemical cell disclosed herein. It is expected that the flow-cells will mitigate any self-discharge by the electrodes thereby increasing areal power delivery.

[0005] In a particular embodiment, the disclosure provides an electrochemical cell comprising metal oxide electrodes and an electrolyte solution comprising at least two metals (e.g., transition metals) capable of forming a redox pair, wherein one of the metals is reduced and deposited on one electrode, while another metal is solubly oxidized at another electrode. In a further embodiment, the electrochemical cell comprises two symmetrical metal oxide electrodes having the same composition. In yet a further embodiment, the metal oxide electrodes are comprised of a transition metal oxide electrocatalyst, such as RuO₂. In another embodiment, the at least two metals are selected from the group consisting of

scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cerium, zinc, and silver. In a certain embodiment, the metals are copper and iron. In yet another embodiment, the electrolyte comprises $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in H_2SO_4 .

[0006] In a particular embodiment, an electrochemical cell disclosed herein, further comprises a finely porous separator that separates the electrolyte solution into an anolyte solution and a catholyte solution, whereby the mobility of the ions resulting from the oxidation of the metal at the cathode is impeded by the separator. In a further embodiment, the separator comprises a glass-frit with pores of 4 μm to 8 μm .

[0007] In a certain embodiment, the disclosure provides for an electrochemical cell disclosed herein, wherein the deposition of a metal on the electrode forms a layer having a thickness of 0.01 μm to 0.6 μm .

[0008] In a particular embodiment, the disclosure also provides for a electrochemical cell which exhibits one or more of the following characteristics: an output voltage of about 0.4 V; a discharge efficiency of at least 42%; an average areal power of at least 62 $\mu\text{W}/\text{cm}^2$; an areal capacity of at least 1.92 C/ cm^2 ; and/or an energy density of at least 85 Wh/kg. In a further embodiment, the electrochemical cell exhibits the following characteristics: an output voltage of about 0.4 V; a discharge efficiency of about 42%; an average areal power of about 62 $\mu\text{W}/\text{cm}^2$; an areal capacity of about 1.92 C/ cm^2 ; and an energy density of about 85 Wh/kg.

[0009] In a certain embodiment, the disclosure further provides for a rechargeable battery or flow cell comprising an electrochemical cell of the disclosure.

BRIEF DESCRIPTION OF THE FIGURES

[0010] **Figure 1** shows a schematic of the electrochemical cell of the disclosure, depicted under charging conditions.

Two symmetric, thin film RuO₂ electrodes (50 or 260 nm thick) with a Cu²⁺, Fe²⁺ electrolyte leads to Cu⁰ deposition on the anode and solvated Fe³⁺ generated at the cathode. A 1 h charge leads to 0.6 μm of Cu deposited. An H-cell separator is depicted by the dotted line.

[0011] **Figure 2** shows a 3-electrode cyclic voltammetry traces (RuO₂ working, Pt counter, and Ag/AgCl (3M NaCl) reference) in a 1M H₂SO₄ (aq) solution, with and without the addition of 60 mM Cu²⁺, 54 mM Fe²⁺. Peaks I and IV correspond to Fe³⁺ reduction and Fe²⁺ oxidation, respectively, while Peaks II and III represent Cu²⁺ reduction and Cu oxidation, respectively. Thermodynamic potentials of Cu²⁺/Cu⁰ deposition and Fe²⁺/Fe³⁺ oxidation are indicated by vertical dotted lines.

[0012] **Figure 3** shows Cyclic-Voltammetry Curves in a 3-electrode cell with a RuO₂ working electrode and Pt counter electrode with Cu²⁺ only solution (left) and Fe²⁺ only solution (right). The Cu²⁺/Cu⁽⁰⁾ reduction, Cu⁽⁰⁾/Cu²⁺ oxidation, Fe²⁺/Fe³⁺ oxidation, and Fe³⁺/Fe²⁺ reduction peaks are in the same locations as in **FIG. 2**. Both ions are included in the electrolyte.

[0013] **Figure 4** shows Cu plating onto the RuO₂ electrode was confirmed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The SEM image is taken on a 10 μm scale at 3500x magnification, using an accelerating voltage of 20 kV and a spot size of 5.0 [arbitrary units]. The EDX shows Cu deposition, Ru electrode, and Si glass substrate peaks.

[0014] **Figure 5** shows UV-vis absorption spectra of 3 [FeSCN]²⁺ solutions comprising undiluted, and 1/4 and 1/8-diluted concentrations. Calibration curve of [FeSCN]²⁺ (inset, lower right). UV-vis absorption spectrum (inset, upper right) of the solution of unknown concentration of [FeSCN]²⁺. The vertical dotted line indicates the wavelength (450 nm) at which the [FeSCN]²⁺ calibration was performed.

[0015] **Figure 6A-B** shows **(A)** Open-circuit potential measurements for the 2-electrode symmetric RuO_2 cell after a 20 second charge at an applied voltage of -1V . A $1\text{M H}_2\text{SO}_4$ (aq) solution containing 60 mM Cu^{2+} and 54 mM Fe^{2+} is considered with and without an H-cell glass frit separator, as well as with and without the addition of 54 mM Fe^{3+} to the anolyte. **(B)** Discharge curves for six different electrodes in the 2-electrode symmetric configuration, under the same charging and electrolyte conditions as **(A)**, with no separator. Discharge curves are inverted to show positive cell voltage. Galvanostatic discharge rates were 0.04 mA/cm^2 for RuO_2 and glassy Carbon, 0.05 mA/cm^2 for Cu, and 0.1 mA/cm^2 for Pt, Au; the higher rate for Pt, Au helped to discharge the electrode.

[0016] **Figure 7** shows cyclic voltammetry curves of a symmetric 2-electrode cell of either RuO_2 or IrO_2 electrodes containing a 54 mM FeSO_4 and 60 mM CuSO_4 electrolyte. The dotted black line is in pure H_2SO_4 solution. The RuO_2 electrodes have a higher current density at the Cu deposition and stripping peaks, indicating superior Faradaic activity.

