



(51) International Patent Classification:
H01L 41/00 (2013.01)

(21) International Application Number:
PCT/US2019/051421

(22) International Filing Date:
17 September 2019 (17.09.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/732,822 18 September 2018 (18.09.2018) US
62/772,319 28 November 2018 (28.11.2018) US
62/879,923 29 July 2019 (29.07.2019) US

(71) Applicants: **NORTHWESTERN UNIVERSITY**
[US/US]; 633 Clark Street, Evanston, Illinois 60208
(US). **CALIFORNIA INSTITUTE OF TECHNOLOGY**
[US/US]; 1200 East California Blvd, MC 6-32, Pasadena,
California 91125 (US).

(72) Inventors: **BOAMAH, Mavis D.**; 1311 Chicago Ave., Apt.
306, Evanston, Illinois 60201 (US). **GEIGER, Franz M.**;

1314 Wilder St., Evanston, Illinois 60202 (US). **MILLER III, Thomas F.**; 1836 Monterey Road, South Pasadena, California 91030 (US). **KIM, Jeongmin**; 378 S. Catalina Ave, Pasadena, California 91106 (US).

(74) Agent: **MANNING, Michelle** et al.; Bell & Manning, LLC,
2801 West Beltline Highway, Ste. 210, Madison, Wisconsin
53713 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

(54) Title: LIQUID FLOW INDUCED POWER GENERATION USING NANOSCALE METAL LAYERS

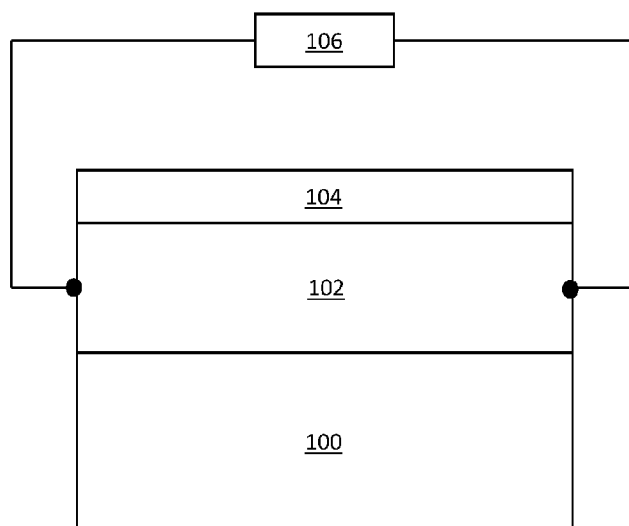


FIG. 1A

(57) Abstract: Energy harvesting devices and methods for converting the mechanical energy of a flowing ionic solution, such as rainwater or seawater, into electric energy are provided. The energy harvesting devices include an electric current generating device that includes a metal layer and an amphoteric metal oxide film disposed over a surface of the metal layer. By moving an electric double layer across the surface of the amphoteric metal oxide film, an electric current is generated in the metal layer.



UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

(88) Date of publication of the international search report:

20 August 2020 (20.08.2020)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 19/51421

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.:
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:

-- See Extra Sheet --

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.:
1-10

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/US 19/51421

A. CLASSIFICATION OF SUBJECT MATTER

IPC - H01L 41/00 (2020.01)

CPC - H02N 2/188; H01L 41/053; H02N 2/00

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.
Y	US 2010/0171394 A1 (Glenn et al.) 8 July 2010 (08.07.2010) Entire document, especially Abstract, para [0028]-[0029]; [0037]-[0038]	1-10
Y	US 6,008,625 A (Gan et al.) 28 December 1999 (28.12.1999) Entire document, especially Abstract, col 2 ln 17-24; col 4 ln 48-51; col 6 ln 13-17	1-10
Y	US 6,791,205 B2 (Woodbridge) 14 September 2004 (14.09.2004) Entire document, especially Abstract, col 1 ln 37-63; col 2 ln 56-60	3
Y	US 2016/0324435 A1 (The Trustees of the University of Pennsylvania) 10 November 2016 (10.11.2016) Entire document, especially Abstract, para [0048]; [0088]	8
Y	US 2015/0124311 A1 (Parrot) 7 May 2015 (07.05.2015) Entire document, especially Abstract, para [0029]; [0039]	10
A	wikipedia. "Vanadium(V) Oxide." Wikipedia, Wikimedia Foundation, 6 Sept. 2018 (06.09.2018), en.wikipedia.org/w/index.php?title=Vanadium%28V%29_oxide&oldid=856169497.	1, 6
A	US 2018/0183038 A1 (University of Houston System) 28 June 2018 (28.06.2018) Entire document, especially para [0037]	10
A	US 2013/0026409 A1 (Baker et al.) 31 January 2013 (31.02.2013) Entire document	1-10

