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(71) Applicant *(for all designated States except US):* **ILLINOIS INSTITUTE OF TECHNOLOGY** [US/US]; 10 West 35th Street, Chicago, IL 60616 (US).

(72) Inventor; and

(71) Applicant *(for US only):* **ASADI, Mohammad;** 530 N. Lake Shore Drive Apt. 1204, Chicago, IL 60611 (US).

(74) Agent: **SWANSON, Mark, D.** et al.; Pauley Erickson & Kottis, 2800 West Higgins Road, Suite 365, Hoffman Estates, IL 60169 (US).

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(54) **Title:** TRANSITION METAL PHOSPHIDES FOR HIGH EFFICIENT AND LONG CYCLE LIFE METAL-AIR BATTERIES

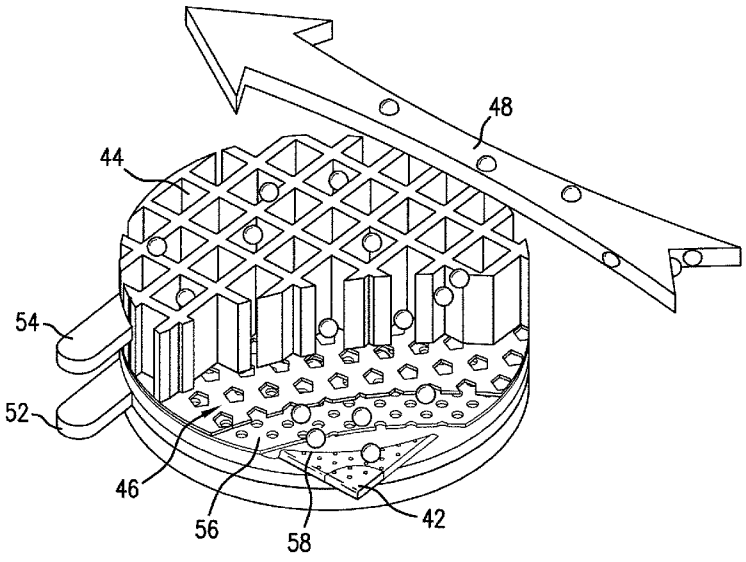

FIG. 2

(57) **Abstract:** An electrochemical cell and method of use, including an anode of metal, an air permeable cathode, an electrolyte between the anode and the cathode, and a transition metal phosphide catalyst on the cathode or between the cathode and the electrolyte. Also, a method of generating electrical current with an electrochemical cell by introducing a transition metal phosphide catalyst on a cathode side of the electrochemical cell. The catalyst can be in the form of any suitable nanostructure, such as molybdenum phosphide nanoflakes.

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[Continued on next page]

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

TRANSITION METAL PHOSPHIDES FOR HIGH EFFICIENT AND LONG CYCLE LIFE METAL-AIR BATTERIES

CROSS REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Application Serial No. 62/642,058, filed on 13 March 2018. This co-pending application is hereby incorporated by reference herein in its entirety and is made a part hereof, including but not limited to those portions which specifically appear hereinafter.

BACKGROUND OF THE INVENTION

This invention relates generally to chemical-based energy production and/or storage and, more particularly, to metal-air batteries and nanostructured catalytic materials for improved batteries.

Recent advances as well as dropping technology costs have made the development of carbon-free energy more feasible than ever. However, a transition toward clean energy technology requires a revolution in energy storage systems, generally known as a bottleneck for this transition. Today, lithium-ion batteries are recognized as the conventional energy storage systems used in many electronic devices. However, this technology has reached its theoretical limits making the goal of an efficient and inexpensive large-scale energy storage system seemingly impossible.

Among different emerging technologies, the metal-air battery is a promising alternative to Li-ion battery due to a several times higher theoretical specific energy. A metal–air battery is an electrochemical cell having an anode generally of pure metal and an external cathode of ambient air. An aqueous or aprotic electrolyte is also typical. During discharge of a metal-air electrochemical cell, an oxygen reduction reaction occurs in the ambient air cathode while the metal anode is oxidized.

The excessive specific energy of this new generation battery compared to the state of the art of existing technologies could result in a very inexpensive and compact battery that is well suited for large-scale application such as long-range electric vehicles (EVs). This technology can also be used as a main energy storage system for solar and wind power planets increasing the contribution of renewable energy in the electricity generation and supply by resolving their intermittency challenges.

SUMMARY OF THE INVENTION

A general object of the invention is to provide improved energy storage systems, particularly metal-air/0_2 batteries, and compositions and components therefore. The invention provides nanostructured catalysts working with electrolytes as a co-catalyst system.

The invention includes an electrochemical cell, such as a metal-air battery, including a metal anode, a cathode that allows an air flow, an electrolyte disposed between the anode and the cathode, and a catalyst in combination with the cathode. The cathode can include an air-permeable porous structure disposed between the cathode and the electrolyte. The cathode can be coated with the catalyst.

Embodiments of this invention incorporate an earth-abundant and inexpensive transition metal phosphide class of catalyst that can be useful in large-scale energy storage technologies. Establishing this class of materials with outstanding catalytic properties will also encourage the researcher to use them in other catalysis processes for sustainable energy technologies that are mainly stymied due to lack of suitable and inexpensive materials.

