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(54) Title: MULTIMODAL FLEXIBLE ALUMINIUM BASED SYSTEM FOR GENERATING ELECTRICAL ENERGY

(57) Abstract: The present disclosure relates to a system for generating electrical energy. The system comprises an electrochemical generator comprising: an anode (104) comprising an aluminium coated with calcium magnesium silicate (106); an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide; a solid electrolyte (110) comprising an oxygen generating biomaterial; a gas inlet (118); and a gas outlet (120); wherein the gas inlet (118) is connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir (112) comprises a first conductive ink or at least a portion of the reservoir (112) wall is coated with a first conductive ink that has the capability to selectively adsorb the gases CO2, SO2, and O2.

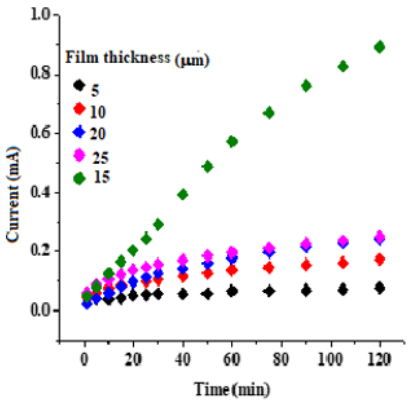

FIG. 1: Electrical performance of calcium-magnesium-silicate sheet modified anodized aluminium

FORM 2

THE PATENTS ACT 1970
(39 OF 1970)
&
The Patent Rules, 2003

Complete Specification
(See Section 10 and Rule 13)

1. TITLE OF THE INVENTION

MULTIMODAL FLEXIBLE ALUMINIUM BASED SYSTEM FOR GENERATING ELECTRICAL ENERGY

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3. PREAMBLE TO THE DESCRIPTION

COMPLETE

The following specification particularly describes the invention and the manner in which it is to be performed

TECHNICAL FIELD

[0001] The present disclosure generally relates to the field of electrochemistry, specifically to an electrochemical generator. More particularly, it pertains to a multimodal flexible aluminium based electrochemical generator and a system for generating electrical energy.

BACKGROUND

[0002] The pursuit of efficient and sustainable energy sources has led to the development and widespread adoption of electrochemical generators as a vital component of various energy storage and conversion systems. These generators encompass a wide range of technologies, including fuel cells, batteries, and electrolyzers. Conventional electrochemical generators operate based on the principles of an electrochemical cell, which can provide an electrical current by employing a set of electrodes. These electrodes consist of a positive electrode and a negative electrode, positioned on either side of an electrolyte. Within these electrodes are specific materials capable of undergoing redox reactions, a process that generates electrons, resulting in the creation of an electric current. Concurrently, ions are produced during these reactions and are transported from one electrode to the other through the electrolyte.

[0003] The basic structure of primary Al–air generator includes an Al anode, an air cathode, and an appropriate electrolyte and in general; the electrolytes used for primary Al–air batteries are aqueous solutions of sodium hydroxide (NaOH), potassium hydroxide (KOH) or sodium chloride (NaCl) in which electrochemical reactions in alkaline electrolytes at the electrodes can be expressed as follows:

$$\text{Anode:} \quad Al \longrightarrow Al^{3+} + 3e^- \qquad (1)$$

$$\text{Cathode:} \quad O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (2)$$

$$\text{Overall:} \quad 4Al + 3O_2 + 6H_2O \rightarrow 4Al(OH)_3 \qquad (3)$$

[0004] Aqueous electrolytes face critical issues involving dendrite formation, electrode corrosion and hydrogen gas evolution. To address these issues, corrosion and hydrogen gas inhibitors can be used in which the basic mechanism of corrosion inhibitors is the adsorption of inhibitor molecules onto Al anode surfaces to suppress corrosion reactions.

[0005] For normal Al–air generator, several issues exist, including: (1) the formation of byproducts such as Al_2O_3 and $Al(OH)_3$ on electrode surfaces that can suppress Al–air battery electrochemical reactions, (2) hydrogen evolution resulting from parasitic corrosion reactions on Al surfaces and (3) the formation of corrosion products such as $Al(OH)_4$ and $Al(OH)_3$. This parasitic chemical side reaction can be expressed as follows:

$$Al + 3H_2O \longrightarrow Al(OH)_3 + 3/2H_2 \quad (4)$$

[0006] Among the critical challenges in optimizing the performance and durability of these electrochemical generators is the inhibition of hydrogen (H_2) evolution, which often plays a dual role in undermining their efficacy – as a product of undesirable side reactions and as a contributor to corrosion.

[0007] The need for inhibiting the hydrogen evolution reaction of the aluminum anode and increasing the specific capacity, stability, and/or longevity of electrochemical generators spans various sectors, ranging from energy and transportation to healthcare and beyond. Addressing these requirements not only improves the efficiency and effectiveness of existing technologies but also enables the development of new, innovative solutions that are more sustainable and environmentally friendly.

SUMMARY OF THE DISCLOSURE

[0008] Accordingly, the disclosure herein provides an electrochemical generator and a system for generating electrical energy. Thus, in an aspect, the present disclosure provides an electrochemical generator and a system as a power supply source. The electrochemical generator and the system provided herein may overcome one or more challenges associated therewith.

[0009] In an aspect, the present disclosure provides an electrochemical generator comprising:

an anode comprising an aluminium coated with calcium magnesium silicate;

an air cathode comprising graphene or graphite coated with calcium-magnesium peroxide layer; and

a solid electrolyte comprising an oxygen generating biomaterial.

In another aspect, the present disclosure provides a system for generating electrical energy, comprising an electrochemical generator comprising:

an anode comprising an aluminium coated with calcium magnesium silicate;

an air cathode comprising graphene or graphite coated with calcium-magnesium peroxide layer;

a solid electrolyte comprising an oxygen generating biomaterial;

a gas inlet; and

a gas outlet;

wherein the gas inlet is connected to a reservoir, which absorbs, or stores, or desorbs air and the reservoir comprises a first conductive ink or at least a portion of the reservoir wall is coated with a first conductive ink that has the capability to selectively adsorb the gases CO_2, SO_2, and O_2.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The features of the present disclosure will become fully apparent from the following description taken in conjunction with the accompanying figures. With the understanding that the figures depict only several embodiments in accordance with the disclosure and are not to be considered limiting of its scope, the disclosure will be described further through use of the accompanying figures:

[0011] FIG. 1 illustrates electrical performance of calcium-magnesium-silicate sheet modified anodized aluminium.

[0012] FIG. 2 illustrates Differential Scanning Calorimetry (DSC) Thermogram of (a) Pure NaAlg, (b) 60 M wt.% NaAlg: 40 M wt.% sodium percarbonate, (c) 40 M wt.% NaAlg: 60 M wt.% sodium percarbonate, (d) 50 M wt.% NaAlg: 50 M wt.% sodium percarbonate and (e) 30 M wt.% NaAlg: 70 M wt.% sodium percarbonate, in accordance with an embodiment.

[0013] FIG. 3 illustrates linear sweep voltammogram for the highest conducting biopolymer electrolyte.

[0014] FIG. 4 illustrates (A) CMPO carbon nanofibers and (B) oxygen release profile of CMPO loaded carbon nanofibers.

[0015] FIG. 5 illustrates electrochemical performance of electrochemical generator under different gas conditions. Galvanostatic discharge of Al under Ar, 100% CO_2, 100% O_2, and 80% CO_2 using sodium percarbonate incorporated alginate hydrogel electrolyte and current density of 80 mA/gCarbon. Inset: CV for three-electrode cell under 100% O_2 and 80% CO_2 with a sweep rate of 0.1 mV/s.

[0016] FIG. 6. illustrates galvanodynamic polarization curves of the anode (blue) and the cathode (green), current-voltage curve (red), and power curve (black) of Aluminium air (AA)cell with solid electrolyte sodium percarbonate incorporated alginate hydrogel at 60 ^oC.

[0017] FIG. 7 illustrates schematic representation of multimodal electrochemical generator.

[0018] FIG. 8 illustrates reservoir's printed conductive ink modified intertwin silver ink response and selectivity for all three gases such as CO_2, SO_2, and O_2.

