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(54) **A METHOD OF PREPARING H2O2**

(57) The present invention provides a method of preparing H_2O_2, the method at least comprising:
a) providing an aqueous solution of potassium bicarbonate ($KHCO_3$) or cesium bicarbonate ($CsHCO_3$);
b) subjecting the aqueous solution provided in step a) to electrochemical oxidation using an electrode, wherein the electrode comprises a metallic anode and a cathode, and wherein a potential of at least 2.0 V is applied, thereby obtaining gaseous H_2 and an aqueous solution of H_2O_2.

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Description

[0001] The present invention relates to a method of preparing H_2O_2 (hydrogen peroxide).

[0002] Various methods of preparing H_2O_2 are known in the art.

[0003] As also acknowledged by the recent article by S. Yang et al., "Toward the decentralized electrochemical production of H2O2: a focus on the catalysis", ACS Catal. 2018, 8, 4064-4081, the so-called 'anthraquinone process' is still the most widely used process for preparing H_2O_2 and accounts for more than 95% of H_2O_2 production. As also indicated in this article by S. Yang et al. (see top of left-hand column of page 4065), the major drawbacks of the anthraquinone process are that it requires large infrastructure and that it is a batch process.

[0004] Hence, there is a continuous desire in the art to provide new and alternative processes for preparing H_2O_2.

[0005] Other recent development in electrochemical production of H_2O_2 are disclosed in:

- X. Shi et al., "Understanding activity trends in electrochemical water oxidation to form hydrogen peroxide", Nature Communications, 8, 701 (published on 26 September 2017) [DOI 10.1038/s41467-017-00585-6], indicating that $BiVO_4$ has the best H_2O_2 generation amount amongst four different metal oxides (viz. WO_3, SnO_2, TiO_2 and $BiVO_4$) used as an electrode.
- K. Fuku, "Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/bismuth vanadate photoanode", Chem. Commun., 2016, 52, 5406-5409, disclosing that an aqueous solution of hydrogen carbonate (HCO_3^-) facilitated oxidative hydrogen peroxide (H_2O_2) production from water on a $WO_3/BiVO_4$ photoanode with the simultaneous production of hydrogen (H_2) on a Pt cathode.
- Z. Chen et al., "Development of a reactor with carbon catalysts for modular-scale, low-cost electrochemical generation of H2O2", React. Chem. Eng., 2017, 2, 239.

[0006] A problem associated with the known electrochemical oxidation routes as described above is that a low Faraday Efficiency (FE) and limited H_2O_2 production are obtained unless a photoanode and illumination is used.

[0007] It is an object of the present invention to overcome or minimize the above problem.

[0008] It is a further object of the present invention to provide an alternative method of preparing H_2O_2 using electrochemical oxidation.

[0009] One or more of the above or other objects can be achieved by providing a method of preparing H_2O_2, the method at least comprising:

a) providing an aqueous solution of potassium bicarbonate ($KHCO_3$) or cesium bicarbonate ($CsHCO_3$);
b) subjecting the aqueous solution provided in step a) to electrochemical oxidation using an electrode, wherein the electrode comprises a metallic anode and a cathode, and wherein a potential of at least 2.0 V is applied, thereby obtaining gaseous H_2 and an aqueous solution of H_2O_2.

[0010] It has surprisingly been found according to the present invention that a high Faraday Efficiency (FE) and H_2O_2 production are obtained even though no photoanode and illumination is used.

[0011] In step a) of the method according to the present invention, an aqueous solution of potassium bicarbonate or cesium bicarbonate is provided. The person skilled in the art will readily understand that the aqueous solution of potassium bicarbonate or cesium bicarbonate ($CsHCO_3$) is not particularly limited and may contain several components in addition to water and potassium bicarbonate or cesium bicarbonate. Also, the aqueous solution may contain a combination of potassium bicarbonate and cesium bicarbonate. Preferably, the aqueous solution provided in step a) comprises at least potassium bicarbonate.