The invention further includes a method of generating electrical current with an electrochemical cell by introducing a transition metal phosphide catalyst on a cathode side of the electrochemical cell. The catalyst provides or improves formation of superoxides in the electrochemical cell over peroxides. In embodiments of this invention, the method includes contacting the cathode to oxygen, allowing the metal of the anode to be oxidized to metal ions, and allowing the oxygen to be reduced at a surface of the transition metal dichalcogenide to form one or more metal oxides with the metal ions, thereby generating the electrical potential between the anode and the cathode.

Other objects and advantages will be apparent to those skilled in the art from the following detailed description taken in conjunction with the appended claims and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a cross-section representation of a Na-air (0_2) battery according to one embodiment of this invention.

Fig. 2 shows a partial sectional representation of a Na-air (0_2) battery according to one embodiment of this invention.

Figs. 3A-F summarize test results according to embodiments of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides energy storage systems incorporating transition metal catalysts, , such as nanostructured transition metal phosphide catalysts (TMPs). The catalysts of this invention provide improved electrocatalytic activity for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which are two basic reactions during battery discharge and charge processes, respectively.

Figs. 1 and 2 illustrate incorporation of the catalyst into battery systems according to embodiments of this invention. Fig. 1 shows a cross-section of a Na-air (O_2) electrochemical cell 20, such as a metal-air battery, according to one embodiment of this invention. The cell 20 includes an anode 22, a cathode 24, and an electrolyte 26 disposed between the anode 22 and the cathode 24. The cathode provides an air flow 28, and is desirable formed of an air-permeable porous material, such as a carbon material. The porous material can also be electrically conductive. As shown in Fig. 1, the cell 20 can also include an optional reference electrode 25 in contact with the electrolyte.

The invention provides a catalyst, such as working with electrolytes as a co-catalyst system. As shown in Fig. 1, the catalyst 30 is disposed on the cathode side, such as between the cathode 24 and the electrolyte 26. In embodiments of this invention, the catalyst is coated on the cathode 24, such as coated on the porous structure. The catalyst 30 is disposed between the sodium-based electrolyte 26 and the air-permeable porous structure 24, which allows oxygen to contact the catalyst 30 and the electrolyte 26.

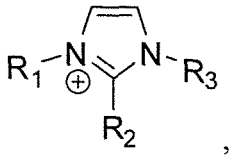
Fig. 2 is an exemplary schematic of a continuous air flow Na-air battery cell 40 according to one embodiment of this invention. The cell includes an anode 42, a cathode 44, and electrode 46. The cell 40 also includes an anode current collector 52, a cathode current collector 54, a cell guard membrane 56, and an anode protection layer 58 In this embodiment the air electrode (cathode) 44 is porous for air stream 48 and coated with the nanostructured catalyst of this invention. Various and alternative sizes (1 to 1000 nm), amounts, shapes, and configurations are available for the battery, the electrodes, and the catalyst material, depending on need.

Anodes of embodiments of this invention are formed of metal, and desirable consisting essentially of metal (meaning fully metal with only minor, insignificant other components/impurities). Exemplary metals include lithium, sodium, potassium, calcium, magnesium, zinc, and aluminum.

Electrolytes of embodiments of this invention include any suitable salt, such as

corresponding to the anode metal. For example, lithium salts are used to increase the lithium ion conductivity in the electrolyte, this is the case for other anode metals such as sodium, calcium, magnesium, zinc, and aluminum. The electrolyte can also include redox mediators, namely chemicals with electrochemical activity used to improve the activity of the reduction and oxidation reactions happening on the catalyst surface.

Electrolytes of embodiments of this invention include any suitable ionic liquid. Exemplary ionic liquids include an anion and a cation selected from imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, choline, sulfonium, prolinate, or methioninate cations. As a further example, an exemplary imdazolium cation is of the formula:



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where each of R_1, R_2, and R_3 is independently one of hydrogen, linear aliphatic C_1-C_6 group, branched aliphatic C_1-C_6 group, or cyclic aliphatic C_1-C_6 group. In one embodiment of this invention R_2 is hydrogen, and each of R_1 and R_3 is independently a linear or branched C1-C4 alkyl. Exemplary anions include C_1-C_6 alkylsulfate, tosylate, methanesulfonate, bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, tetrafluoroborate, triflate, halide, carbamate, sulfamate, and combinations thereof. In one embodiment, the ionic liquid includes 1-ethyl-3-methylimidazolium tetrafluoroborate. The electrolyte desirably includes at least 90% of the ionic liquid, and preferably is substantially free of water or non-ionic liquid organic solvents.

Catalysts of embodiments of this invention include a transition metal catalyst, and desirably a tri-transition metal catalyst. Exemplary catalysts include transition metal phosphide catalysts, such as, without limitation, Ti_nP_m, V_nP_m, Cr_nP_m, Z_mP_m, Nb_nP_m, $MonPm$, $HfnP_m$, W_nP_m, Ta_nP_m, Tc_nP_m, and Re_nP_m, wherein each n and m is independently one of 1, 2, 3, 4 and 5.

In embodiments of this invention, the catalyst comprises a plurality of nanoparticles. The nanoparticles have an average size between about 1 nm and 1000 nm, more between 1 nm and about 400 nm. Exemplary nanoparticle shapes include, without limitation, nanoflakes, nanosheets, nanoribbons, and combinations thereof.