[0017] **Figure 8A-D** shows graphs of discharge capacity and time-dependent power density on discharge. The top graphs compare the discharge capacity for a -0.6V charge for different charging times of **(A)** 20 sec and **(B)** 1 h, delivered at 0.4V with a Galvanostatic discharge rate of 0.2 mA/cm^2 . The bottom graphs compare the corresponding time-dependent power density on discharge for the same charging times of **(C)** 20 sec and **(D)** 1 hour.

DETAILED DESCRIPTION

[0018] As used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise.

[0019] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as

commonly understood by one of ordinary skill in the art to which the invention pertains. Although any methods and materials similar or equivalent to those described herein can be used in the practice for testing of the invention(s), specific examples of appropriate materials and methods are described herein.

[0020] Also, the use of "or" means "and/or" unless stated otherwise. Similarly, "comprise," "comprises," "comprising" "include," "includes," and "including" are interchangeable and not intended to be limiting.

[0021] It is to be further understood that where descriptions of various embodiments use the term "comprising," those skilled in the art would understand that in some specific instances, an embodiment can be alternatively described using language "consisting essentially of" or "consisting of."

[0022] All publications mentioned herein are incorporated herein by reference in full for the purpose of describing and disclosing the methodologies, which are described in the publications, which might be used in connection with the description herein. The publications discussed above and throughout the text are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior disclosure.

[0023] While batteries store energy in chemical reactions, supercapacitors store their energy in a thin, two-dimensional electric double layer at the solid/electrolyte interface. The most energy dense batteries (e.g. Li-ion) rely on solid-state ion diffusion and complex chemical transformations to store high energy densities in three-dimensional materials. Since supercapacitors do not rely on these solid-state Faradaic processes, they can have higher power density and longer

cycle life but also exhibit lower energy density. Recently, facile soluble redox reactions that involve either solvated transition metal ions or quinones, have been used to enhance the stored energy in supercapacitors; others have combined Li-ion solid-state reactions with supercapacitor electrodes to create hybrid devices. Another electrochemical process that sits in between supercapacitor and battery technologies in terms of balancing power density, energy density, and cycle life is facile and reversible metal deposition. If alloy formation with the electrode, ion diffusion into the electrode, and dendritic growth can be avoided, the deposition of metal layers should increase energy densities without hampering power delivery and cycle life significantly. Pure Li metal would be used in Li-ion batteries if its growth did not also involve dendrites through a solid electrolyte interface, though progress on this front is being made.

[0024] The disclosure provides an electrochemical cell (See, **FIG. 1**) that involves transition metal ion deposition and soluble transition metal ion oxidation on RuO₂ electrodes traditionally used as supercapacitors. During charging, Cu²⁺/Cu⁰ deposition occurs on one RuO₂ electrode and soluble Fe²⁺/Fe³⁺ oxidation occurs on a symmetric RuO₂ electrode in aqueous electrolyte. While Cu can adhere strongly to RuO₂, it does not alloy or let Cu penetrate as has been shown in electrochemical cells that have been investigated for Cu deposition; for this reason, RuO₂ is suggested as a barrier to Cu diffusion in the semiconductor industry and has been used for Al interconnects. Characterized by a large 4d density of states, RuO₂ is highly conductive and supports many redox processes, making it a good supercapacitor and catalyst in aqueous electrolytes. The plating of thin Cu layers on RuO₂ in this cell was shown to lead to areal power delivery during discharge that is nearly constant (70 μW/cm²), whether charged for seconds or hours. This means that the achievable energy

density is not limited by slow solid-state processes. A 20 sec charge gives a 0.02 C/cm² discharge capacity and 8.5 Wh/kg; a 1 h charge gives a 1.9 C/cm² areal discharge capacity and 85 Wh/kg (calculated with the active electrolyte and electrode mass). In comparison, pure transition metals (Pt, Au, and Cu) exhibit negligible capacity under the same electrochemical conditions, glassy carbon exhibits approximately 10% of the capacity, and IrO₂, being similar to RuO₂, exhibits 50 % of the capacity.

[0025] In general, facile Faradaic processes can lead to self-discharge at open circuit, either by back reactions at the electrode or within the electrolyte and this cell exhibits significant self-discharge. It is therefore of interest in applications where it is not required to hold charge for long periods on its own, such as back-up storage in tandem with the main source. Alternatively, flow-cell technologies can mitigate the discharge and the Zn-Cerium flow-cell battery involves the most comparable electrochemical process to that described herein.

[0026] The disclosure also demonstrates that non-alloying/reversible deposition of metal layers to tune energy density of storage technologies can be achieved using transition metal oxide electrodes and a facile, soluble cation reaction on the counter electrode. This electrochemical process could be utilized together with existing nanoporous electrode geometries that boost the energy density of materials such as RuO₂.

[0027] In embodiments presented herein, a method of manufacture of an electrode is provided, in which metal-organic compounds are applied to the surface of an electrode substrate and are then subjected to thermal decomposition in an oxidizing atmosphere so as to form a mixed metal oxide electrocatalytic layer on the substrate. In a particular embodiment, the electrode substrate comprises glass (e.g.,

fluorine doped tin oxide coated glass); silicon wafer or wire; or a single crystal substrate, such as aluminum oxide, gallium antimonide, gallium arsenide, gallium phosphide, LSAT, Lanthanum aluminum oxide, magnesium aluminate, magnesium oxide, silicon dioxide, strontium lanthanum aluminate, strontium titanate, and titanium oxide. In a further embodiment, the electrode substrate may further comprise a coating of gold or indium tin oxide. In additional embodiments, a compound comprising a metal, or a mixture comprising at least two different metal containing compounds, is applied to the surface of the electrode substrate to produce a thin metal film on the electrode. Examples of metals that could be used to coat the substrate include, but are not limited to, manganese, iron, cobalt, nickel, titanium, zirconium, vanadium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, rhodium, iridium, palladium, platinum, aluminum, lead, and bismuth. In further embodiments, the metal coated electrode is then heated in an oxidizing atmosphere at an elevated temperature which then converts the thin metal film into a film of a mixed metal oxide electrocatalyst.