[0012] Preferably, the aqueous solution provided in step a) is 1.0-3.0 M potassium bicarbonate, preferably at least 2.0 M, more preferably at least 2.5 M.

[0013] Further, it is preferred that the aqueous solution provided in step a) has a temperature in the range from 0-50°C, preferably at least 3°C and preferably at most 30°C, more preferably at most 25°C, even more preferably at most 20°C yet even more preferably at most 10°C or even at most 8°C.

[0014] Also, it is preferred that the aqueous solution provided in step a) has a pressure in the range from 0.5-5.0 bara, preferably at most 4.0 bara, more preferably at most 3.0 bara.

[0015] Furthermore, it is preferred that the aqueous solution provided in step a) has a pH in the range of from 4.0 to 9.5, preferably at least 6.0 and preferably at least 8.5.

[0016] In step b), the aqueous solution provided in step a) is subjected (in a vessel or the like) to electrochemical oxidation using an electrode, wherein the electrode comprises a metallic anode and a cathode, and wherein a potential of at least 2.0 V is applied, thereby obtaining gaseous H_2 (at the cathode) and an aqueous solution of H_2O_2 (at the anode).

[0017] Again, the person skilled in the art will readily understand that the electrochemical oxidation and the electrode (and the anode and cathode forming part thereof) are not particularly limited and can vary widely. Preferably, no membrane

is placed between the anode and the cathode.

[0018] Typically, the electrode comprises a 'working electrode' (WE) as the metallic anode and a 'counter electrode' (CE) as the cathode. Usually, also a 'reference electrode' (RE) is present in case it is desired to measure the potential between the anode and the cathode. As the person skilled in the art is familiar with the function of the WE, the CE and the RE, this is not discussed here in detail. Suitable reference electrodes are for example Ag/AgCl, Hg/HgO, and Hg/Hg_2SO_4.

[0019] As mentioned above, the electrode comprises a metallic anode. The person skilled in the art will understand that, in particular at higher applied potentials (such as above 3.0 V) between the anode and the cathode, some limited oxidation of the metallic anode may occur at the surface thereof. However, preferably, the metallic anode is substantially free from oxides, other than potentially formed at the surface thereof, i.e. the metallic anode comprises at most 2.0 wt.%, preferably at most 1.0 wt.% metal oxides.

[0020] Preferably, the metallic anode comprises Pt (platinum). According to an especially preferred embodiment of the present invention, the metallic anode consists of Pt.

[0021] Although the metallic anode can take various shapes such as a rod, foil, mesh, etc., the metallic anode preferably has the shape of a mesh.

[0022] The cathode is not particularly limited and can be selected from a broad range. Examples of suitable cathodes are Pt, carbon, graphene, etc. Preferably, the cathode comprises or even consist of Pt as well.

[0023] Preferably, during electrochemical oxidation a potential in the range of from 2.0 to 5.0 V is applied (between the anode and the cathode), preferably at least 2.4 V, more preferably at least 3.0 V, and preferably at most 4.6 V, more preferably at most 4.0, even more preferably at most 3.8 V.

[0024] Further it is preferred that the aqueous solution of H_2O_2 obtained in step b) comprises from 0.1 to 10.0 wt.% H_2O_2, more preferably at most 4.0 wt.% H_2O_2.

[0025] Hereinafter the invention will be further illustrated by the following non-limiting examples.

Examples

[0026] Various experiments (Examples 1-7 and Comparative Examples 1-9) were performed to show the effect of H_2O_2 production in accordance with the present invention.

[0027] In Table 1, several variations in conditions, electrolytes and anodes have been shown for the experiments.

[0028] The electrolytes $KHCO_3$, $NaHCO_3$, $KHSO_4$, K_2SO_4, Na_2SO_4 and $NaHSO_4$ were obtained from Merck (Bangalore, India), whilst $CsHCO_3$ was obtained from Sigma Aldrich (Bangalore, India).