[0019] FIG. 9 illustrates response of electrochemical generators at different concentrations of gas mixture.

DETAILED DESCRIPTION

[0020] Before the methods of the present disclosure are described in greater detail, it is to be understood that the methods are not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the methods will be limited only by the appended claims.

[0021] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the methods. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the methods, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the methods.

[0022] Certain ranges are presented herein with numerical values being preceded by the term "about." The term "about" is used herein to provide literal support for the exact number that it precedes, as well as a number that is near to or approximately the number that the term precedes. In determining whether a number is near to or approximately a specifically

recited number, the near or approximating unrecited number may be a number which, in the context in which it is presented, provides the substantial equivalent of the specifically recited number.

[0023] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by those of ordinary skill in the art to which the disclosure belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, preferred methods and materials are described. For the purposes of the present disclosure, the following terms are defined below.

[0024] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

[0025] As used herein, the term "comprises" or "comprising" is generally used in the sense of include, that is to say permitting the presence of one or more features or components.

[0026] As used herein, “conductive ink” refers to a material capable of conducting electricity.

[0027] As used herein, "oxygen-generating biomaterial" refers to a biomaterial or substance that has the capability to produce oxygen under specific conditions.

[0028] As used herein, “intertwin printed ink” refers to material that have printed/memorable sites for specific templates/ gases.

[0029] As used herein, “silver ink modified with intertwin printed ink” refers to material that have electrical conductivity modified with material that have printed/memorable sites for specific templates/ gases selectively adsorbs template/gases without change its physical &chemical properties.

[0030] Disclosed are an electrochemical generator and a system for generating electrical energy.

[0031] In an embodiment, the present disclosure provides an electrochemical generator comprising:

an anode comprising an aluminium coated with calcium magnesium silicate;

an air cathode comprising graphene or graphite coated with calcium-magnesium peroxide layer; and

a solid electrolyte comprising an oxygen generating biomaterial.

[0032] In certain embodiments, the anode comprises an aluminium coated with calcium magnesium (Ca-Mg) silicate. Examples of Ca-Mg silicates include, but are not limited to akermanite ($Ca_2MgSi_2O_7$), bredigite ($Ca_7MgSi_4O_{16}$), diopside ($CaMgSi_2O_6$), merwinite and larnite. In some instances, asbestos is used to coat the aluminium. Any form of asbestos may be used for coating the aluminium. The coating of Ca-Mg silicate can be of any thickness. In certain embodiments, the coating of Ca-Mg silicate is of a predetermined thickness. In some embodiments, the thickness of the coated Ca-Mg silicate is about 5 mm or more. In some embodiments, the thickness of the coated Ca-Mg silicate is from about 5 mm to about 15 mm, including about 5 mm, about 5.5 mm, about 6 mm, about 6.5 mm, about 7 mm, about 7.5 mm, about 8 mm about 8.5 mm, about 9 mm, about 9.5 mm, about 10 mm, about 10.5 mm, about 11 mm, about 11.5 mm, about 12 mm, about 12.5 mm, about 13 mm, about 13.5 mm, about 14 mm, about 14.5 mm, or about 15 mm. In some instances, the thickness of the coated Ca-Mg silicate is 15 mm.

[0033] The Ca-Mg silicate may be coated or deposited on aluminium by any conventional technique known in art. In certain embodiments, Ca-Mg silicate is coated on the aluminium using drop coating method.

[0034] In certain embodiments, the anode having an aluminium coated with calcium magnesium silicate is highly mesoporous and enhances the gas adsorption and ion exchange of the anode.

[0035] In certain embodiments, the Ca-Mg-silicate coating on Al anode inhibits self-corrosion. All the elements of Ca-Mg-silicate have lower melting temperatures than Al, have a degree of solubility in Al, soluble in an alkaline electrolyte and have high hydrogen overpotential. The ions dissolved into the solution and redeposited on the cathodic surface to decrease the hydrogen evolution. Silica, calcium, and magnesium react with unwanted OH^- which forms silicates, calcium hydroxide and magnesium hydroxides. These hydroxides are an adsorber of oxygen, carbon dioxide and sulphur dioxide, facilitate the electron flow and consumption of more gases which increase the specific power density of electrochemical generator.

$$SiO_2 + OH^- = SiO_3^{2-} + H_2O$$

$$Ca^{2+} + OH^- = Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

$$Mg^{2+} + OH^- = Mg(OH)_2 + CO_2 = MgCO_3 + H_2O$$

[0036] Thus, modified anode (i.e., the anode comprising an aluminium coated with calcium magnesium silicate) inhibits hydrogen evolution, generates water which facilitates more electron flow by reacting with oxygen. This also highly facilitates the absorption of greenhouse gases such as carbon dioxide and sulphur dioxide (FIG. 7`).

Their chemical reaction mechanism to produce the performance is shown to be $4Al + 9CO_2 \leftrightarrow 2Al_2(CO_3)_3 + 3C$, by which CO_2 is reversibly utilized.

[0037] The air cathode of the electrochemical generator adsorbs O_2, CO_2, SO_2, moisture, or a mixture thereof. In the air cathode, the calcium-magnesium (Ca-Mg) peroxide layer coated or deposited on graphene or graphite acts as a catalyst for electrochemical oxidation of gas(es) in presence water vapor. The coating of Ca-Mg peroxide layer can be of any thickness. In certain embodiments, the coating of Ca-Mg peroxide layer is of a predetermined thickness. In some embodiments, the thickness of the coated Ca-Mg peroxide layer is about 25 mm or more. In some embodiments, the thickness of the Ca-Mg peroxide layer is from about 25 mm to about 100 mm, including about 25 mm, about 30 mm, about 35 mm, about 40 mm, about 45 mm, about 50 mm, about 55 mm, about 60 mm, about 65 mm, about 70 mm, about 75 mm, about 80 mm, about 85 mm, about 95 mm, or about 100 mm. The calcium-magnesium peroxide layer may be coated or deposited on graphene or graphite by any conventional technique known in art. In certain embodiments, Ca-Mg peroxide layer is coated on the graphene or graphite using spin coating or electrospinning.

[0038] Calcium peroxide (CaO_2), magnesium peroxide (MgO_2), and sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$), are proposed as oxygen generating biomaterials. Oxygen release from the solid peroxides, contrary to liquid hydrogen peroxide directly decomposing to molecular oxygen, is a two-step process (see below).

$$CaO_2\,(s) + 2H_2O \longrightarrow Ca(OH)_2 + H_2O_2 \qquad (1)$$

$$2H_2O_2 \longrightarrow O_2 + 2H_2O \qquad (2)$$

[0039] In certain embodiments, the electrochemical generator provided herein comprises a solid electrolyte comprising an oxygen generating biomaterial. In some embodiments, the oxygen generating biomaterial also has high CO_2 and SO_2 adsorption capacity. Any oxygen generating biomaterial suitable for employing in a solid electrolyte may be used. In certain embodiments, the oxygen generating biomaterial comprises sodium

percarbonate incorporated into or onto alginate. The solid electrolyte may comprise sodium percarbonate and alginate in any ratio. In certain embodiments, the solid electrolyte comprises sodium percarbonate and alginate in a ratio from about 30 to about 70, including about 30, about 35, about 40, about 45, about 50, about 55, about 60, about 65, or about 70. In some instances, the solid electrolyte comprises: 50 M wt.% sodium alginate (NaAlg): 50 M wt.% sodium percarbonate composition.

[0040] The solid electrolyte comprising sodium percarbonate incorporated into or onto alginate may be prepared by any conventional method known in the art. In certain embodiments, the sodium percarbonate incorporated into or onto alginate is prepared by solution casting method. In some embodiments, the method comprises adding solutions of sodium alginate and sodium percarbonate dissolved in a solvent separately, to a solution of alginate in a solvent; and evaporating the solvent to obtain sodium percarbonate incorporated into or onto alginate. The solvent may be evaporated by any conventional technique known in art. The solvent may be evaporated by any conventional method including, but not limited to, air/gas drying, heating, or vacuum drying. The method further comprises a drying step after the solvent evaporation step.

