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(54) Title: DOPED BISMUTH OXIDE THIN FILMS, ELECTROCHEMICAL DEVICES, METHODS OF MAKING, AND USE THEREOF

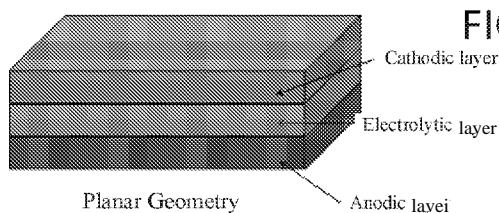


FIG. 1A

(57) Abstract: Embodiments of the present disclosure provide for electrochemical devices, methods of converting chemical energy to electrical energy, and the like.

**DOPED BISMUTH OXIDE THIN FILMS, ELECTROCHEMICAL DEVICES,
METHODS OF MAKING, AND USE THEREOF**

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of and priority to U.S. Provisional Application Serial No. 62/379,785, having the title "DOPED BISMUTH OXIDE THIN FILMS, ELECTROCHEMICAL DEVICES, METHODS OF MAKING, AND METHODS OF USE THEREOF," filed on August 26, 2016, the disclosure of which is incorporated herein in by reference in its entirety.

BACKGROUND

Electrochemical devices can include solid oxide fuel cells (SOFC) and/or solid oxide electrolyser cells (SOEC). Solid oxide fuel cells (SOFC) are capable of converting chemical energy directly to electrical energy. Solid oxide electrolyser cells (SOEC) have the capability to convert electrical energy to chemical energy. However, both devices suffer from limiting factors such as electrolyte ionic conductivity.

SUMMARY

Embodiments of the present disclosure provide for electrochemical devices, electrochemical systems, methods of converting chemical energy to electrical energy, and the like.

An aspect of the present disclosure provides for an electrochemical device, among others, that includes: at least one stack including an anodic layer, an electrolytic layer, and a cathodic layer, wherein the electrolytic layer is disposed between the anodic layer and the cathodic layer, wherein the electrolytic layer has a thickness of about 0.5 nm and 100 μm , wherein the electrolytic layer is a doped bismuth oxide. In an embodiment, the electrochemical device can be used to convert chemical energy to electrical energy or convert electrical energy to chemical energy.

An aspect of the present disclosure provides for an electrochemical system, among others, that includes: at least one stack including an anodic layer, an electrolytic layer, and a cathodic layer, wherein the electrolytic layer is disposed between the anodic layer and the cathodic layer, wherein the electrolytic layer has a thickness of about 0.5 nm and 100 μm , wherein the electrolytic layer is a doped bismuth oxide, wherein the system is configured to

operate at temperature of about room temperature to 550°C, wherein the system is configured to convert chemical energy to electrical energy, electrical energy to chemical energy, or a combination thereof.

Other systems, methods, features, and advantages will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional compositions, apparatus, methods, features and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A-1E illustrates embodiments of various geometries.

Fig. 2A illustrates a cross-section while Fig. 2B illustrates a top view of the dense DGSB electrolytic layer over a nanoporous anode.

DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is 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 present disclosure will be limited only by the appended claims.

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 disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, 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 disclosure.

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

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, inorganic chemistry, material science, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is in atmosphere. Standard temperature and pressure are defined as 25 °C and 1 atmosphere.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

Discussion

Embodiments of the present disclosure provide for electrochemical devices, electrochemical systems, methods of converting chemical energy to electrical energy, and the like. Embodiments of the electrochemical devices can be used to store or produce energy, for example to convert chemical energy to electrical energy.

In an embodiment, the electrochemical devices can include solid oxide fuel cells (SOFC) and/or solid oxide electrolyser cells (SOEC). SOFCs are capable of converting chemical energy directly to electrical energy. SOECs have the capability to convert electrical energy to chemical energy. Both devices include of an anode, an electrolyte, and a cathode. However, one of the limiting factors in both devices is the electrolyte ionic conductivity.