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

1 May 2020

Date of mailing of the international search report

09 JUL 2020

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300

Continuation of Box III: Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-10 directed to a method of harvesting energy using a liquid flow-based device comprising: a metal layer comprising a metal; an amphoteric metal oxide film adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface; and at least one of: an electronic device that consumes electrical power connected laterally across the metal layer and configured to be powered by a current running parallel to the interface; and an energy storage device connected laterally across the metal layer and configured to be charged by a current running parallel to the interface, the method comprising: exposing the surface of the amphoteric metal oxide film to a flow of an ionic solution having a temporally varying flow rate or a temporally varying flow direction, wherein the temporally varying flow rate or the temporally varying flow direction generates a current in the metal layer; and powering the electronic device or charging the energy storage device with the generated current.

Group II: Claims 11-19 directed to a method of monitoring the flow of an ionic solution and pumping an ionic solution using a liquid flow-based device comprising: a metal layer comprising a metal; an amphoteric metal oxide film adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface; and at least one of: a voltage measuring device configured to measure a voltage across the metal layer; and a current measuring device connected laterally across the metal layer and configured to measure a current running parallel to the interface, the method comprising: exposing the surface of the amphoteric metal oxide film to a flow of an ionic solution to generate a current in the metal layer, the flow of the ionic solution having a temporally varying ionic conductivity, wherein the temporally varying ionic conductivity is provided by a temporally varying flow rate, a temporally varying flow direction, or both; and measuring changes in the voltage across the metal layer or the current through, the metal layer as the ionic solution passes over the surface of the amphoteric metal oxide film.

Group III: Claims 20-23 directed to a liquid flow-based device comprising: a metal layer comprising vanadium, copper, or tin; an amphoteric metal oxide film comprising vanadium oxide, copper oxide, or tin oxide adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface; and at least one of: an electronic device that consumes electrical power connected laterally across the metal layer and configured to be powered by a current running parallel to the interface; an energy storage device connected laterally across the metal layer and configured to be charged by a current running parallel to the interface; a voltage measuring device configured to measure a voltage across the metal layer; and a current measuring device connected laterally across the metal layer and configured to measure a current running parallel to the interface.

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I requires a method of harvesting energy using a liquid flow-based device comprising: at least one of: an electronic device that consumes electrical power connected laterally across the metal layer and configured to be powered by a current running parallel to the interface; and an energy storage device connected laterally across the metal layer and configured to be charged by a current running parallel to the interface, the method comprising: powering the electronic device or charging the energy storage device with the generated current, not specifically required by Groups II-III.

Group II requires a method of monitoring the flow of an ionic solution and pumping an ionic solution using a liquid flow-based device comprising: at least one of: a voltage measuring device configured to measure a voltage across the metal layer; and a current measuring device connected laterally across the metal layer and configured to measure a current running parallel to the interface, the method comprising: measuring changes in the voltage across the metal layer or the current through, the metal layer as the ionic solution passes over the surface of the amphoteric metal oxide film, not specifically required by Groups I or III.

Group III requires a liquid flow-based device comprising: a metal layer comprising vanadium, copper, or tin; an amphoteric metal oxide film comprising vanadium oxide, copper oxide, or tin oxide adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface; and at least one of: an electronic device that consumes electrical power connected laterally across the metal layer and configured to be powered by a current running parallel to the interface; an energy storage device connected laterally across the metal layer and configured to be charged by a current running parallel to the interface; a voltage measuring device configured to measure a voltage across the metal layer; and a current measuring device connected laterally across the metal layer and configured to measure a current running parallel to the interface, not specifically required by Groups I-II.