[0028] In a certain embodiment, the electrodes of the electrochemical cell disclosed herein are symmetric by having the same compositions. In another or further embodiment, the electrodes comprise RuO_2 .

[0029] In a particular embodiment, the electrochemical cell comprises an electrolyte solution that contains transition metals capable of forming a redox pair. Examples of transition metals that can be used in the electrochemical cell disclosed herein, include, but are not limited to, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, and silver. In a further embodiment, after undergoing a redox reaction, one of the transition metals remains in solution while another

transition metal forms a thin layer on an electrode by deposition. In yet a further embodiment, the deposited layer a transition metal has a thickness of about 0.005 μm to about 1 μm , about 0.0075 μm to about 0.8 μm , or about 0.01 μm to about 0.6 μm . In yet a further embodiment, the electrochemical cell disclosed herein comprises an anolyte solution that is separated from a catholyte solution by a separator having fine porosity (e.g., pores having diameters of 0.1 to 10 μm , 0.5-9.5 μm , 1-9 μm , 2-8.5 μm , or 4-8 μm or a value between any of the two foregoing), wherein the solutions are fluidly in contact. In another embodiment, the catholyte solution comprises a higher concentration of one transition metal while the anolyte solution comprises a higher concentration of a different transition metal. In a further embodiment, the anolyte solution comprises copper or copper and iron while the catholyte solution comprises iron, wherein Cu^0 is deposited on the anode electrode and wherein Fe^{3+} is generated at the cathode electrode from an electrolyte comprising Fe^{2+} .

[0030] The disclosure also provides for rechargeable batteries comprising the electrochemical cell disclosed herein. A rechargeable battery is a type of electrical battery which can be charged, discharged into a load, and recharged many times. In a further embodiment the disclosure provides for automobile starters, portable consumer devices, light vehicles (such as motorized wheelchairs, golf carts, electric bicycles, and electric forklifts), tools, and uninterruptible power supplies, hybrid internal combustion-batteries and electric vehicles comprising a rechargeable battery disclosed herein.

[0031] The disclosure further provides for flow cells comprising the electrochemical cell disclosed herein. A flow cell refers to a type of rechargeable battery where rechargeability is provided by two chemical components

dissolved in liquids contained within the system and separated by a membrane. Ion exchange (providing flow of electric current) occurs through the membrane while both liquids circulate in their own respective space. A "flow cell" as used herein encompasses fuel cells and electrochemical accumulator cells (electrochemical reversibility). Flow cells have technical advantages such as potentially separable liquid tanks and near unlimited longevity over most conventional rechargeable batteries.

[0032] The following examples are intended to illustrate but not limit the disclosure. While they are typical of those that might be used, other procedures known to those skilled in the art may alternatively be used.

EXAMPLES

[0033] ***Thin Film Deposition (RuO_2 , IrO_2):*** RuO_2 films were deposited by radio frequency (RF) reactive sputtering (ATC Orion; AJA International, North Scituate, MA) on glass substrates from a 2" Ru target of 99.95% purity. A total working pressure of 5 mTorr (4.5 mTorr Ar/0.5 mTorr O_2) was used with a growth temperature of 250 °C and an input power of 150 W. Glass substrates were sonicated prior to deposition 10 minutes each in acetone and isopropanol sequentially, then dried with nitrogen. Film thicknesses of 260 nm were verified using a Dektak IID profilometer. A similar deposition technique was used for IrO_2 .

[0034] ***Other Electrodes (Au, Pt, Cu, and Glassy Carbon):*** Thin foils (of Cu, Pt, and Au) were mounted on steel substrates and lacquer was applied to the portions of steel submerged in solution. As for Glassy Carbon (SPI-Glas™) electrodes, the carbon samples were used directly without a substrate; electrically insulating tape was used to cover the submerged portions.

[0035] ***Electrochemical setup and measurements:*** All electrochemical measurements were carried out on a CH

Instruments Electrochemical Analyzer (model 1140B). For the best performing configuration, an electrochemical H-cell (Pine Research Instrumentation, Inc.) with a glass-frit separator of fine porosity (4-8 μm) was used to contain 20 mL of anolyte and catholyte separately. The anolyte is 300 mg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 300 mg of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in 20 mL of 1 M H_2SO_4 ; the catholyte contained an additional 175 mg of FeCl_3 in experiments containing the separator. All CV measurements were conducted at 20 mV/s sweep rate on a three-electrode configuration (consisting of RuO_2 working, Pt counter, and Ag/AgCl (3 M NaCl) reference electrodes). For the Galvanostatic discharge, the electrodes were discharged immediately after charging. The x-axis of the Galvanostatic discharge is converted to the stored charge Capacity (C/cm^2) by multiplying Δt , the discharge duration, by the Galvanostatic discharge rate ($I = A/\text{cm}^2$). For reporting the discharged power density vs. time, the voltage on the y-axis is converted to power by multiplying by the Galvanostatic discharge rate, $V(t) \cdot I$. The discharged energy density then is simply the area under this curve, or $I \cdot \int V(t) dt$. The overall energy efficiency is calculated as the total discharged (output) energy over the input energy. Since on charging, V is held constant, $E = V \cdot \int i(t) dt$, where $\int i(t) dt$ is the integral of the current during charging. Some of the initial charge is capacitive (~10 sec) until the current stabilizes to a constant value, and therefore this formula overestimates the energy input slightly.