Doped bismuth oxides (DBO) exhibit the highest oxygen ionic conductivity known to date. What has hindered the utilization of DBO is its degradability under usual SOFC operating conditions. Operational conditions require a reducing environment (*e.g.*, hydrogen, methane, biogas, etc.) and temperatures above 400°C. High temperatures are usually employed for it has been found that the ionic conductivity increases with temperature.

Embodiments of the present disclosure are directed towards electrochemical devices and systems whose electrolyte or membrane utilizes an oxygen ion conductor, such as fuel cells, and electrolyzers; especially for thin film (TF) SOFC and TF SOEC. Embodiments of the present disclosure use doped (*e.g.*, doped, co-doped, and poly-doped) bismuth oxide thin films as a stable electrolyte. Embodiments of the present disclosure lower the operation temperature of SOFC with doped bismuth oxide electrolytes to the domain where the doped bismuth oxide electrolytes are stable to operate continuously. The ionic resistivity of doped bismuth oxide electrolytes is inversely related with temperature. By utilizing thin films of dense doped bismuth oxide electrolytes, the total ionic resistance of the electrolyte is reduced. By lowering the thickness of the electrolyte the overall ionic resistance is maintained at lower temperatures although the ionic resistivity is higher.

Additional advantages arise from lowering the operating temperature of the doped bismuth oxide based SOFC and SOEC. Doped bismuth oxide can exhibit different crystallographic structures at different temperatures. The crystallographic structure of DBOs with the highest ionic conductivity is the δ -phase. The δ -phase is formed around 750°C for undoped bismuth oxide. The δ -phase of doped bismuth oxide is not thermodynamically stable at lower temperatures. By operating the SOEC and SOEC at lower temperatures the phase transition is kinematically limited. The δ -phase doped bismuth oxide (δ -DBO) does not have the sufficient energy to restructure into another phase, unlike as when operating at higher temperatures. Operation at lower temperatures allows the use of less expensive interconnecting materials and the use of polymeric resins as sealants.

In an embodiment, the electrochemical device or system can include at least one stack including an anodic layer, an electrolytic layer, and a cathodic layer. The electrolytic layer is disposed between the anodic layer and the cathodic layer. In an embodiment, the doped

bismuth oxide electrolyte can have a thickness of about 100 μm or less (*e.g.*, about 0.1 to 100 μm) and/or about 0.5 nm or more (*e.g.*, about 0.5 nm to 100 μm). In an embodiment, the cathodic layer can include a partially or entirely a mixture of electronic conductors, catalysts, ionic conductors and/or a mixture thereof. In an embodiment, the cathodic layer can include materials such as, but not limited to, metals, alloys of metals, oxides, conductive polymers and/or electronically conductive ceramics. In an embodiment, the cathodic layer can be subdivided into thinner sub-layers or sections, disposing of homogenous or heterogeneous materials with one or more features with a size of about 100 μm or less (*e.g.*, about 0.1 to 100 μm) and/or about 0.5 nm or more (*e.g.*, about 0.5 to 500 nm).

In an embodiment, the anodic layer can include partially or entirely a mixture of electronic conductors, catalysts, ionic conductors and/or a mixture thereof. In an embodiment, the anodic layer can include materials such as, but not limited to, metals, alloys of metals, oxides, conductive polymers and/or electronically conductive ceramics. In an embodiment, the anodic layer can be subdivided into thinner sub-layers or sections, disposing of homogenous or heterogeneous materials with one or more feature with a size of about 100 μm or less (*e.g.*, about 0.1 to 100 μm) and/or about 0.5 nm or more (*e.g.*, about 0.5 to 500 nm).

In an embodiment, the electrochemical device or system can include one or more support layers, whose central and/or auxiliary purpose is to bring mechanical integrity to the electrochemical device. The support layer can include partially or entirely a mixture of electronic conductors, electronic insulators, catalysts, ionic conductors and/or a mixture thereof; examples of such can include, but are not limited to, metals, alloys of metals, oxides, conductive polymers, high temperature withstanding polymers, and/or electronically conductive ceramics. The support layer can be subdivided into thinner sub-layers or sections, disposing of homogenous or heterogeneous materials with one or more feature with a size of about 100 μm or less (*e.g.*, about 0.1 to 100 μm) and/or about 0.5 nm or more (*e.g.*, about 0.5 to 500 nm).