[0029] The Pt mesh (6.25 cm^2; openings of 1 mm, with Pt wire) as used as the metallic anode was 'platinum mesh' as commercially available from Techsol Instruments (Bangalore, India). In all cases, a Hg/Hg_2SO_4 reference electrode (commercially available from Gamry Instruments (Warminster, Pennsylvania, USA)) and a Pt mesh cathode ('platinum mesh'; 6.25 cm^2, mesh size 2 mm x 2 mm with silver frame and silver rod, commercially available from Techsol Instruments (Bangalore, India)) were used.

[0030] All experiments were performed in a 250 ml glass cell (obtained from Hi Tech Pvt Ltd. (Bangalore, India)) with six openings (three openings for the 3 electrodes, one opening for N_2 purging, one opening as sampling port and the remaining opening is normally left open for venting out the gases generated) at atmospheric pressure (1.0 bara) using a water bath to control the temperature of the electrolyte. In each Example 200 ml of the aqueous solution (used as the electrolyte) was used.

Table 1

Example	T [°C]	pH	electrolyte	Anode	Applied potential [V]	Time [h]	H_2O_2 produced[1] [ppm]	FE[2] [%]
Ex. 1	55.0	8.2	2M $KHCO_3$	Pt mesh	2.5	2	2120	12
Ex. 2	55.0	8.2	2M $KHCO_3$	Pt mesh	2.5	3	2487	12
Ex. 3	55.0	8.2	2M $KHCO_3$	Pt mesh	2.5	5	2300	12
Ex. 4	5.0	9.0	3M $KHCO_3$	Pt mesh	2.5	3	720	25
Ex. 5	5.0	9.0	3M $KHCO_3$	Pt mesh	3.5	5	5923	47

(continued)

Example	T [°C]	pH	electrolyte	Anode	Applied potential [V]	Time [h]	H_2O_2 produced[1] [ppm]	FE[2] [%]
Ex. 6	5.0	9.0	3M $KHCO_3$	Pt mesh	4.5	3	770	23
Ex. 7	5.0	8.9	3M $CsHCO_3$	Pt mesh	3.5	5	2195	16
C. Ex. 1	5.0	8.2	2M $KHCO_3$	Pt mesh	1.5	5	724	5
C. Ex. 2	5.0	9.0	3M $KHCO_3$	Pt mesh	1.5	3	43	4.3
C. Ex. 3	5.0	-0.3	2M $NaHSO_4$	Pt mesh	3.5	5	46	2
C. Ex. 4	5.0	0.0	1M $NaHSO_4$	Pt mesh	3.5	5	-	0
C. Ex. 5	5.0	0.3	0.5M $NaHSO_4$	Pt mesh	3.5	5	-	0
C. Ex. 6	5.0	-0.3	2M $KHSO_4$	Pt mesh	3.5	3	-	0
C. Ex. 7	5.0	1	2M Na_2SO_4	Pt mesh	3.5	3	-	0
C. Ex. 8	5.0	8.2	0.5M $NaHCO_3$	Pt mesh	3.5	5	52	0.5
C. Ex. 9	5.0	1	2M K_2SO_4	Pt mesh	3.5	3	-	0

[1]Determined using the commonly used permanganate titration (as also described on page 5 of the above-mentioned article by Shi in Nature Communications).
[2]FE = Faraday Efficiency, calculated using the formula FE = (amount of generated H_2O_2 (mol)/theoretical generated H_2O_2) x 100; see again the article of Shi.

Discussion

[0031] As can be seen from the Examples, the present invention surprisingly provides a new method of preparing H_2O_2, resulting in desirable amounts of H_2O_2 production with a good Faraday Efficiency (i.e. above 10%).

[0032] The Examples surprisingly show that potassium carbonate ($KHCO_3$) and cesium carbonate ($CsHCO_3$) are better electrolytes than $NaHCO_3$ (and the other listed electrolytes) with a preference for $KHCO_3$ above $CsHCO_3$.