One exemplary catalyst of this invention includes molybdenum (Mo) terminated molybdenum phosphide nanoflakes (MoP NFs). The catalyst can be, without limition, Mo_3P, MoP, or M0P2. Experimental data has revealed the turn over frequency

(TOF)) per atom activity of MoP NFs is more than two orders of magnitude higher than noble metal catalysts such as gold (Au) and platinum (Pt) nanoparticles. The performance of this catalyst in sodium-oxygen (Na-O_2) batteries has revealed that using MoP NFs on the cathode side and an ionic liquid/DMSO electrolyte of the cell make the formation of the sodium superoxide (NaO_2) more favorable than sodium peroxide (Na_2O_2). As a result, the cell overpotential of 600 mV can be obtained, which is approximately two times lower than the state of the art existing system in the literature (1000 mV). The formation of the NaO_2 as the product was confirmed by using *in-situ* differential electrochemical mass spectroscopy (DEMS) where the number of the electron per mole of O_2 was calculated to be 1.07 during the charging process. Preliminary results also revealed that this system can work up to 100 cycles in a pure O_2 environment.

Figs. 3A-F summarize testing using of a cell according to this invention. The electrolyte was 0.3M LiTFSI dissolved in DMSOTL (75/25) with redox mediators as additives. The amount of Mo_3P coating is 0.1 mg cm^{-2}. Fig. 3A shows charge/discharge profiles over 1000 cycles at constant density of 500 mA/g and the constant specific capacity of 500 mAh/g. Fig. 3B shows changes in discharge specific capacity, charge specific capacity (lower dots), and the corresponding coulombic efficiency (upper dots) over 1000 cycles. Fig. 3C shows changes in polarization gap and energy efficiency over 1000 cycles. Fig. 3D shows discharge and charge potential values over 1000 cycles. The graph shows the stable discharge overpotential up to 600 cycles with respect to the electrochemical potential for Li_2O_2 formation, at 2.96V. Fig. 3E shows the polarization gap as a function of current density while the specific capacity is constant at 500 mAh/g. FIG. 3F shows charge/discharge profiles over 300 cycles at a constant density of 500 mA/g and the specific capacity of 1250 mAh/g.

The invention thus provides transition metal catalysts for use in battery systems. The catalysts of this invention provide improved electro catalytic activity for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which are two basic reactions during battery discharge and charge processes, respectively.

The invention illustratively disclosed herein suitably may be practiced in the absence of any element, part, step, component, or ingredient which is not specifically disclosed herein.

While in the foregoing detailed description this invention has been described in relation to certain preferred embodiments thereof, and many details have been set forth for

purposes of illustration, it will be apparent to those skilled in the art that the invention is susceptible to additional embodiments and that certain of the details described herein can be varied considerably without departing from the basic principles of the invention.

What is claimed is:

1. An electrochemical cell, comprising:

an anode comprising metal;

a cathode comprising an air flow;

an electrolyte disposed between the anode and the cathode; and

a catalyst in combination with the cathode.

2. The electrochemical cell according to claim 1, wherein the anode consists essentially of the metal.

3. The electrochemical cell according to claim 1 or claim 2, wherein the metal of the anode is selected from lithium, sodium, potassium, calcium, magnesium, zinc, and aluminum.

4. The electrochemical cell according to any one of claims 1 to 3, wherein the metal of the anode is lithium.

5. The electrochemical cell according to any one of claims 1 to 4, wherein the cathode is coated with the catalyst.

6. The electrochemical cell according to any one of claims 1 to 5, wherein the cathode comprises an air-permeable porous structure.

7. The electrochemical cell according to any one of claims 9-11, wherein the porous member is electrically-conductive.

8. The electrochemical cell according to any one of claims 1 to 7, wherein the catalyst is disposed between the cathode and the electrolyte.

9. The electrochemical cell according to any one of claims 1 to 8, wherein the catalyst comprises a transition metal phosphide catalyst.

10. The electrochemical cell according to claim 9, wherein the catalyst comprises a tri-transition metal phosphide catalyst.

11. The electrochemical cell according to any one of claims 1 to 10, wherein the catalyst comprises a nanosized catalyst (1-1000nm).

12. The electrochemical cell according to any one of claims 1 to 11, further comprising a reference electrode disposed in contact with the electrolyte.

13. The electrochemical cell according to any one of claims 1 to 12, wherein the catalyst is selected from the group consisting of Ti_nP_m, V_nP_m, Cr_nP_m, Zr_nP_m, Nb_nP_m, Mo_nP_m, Hf_nP_m, W_nP_m, Ta_nP_m, Tc_nP_m, and Re_nP_m, wherein each n and m is independently one of 1, 2, 3, 4 and 5.

14. The electrochemical cell according to any one of claims 1 to 12, wherein the catalyst comprises Mo_3P, MoP, or MoP_2.

15. The electrochemical cell according to any one of claims 1 to 14, wherein the catalyst comprises a plurality of nanoparticles.

16. The electrochemical cell according to claim 15, wherein the nanoparticles have an average size between about 1 nm and 400 nm.

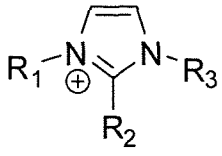
17. The electrochemical cell according to any one of claims 1-16, wherein the catalyst comprises nanoflakes.

18. The electrochemical cell according to any one of claims 1-16, wherein the catalyst comprises a nanosheet or nanoribbon.