[0041] The solid electrolyte provided herein adsorbs moisture and water from the atmosphere and inhibits the hydrogen producing/evolution reactions, and simultaneously provides more air. These unique features give long life, high electrochemical performance with high energy density.

$$Al^{3+}\,(aq) + 6H_2O\,(l) \longrightarrow Al(H_2O)_6^{3+}\,(aq)$$

$$Al(H_2O)_n^{m+} + H_2O\,(l) \longleftrightarrow Al(H_2O)_{n-1}(OH)^{(m-1)+} + H_3O^+$$

[0042] Alginate adsorbs moisture, efficient oxygen carrier and facilitates the Al ions by crosslinking it. Alginate can crosslink Al^{3+} effectively. It releases Al^{3+} ions mechanism from Aluminium-alignate crosslinked surface layer.

[0043] Sodium percarbonate (SPO) is an adduct of sodium carbonate and hydrogen peroxide which in the presence of water will rapidly decompose to generate oxygen as shown in equations below:

$$2[Na_2CO_3 \cdot 1.5H_2O_2] \longrightarrow 2Na_2CO_3 + H_2O_2$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

[0044] The solid electrolyte enhances electrochemical performance with very high specific energy and power. It provides more water and inhibits hydrogen evolution reactions and simultaneously provides more air. These unique features give long life, high electrochemical performance with high energy density.

[0045] In certain embodiments, the electrochemical generator as provided herein further comprises a gas inlet, and a gas outlet; wherein the gas inlet is connected to a reservoir, which absorbs, or stores, or desorbs air. The reservoir comprises a first conductive ink or at least a portion of the reservoir wall is coated with a first conductive ink that has the capability to selectively adsorb the gases CO_2, SO_2, and/or O_2. In certain embodiments, the first conductive ink comprises a silver ink modified with intertwin printed ink. The silver ink modified with intertwin printed ink is optionally coated with a second conductive ink. In certain embodiments, the second conductive ink has optionally printed cavities/sites to adsorb the respective gases SO_2, CO_2 and/or O_2. In some embodiments, the silver ink modified with intertwin printed ink is coated with a second conductive ink having printed cavities/sites to adsorb the respective gases SO_2, CO_2 and/or O_2. As per adsorption in the printed cavities of the second conductive ink, there would be a change in conductive path. The comparative study of a reference conductive path without gas adsorption and change in conductive path after adsorption can be monitored by a change in current/resistance. Once saturation level is reached, there would be no change in current/resister observed, which indicates saturation. Thus, the whole acts as a sensor.

[0046] In certain embodiments, the second conductive ink comprises a polymeric ink. Polymeric ink may comprise any conductive polymer. In some embodiments, the polymeric ink comprises a polymer and/or co-polymer of one or more acrylic acid, (alkyl)acrylic acid, acrylate, (alkyl)acrylate, urethane/acrylic acid, and urethane acrylate. In some embodiments, the polymeric ink comprises a polymer of (alkyl)acrylic acid. In some instances, the polymeric comprises a polymer of (meth)acrylic acid. The second conductive ink may further comprise cellulose such as acetate/cellulose nanofibrils.

[0047] In certain embodiments, printed ink modified reservoir has the following advantages:

- Effective adsorption and desorption can be Monitored by multiple ways- Swelling of inks, UV light and temperature.
- Effect of humidity is negligible.
- Effect of very low and very high temperature, pressure is negligible.

- Cost effective, quick response (60 s) and simple method to adsorb-desorb gases in reservoirs.
- Wide application in automotive, aerospace and space mission in storing gases and generating electricity.
- These conductive printed inks act as sensor which provide accurate measurements of all three gases at wide temperature, pressure, and humidity.

[0048] FIG. 7 illustrates a typical schematic representation of multimodal electrochemical generator in accordance with an embodiment of the invention. As shown in FIG. 7, the electrochemical generator of the present disclosure comprises: an anode (104) comprising an aluminium coated with calcium magnesium silicate (106); an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide; a solid electrolyte (110) comprising an oxygen generating biomaterial; a gas inlet (118); and a gas outlet (120); wherein the gas inlet (118) is connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir is same as described above.

[0049] Thus, in certain embodiments, the present disclosure provides a system for generating electrical energy. The system comprises an electrochemical generator comprising:

an anode (104) comprising an aluminium coated with calcium magnesium silicate (106);

an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide;

a solid electrolyte (110) comprising an oxygen generating biomaterial;

a gas inlet (118); and

a gas outlet (120);

wherein the gas inlet (118) is connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir is same as defined above.

[0050] In certain embodiments, the system comprises an anode assembly (104a) comprising an anode (104), a cathode assembly (108a) comprising a cathode (108), and a heat exchanger (116), wherein the heat exchanger (116) is connected to the anode assembly

(104a). In further embodiments, the system comprises a positive chamber (100) comprising an anode (104), and a negative chamber (102) comprising an air cathode (108). In some instances, the system comprises metal terminals attached to said anode (104) and said cathode (108); wherein the metal terminals configured to allow electrical connections to be made with an external device or circuit. In further instances, the system may further comprise a casing enclosing said anode (104), cathode (108), metal terminals, and solid electrolyte (110).

[0051] Accordingly, in certain embodiments, the present disclosure provides a system for generating electrical energy, the system comprises:

an anode (104) comprising an aluminium coated with calcium magnesium silicate (106);

an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide;

a solid electrolyte (110) comprising an oxygen generating biomaterial;

a gas inlet (118);

a gas outlet (120) connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir is same as defined above;

metal terminals attached to said anode (104) and said cathode (108); said metal terminals configured to allow electrical connections to be made with an external device or circuit; and

a casing enclosing said anode (104), cathode (108), metal terminals, and solid electrolyte (110).

[0052] The present disclosure is further described with reference to the following examples, which are only illustrative in nature and should not be construed to limit the scope of the present disclosure in any manner.

EXAMPLES

Example 1: Aluminium anode and its characterization

[0053] 99.99% pure 3.5 x3.5 mm thickness Aluminium sheet was purchased from local market. Firstly, 5% acetone solution was used to clean the surface of aluminum alloy. After that, the aluminum alloy was put into an alkali solution (15 % sodium hydroxide solution) to

remove unwanted oil coating (if any) for 5 mins. Secondly, an acid solution (10 % hydrofluoric acid) was used to etch the aluminum alloy for 5 min. After the pretreatment of the alkali and acid solution, the aluminum alloy was washed with pure water and put into a solution of phosphoric acid and sulphuric acid solution. Finally, after the anodic oxidation process, the anodized aluminum alloy is sealed by boiling water and potassium dichromate solution respectively. The treated anode was coated with Ca-Mg-silicate sheet by drop coating and kept it for 2 hrs to dry at room temperature.

Example 2: Calcium Magnesium silicate preparation ($Ca_2MgSi_2O_7$)

[0054] (1 M) magnesium nitrate and (3.5 M) citric acid stock solutions were prepared in deionized water. 20 ml of eggshell solution, 20 mL of palm oil, 20 mL of magnesium nitrate and 30 mL of citric acid were pipetted out from the stock solution and 9 mL of TEOS was mixed sequentially in a beaker. The pH of the reaction mixture was adjusted to 1 by using concentrated nitric acid. Finally, the reaction mixture was kept for stirring at room temperature for 28 h. Nitric acid plays dual role in sol–gel combustion method by maintaining the pH of the reaction mixture at 1 and also facilitates hydrolysis of TEOS into silanol and ethyl alcohol. The resultant silanol and ethyl alcohol undergo poly-condensation reaction with the citric acid, leading to the formation of a gel-like complex. The complex was later kept for ageing for 5 days to obtain dense gel. The gel formed was dried at 100 °C for 6 h in hot air oven and eventually decomposed at 300 ◦C in a preheated muffle furnace for combustion. Combustion initiates with exothermic redox reaction between fuel and nitrate ions present in gel. Brown color precursor formed after combustion indicates the existence of nitrate and carbon groups. The precursor was finely powdered by using mortar pestle and calcined at 350 °C temperature for 6 h.