[0036] Energy and power mass densities were calculated using the mass of the thin films on both electrodes, the mass of the Cu that plates onto the anode, and the mass of the Fe ions oxidized at the cathode. The actual device energy density will be lower due to the glass substrates, the

aqueous electrolyte, and the separator. It was found that a pair of RuO₂ electrodes of 260-nm thickness lasted 59 charge-discharge cycles and 25 CV's which were subsequently replaced due to handling issues that lowered the conductivity.

[0037] UV-VIS Spectroelectrochemistry: Two solutions were prepared: Solution A consisted of FeSO₄ (54 mM, + unknown amount of Fe(III)) in H₂SO₄ (1 M, 20 mL); Solution B was similar to A with additional FeCl₃ (54 mM). Aqueous NaSCN 20 M (2 mL, 0.04 mmol) was added into each solution. The complexation reaction occurred between the thiocyanide anion and Fe(III): $\text{Fe}^{3+} + \text{SCN}^- \rightleftharpoons [\text{FeSCN}]^{2+}$. A dilution series was then prepared for solution B ($\times 1$, $\times 1/4$ and $\times 1/8$). UV-Vis absorption spectra (300–700 nm, H₂SO₄ reference) were obtained for all resulted solutions. The calibration curve for $[\text{FeSCN}]^{2+}$ was deduced by plotting the absorbance at 450 nm against the concentration of $[\text{FeSCN}]^{2+}$. This was fit to the straight line from which, together with the equilibrium constant of the complexation reaction (138 M^{-1}), the unknown amount of Fe(III) present in Solution A can be calculated to be 0.5 mM.

[0038] Evaluating the cell's electrochemical properties.

FIG. 2 shows the cyclic-voltammetry curves (CVs) for an aqueous solution of Cu²⁺/Fe²⁺ with a RuO₂ working electrode and Pt counter electrode in a 3-electrode cell. Peak I corresponds to the reduction of Fe³⁺ to Fe²⁺ and Peak IV to the oxidation of Fe²⁺ to Fe³⁺. Peak II corresponds to the reduction of Cu²⁺ to Cu, and Peak III to the oxidation of Cu to Cu²⁺. CV's of Fe²⁺-only solution and a Cu²⁺-only solution each show the corresponding peak pairs at the same locations (see **FIG. 3**). While there should be under-potential deposition (UPD) of Cu as well as bulk deposition, only the bulk deposition peak is seen at these elevated concentrations (60 mM Cu²⁺, 54 mM Fe²⁺). The Cu plating onto the RuO₂ electrode is seen

visually, and confirmed by elemental analysis with an SEM (see **FIG. 4**).

[0039] From the thermodynamic potentials of Cu^{2+}/Cu (0.11 V) and $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.45 V), an equilibrium cell voltage of -0.34 V is obtained for the 2-electrode, symmetric RuO_2 cell. For the calculations, a UV-Vis absorption experiment was done to determine the amount of Fe^{3+} dissolved in air (0.5 mM, **FIG. 5**). As shown in **FIG. 6A**, the open-circuit voltage stabilizes at -0.3 V for the 2-electrode cell, in good agreement with the calculated value. The cell voltage is increased to -0.4 V by explicitly introducing Fe^{3+} ions (54 mM) into the catholyte in the presence of the H-cell glass frit (see **FIG. 6A**), in good agreement with the calculated value of -0.46 V.

[0040] The consequence of facilitating the Cu plating on the negative electrode by a solvated Fe ion oxidation reaction on the positive electrode is a back reaction between the diffusive and mobile solvated ions and the plated metal. This self-discharge is evident from the decay of the open circuit voltage after ~1000s, when it decreases rapidly to zero (see **FIG. 6A**). Visually, the plated Cu is seen as leaving the RuO_2 surface. After charging, the feasible reaction at open-circuit thermodynamically is: $2\text{Fe}^{3+}(\text{aq}) + \text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$. Impeding the mobility of the Fe^{3+} ions by introducing the H-cell glass frit lengthens the duration for which the cell voltage is held by a factor of 2 (see **FIG. 6A**). In the case when additional Fe^{3+} ions (54 mM) are added to the catholyte, the open-circuit voltage does not drop completely to zero and remains at -0.1V for some time, which may be due to the strongly adhering, under-potential deposited Cu layer seen previously on RuO_2 .

[0041] Useful in the Faradaic facility of the metal plating is the transition metal oxide electrode itself.

Figure 6B compares the Galvanostatic discharge curves for several pure transition metals, glassy carbon, and two

transition metal oxide electrode materials in a 2-electrode cell. In all cases, the cell was charged for 20 sec at -1V and with a Cu^{2+} (60 mM) / Fe^{2+} (54 mM) solution (no H-cell separator) and then discharged just after it reached the equilibrium cell voltage. The discharge capacity is given in C/cm^2 to compare the performance of the electrode/electrolyte interface independent of the material density. While the RuO_2 electrodes have a high discharge capacity, the capacity is insignificant for the pure transition metal electrodes (Cu, Pt, and Au); the negligible capacity is attributed to the irreversible formation of an alloy on Pt, Au and Cu plating on the Cu electrode that doesn't undergo under-potential deposition first. Conductive glassy carbon does have a measurable discharge capacity, though with only 10% of the capacity of the RuO_2 electrodes. Here, the lower capacity could be related to intercalation of the metal ions within the carbon that is prevented on the transition metal oxides; the lack of a significant plateau in the discharge curve attests to a Nernstian potential that decreases on discharge due to an additional, slower electrochemical process. Finally, IrO_2 has a 50% lower discharge capacity than RuO_2 . The 2-electrode CV curves (see **FIG. 7**) show a lower peak current at the Cu plating and stripping potentials in the IrO_2 films, which indicates an inferior Faradaic activity for $\text{Cu}^{2+}/\text{Cu}^0$.