19. The electrochemical cell according to any one of claims 1 to 18, wherein the electrolyte comprises an ionic liquid including an anion and a cation selected from imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, choline, sulfonium, prolinate or methioninate cations.

20. The electrochemical cell of claim 19, wherein the cation comprises imidazolium.

21. The electrochemical cell of claim 20, wherein the imdazolium cation is of the formula:



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where each of Ri, R_2, and R_3 is independently one of hydrogen, linear aliphatic Ci-C_6 group, branched aliphatic Ci-C_6 group, or cyclic aliphatic Ci-C_6 group.

22. The electrochemical cell of claim 21, wherein R_2 is hydrogen, and each of R_1 and R_3 is independently a linear or branched Ci-C_4 alkyl.

23. The electrochemical cell of any one of claims 19 to 22, wherein the anion is selected from the group consisting of Ci-C_6 alkylsulfate, tosylate, methanesulfonate, bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, tetrafluoroborate, triflate, halide, carbamate, sulfamate, and combinations thereof.

24. The electrochemical cell according to any one of claims 19 to 23, wherein the ionic liquid comprises 1-ethyl-3-methylimidazolium tetrafluoroborate.

25. The electrochemical according to any one of claims 19 to 24, wherein the electrolyte comprises at least 90 % of the ionic liquid.

26. The electrochemical cell according to any one of claims 1 to 25, wherein the electrolyte is substantially free of water or non-ionic liquid organic solvents.

27. A method of generating an electrical potential, comprising:

providing a electrochemical cell according to any one of claims 1 to 26;

contacting the cathode to oxygen;

allowing the metal of the anode to be oxidized to metal ions; and

allowing the oxygen to be reduced at a surface of the transition metal dichalcogenide to form one or more metal oxides with the metal ions, thereby generating the electrical potential between the anode and the cathode.

28. The electrochemical cell according to any of claims claim 1 to 27, wherein the catalyst comprises molybdenum.

29. The electrochemical cell according to any of claims 1 to 28, wherein the catalyst comprises molybdenum phosphide nanoflakes.

30. The electrochemical cell according to any of claims 1 to 29, further comprising an appropriate salt disposed between the anode and the cathode.

31. The electrochemical cell according to any of claims 1 to 30, further comprising a mediator disposed between the anode and the cathode.

32. An electrochemical cell, comprising:

an anode comprising metal;

an air permeable cathode;

an electrolyte between the anode and the cathode; and

a transition metal phosphide catalyst on the cathode or between the cathode and the electrolyte.

33. A method of generating electrical current with an electrochemical cell by introducing a transition metal phosphide catalyst on a cathode side of the electrochemical cell.

34. The method of Claim 33, wherein the catalyst improves formation of superoxides in the electrochemical cell over peroxides.