Table 1. Anti-corrosion performance of different modified anode surface dipped in 3% NaCl solution

Sample	BET area (m^2/g)	V_t (cc/g)	V_{micro} (cc/g)	V_{meso} (cc/g)	E corrosion potential immersed in 3% Nacl Solution	Weight loss mg cm^{-2}
Aluminium sheet	1006	0.558	0.422	0.080	-1.45 V (0 days) -1.37 (10 days)	70.4 (0 days) 90.5 (10 days)
Anodized Aluminium sheet	426	0.378	0.228	0.277	-0.93V (0 days) -0.92V (10 days)	10.3 (0 days) 12.4 (0 days)
Ca-Mg-Silicate coating	502	0.364	0.234	0.345	-0.65V (0 days) -0.60V (10 days)	0.03 (0 days) 0.03 (10 days)

Anodized Aluminium sheet						

[0055] Calcium-Mg-silicate sheet modified anodized Aluminium showed high mesoporous properties which enhance the gas adsorption and ion exchange of anode. Corrosion potential (E corrosion) found to close to 1 in case of Calcium-Mg-silicate sheet modified anodized Aluminium, comparative to other anode or anodized aluminum sheet/aluminum sheet confirms the anticorrosion behavior of Ca-Mg-Silicate coating Anodized Aluminium sheet and weight loss is also found to be less.

Example 3: Thickness optimization of Ca-Mg-silicate coating on Aluminium

[0056] Calcium-Mg-silicate sheet modified anodized Aluminium electrical performance was examined using Potentiostate (Autolab) using 5 M NaOH and 0.02M $Na_2SnO_3.3H_2O$ electrolyte (50 mL) and calcium and magnesium peroxide on carbon nanofibers mesh (air cathode) in 100 mL cell. The 15 mm thickness of Ca-Mg-silicate modified anodized aluminum sheet showed good performance comparative to other modified anodized aluminum sheet (see FIG. 1).

Example 4: Solid electrolyte preparation

[0057] In the example, sodium alginate (M.wt 216.12 $gmol^{-1}$) and sodium percarbonate [$Na_2CO_3 \cdot 1.5H_2O_2$] (M.wt 157.01 $gmol^{-1}$) were used as the raw materials, and hot water has been used as a solvent to make solid biopolymer electrolytes using the solution casting technique. All the chemicals used in this study are purchased from Merck (India). The different M wt.% of sodium alginate (60 to 30%) was dissolved in hot water (95 ^oC) using a magnetic stirrer. [$Na_2CO_3 \cdot 1.5H_2O_2$] of various M wt.% (40 to 70%) was dissolved separately and added with the biopolymer solution. In order to obtain a homogeneous solution, the solution was stirred well for 1.6 h. The solution was then cast into a polypropylene petri dish and kept in an oven at 75^oC for 20 hrs to obtain a clear and freestanding film.

[0058] The DSC curve for the biopolymer electrolyte of pure sodium alginate and sodium alginate with various compositions of sodium percarbonate are shown in FIG. 2. Tg values for pure sodium alginate and sodium alginate with different compositions of salt are provided in FIG. 2. The Tg value obtained for the host biopolymer is 69.2 °C. The Tg values decrease with increase of sodium percarbonate which shows that incorporation of sodium percarbonates in alginate increase the plasticization and flexibility enhances the electron/ions movements of resultant solid electrolyte. The lowest Tg value obtained for 50 M wt.% NaAlg:

50 M wt.% sodium percarbonate. The increase in sodium percarbonate contents in sodium percarbonate showed a high Tg value compared to the Tg value obtained for 50 M wt.% NaAlg: 50 M wt.% sodium percarbonate. This may be due to undissociated and loose incorporation of salt which results in poor electron/ions mobility within the electrolyte and enhances the hardness of the solid electrolyte results in poor permeability of ions, gases, and electrons. As per the comparative study of different compositions of fabricated solid electrolyte, 50 M wt.% NaAlg: 50 M wt.% sodium percarbonate composition of solid electrolyte is excellent for fabrication of electrochemical generator.

Electrochemical stability of the solid electrolyte:

[0059] In electrochemical devices applications, the stability of solid biopolymer electrolytes is an auspicious parameter. The electrochemical stability of maximum ionic conducting solid biopolymer electrolyte was measured using Linear sweep voltammetry at the scanning rate of 1 mVs-1 and the voltage is between 0 and 5 V at room temperature. The electrochemical stability of the largest ionic conducting biopolymer electrolyte (50 M wt.% NaAlg: 50 M wt.% sodium percarbonate is shown in FIG. 3.

Example 5: Synthesis of air cathode

[0060] Activated carbon was produced by using hydrothermal carbonization and pyrolysis activation process. Hydrothermal carbonization was carried out in a hydrothermal reactor at 300 °C for 40 minutes using $ZnCl_2$ solution in waste palm oil. Meanwhile, the activation process was performed in a tubular furnace at 650 °C in the presence of flowing hydrogen for 3 hours. Graphene was prepared by mixing the biomass with $FeCl_3$, $ZnCl_2$ and water, followed by stirring and heating at 90 °C for 1.5 hours. Afterwards the mixture dried for 24 hours at 95 °C. The graphene precursor then heated in an atmospheric furnace at 900 °C for 25 minutes.

Example 6: Synthesis of calcium-magnesium peroxide nanoparticles (CMPO)

[0061] CMPO nanoparticles were synthesized using a hydrolysis–precipitation procedure. To this end, 5 g of $CaCl_2$ (Merck, India) and 5 g $MgCl_2$(Merck India) was dissolved in 5 mL distilled water. Later on, 2.5 mL of 1.7% w/w ammonia solution and 15 mL of PEG 200 were consecutively added to the content and stirred for 25 min. Next, 2.5 mL of 30% w/w H_2O_2 was poured into the stirring mixture with a rate of 1.0 ml/h via a programmable infusion pump. Thereafter, 0.5% w/w NaOH solution was added to increase the pH to 12 and render a precipitate from reaction mixture. The precipitate was then

centrifuged and washed with 0.5% w/w NaOH three times. The resulting product was extensively rinsed with water and dried in a vacuum oven at 90 °C and 20 mmHg.

Example 7: Fabrication of CMPO carbon nanofibers

[0062] CMPO carbon nanofibers were fabricated via electrospinning process. For this purpose, polyacrylonitride (PAN) pellets were dissolved in hydrogen fluoride and isopropyl to yield 10 % (w/v) solutions. Then, 0.005 g of both CaO_2+MgO_2 nanoparticles were dispersed in 2 mL of each solution via vigorous stirring for 6 h. The resulting suspensions were separately delivered to 5 mL plastic syringes fitted with 20 gauge rounded-end needle. The needles were positioned 12.5 cm from a grounded, aluminum foil covered rotating collector and the spinning voltage was kept constant at 15 kV. The flow rate and drum rotation speed were set as 2 mL/h and 300 rpm, respectively. The obtained CMPO carbon nanofibers SEM images are shown in FIG. 4.

[0063] Oxygen release from CMPO-loaded carbon nanofibers was measured using an Abott portable blood gas analyzer. About 2 mL of phosphate-buffered solution became deoxygenated by nitrogen purging and the CMPO carbon nanofiber sheets (1x1cm) were immersed in deoxygenated phosphate-buffered solution for intended intervals over 10 days. At each point, a small aliquot of each incubating fluid was removed, and the oxygen content was measured in mmHg. Moreover, the calcium and magnesium content and pH evolutions of the incubating fluid were recorded by the analyzer. The deoxygenated buffer was used as a control to minimize the unwanted interferences from surrounding. The measurements were performed in triplicate.

[0064] The cathode material, graphite (10 g) was mixed with 15% wt polyvinyl difluoride dissolved in N-methyl pyrrolidone (50 mL) solution using agitated stirring and agitated for 30 minutes using homogenizer. The solution obtained was kept for drying in an oven at 35 ^{o}C. The obtained graphite film (25 mm thickness) was further modified with carbon nanofibers film coating. CMPO modified carbon nanofibers were dissolved in 2 mL of DMF and spin coated on graphite film. CMPO carbon nanofibers graphite film was dried at 65 ^{o}C for 16 hrs. This film (GP) cut into pieces with size of 200 × 200 mm2 was connected with stainless wire and encapsulated by epoxy resin.

