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(54) Title: NANOCOMPOSITE-BASED FUEL CELL ELECTRODE AND METHOD THEREOF

(57) Abstract: The present disclosure relates to nanocomposite-based fuel cell electrode. The nanocomposite-based fuel cell electrode comprises of a cathode substrate of N-S doped polymeric carbon quantum dot act as a porous metal free carbon catalyst layer formed on the substrate. The porous metal free carbon catalyst layer and polymer film exhibit dual function of generating and storing hydrogen with no dependency of sun and water. The nanocomposite-based fuel cell electrode can work in solar light and night as well. The developed PEM-URFCs having the nanocomposite-based fuel cell electrode shows high power density, reduced hydrogen storage tank size with ambient pressure and temperature. Further, the present disclosure relates to method of preparing a nanocomposite-based fuel cell electrode. The present disclosure also relates to a unitized regenerative fuel cell and a method of operating a unitized regenerative fuel cell.

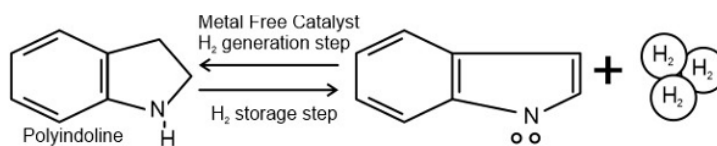


Figure 1

FORM 2

THE PATENTS ACT, 1970

(39 OF 1970)

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THE PATENTS RULES, 2003

COMPLETE SPECIFICATION

(See section 10, rule 13)

1. TITLE OF THE INVENTION

NANOCOMPOSITE-BASED FUEL CELL ELECTRODE AND METHOD THEREOF

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3. PREAMBLE TO THE DESCRIPTION

COMPLETE

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

DESCRIPTION

FIELD OF THE INVENTION

[0001] The present disclosure relates to a fuel cell electrode. Particularly, the present disclosure relates to a nanocomposite-based fuel cell electrode. More particularly, the present disclosure relates to a nanocomposite-based fuel cell electrode comprising a porous metal free carbon catalyst layer. The porous metal free carbon catalyst layer has dual function of generating and storing hydrogen with no dependency of sun and water. Further, the present disclosure relates to method of preparing a nanocomposite-based fuel cell electrode. The present disclosure also relates to a unitized regenerative fuel cell and a method of operating a unitized regenerative fuel cell.

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BACKGROUND OF THE INVENTION

[0002] Green hydrogen as a fuel in a proton exchange membrane-unitized regenerative fuel cells (PEM-URFCs) is a promising candidate for the powering electric vehicles, unmanned vehicles and space mission. The production of green hydrogen and storing the same is however challenging in PEM-URFCs. In commercial PEM based fuel cells, a high-pressure (>80 MPa) tank with a gravimetric hydrogen-storage capacity of wt% (hydrogen weight/total weight of the tank system), is used as the state-of-the-art mode of hydrogen storage; however, this system suffers from issues of volumetric hydrogen-storage capacity (or portability), safety, and energy cost.

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[0003] On the other hand, for hydrogen evolution reactions mostly transition metals such as platinum and iridium are used as catalysts. However, these catalysts have limited natural abundance and commonly suffer from the drawbacks like coking, restricting continuous large-scale application.

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[0004] Research has been carried out address these challenges. Non-patent literature “*Chitosan-Based N-Doped Carbon Materials for Electrocatalytic and Photocatalytic Applications*, American Chemical Society (Ayesha Khan,* Michael Goepel, Juan Carlos Colmenares,* and Roger Glaser), March 8, 2020” discloses a method to produce a carbon material derived from seafood waste which functions as electro catalyst for fuel cells by oxygen reduction and photo catalyst to produce hydrogen by carbonization.

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[0005] Non-patent literature “*Membrane-Based Electrolysis for Hydrogen Production: A Review, Membranes, 2021 - mdpi.com*” discloses about hydrogen production by water splitting technologies using different types of membrane-based electrolysis like photoelectrochemical electrolysis, microbial, acid-alkaline amphoteric, AEM, PEM, solid oxide and alkaline.