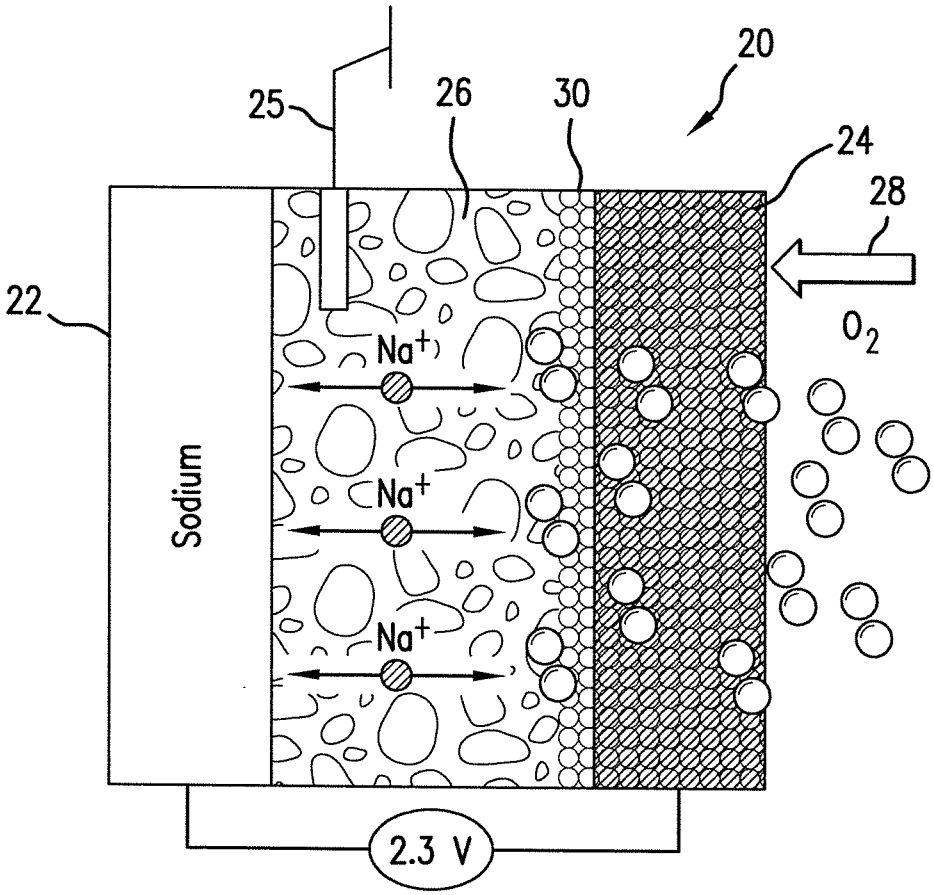

FIG. 1

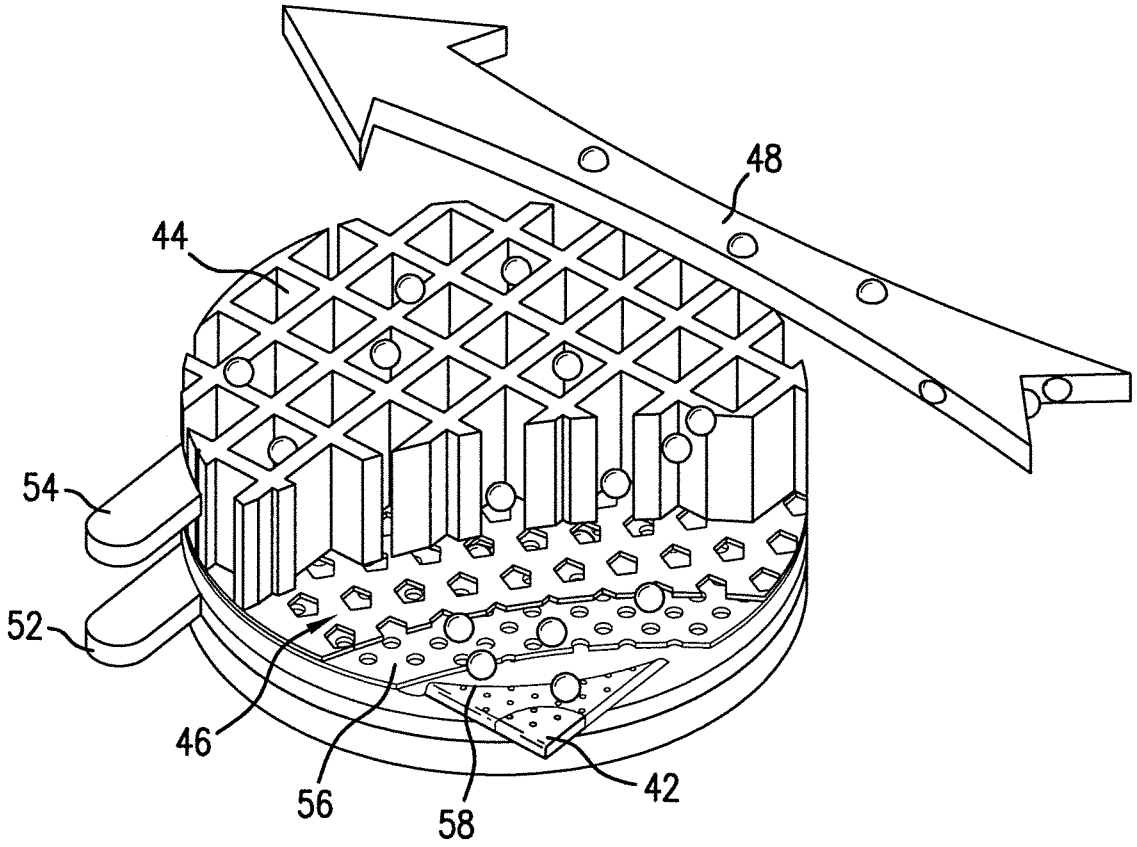

FIG.2

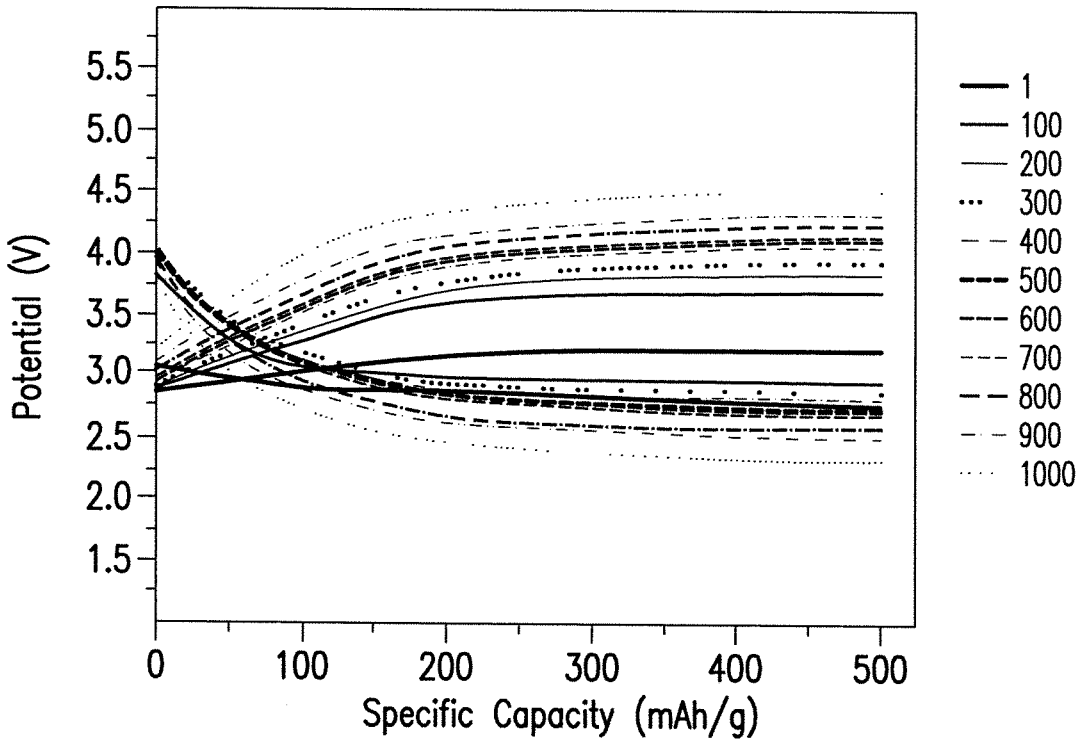
Potential (V)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
0
100
200
300
400
500
Specific Capacity (mAh/g)
1
100
200
300
400
500
600
700
800
900
1000