[0065] As per FIG. 4 (B), CMPO-loaded carbon nanofibers release more oxygen than magnesium peroxide and calcium peroxide. It showed high oxygen release due to good water permeability and diffusion of Ca^{2+}/Mg^{2+} ions in the networked carbon nanofibers.

Example 8: Electrochemical Generator

[0066] Electrochemical generator includes a body with bottom inlet/upper outlet gas channel for gas circulation. Inlet gas channel connected with reservoir (FIG. 7) The volume of the gases pumped through the cell was 1.4 l. A 100 mmx 200 mm. 3.5 x3.5 mm thick aluminum anode was installed between a pair of electrically connected air cathodes with the dimensions of 100 mmx200 mm each. The total working surface area of the anode-cathodes assembly was 400 cm^2.

[0067] An anodized aluminum sheet plate with a mass of 5 g and the corresponding capacity of ~500 Ah was used as an anode. Other components of electrochemical generators include heat exchanger, air shutters attached to reservoir to capture air, circulation pump, and deflector.

Electrochemical method for testing electrochemical generator performance:

[0068] The electrochemical generator performance was examined by galvanostatic discharge method. In the presence of various gases such as oxygen, carbon dioxide, mixture of carbon dioxide and argon, galvanostatic discharge test for Al anode-based electrochemical generator was examined and voltage profiles were recorded. The obtained data is shown in FIG. 5. Under pure oxygen (100% O_2), electrical energy produced (about 1800 mA·hour/gCarbon) at about 2.1 V. Under pure carbon dioxide (100% CO_2), electrical energy produced (about 1200 mA·hour/gCarbon) at about 1.5 V. This capacity was increased about 20-fold at CO_2:O_2 mixture (80 % Carbon dioxide: 20% O2) with noticeable voltage plateau at higher potential about 2.4 V. Under argon, the generator produced insignificant electrical energy at a lower potential 0.3 V.

Examination of electrochemical generator cell:

[0069] FIG. 6 shows the current-voltage curve of current invention with the working surface area 200 cm^2 tested in galvanodynamic regime and the corresponding polarization curves of its electrodes. The open circuit potential of the cell was 2.56V (red). The equilibrium potential was 0.42 V vs. SHE for the cathode (green) and -2.53 V vs. SHE for the anode (blue). The maximum power density of the cell was 198 mW cm^{-2}. The power of the electrochemical generator (10 cells in each module) at the beginning of the discharge was 100 W, and it remained almost constant to 95 W at the end of discharge. The negligible power drop was caused by the thermal stable and heat absorption properties of solid electrolyte and air-CO_2 cathode, with no decrease in electrolyte concentration and increase of gap between electrodes which accompanied by retention of electrical conductivity.

Working mechanism of electrochemical generator:

[0070] As a special electrochemical generator, the Al–gas generator uses oxygen, CO_2, sulphur dioxide from surrounding as the material to activate the cathode and aluminum as the anode reactant. It is a converter which uses air, carbon dioxide and water vapour to generate electricity. Electricity supply depends upon the availability of gases. It is not a storage device. It has the advantages of being lightweight, very safe, and having high specific power. The generator showed 200 W electrochemical generator with specific energy of 300 Wh kg-1 after testing.

Example 9: Gas reservoir of electrochemical generator

[0071] The reservoir was modified with intertwine silver ink materials. The intertwin silver ink surface was further coated with conductive SO_2, CO_2 and O_2 selective printed sites containing polymeric inks. These inks adsorb selectively the three gases in printed cavities. As per adsorption in the printed cavities of the polymeric inks there is change in conductive path. The comparative study of reference conductive path without gas adsorption and change in conductive path after adsorption can be monitored by change in current/resistance. Once saturation level is reached, there is no change in current/resister is observed, which indicates saturation. The whole acts as a sensor FIG. 8 illustrates a reservoir's printed conductive ink modified intertwin silver ink response and selectivity for all three gases.

Preparation of gas printed conductive films:

[0072] The following reagents were mixed into N-N-ethyl-2-pyrrolidone 30 mL, bamboo derived activated carbon (particle size 10 nm) 25 mg as conductive poly-methacrylic acid, 1.0 g, hydrochloric acid methanolic solution 250 mL, cellulose acetate/cellulose nanofibrils 40 mg as binder and template (CO_2, SO_2, O_2) 1.2 mmol. After that, they were ultrasonicated to prevent aggregation of bamboo derived activated carbon and were stirred for 5 hours to absorb template molecule gases into polymer matrix. Next, absorption properties of the inks were evaluated. In this study two types of inks were prepared; 1. Printed by all three gases and non-printed polymer (2) which was synthesized without printing treatment. Each 15 μL ink were drop-casted onto a spot of 1 cm^2 on silica substrates. Then heated at 85 °C on a hot plate to volatilize ink solvent. After this treatment, the substrates were heated at 90 °C in a vacuum for 1.2 hour to remove template molecules (all three gases). Thereafter, these inks were placed into a chamber in an adsorption experiment system. Then all three gases were flown into the chamber 0.5 L/min, 100 ppm in flow rate for 15 minutes. In this process, all three gases were adsorbed to the inks. After the absorption process, amount of absorbed gases in inks were measured by measuring change in current/resister. At 5 ppm-

10 ppm gas mixture, the electrochemical generation process runs. FIG. 9 shows the response of change in resistance in the electrochemical generator at various concentrations of gas mixture.

[0073] Although the foregoing disclosure has been described in some detail by way of illustration and examples for purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this disclosure that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

[0074] Accordingly, the preceding merely illustrates the principles of the disclosure. It will be appreciated that those skilled in the art will be able to devise various arrangements which, although not explicitly described or shown herein, embody the principles of the disclosure and are included within its spirit and scope. Furthermore, all examples and conditional language recited herein are principally intended to aid the reader in understanding the principles of the disclosure and the concepts contributed by the inventors to furthering the art and are to be construed as being without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting principles, aspects, and embodiments of the disclosure as well as specific examples thereof, are intended to encompass both structural and functional equivalents thereof. Additionally, it is intended that such equivalents include both currently known equivalents and equivalents developed in the future, i.e., any elements developed that perform the same function, regardless of structure. The scope of the present disclosure, therefore, is not intended to be limited to the exemplary embodiments shown and described herein. Rather, the scope and spirit of present disclosure is embodied by the appended claims.

WE CLAIM:

1. An electrochemical generator comprising:

    an anode (104) comprising an aluminium coated with calcium magnesium silicate (106);

    an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide layer; and

    a solid electrolyte (110) comprising an oxygen generating biomaterial.

2. The electrochemical generator as claimed in claim 1, wherein calcium magnesium silicate (106) is asbestos.

3. The electrochemical generator as claimed in claim 1, wherein the air cathode (108) adsorbs O_2, CO_2, SO_2, moisture, or a mixture thereof.

4. The electrochemical generator as claimed in claim 1, wherein the oxygen generating biomaterial is sodium percarbonate incorporated into or onto alginate.

5. The electrochemical generator as claimed in claim 4, wherein ratio of sodium percarbonate to alginate is from about 30 to 70.

6. The electrochemical generator as claimed in claim 1, wherein calcium magnesium silicate (106) has a thickness ranging from 5 mm to 15 mm; and/or calcium-magnesium peroxide layer has a thickness ranging from 25 mm to 100 mm.

7. The electrochemical generator as claimed claim 1, further comprises a gas inlet (118), and a gas outlet (120); wherein the gas inlet (118) is connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir (112) comprises a first conductive ink or at least a portion of the reservoir (112) wall is coated with a first conductive ink that has the capability to selectively adsorb the gases CO_2, SO_2, and/or O_2.

8. The electrochemical generator as claimed in claim 7, wherein the first conductive ink comprises a silver ink modified with intertwin printed ink, which is optionally coated

with a second conductive ink having optionally printed cavities/sites to adsorb the respective gases SO_2, CO_2 and/or O_2.