In an embodiment, the doped bismuth oxide can include about 0.001 mole per cent to 0.4 mole per cent of at least one or more (*e.g.*, 2 or 3) rare earth oxides, when more than one rare earth metal is present each can be about 0.001 mole per cent to 0.4 mole per cent. In an embodiment, the rare earth oxides can include La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Th, U, Lu, or a combination thereof.

In an embodiment, the doped bismuth oxide can also include one or more (*e.g.*, 2 or 3) of the following ions of: Ca, Sr, Ba, Hf, Zr, Sn, Pb, W, Mo, Cr, Cd, In, Mg, Li, or Zn, where each ion can be about 0.001 mole percent to 0.4 mole percent of the doped bismuth oxide.

Embodiments of the doped bismuth oxide can include $\text{Er}_{0.4}\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.16}\text{W}_{0.08}\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.16}\text{Gd}_{0.08}\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.16}\text{Sm}_{0.08}\text{Bi}_{1.6}\text{O}_3$ and stoichiometric variations thereof.

Other possible dopants, co-dopants and polydopants might include, but are not limited to, the complete or partial use of lanthanide oxides, actinide oxides, CaO, SrO, BaO, Y_2O_3 , HfO_2 , ZrO_2 , Sc_2O_3 , SnO, lead oxide, tungsten oxide, molybdenum oxide and Cr_2O_3 as dopants.

In an embodiment, the device or system can be operated at about room temperature to about 550° C or about room temperature to about 400° C.

In an embodiment, the doped bismuth oxide electrolyte layer can be fabricated completely or partially by, but not limiting to, pulsed laser deposition, pulsed electron deposition, pulsed plasma deposition, sputtering, atomic layer deposition, pressing, spin coating, screen printing, tape casting, ink-jet printing, thermal treatment, spark sintering, spray pyrolysis, hydrothermal synthesis, solvothermal synthesis and/or a mixture thereof.

Embodiments of the device and the doped bismuth oxide layer can have a geometry such as planar, tubular, and/or monolithic. Figs. 1A-E illustrates embodiments of various geometries. In an embodiment with a planar geometry, the electrochemical device disposes entirely or partially of flat or nearly flat layers. In an embodiment with a tubular geometry, the electrochemical device disposes entirely or partially of curved or ellipsoidal layers. In an embodiment, a tubular geometry can dispose of a cylindrical geometry, with an open base. In an embodiment with a monolithic geometry, the electrochemical device disposes entirely or partially of patterned layers. In an embodiment, a monolithic geometry can embody at least one or more layers disposed for the electrochemical device or devices and can include subsequent layers whose central or auxiliary purpose is to feed fluids onto the electrochemical device. The illustrations in Figs. 1A-E, pertaining to the geometry, is for illustration purposes and it is not intended to limit the geometry of a particular electrochemical device.

In an embodiment, the device or system can be configured (*e.g.*, stacked) with the appropriately selected electrolyte thickness to decrement the ionic resistance, increment the electrical current, voltage and/or power. In an embodiment each layer of doped bismuth oxide can be of the same type while in another embodiment at least two of the layers are of different types of doped bismuth oxide. In this regard the type of doped bismuth oxide

material and the thickness of the doped bismuth oxide layer can be designed to achieve the desired results in regard to at least ionic resistance, current, voltage, and/or power. In a particular embodiment, when the doped bismuth oxide is $\text{D}_{0.16}\text{W}_{0.08}\text{Bi}_{1.6}\text{O}_3$ (DWSB) electrolyte and has a thickness of about 1 cm, while operating at 500°C, has an ionic resistance of 10Ω. The same electrolyte operating at 400°C would have a total ionic resistance of 100Ω. A second electrolyte of about 0.1 cm thickness would have a resistance of 10Ω when operating at 400°C. A third electrolyte of about 0.015 cm in thickness to operate at 350°C would exhibit a total ionic resistance of 10Ω.