Common Technical Features:

Groups I-III share the common feature of a liquid flow-based device comprising: a metal layer; adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface; and an electrical device.

Groups I-II share the common feature of a method comprising disposing an ionic solution on the surface of the amphoteric metal oxide film; and applying a temporally varying voltage across the metal layer, whereby the temporally varying voltage induces the ionic solution to move along the surface of the amphoteric metal oxide film.

-- See Extra Sheet --

Continuation of Box III: Observations where unity of invention is lacking

Groups I and III share the technical feature of a liquid flow-based device comprising at least one of: an electronic device that consumes electrical power connected laterally across the metal layer and configured to be powered by a current running parallel to the interface; or an energy storage device connected laterally across the metal layer and configured to be charged by a current running parallel to the interface.

Groups II-III share the technical feature of a liquid flow-based device comprising at least one of: a voltage measuring device configured to measure a voltage across the metal layer; and a current measuring device connected laterally across the metal layer and configured to measure a current running parallel to the interface.

However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is obvious over US 2010/0171394 A1 to Glenn et al. (hereinafter 'Glenn') in view of US 6,008,625 A to Gan et al. (hereinafter 'Gan'). Glenn discloses a liquid flow-based device (Abstract - '... An energy harvesting device positionable within a blood vessel... the energy harvesting device includes piezoelectric elements arranged to generate a voltage in response to... or flow of blood through the blood vessel...'; see instant claims 4 and 5) that comprises a metal layer comprising a metal (para [0038] - '... the energy harvesting implant may be a stent-like device in the form of a band, sleeve, mesh, laser cut tubing, or other framework formed of one or more shape memory elements (e.g. nickel titanium alloy... or stainless steel); a film having a surface disposed opposite the interface (para [0028] - '...The harvesting elements disclosed herein utilize piezoelectric elements that convert mechanical stress, strain, vibration, or bending into an electrical potential that can be used to provide operating power to components of the implant system or that can be stored in a capacitor or rechargeable battery for later use. Suitable piezoelectric materials include... The piezoelectric elements are positioned in electrical contact with electrodes and conductors that conduct the electrical energy to the device 12 for immediate use or for storage for later use. piezoelectric films...'); and an electrical device, (Abstract - '...The energy harvesting device includes piezoelectric elements arranged to generate a voltage in response to mechanical blood vessel activity such as bending, expansion or contraction of the blood vessel, or flow of blood through the blood vessel...'; para [0029] - '...the piezoelectric material may be arranged to generate electrical current in response to strain during expansion of the vessel, or forces incurred when patient movement bends the vessel...') but does not further specifically disclose the device comprising an amphoteric metal oxide film adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface. Gan discloses a similar implant (Abstract - '...A power source including two alkali metal/transition metal oxide cells discharged in parallel to power an implantable medical device is described...') wherein an amphoteric oxide anode material is chosen to facilitate charge carrying (col 2 ln 17-20 - '...In the present invention, the preferred anode is lithium metal and the preferred cathode is a transition metal oxide for example, silver vanadium oxide (SVO) or copper silver vanadium oxide (CSVO)...'; see the document entitled "Vanadium Oxide" to Wikipedia, see page 1; see instant claim 7), but does not further specifically disclose wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface. However, as the electronic device is capable of charging via the voltage supplies by flowing blood, it would have been obvious to one of ordinary skill in the art to create the method wherein the metal layer has a thickness that facilitates charge carrier motion parallel to the interface, through routine experimentation. Further, it would have been obvious to one of ordinary skill in the art to combine these references, and create the method wherein the device comprises an amphoteric metal oxide film adjacent to the metal layer at an interface, the amphoteric metal oxide film having a surface disposed opposite the interface, because amphoteric metal oxides, such as vanadium oxide, are known to possess the vigorous energy density and discharge capacity required for use in medical devices, making them ideal for the coating on the metal layer of the device (see Gan, col 6 ln 13-17).

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-III lack unity under PCT Rule 13.