9. A system for generating electrical energy, comprising an electrochemical generator comprising:

an anode (104) comprising an aluminium coated with calcium magnesium silicate (106);

an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide;

a solid electrolyte (110) comprising an oxygen generating biomaterial;

a gas inlet (118); and

a gas outlet (120);

wherein the gas inlet (118) is connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir (112) comprises a first conductive ink or at least a portion of the reservoir (112) wall is coated with a first conductive ink that has the capability to selectively adsorb the gases CO_2, SO_2, and O_2.

10. The system as claimed in claim 9, wherein the conductive ink comprises a silver ink modified with intertwin printed ink, which is optionally coated with a second conductive ink having optionally printed cavities/sites to absorb the respective gases SO_2, CO_2 and/or O_2.

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ABSTRACT

MULTIMODAL FLEXIBLE ALUMINIUM BASED SYSTEM FOR GENERATING ELECTRICAL ENERGY

The present disclosure relates to a system for generating electrical energy. The system comprises an electrochemical generator comprising: an anode (104) comprising an aluminium coated with calcium magnesium silicate (106); an air cathode (108) comprising graphene or graphite coated with calcium-magnesium peroxide; a solid electrolyte (110) comprising an oxygen generating biomaterial; a gas inlet (118); and a gas outlet (120); wherein the gas inlet (118) is connected to a reservoir (112), which absorbs, or stores, or desorbs air and the reservoir (112) comprises a first conductive ink or at least a portion of the reservoir (112) wall is coated with a first conductive ink that has the capability to selectively adsorb the gases CO_2, SO_2, and O_2.

[Fig 7(a) & 7(b)]

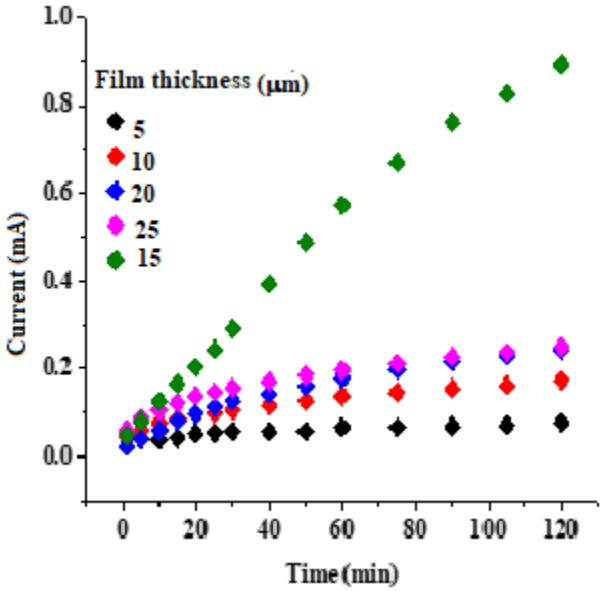

FIG. 1: Electrical performance of calcium-magnesium-silicate sheet modified anodized aluminium

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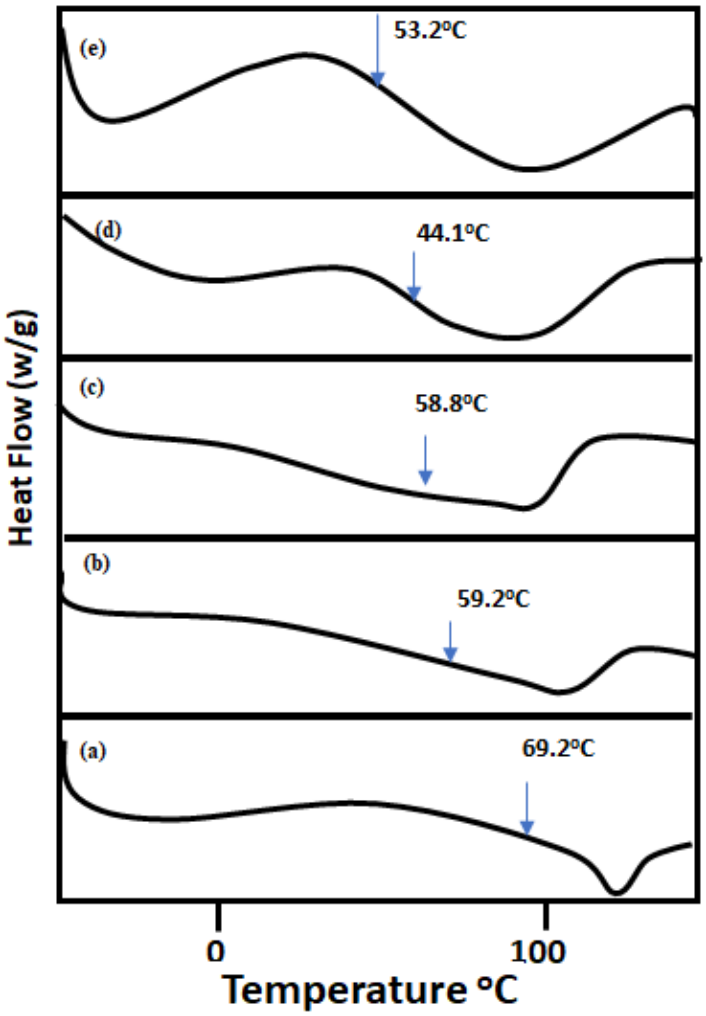

FIG. 2. DSC Thermogram of (a) Pure NaAlg, (b) 60 M wt.% NaAlg: 40 M wt.% sodium percarbonate, (c) 40 M wt.% NaAlg: 60 M wt.% sodium percarbonate, (d) 50 M wt.% NaAlg: 50 M wt.% sodium percarbonate and (e) 30 M wt.% NaAlg: 70 M wt.% sodium percarbonate

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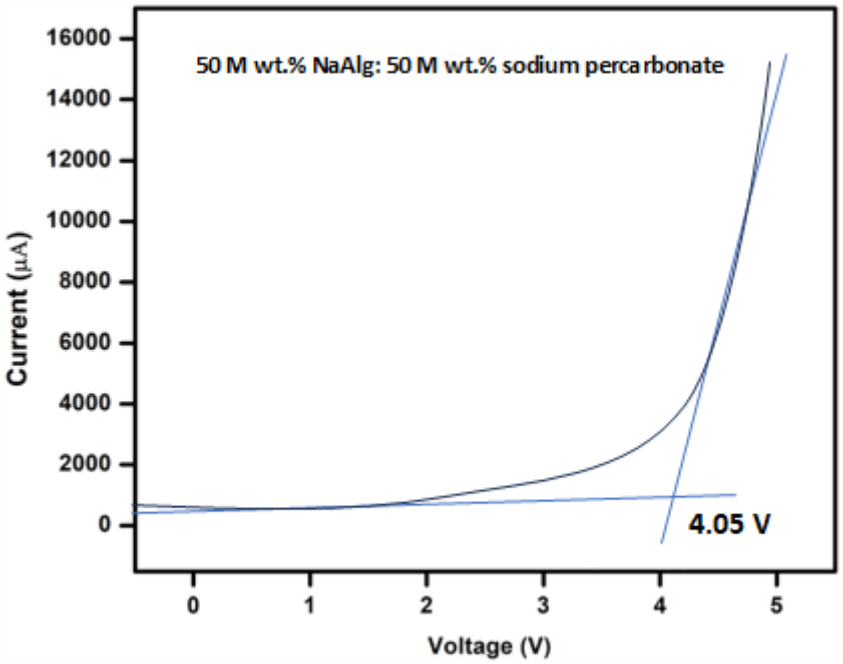

FIG. 3 Linear sweep voltammogram for the highest conducting biopolymer electrolyte