Example 1

Figs. 2A and 2B illustrate dense DGSB electrolytic layer over a nanoporous anode. Fig. 2A illustrates a cross-section while Fig. 2B illustrates a top view of the dense DGSB electrolytic layer over a nanoporous anode.

It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1% to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (*e.g.*, 1%, 2%, 3%, and 4%) and the sub-ranges (*e.g.*, 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term "about" can include traditional rounding according to how the numerical value determined. In addition, the phrase "about 'x' to 'y'" includes "about 'x' to about 'y'".

Many variations and modifications may be made to the above-described embodiments. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

CLAIMS

At least the following is claimed:

1. An electrochemical device, comprising:
at least one stack including an anodic layer, an electrolytic layer, and a cathodic layer, wherein the electrolytic layer is disposed between the anodic layer and the cathodic layer, wherein the electrolytic layer has a thickness of about 0.5 nm and 100 μm , wherein the electrolytic layer is a doped bismuth oxide.
2. The device of claim 1, wherein doped bismuth oxide includes about 0.001 mole per cent to 0.4 mole per cent of at least one or more rare earth oxides.
3. The device of claims 1 or 2, wherein doped bismuth oxide includes about 0.001 mole per cent to 0.4 mole per cent of at least one or more of La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Th, U and Lu.
4. The device of claims 1-3, wherein doped bismuth oxide also includes one or more of the following ions of: Ca, Sr, Ba, Hf, Zr, Sn, Pb, W, Mo, Cr, Cd, In, Mg, Li, or Zn, wherein each ion is about 0.001 mole percent to 0.4 mole percent of the doped bismuth oxide.
5. The device of claim 1, wherein the doped bismuth oxide is selected from the group consisting of: $\text{Er}_{0.4}\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.6}\text{W}_{0.8}\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.6}\text{Gd}_{0.8}\text{Bi}_{1.6}\text{O}_3$, and $\text{Dy}_{0.6}\text{Sm}_{0.8}\text{Bi}_{1.6}\text{O}_3$.
6. The device of claims 1-5, wherein the device operates at temperature of about room temperature to 550°C.
7. The device of claims 1-5, wherein the device operates at temperature of about room temperature to less than 400°C.
8. The device of claims 1-7, wherein multiple stacks are included to convert chemical energy to electrical energy, electrical energy to chemical energy, or a combination thereof.
9. The device of claim 8, wherein at least two of the stacks are made of a different doped bismuth oxide.

10. The device of claim 8, wherein at least two of the stacks have different thickness.
11. The device of claim 8, wherein the structure of the device is selected from the group consisting of: planar, tubular, and monolith.
12. The device of claim 8, wherein selection of the thickness of the doped bismuth oxide is used to decrease total ionic resistance.
13. An electrochemical system, comprising:
 - at least one stack including an anodic layer, an electrolytic layer, and a cathodic layer, wherein the electrolytic layer is disposed between the anodic layer and the cathodic layer, wherein the electrolytic layer has a thickness of about 0.5 nm and 100 μm , wherein the electrolytic layer is a doped bismuth oxide,
 - wherein the system is configured to operate at temperature of about room temperature to 550°C, and
 - wherein the system is configured to convert chemical energy to electrical energy, electrical energy to chemical energy, or a combination thereof.
14. The electrochemical system of claim 13, wherein the device operates at temperature of about room temperature to less than 400°C.
15. The electrochemical system of claim 14, wherein doped bismuth oxide includes about 0.001 mole per cent to 0.4 mole per cent of at least one or more rare earth oxides and optionally wherein doped bismuth oxide includes about 0.001 mole per cent to 0.4 mole per cent of at least one or more of La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Th, U and Lu, and optionally wherein doped bismuth oxide also includes one or more of the following ions of: Ca, Sr, Ba, Hf, Zr, Sn, Pb, W, Mo, Cr, Cd, In, Mg, Li, or Zn, wherein each ion is about 0.001 mole percent to 0.4 mole percent of the doped bismuth oxide.
16. The electrochemical system of claim 13, wherein the doped bismuth oxide is selected from the group consisting of: $\text{Er}_0.4\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.6}\text{W}_{0.8}\text{Bi}_{1.6}\text{O}_3$, $\text{Dy}_{0.6}\text{Gd}_{0.8}\text{Bi}_{1.6}\text{O}_3$, and $\text{Dy}_{0.6}\text{Sm}_{0.8}\text{Bi}_{1.6}\text{O}_3$.