5 [0006][Patent literature US11127967B2 discloses a membrane electrode assembly for a unitized regenerative fuel cell that includes a polymer electrolyte membrane capable of conducting cations between the first electrode and the second electrode, a water vapor supply unit for supplying water vapor to the first electrode, wherein the first electrode is an oxidation electrode during water electrolysis operation and an oxidation electrode or a reduction electrode during fuel cell operation,
10 and the second electrode is a reduction electrode during water electrolysis operation and an oxidation electrode or a reduction electrode during fuel cell operation.

[0007] However, there still exists a need for improvement in electrodes which are capable of reversible fix-release hydrogen at ambient temperature without using precious transition metals.

[0008] The present disclosure provides a nanocomposite-based fuel cell electrode comprising a
15 porous metal free carbon catalyst layer. The nanocomposite-based fuel cell electrode can work in solar light and night as well. The developed PEM-URFCs having the nanocomposite-based fuel cell electrode shows high power density, reduced hydrogen storage tank size with ambient pressure and temperature.

SUMMARY OF THE INVENTION

20 [0009] The present disclosure relates to nanocomposite-based fuel cell electrode. The nanocomposite-based fuel cell electrode comprises of a cathode substrate of N-S doped polymeric carbon quantum dot and a porous metal free carbon catalyst layer formed on the substrate. The porous metal free carbon catalyst layer has dual function of generating and storing hydrogen with no dependency of sun and water. The nanocomposite-based fuel cell electrode can work in solar
25 light and night as well. The developed PEM-URFCs having the nanocomposite-based fuel cell electrode shows high power density, reduced hydrogen storage tank size with ambient pressure and temperature. Further, the present disclosure relates to method of preparing a nanocomposite-based fuel cell electrode. The present disclosure also relates to a unitized regenerative fuel cell and a method of operating a unitized regenerative fuel cell.

BRIEF DESCRIPTION OF ACCOMPANYING DRAWINGS

[0010] The present disclosure will be further understood with reference to the accompanying drawings. More specifically, the purposes of drawings are to illustrate the preferred and alternate embodiments and are not to be construed as limitations. Furthermore, drawings are not drawn to
5 scale.

[0011] **Figure 1** illustrates the hydrogen storage and evolution reaction.

[0012] **Figure 2** illustrates the PEM-URFCs – (A) Photocatalysis water splitting (B) Electrocatalysis.

DETAILED DESCRIPTION OF THE INVENTION

10 [0013] While the disclosure is susceptible to various modifications and alternative forms, specific aspect thereof has been shown by way of example and will be described in detail below. It should be understood, however that it is not intended to limit the invention to the particular forms disclosed, but on the contrary, the invention is to cover all modifications, equivalents, and alternative falling within the scope of the invention.

15 [0014] Before describing in detail embodiments, it is to be noted that a person skilled in the art can be motivated from the present disclosure and modify the various constructions of system and method. However, such modification should be construed within the scope of the invention. Accordingly, applicant would like to mention that the examples and comparative studies are mentioned to show only those specific details that are pertinent to understanding the embodiments
20 of the present invention so as not to obscure the disclosure with details that will be readily apparent to those of ordinary skill in the art having benefit of the description herein.

[0015] The terms “comprises”, “comprising”, or any other variations thereof, are intended to cover a non-exclusive inclusion, that comprises a list of components does not include only those
25 components but may include other components not expressly listed or inherent to such system or device. In other words, one or more elements in a system or method preceded by “comprises... a” does not, without more constraints, preclude the existence of other elements or additional elements in the system or method.

[0016] The present disclosure discloses nanocomposite-based fuel cell electrode comprising a cathode substrate of N-S doped polymeric carbon quantum dots, and a porous metal free carbon catalyst layer formed on the substrate, wherein the porous metal free carbon catalyst layer is selected from a non-reactive thermoplastic fluoropolymer, an organic compound, or a combination thereof.