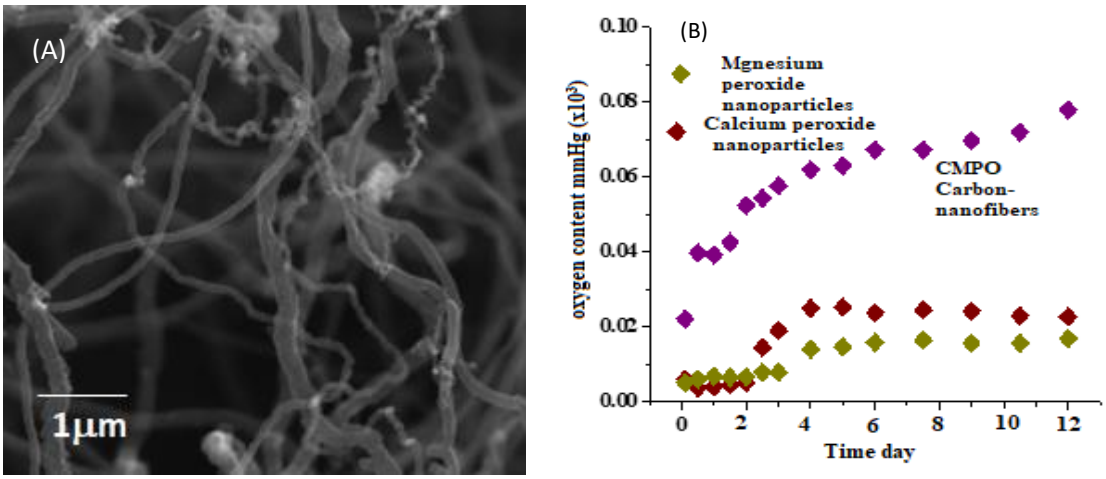

FIG. 4 (A) CMPO carbon nanofibers and (B) oxygen release profile of CMPO loaded carbon nanofibers

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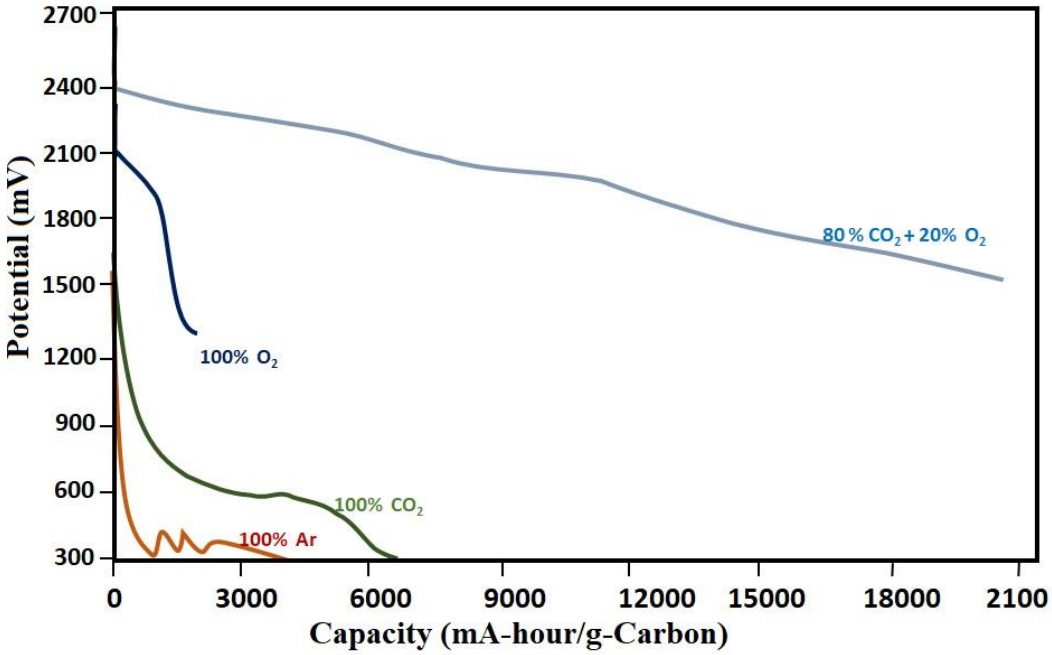

FIG. 5: Electrochemical performance of Electrochemical generator under different gas conditions. Galvanostatic discharge of Al under Ar, 100% CO_2, 100% O_2, and 80% CO_2 using Sodium percarbonate incorporated alginate hydrogel electrolyte and current density of 80 mA/g Carbon. Inset: CV for three-electrode cell under 100% O_2 and 80% CO_2 with a sweep rate of 0.1 mV/s.

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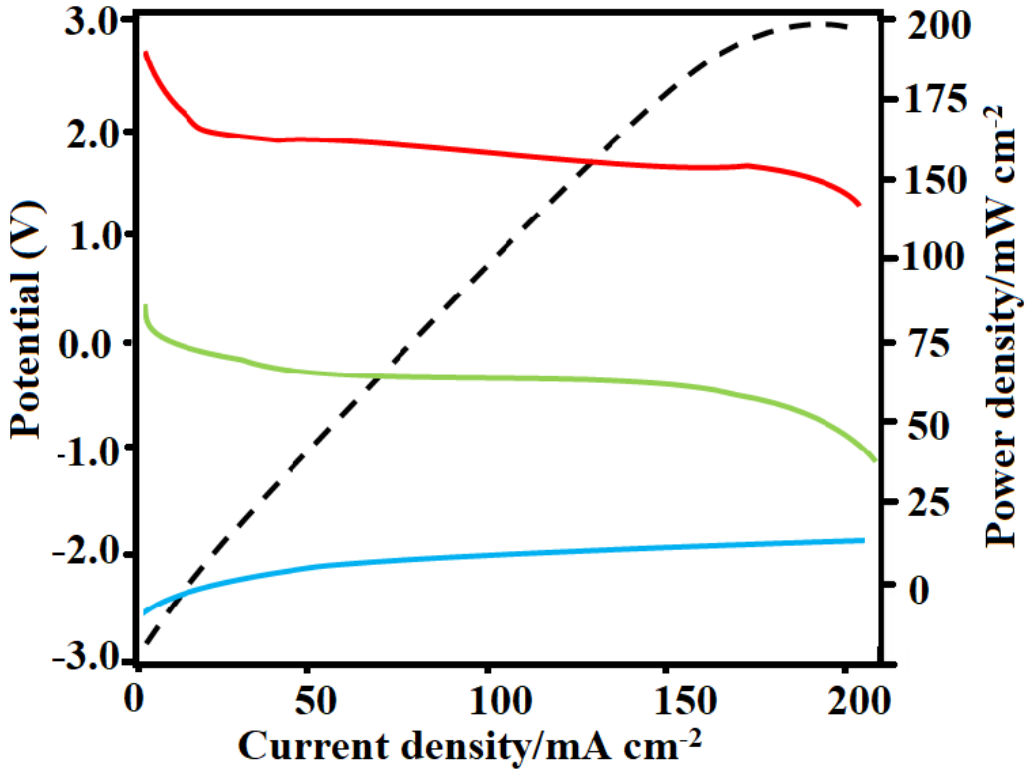

FIG. 6. Galvanodynamic polarization curves of the anode (blue) and the cathode (green), current-voltage curve (red), and power curve (black) of AA cell with solid electrolyte Sodium percarbonate incorporated alginate hydrogel at 60 ºC.