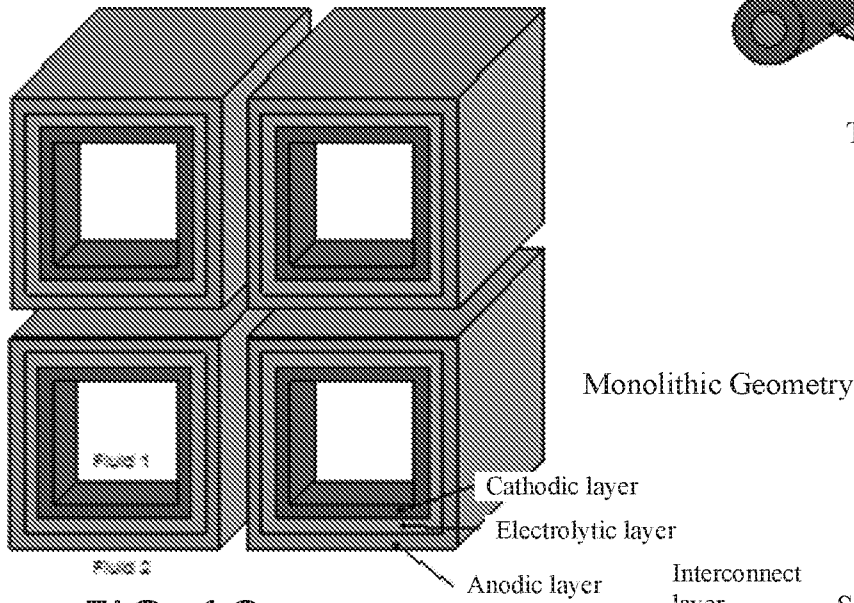
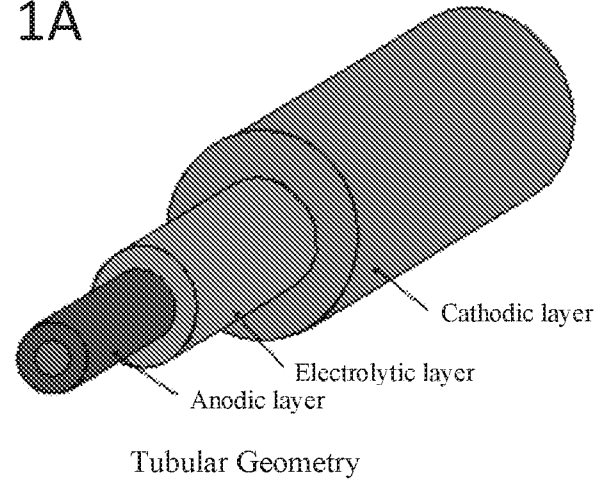
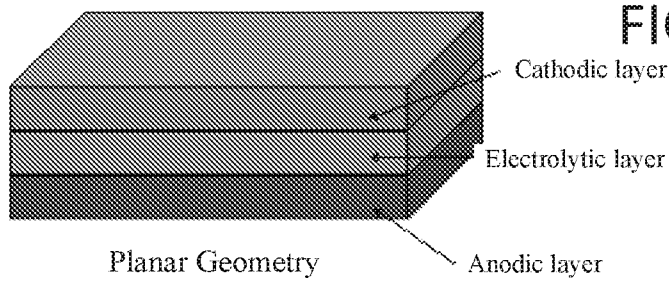