[0033] Noteworthy is also the outcome of the comparison of Comparative Examples 1 and 2 (wherein a potential of below 2.0 V was applied) with Examples 3 and 4, showing that the applied potential of at least 2.0 V results in a better FE and H_2O_2 production. On the other hand, it can be seen from Examples 3-7 that there is a preference for a potential of at most 4.0, in particular at a pH above 8.5.

[0034] An especially preferred embodiment was found for Example 5 (3M $KHCO_3$ at 5°C and 3.5 V, with 5923 ppm H_2O_2 produced at a FE of 47%).

[0035] The person skilled in the art will readily understand that many modifications may be made without departing from the scope of the invention.

Claims

1. A method of preparing H_2O_2, the method at least comprising:

a) providing an aqueous solution of potassium bicarbonate ($KHCO_3$) or cesium bicarbonate ($CsHCO_3$) ;
b) subjecting the aqueous solution provided in step a) to electrochemical oxidation using an electrode, wherein

the electrode comprises a metallic anode and a cathode, and wherein a potential of at least 2.0 V is applied, thereby obtaining gaseous H_2 and an aqueous solution of H_2O_2.

2. The method according to claim 1, wherein the aqueous solution provided in step a) is 1.0-3.0 M potassium bicarbonate, preferably at least 2.0 M, more preferably at least 2.5 M.

3. The method according to claim 1 or 2, wherein the aqueous solution provided in step a) has a temperature in the range from 0-50°C, preferably at least 3°C and preferably at most 30°C, more preferably at most 25°C, even more preferably at most 20°C yet even more preferably at most 10°C or even at most 8°C.

4. The method according to any one of the preceding claims, wherein the aqueous solution provided in step a) has a pressure in the range from 0.5-5.0 bara, preferably at most 4.0 bara, more preferably at most 3.0 bara.

5. The method according to any one of the preceding claims, wherein the aqueous solution provided in step a) has a pH in the range of from 4.0 to 9.5, preferably at least 6.0 and preferably at least 8.5.

6. The method according to any one of the preceding claims, wherein the metallic anode comprises Pt.

7. The method according to any one of the preceding claims, wherein the metallic anode has the shape of a mesh.

8. The method according to any one of the preceding claims, wherein during electrochemical oxidation a potential in the range of from 2.0 to 5.0 V is applied, preferably at least 2.4 V, more preferably at least 3.0 V, and preferably at most 4.6 V, more preferably at most 4.0, even more preferably at most 3.8 V.

9. The method according to any one of the preceding claims, wherein the aqueous solution of H_2O_2 obtained in step b) comprises from 0.1 to 10.0 wt.% H_2O_2.

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EUROPEAN SEARCH REPORT

Application Number
EP 19 15 6112

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2016/068973 A1 (STEPHENS IFAN [DK] ET AL) 10 March 2016 (2016-03-10) * paragraph [0070]; claims 1,5 * -----	1-9	INV. C25B1/30
A	DATABASE WPI Week 199624 Thomson Scientific, London, GB; AN 1996-235904 XP002793372, & JP H08 92018 A (FURUKAWA KIKAI KINZOKU KK) 9 April 1996 (1996-04-09) * abstract * -----	1-9	

TECHNICAL FIELDS SEARCHED (IPC)

C25B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	5 August 2019	Hammerstein, G

CATEGORY OF CITED DOCUMENTS

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05-08-2019

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- **S. YANG et al.** Toward the decentralized electrochemical production of H2O2: a focus on the catalysis. *ACS Catal.,* 2018, vol. 8, 4064-4081 **[0003]**
- **X. SHI et al.** Understanding activity trends in electrochemical water oxidation to form hydrogen peroxide. *Nature Communications,* 26 September 2017, vol. 8, 701 **[0005]**
- **K. FUKU.** Efficient oxidative hydrogen peroxide production and accumulation in photoelectrochemical water splitting using a tungsten trioxide/bismuth vanadate photoanode. *Chem. Commun.,* 2016, vol. 52, 5406-5409 **[0005]**
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