[0017] In one of the embodiments, the non-reactive thermoplastic polymer is selected from polyvinyl indoline, 2,2' dipyridylamine, quinoxaline or a combination thereof. The indoline is sourced from plants and human feces so it is one of the waste management solution.

[0018] In another one of the embodiments, the organic compound is selected from N-heterocycle compounds.

[0019] In yet another one of the embodiments, the porous metal free carbon catalyst layer has a weight of 0.4 g to 0.75g.

[0020] In one of the embodiments, the N-S doped polymeric carbon quantum dots are in the form of a conductive nanofilm.

[0021] In another one of the embodiments, the N-S doped polymeric carbon quantum dots are selected from the group consisting of graphite, graphene oxide, reduced graphene oxide, graphene fluoride, graphene chloride, graphene bromide, graphene iodide, hydrogenated graphene, nitrogenated graphene, chemically functionalized graphene, polymerized and carbonized small molecules or combinations thereof.

[0022] The present disclosure further discloses method of preparing a nanocomposite-based fuel cell electrode, comprising

- preparing a cathode substrate of N-S doped polymeric carbon quantum dots by electrochemical ablation of graphitic materials in presence of thiourea,
- providing a porous metal free carbon catalyst layer on a surface of the substrate by electrochemical layer deposition method,

wherein the porous metal free carbon catalyst layer is selected from non-reactive thermoplastic polymer, organic compound, or a combination thereof.

5 [0023] In one of the embodiments, the porous metal free carbon catalyst layer is developed by incorporating a polyvinyl indoline redox couple coated on N-S doped polymeric carbon quantum dots. Polyvinylindoline is electrochemically grown from a solution containing 0.05 M concentration of the vinylindole monomer and 0.1 M NaClO₄ in acetonitrile electrolyte. In cyclic voltammetry the potential range was set up from -1.0 V to 1.5 V, and back to -1.0V at the sweep rate of 5 mV s⁻¹ at 25°C. The N-S doped polymeric carbon quantum dots exhibit excellent photo,
10 electro and photo-luminesce properties.

[0024] Further, the present disclosure relates to unitized regenerative fuel cell comprising, at least two electrodes, a polymer electrolyte membrane disposed between the two electrodes, at least two gas storage tanks for storing hydrogen gas and oxygen gas, a water storage tank, an external energy source, and a power reservoir for storing energy, wherein at least one of the two electrodes is a
15 nanocomposite-based fuel cell electrode. The nanocomposite-based fuel cell electrode comprising a cathode substrate of N-S doped polymeric carbon quantum dots, and a porous metal free carbon catalyst layer formed on the substrate, wherein the porous metal free carbon catalyst layer is selected from a non-reactive thermoplastic fluoropolymer, an organic compound, or a combination thereof.

20 [0025] In yet another one of the embodiments, the polymer electrolyte membrane is selected from polyvinylidene-based polymer electrolyte membrane for cathode and oxygen capturing polymers such as polylactic acid, N-doped butadiene polymers on carbon fibers composite for anode.

[0026] In one of the embodiments, the unitized regenerative fuel cell comprises a water electrolysis mode and a fuel cell mode. Water electrolysis is one mode of URFCs and other mode
25 is fuel cell mode that is generation of electricity and water as byproduct. This byproduct reacts with water which helps to regenerate the polymers. The polymer network along with porous metal free carbon catalyst is suitable to store hydrogen. Without photolysis/electrolysis also, the designed URFCs can generate electricity by taking hydrogen from polymers and oxygen from air. Thus, it is looped energy storage system with dual mechanism. Figure 1 illustrates the hydrogen storage

and evolution reaction, and Figure 2 illustrates the PEM-URFCs – (A) Photocatalysis water splitting (B) Electrocatalysis.

[0027] In another one of the embodiments, at least one of the two electrodes is an oxidation electrode during the water electrolysis mode and a reduction electrode during the fuel cell mode.

5 [0028] In yet another one of the embodiments, another one of the two electrodes is a reduction electrode during the water electrolysis mode and an oxidation electrode during the fuel cell mode.