[0042] The overall performance of the cell is demonstrated by the power delivery and discharge capacity for the symmetric RuO_2 cell when initially charged for 20 seconds, and for 1 h (see **FIG. 8**). Here, the cell is charged at -0.6 V, near the operating voltage of -0.4 V, uses the H-cell glass frit, and contains the additional Fe^{3+} catholyte. The performance is first demonstrated per electrode area. The cell is discharged at a Galvanostatic rate of 0.2 mA/cm², which translates to a C-rate (1/nC is the time to fully

discharge) of 0.4C for the 1 h charge. This is a C-rate typical of Li-ion batteries that utilizes nearly all of the stored charge. The top graphs (see **FIG. 8A, 8B**) show that the discharge capacity for both the 20 sec and 1 hour charge are near-ideal square curves, indicative of a single Nernstian reaction that dominates at either electrode. The bottom graphs show the time range for which the areal power can be delivered. A constant power ($\sim 70 \mu\text{W}/\text{cm}^2$) is delivered regardless of whether the cell was charged for 20 s (see **FIG. 8C**) or for 1 h (see **FIG. 8D**)—only the time range is extended from ~ 120 s to $\sim 9,000$ s. Therefore, significantly higher discharge capacities (from 0.03 to 2 C/cm²) translate to proportionally higher energy stored per area (from 2.3 Wh/cm² to 175 Wh/cm²) upon integrating the curves in **FIG. 8C, 8D**. With more complex solid-state reactions and ion diffusion, the voltage and power lower during discharge over minutes to hours, even in high performing Li-ion cells and limits their usable capacity. Additionally, given that the performance of the cell is maintained equivalently for Cu layers of 0.01 μm (20 second charge) and 0.6 μm (1 hour charge), evidence of a solid electrolyte layer that accompanies Li metal deposition was not found. **TABLE 1** reports the achievable energy density, areal power, and energy efficiency for the two films, and for the two different charge times. The 1 h charge leads to 85 Wh/kg and the 20 second charge leads to 6 Wh/kg. The average areal power is calculated by integrating **FIG. 8B, D** over time and then dividing by the overall discharge time ($62 \mu\text{W}/\text{cm}^2$ for the 1 h charge). The energy efficiency is around 30-40%, if the cell is discharged right after equilibrating to the cell voltage.

[0043] **TABLE 1: Wh/kg and the 20 second charge leads to 6 Wh/kg. The average areal power is calculated by integrating FIG. 8B, 8D over time and then dividing by the overall discharge time ($62 \mu\text{W}/\text{cm}^2$ for the 1 h charge). The energy**

efficiency is around 30-40%, if the cell is discharged right after equilibrating to the cell voltage.

RuO ₂ Films	Charged For:	Output Voltage (V)	Discharge Efficiency (%)	Average Areal Power ($\mu\text{W}/\text{cm}^2$)	Areal Capacity (C/cm^2)	Energy Density (Wh/kg)
260 nm	1 h	0.4	42	62	1.92	85
260 nm	20 sec	0.4	46	52	0.03	6

[0044] One can compare the performance of this cell with both flow-cell and stand-alone battery architectures. The areal power is much lower than Zn-Ce flow-cell batteries that involve simple 2-electron metal plating and 1-electron soluble cation oxidation ($100 \text{ mW}/\text{cm}^2$). However, flow cells use 1M rather than 60 mM electrolyte concentrations. Electrolytes with higher Cu^{2+} , Fe^{2+} concentrations than 60 mM do deposit Cu layers at a higher rate. Both higher areal power and energy efficiency could be achieved with highly concentrated electrolytes and a full flow-cell architecture that mitigates discharge; interestingly, the performance of the Zn-Ce flow cell is also highly dependent on electrode material and transition metal oxide electrodes haven't been explored. To compare to stand-alone batteries on a per volume basis, the 1 hour charge corresponds to a volumetric power of $6.2 \mu\text{W}/\text{cm}^2\text{-}\mu\text{m}$ and energy of $17.5 \mu\text{Wh}/\text{cm}^2\text{-}\mu\text{m}$ in a packaging where the electrodes are 10 μm apart. This is in the range of that reported for Ni-Zn and Lithium-ion batteries, though at a lower voltage.

[0045] Other embodiments, combinations and modifications of this invention will occur readily to those of ordinary skill in the art in view of these teachings. Therefore, this invention is to be limited only by the following claims, which include all such embodiments and modifications when viewed in conjunction with the above specification and accompanying drawings.

WHAT IS CLAIMED IS:

1. An electrochemical cell comprising metal oxide electrodes and an electrolyte solution comprising at least two metals capable of forming a redox pair, wherein one of the metals is reduced and deposited on one electrode, while another metal is solubly oxidized at another electrode.
2. The electrochemical cell of claim 1, wherein the electrochemical cell comprises two symmetrical metal oxide electrodes having the same composition.
3. The electrochemical cell of claim 1 or claim 2, wherein the metal oxide electrodes are comprised of a transition metal oxide electrocatalyst.
4. The electrochemical cell of claim 3, wherein the metal oxide electrodes comprise RuO_2 .
5. The electrochemical cell of claim 1, wherein the at least two metals are selected from the group consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, cerium, zinc, and silver.
6. The electrochemical cell of claim 5, wherein the metals are copper and iron.
7. The electrochemical cell of claim 6, wherein the electrolyte comprises $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ dissolved in H_2SO_4 .
8. The electrochemical cell of claim 1, wherein the cell further comprises a porous separator that separates the electrolyte solution into an anolyte solution and a catholyte

solution, whereby the mobility of the ions resulting from the oxidation of the metal at the cathode is impeded by the separator.

9. The electrochemical cell of claim 8, where the separator comprises a glass-frit with pores of 4 μm to 8 μm .

10. The electrochemical cell of claim 1, wherein the deposition of a metal on the electrode forms a layer having a thickness of 0.01 μm to 0.6 μm .