FIG.3A

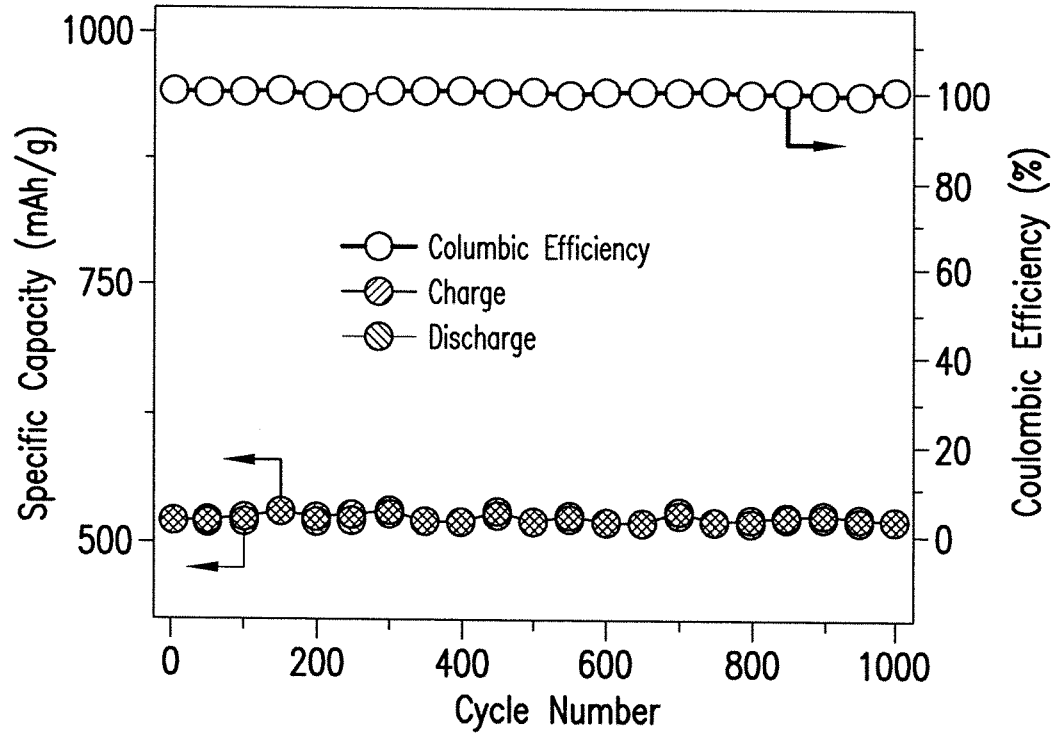
Specific Capacity (mAh/g)
1000
750
500
Columbic Efficiency
Charge
Discharge
100
80
60
40
20
0
Coulombic Efficiency (%)
0
200
400
600
800
1000
Cycle Number

FIG.3B

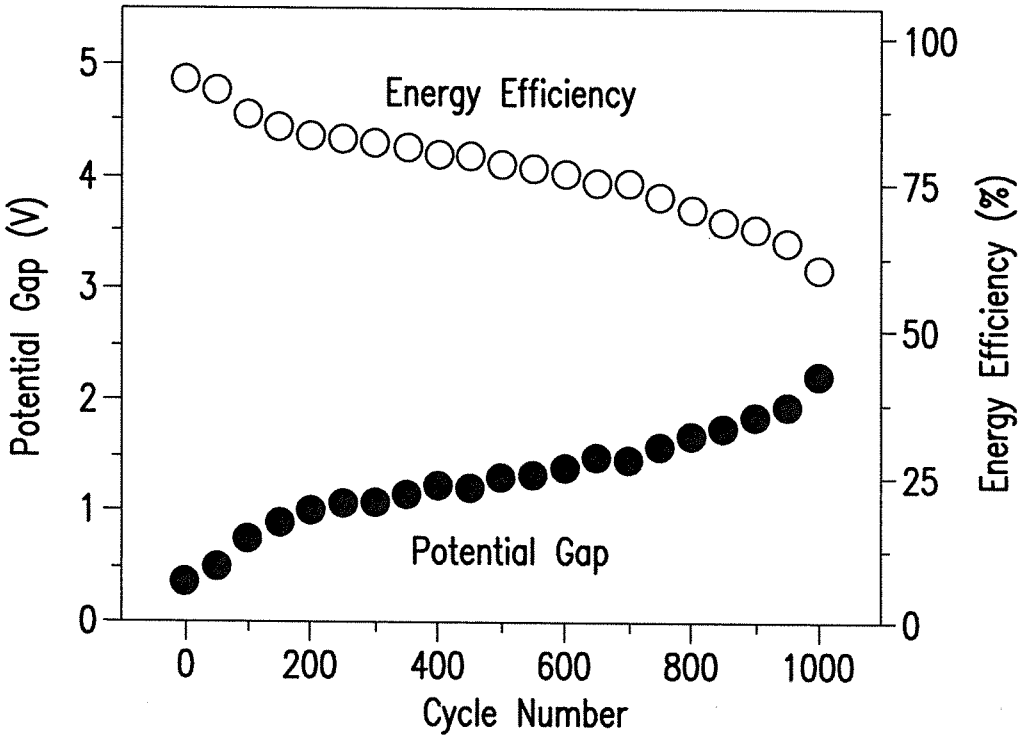
Energy Efficiency
Potential Gap
Potential Gap (V)
Energy Efficiency (%)
Cycle Number
0
1
2
3
4
5
0
25
50
75
100
0
200
400
600
800
1000