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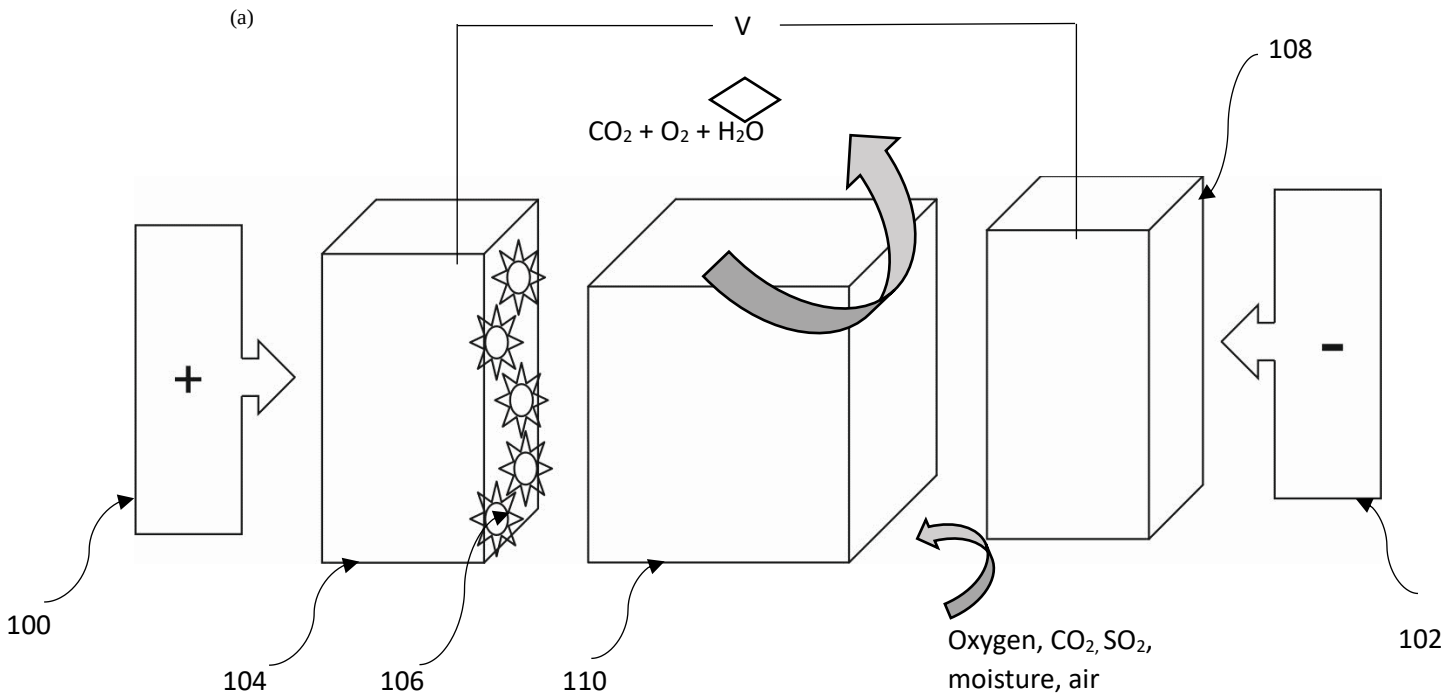

FIG. 7(a)

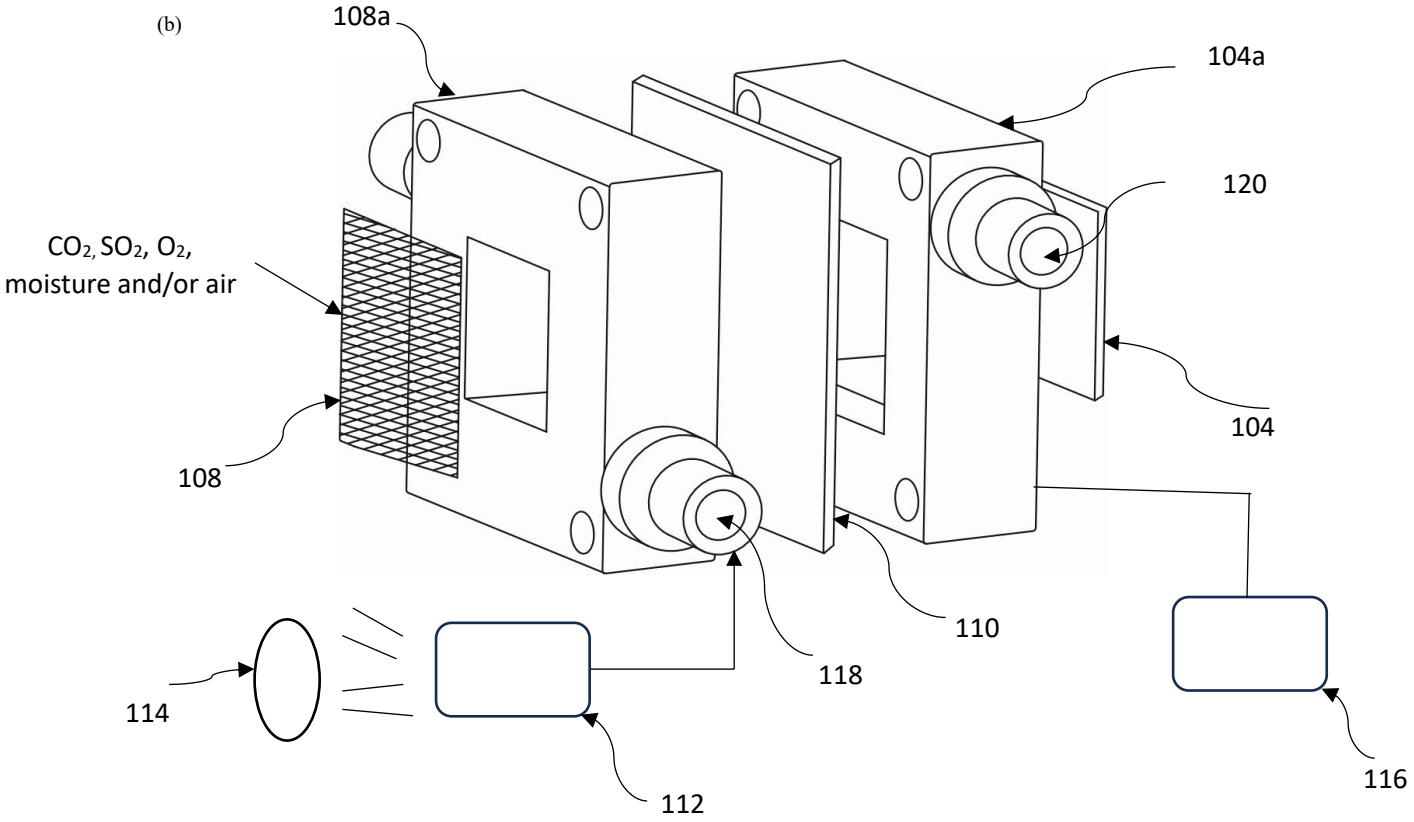

FIG. 7(b): Schematic representation of multimodal electrochemical generator

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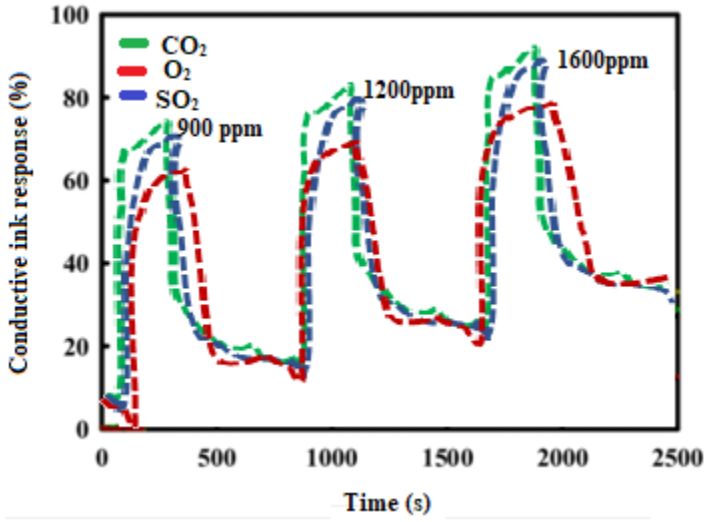

FIG. 8: Reservoir's printed conductive ink modified intertwin silver ink response and selectivity for all three gases such as CO_2, SO_2, and O_2

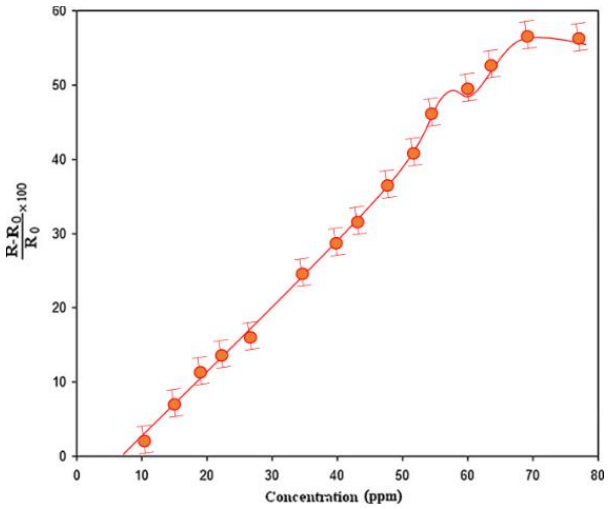

FIG. 9: Response of electrochemical generators at different concentrations of gas mixture

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