11. The electrochemical cell of claim 1, where the cell exhibits one or more of the following characteristics:

- an output voltage of about 0.4 V;
- a discharge efficiency of at least 42%;
- an average areal power of at least 62 $\mu\text{W}/\text{cm}^2$;
- an areal capacity of at least 1.92 C/ cm^2 ; and/or
- an energy density of at least 85 Wh/kg.

12. The electrochemical cell of claim 11 wherein the cell exhibits the following characteristics:

- an output voltage of about 0.4 V;
- a discharge efficiency of about 42%;
- an average areal power of about 62 $\mu\text{W}/\text{cm}^2$;
- an areal capacity of about 1.92 C/ cm^2 ; and
- an energy density of about 85 Wh/kg.

13. A rechargeable battery comprising the electrochemical cell of claim 1.

14. A flow cell comprising the electrochemical cell of claim 1.

1 / 4

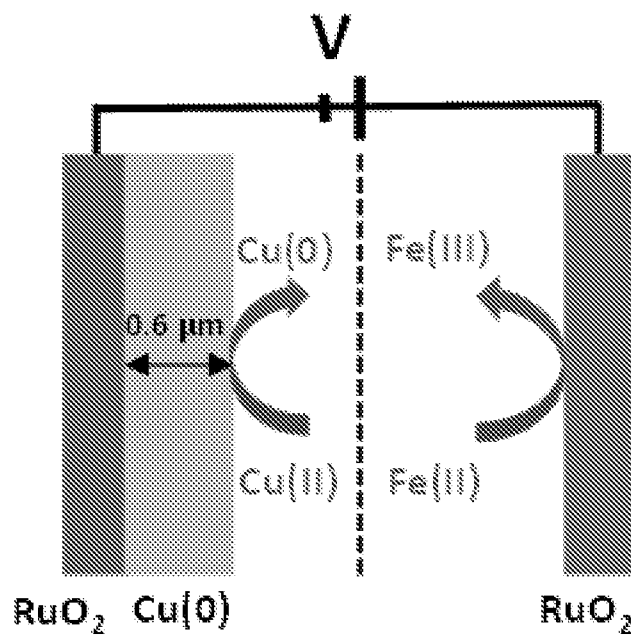


FIG. 1

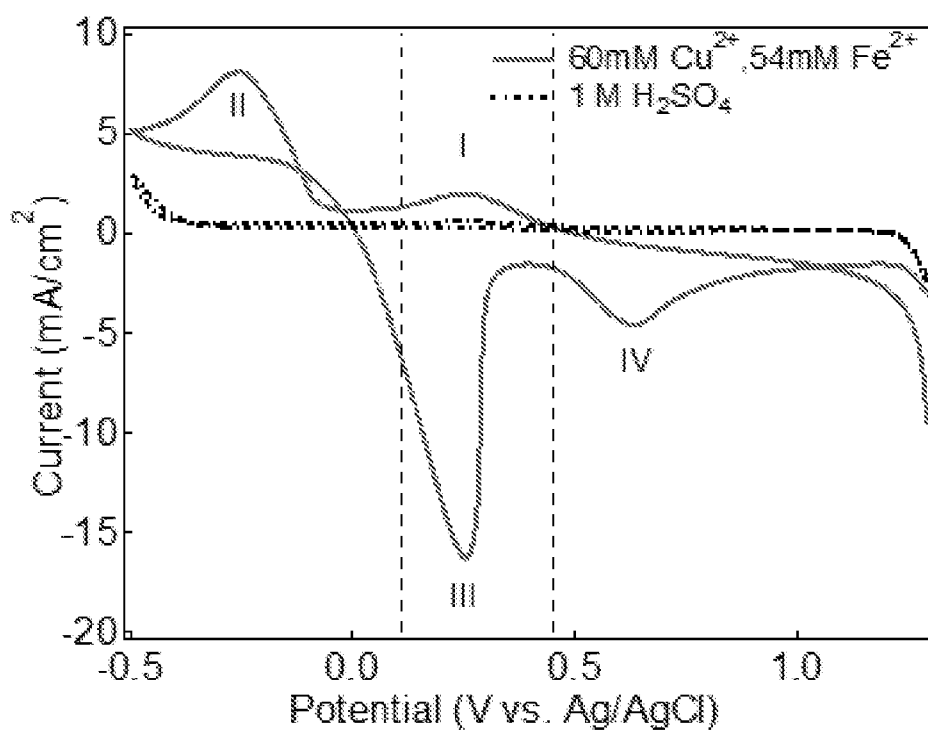


FIG. 2