FIG.3C

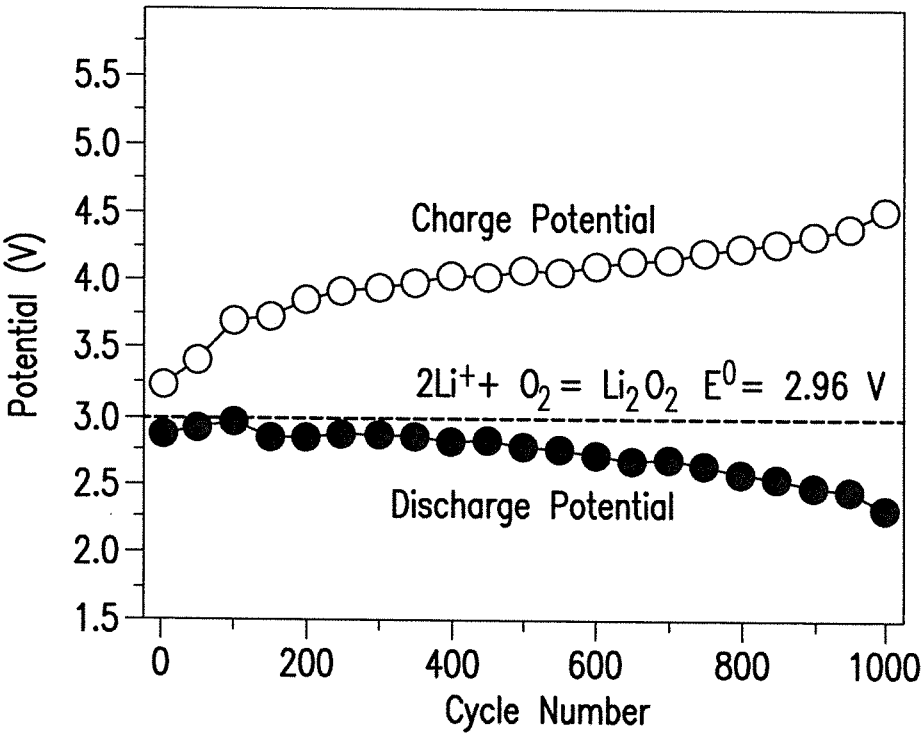
Charge Potential
2Li+ + O2 = Li2O2 E0 = 2.96 V
Discharge Potential
Potential (V)
Cycle Number
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
0
200
400
600
800
1000

FIG.3D

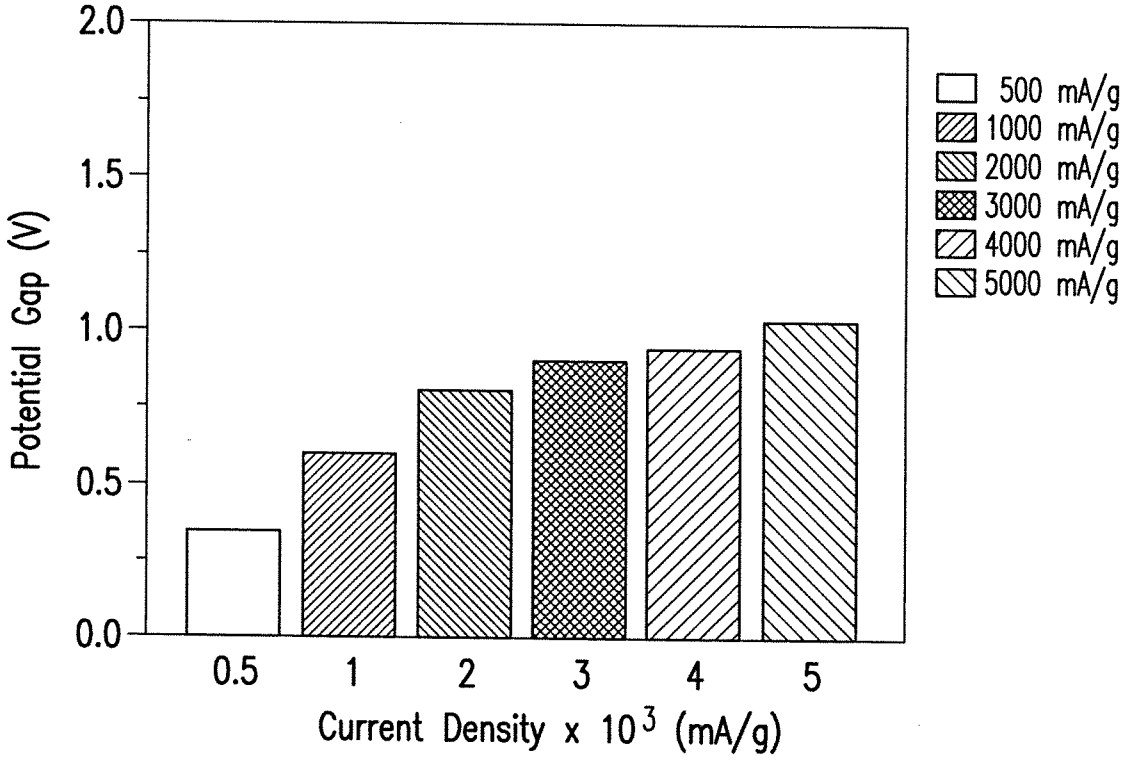
2.0
1.5
1.0
0.5
0.0
Potential Gap (V)
0.5
1
2
3
4
5
Current Density x 10^3 (mA/g)
500 mA/g
1000 mA/g
2000 mA/g
3000 mA/g
4000 mA/g
5000 mA/g