FIG. 1C

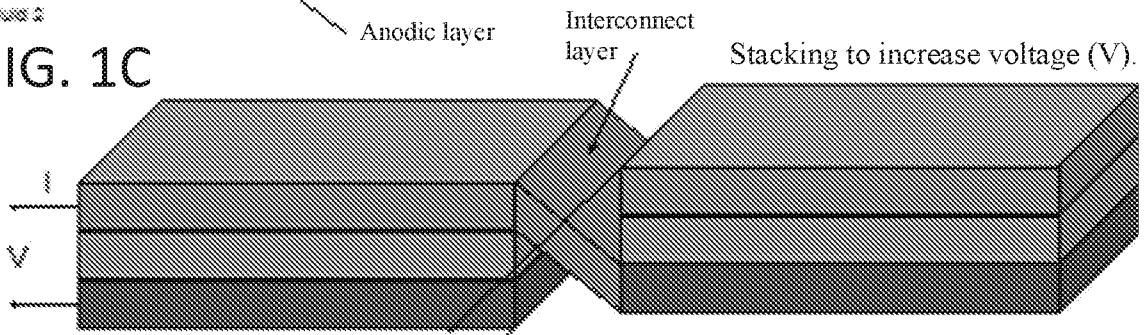


FIG. 1D

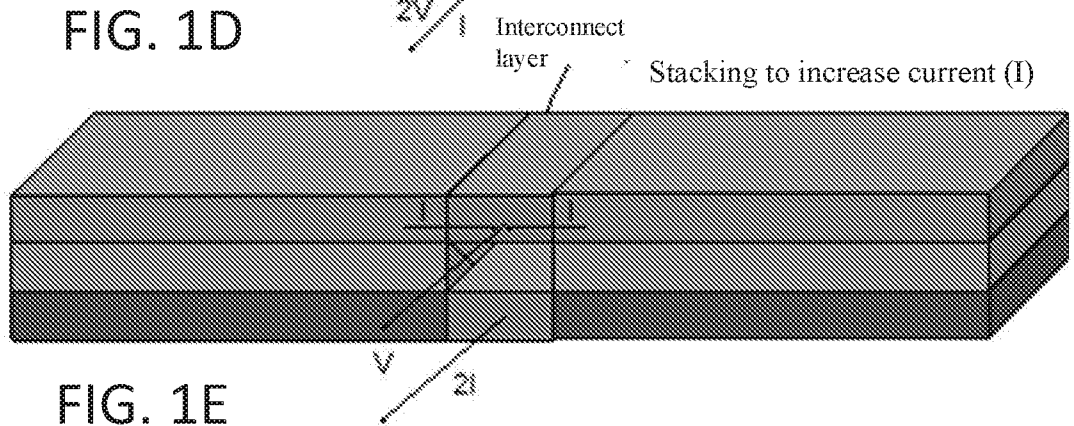


FIG. 1E

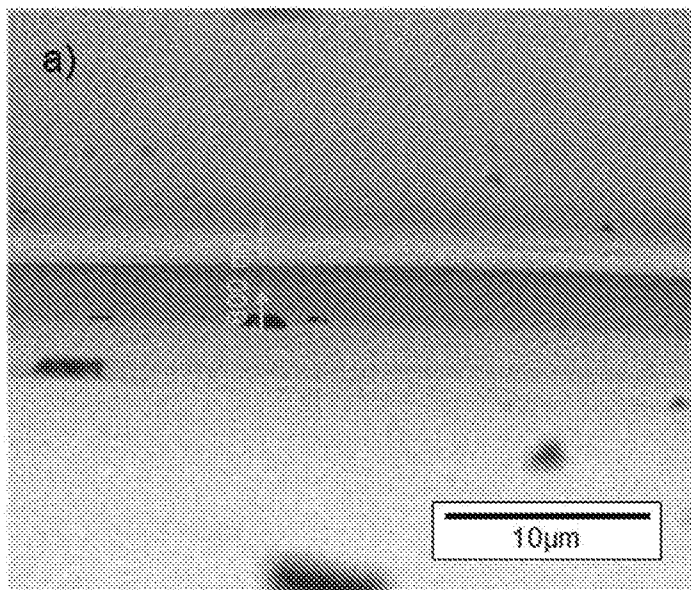


FIG. 2A

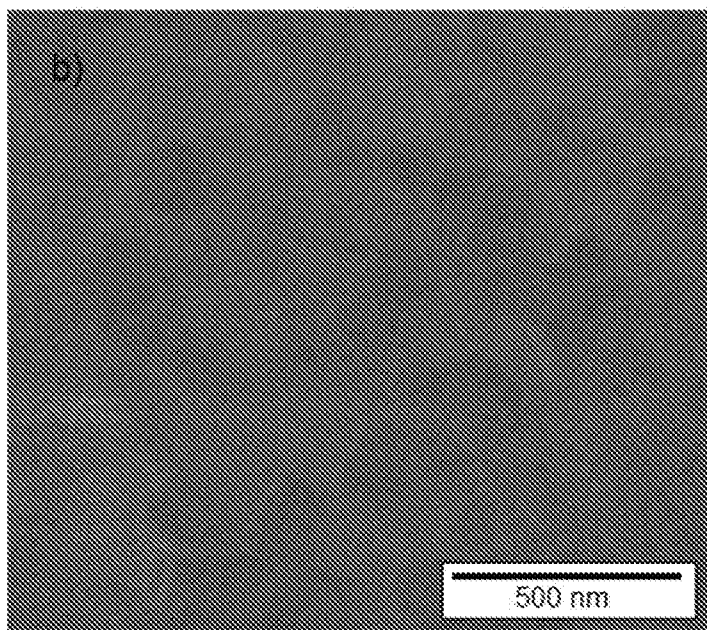


FIG. 2B

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054674

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M8/1246 H01M8/249 ADD.				
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) H01M				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal , WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2006/134492 AI (HI LCHENKO GALINA V [RU] ET AL) 22 June 2006 (2006-06-22) paragraphs [0003] , [0036] , [0038] , [0052] , [0064] , [0078] - [0082] , [0089] , [0147] ; figure 1; examples 1-5 -----	1-4, 6-10, 12-15		
X	US 6 593 020 BI (Y00 YOUNG SUNG [KR] ET AL) 15 July 2003 (2003-07-15) column 2, line 55 column 3, line 46 - line 63 column 5, line 34 - line 35 column 5, line 50 - line 54 figures 2a, 2c claims 1,2,5 ; example 1 ----- - / - -	1,8, 11, 13, 14		
<table style="width:100%; border:none;"> <tr> <td style="width:50%; border:none;"><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</td> <td style="width:50%; border:none;"><input checked="" type="checkbox"/> See patent family annex.