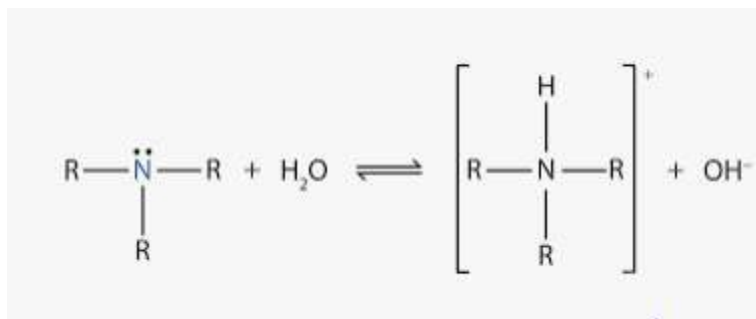
[0029] The unitized regenerative fuel cells having nanocomposite-based fuel cell electrode as per present disclosure are equipped with self-hydrogen generation and have excellent storage properties. They can be used as hydrogen fuel cell source where water splitting is less efficient
10 that is zero gravity.

[0030] Further, the present disclosure relates to method of operating a unitized regenerative fuel cell, comprising steps of:

- operating a water electrolysis mode by supplying energy from an external energy source and water from a water storage tank to a unitized regenerative fuel cell;
- 15 - storing hydrogen gas as generated into one of the gas storage tank;
- storing oxygen gas as generated into another gas storage tank;
- operating fuel cell mode by supplying hydrogen gas from one of the gas storage tank and oxygen gas from another gas storage tank to the unitized regenerative fuel cell;
- storing water as generated into the water storage tank;
- 20 - storing electricity as generated into a power reservoir;

wherein the unitized regenerative fuel cell comprises at least one nanocomposite-based fuel cell electrode comprising a cathode substrate of N-S doped polymeric carbon quantum dots, and a porous metal free carbon catalyst layer formed on the substrate, wherein the porous metal free carbon catalyst layer is selected from a non-reactive thermoplastic fluoropolymer, an organic
25 compound, or a combination thereof.

[0031] Regeneration of polymer from water is shown in scheme below, where R =polyvinylindoline.



[0032] In one of the embodiments, the unitized regenerative fuel cell is used in unmanned vehicles, long range electric vehicles, smart grids, aircrafts, space applications and portable systems such as mobiles, laptops and medical devices.

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[0033] The advantage of the nanocomposite-based fuel cell electrode of the present disclosure is that it is basically alternative solution of generation of green hydrogen by polymers. These indoline is sourced from plants and human feces so it is one of the waste management solution. The unitized regenerative fuel cell comprising the nanocomposite-based fuel cell electrode of the present disclosure has advantage as it is eco-friendly, cost-effective, and works as an independent energy storage and power generation device that requires less space for operation. It can be one of the best alternatives of powering system in comparison to battery-based energy storage system. Further, the storage issue of hydrogen also resolved, and it provides a very high gravimetric hydrogen storage capacity of 8.5 wt%-10 wt % (hydrogen weight/total weight of the tank). It also reduces the issue of volumetric hydrogen-storage capacity, can fix and release hydrogen at ambient temperature (40°C) and pressure (30 bar).

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[0034] The advantages of the disclosed invention are thus attained in an economical, practical, and facile manner. While example have been shown and described, it is to be understood that various further modifications and additional configurations will be apparent to those skilled in the art.

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WE CLAIM:

1. A nanocomposite-based fuel cell electrode comprising
 - (a) a cathode substrate of N-S doped polymeric carbon quantum dots,
 - (b) a porous metal free carbon catalyst layer formed on the substrate,wherein the porous metal free carbon catalyst layer is selected from a non-reactive thermoplastic fluoropolymer, an organic compound, or a combination thereof.
2. The nanocomposite-based fuel cell electrode as claimed in claim 1, wherein the non-reactive thermoplastic fluoropolymer is selected from polyvinyl indoline, 2,2' dipyridylamine, quinoxaline or a combination thereof.
3. The nanocomposite-based fuel cell electrode as claimed in claim 1, wherein the organic compound is selected from N-heterocyclic polymers.
4. The nanocomposite-based fuel cell electrode as claimed in claim 1, wherein the porous metal free carbon catalyst layer has a weight of 0.4 g to 0.75g.
5. The nanocomposite-based fuel cell electrode as claimed in claim 1, wherein the N-S doped polymeric carbon quantum dots are in the form of a conductive film.
6. The nanocomposite-based fuel cell electrode as claimed in claim 1, wherein the N-S doped polymeric carbon quantum dots are selected from the group consisting of graphite, graphene oxide, reduced graphene oxide, graphene fluoride, graphene chloride, graphene bromide, graphene iodide, hydrogenated graphene, nitrogenated graphene, chemically functionalized graphene, polymerized and carbonized small molecules or combinations thereof.
7. A method of preparing a nanocomposite-based fuel cell electrode, comprising
 - preparing a cathode substrate of N-S doped polymeric carbon quantum dots by electrochemical ablation of graphitic materials in presence of thiourea,
 - providing a porous metal free carbon catalyst layer on a surface of the substrate by electrochemical layer deposition method,

wherein the porous metal free carbon catalyst layer is selected from non-reactive thermoplastic fluoropolymer, organic compound, or a combination thereof.

8. The method as claimed in claim 7, wherein the porous metal free carbon catalyst layer is developed by incorporating a polyvinyl indoline redox couple coated on N-S doped polymeric carbon quantum dots.

9. A unitized regenerative fuel cell comprising,

- at least two electrodes,
- a polymer electrolyte membrane disposed between the two electrodes,
- at least two gas storage tanks for storing hydrogen gas and oxygen gas,
- a water storage tank,
- an external energy source, and
- a power reservoir for storing energy,

wherein at least one of the two electrodes is a nanocomposite-based fuel cell electrode comprising,

(a) a cathode substrate of N-S doped polymeric carbon quantum dots,

(b) a porous metal free carbon catalyst layer formed on the substrate,

wherein the porous metal free carbon catalyst layer is selected from non-reactive thermoplastic fluoropolymer, organic compound, or a combination thereof.

10. The unitized regenerative fuel cell as claimed in claim 9, wherein the polymer electrolyte membrane is selected from polyvinylindoline-based polymer electrolyte membrane for cathode generates and store hydrogen gas properties. The oxygen capturing polymers such as polylactic acid, N-doped butadiene polymers on carbon fibers composite for anode.

11. The unitized regenerative fuel cell as claimed in claim 9, comprises a water electrolysis mode and a fuel cell mode.

12. The unitized regenerative fuel cell as claimed in claim 9, wherein at least one of the two electrodes is an oxidation electrode during the water electrolysis mode and a reduction electrode during the fuel cell mode.

13. The unitized regenerative fuel cell as claimed in claim 9 wherein another one of the two electrodes is a reduction electrode during the water electrolysis mode and an oxidation electrode during the fuel cell mode.

14. A method of operating a unitized regenerative fuel cell, comprising steps of:

- operating a water electrolysis mode by supplying energy from an external energy source and water from a water storage tank to a unitized regenerative fuel cell;
- storing hydrogen gas as generated into one of the gas storage tank;
- storing oxygen gas as generated into another gas storage tank;
- operating fuel cell mode by supplying hydrogen gas from one of the gas storage tank and oxygen gas from another gas storage tank to the unitized regenerative fuel cell;
- storing water as generated into the water storage tank;
- storing electricity as generated into a power reservoir;

wherein the unitized regenerative fuel cell comprises at least one nanocomposite-based fuel cell electrode comprising,

(a) a cathode substrate of N-S doped polymeric carbon quantum dots,

(b) a porous metal free carbon catalyst layer formed on the substrate,

wherein the porous metal free carbon catalyst layer is selected from non-reactive thermoplastic fluoropolymer, organic compound, or a combination thereof.

15. The unitized regenerative fuel cell as claimed in claim 9, is used in unmanned vehicles, long range electric vehicles, smart grids, aircrafts, space applications and portable systems such as mobiles, laptops and medical devices.