2 / 4

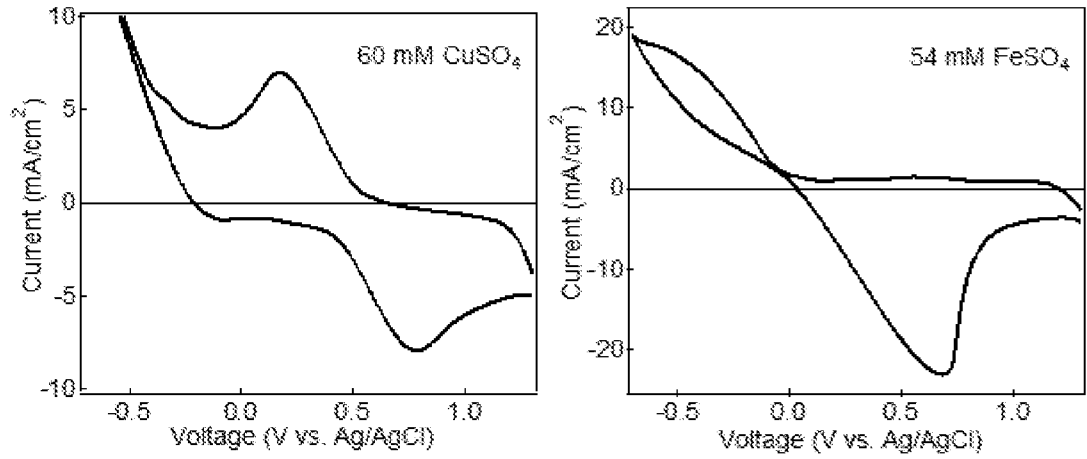


FIG. 3

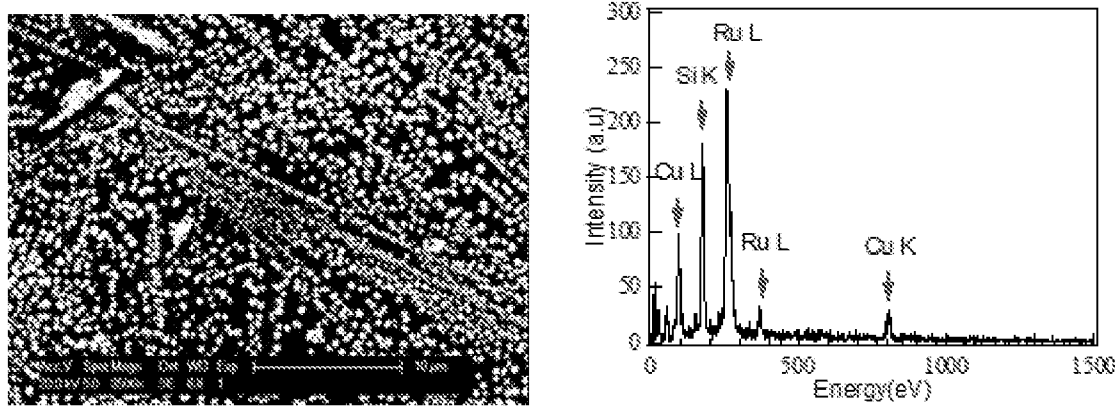


FIG. 4

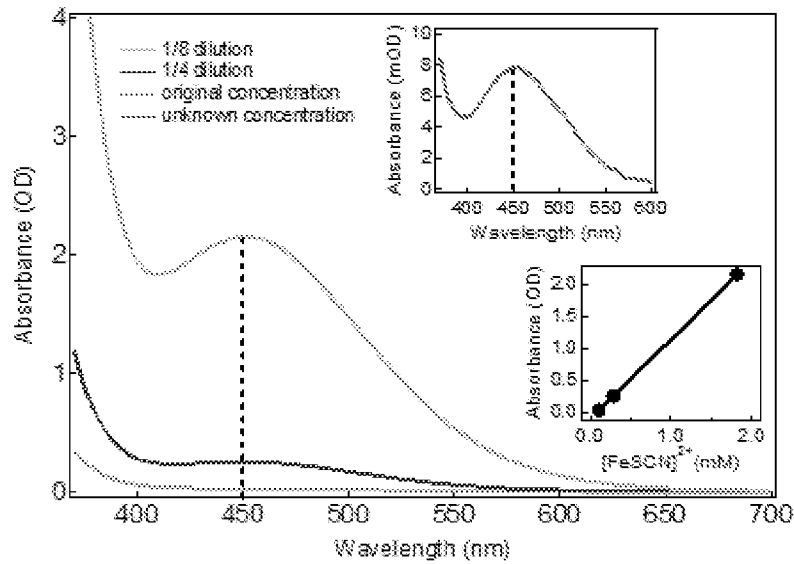


FIG. 5

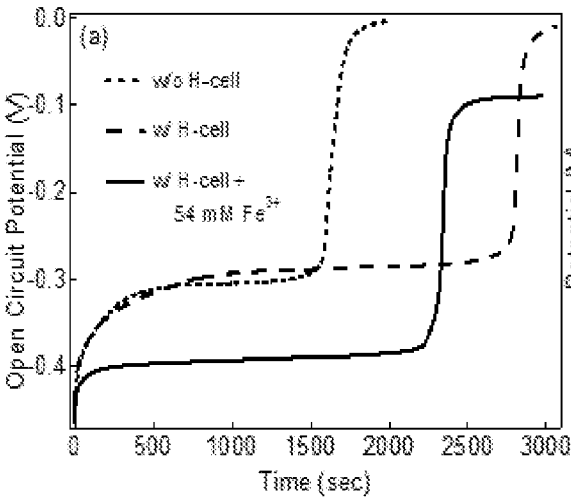


FIG. 6A

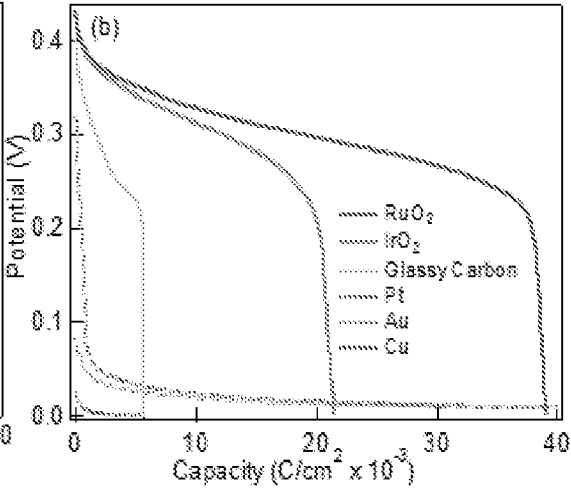


FIG. 6B

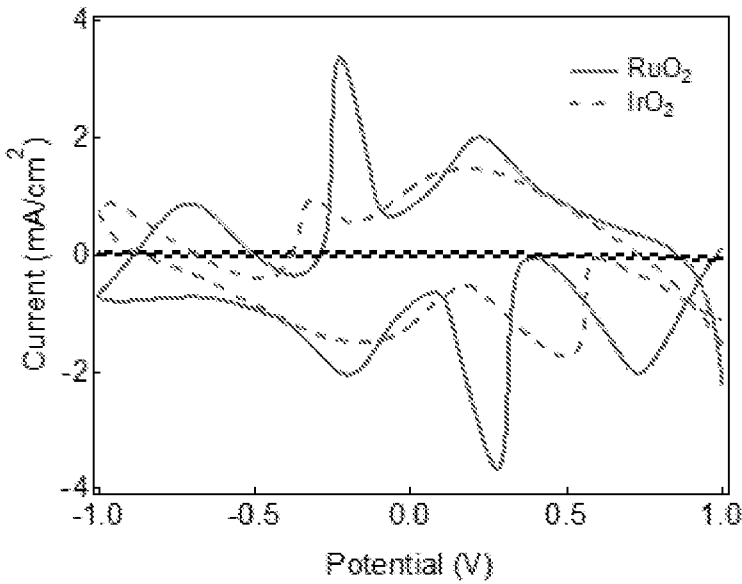


FIG. 7

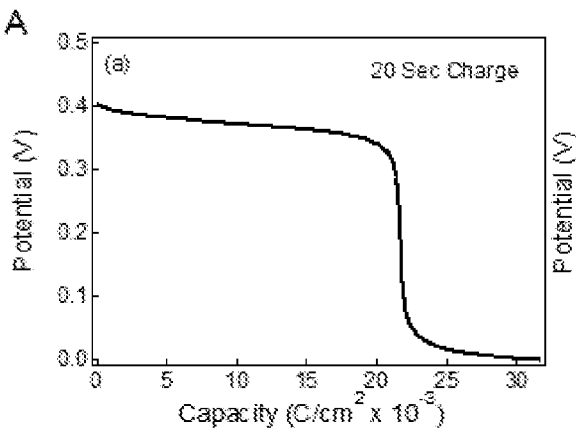


FIG. 8A

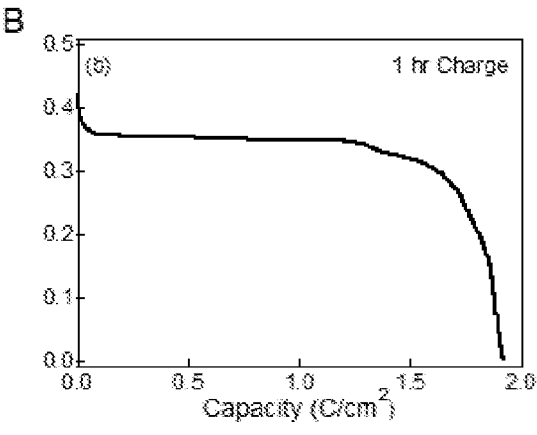


FIG. 8B

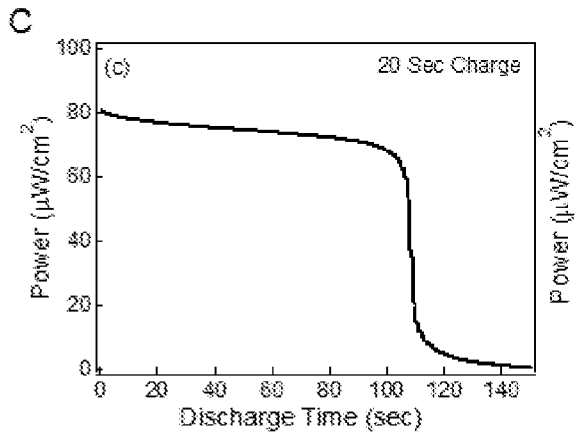


FIG. 8C

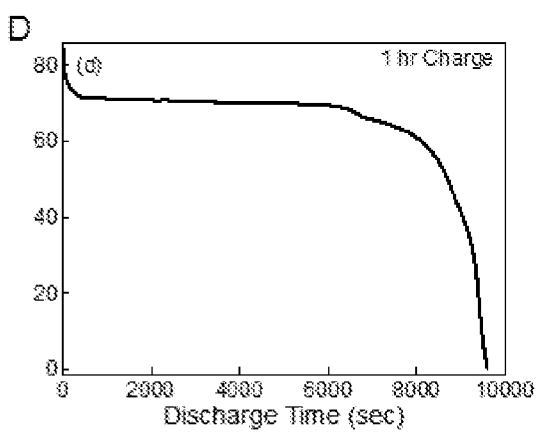


FIG. 8D

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/62949

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C25D 3/02, 3/20, 3/38, 7/10; B82Y 30/00; H01M 4/86; H01G 11/46; H01M 4/90, 8/20 (2017.01)
 CPC - H01M 4/8605, 4/8615, 4/8647, 4/9016, 8/188; H01G 11/46, 11/52; C25D 3/20, 3/38

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y --- A	WO 2015/148358 A1 (CORNELL UNIVERSITY) October 1, 2015; figure 1; paragraphs [0006], [0017]-[0020], [0058], [0076] ; claims 1, 21, 28	1-6, 8, 13-14 --- 7, 9 --- 11, 12
X --- Y	US 2014/0335918 A1 (GARDNER, D et al.) November 13, 2014; figure 5; paragraphs [0016], [0043], [0045], [0047], [0049], [0051]-[0052]; claim 42	1 --- 10
Y	US 2003/0085132 A1 (COBLEY, A et al.) May 8, 2003; paragraphs [0066] & [0080]	7
Y	US 2012/0067417 A1 (MACHIDA, T et al.) March 22, 2012; paragraph [0044]	9
Y	US 5,512,387 A (OVSHINSKY, S) April 30, 1996; Column 13, Lines 13-26	10
A	WO 2015/148357 A1 (CORNELL UNIVERSITY) October 1, 2015; figure 2; paragraphs [0007] & [0015]; claims 1&16	1-14

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

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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

24 January 2017 (24.01.2017)

Date of mailing of the international search report

24 MAR 2017

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