</td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> 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 "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 16 October 2017		Date of mailing of the international search report 14/11/2017		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Mugnaini , Veronica		

INTERNATIONAL SEARCH REPORT

International application No PCT/IB2017/054674

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>A M Azad ET AL: "Revi ew Bi smuth oxide-based sol i d electrolytes for fuel cel l s" , JOURNAL OF MATERIALS SCI ENCE, vol . 29 16 February 1994 (1994-02-16) , pages 4135-4151 , XP055413114, ISSN : 0022-2461, DOI : https ://doi .org/10. 1007/BF00414192 Retri eved from the Internet: URL: https ://rd. springer.com/arti cle/10. 1007/BF00414192# [retri eved on 2017-10-06] secti on 2</p>	<p>1-3,5-8, 13-16</p>
A	<p align="center">-----</p> <p>B. DUNN ET AL: "Electri cal Energy Storage for the Grid: A Battery of Choi ces" , SCI ENCE, vol . 334, no. 6058, 17 November 2011 (2011-11-17) , pages 928-935, XP055413119 , ISSN : 0036-8075, DOI : 10.1126/science.1212741 Headi ng 2 and Col . 10, 1. 34-45; f i g u r e 2</p> <p align="center">-----</p>	<p>1-16</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/IB2017/054674

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