Dated this 20th day of June 2022

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ABSTRACT

NANOCOMPOSITE-BASED FUEL CELL ELECTRODE AND METHOD THEREOF

The present disclosure relates to nanocomposite-based fuel cell electrode. The nanocomposite-based fuel cell electrode comprises of a cathode substrate of N-S doped polymeric carbon quantum dot act as a porous metal free carbon catalyst layer formed on the substrate. The porous metal free carbon catalyst layer and polymer film exhibit dual function of generating and storing hydrogen with no dependency of sun and water. The nanocomposite-based fuel cell electrode can work in solar light and night as well. The developed PEM-URFCs having the nanocomposite-based fuel cell electrode shows high power density, reduced hydrogen storage tank size with ambient pressure and temperature. Further, the present disclosure relates to method of preparing a nanocomposite-based fuel cell electrode. The present disclosure also relates to a unitized regenerative fuel cell and a method of operating a unitized regenerative fuel cell.

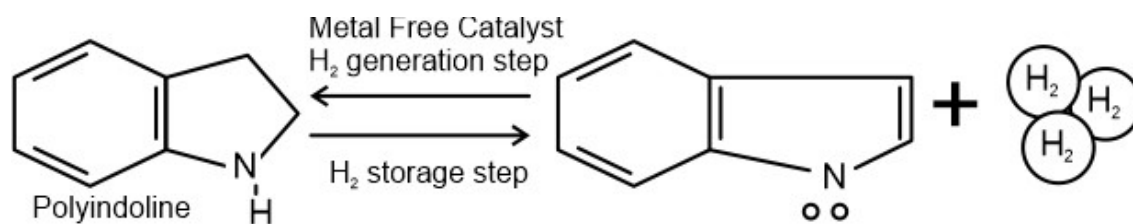


Figure 1

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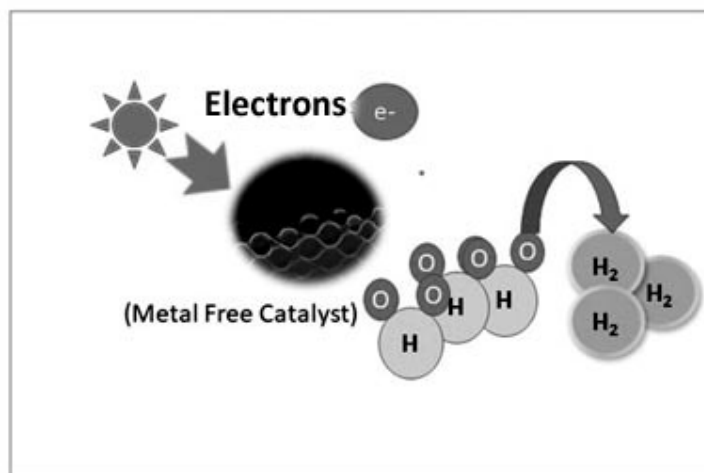


Figure 2(A)

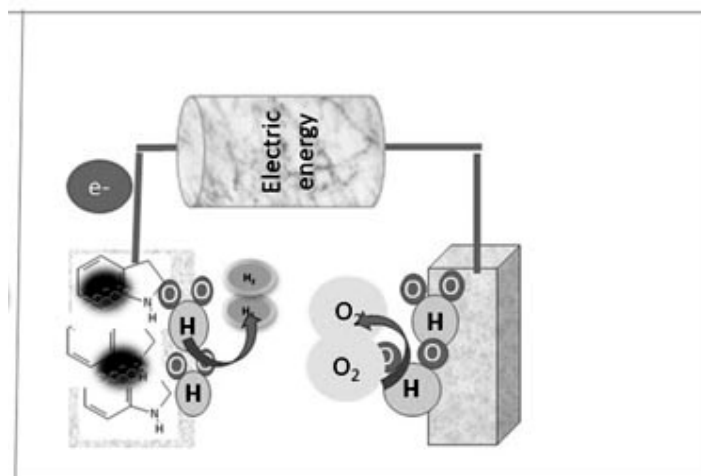


Figure 2(B)

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