FIG.3E

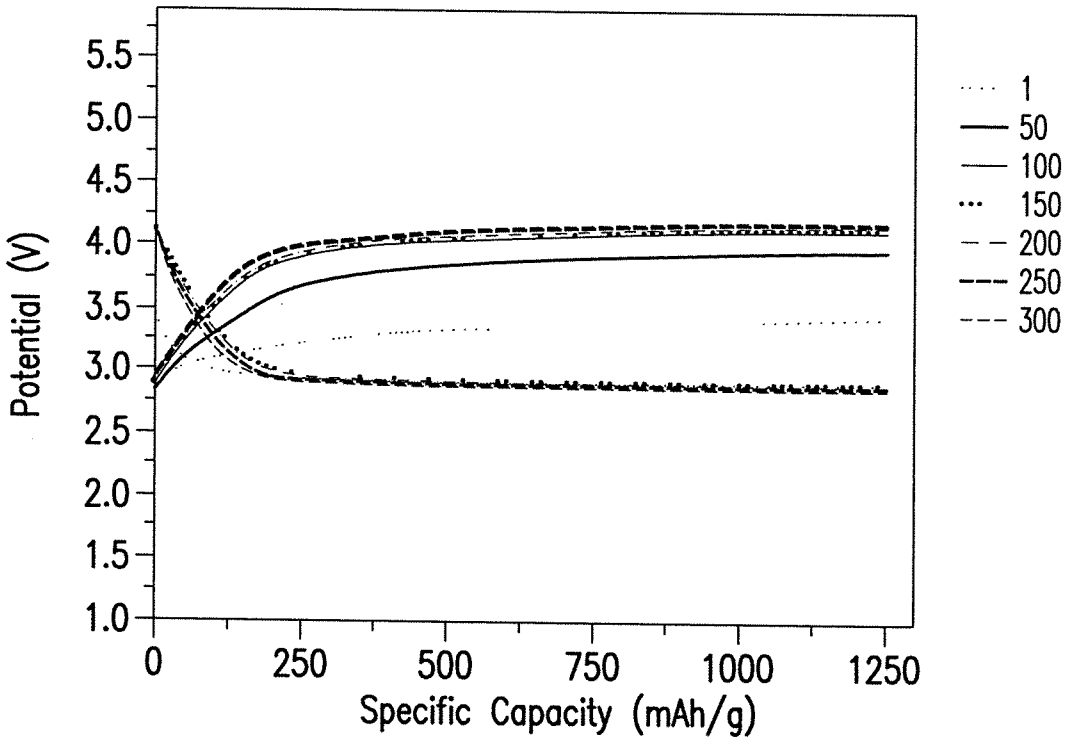
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Potential (V)
0
250
500
750
1000
1250
Specific Capacity (mAh/g)
1
50
100
150
200
250
300

FIG.3F

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/022024

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-26, 28-31
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/022024

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/02; H01M 2/00; H01M 4/134; H01M 4/36; H01M 6/14; H01M 14/00 (2019.01)
CPC - H01M 4/02; H01M 2/00; H01M 4/134; H01M 4/36; H01M 6/14; H01M 14/00 (2019.05)

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
USPC - 204/194; 204/242; 204/279; 320/127 (keyword delimited)

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	WO 2016/100204 A2 (BOARD OF TRUSTEES OF THE UNIVERSITY OF ILLINOIS) 23 June 2016 (23.06.2016) entire document	1-3, 27 --- 32-34
Y	US 9,799,893 B2 (CAMPBELL) 24 October 2017 (24.10.2017) entire document	32-34
A	US 2016/0172688 A1 (HYUNDAI MOTOR COMPANY) 16 June 2016 (16.06.2016) entire document	1-3, 27, 32-34
A	US 2017/0267109 A1 (MANN+HUMMEL GMBH) 21 September 2017 (21.09.2017) entire document	1-3, 27, 32-34

☐ 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	Date of mailing of the international search report
10 May 2019	24 MAY 2019
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Authorized officer Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774