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[Continued on next page]

(54) Title: ELECTROLYSIS CELL WITH MULTIPLE MEMBRANES FOR CUCI/HCI ELECTROLYSIS IN HYDROGEN PRODUCTION

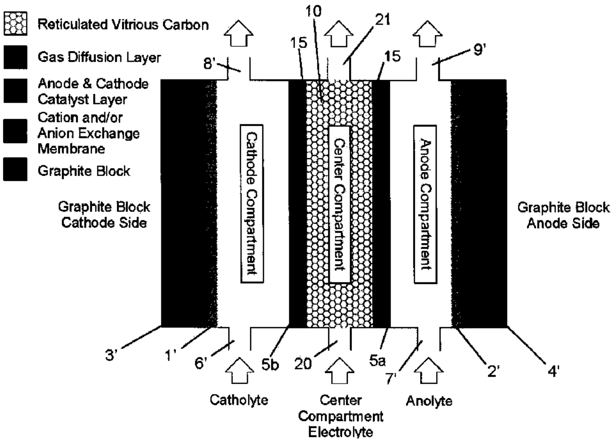

Figure 3

(57) **Abstract**: An electrochemical cell for producing hydrogen gas and cupric chloride. The cell comprises: an anode compartment comprising an anode for disposition in an anolyte, wherein the anolyte is cuprous chloride in hydrochloric acid; a cathode compartment comprising a cathode, wherein the cathode comprises an electrocatalyst; a plurality of ion exchange membranes disposed between the anode compartment and the cathode compartment; and at least one center compartment defined by a pair of said ion exchange membranes and comprising at least one element for removal or sequestering of copper ions that cross at least one of said membranes from the anode compartment. Also described is a method for CuC1/HC1 electrolysis in the production of hydrogen using the electrochemical cell.

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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

Electrolysis Cell with Multiple Membranes
for CuCl/HCl Electrolysis in Hydrogen Production

FIELD OF INVENTION

[0001] The present invention relates to the production of hydrogen, especially those processes which use the Cu–Cl cycle. In particular, the invention relates to an improved electrolysis cell and method for CuCl/HCl electrolysis in the production of hydrogen.

BACKGROUND OF THE INVENTION

[0002] The Copper–Chlorine (Cu–Cl) cycle is a thermochemical cycle used for the production of hydrogen, and can be linked with nuclear plants, or other heat sources such as solar and industrial waste heat, to potentially achieve higher efficiencies, lower environmental impact, and lower costs than other conventional hydrogen production technologies.

[0003] The Cu–Cl cycle is of interest to Atomic Energy of Canada Limited (AECL) because all of the chemical and electrochemical reactions can be carried out at temperatures that do not exceed about 530° C. This means that the heat requirement of this process can be supplied by the Generation IV Supercritical-Water-Cooled Reactor (SCWR) that is being developed by AECL, which can produce heat at temperatures up to 625°C. The Sodium cooled Fast Reactor (SFR) is another nuclear reactor capable of providing heat at around 530°C. Both the SCWR and SFR, therefore, are ideally suited for electricity production and co-generation of hydrogen.

[0004] The Cu–Cl cycle has been developed with several variations, including a four-step process with the following reaction steps:

Step	Reaction
1	$2CuCl(aq) + 2HCl(aq) \rightarrow H_2(g) + 2CuCl_2(aq)$
2	$CuCl_2(aq) \rightarrow CuCl_2(s)$ (drying step)
3	$2CuCl_2(s) + H_2O(g) \rightarrow Cu_2OCl_2(s) + 2HCl(g)$
4	$Cu_2OCl_2(s) \rightarrow 2CuCl(l) + \frac{1}{2}O_2(g)$

[0005] In the four-step Cu–Cl cycle, a chemical species that is consumed in one reaction, such as HCl in Step 1, is produced in a different reaction step, which is Step 3 for HCl. Thus, all of the chemicals are recycled except for water, hydrogen and oxygen, which is consistent with the net reaction being the splitting of water as follows:

$$H_2O(g) \rightarrow H_2(g) + 1/2\ O_2(g)$$

[0006] In the electrochemical reaction step of the Cu-Cl cycle, the anolyte is a solution of CuCl dissolved in HCl. The catholyte is typically an HCl solution, but in certain variations can be water and in others the catholyte is not required. During the electrolysis step, cuprous ions (Cu^+) are oxidized to cupric ions (Cu^{2+}) at the anode while protons are reduced at the cathode to produce hydrogen.

[0007] U.S. 2010/0051469 (Stolberg) describes a single membrane electrolysis cell for CuCl/HCl electrolysis. Stolberg demonstrated that a cell configuration of the type shown in Figure 1 can be used to produce hydrogen by electrolysing a solution of CuCl/HCl at various concentrations of these species.

SUMMARY OF THE INVENTION

[0008] It is an object of the invention to provide an improved electrolysis cell and method for CuCl/HCl electrolysis in the production of hydrogen.

[0009] According to an aspect of the present invention there is provided an electrochemical cell for producing hydrogen gas and cupric chloride, comprising: an anode compartment comprising an anode (and optionally an electrocatalyst) for disposition in an anolyte, wherein the anolyte is cuprous chloride in hydrochloric acid; a cathode compartment comprising a cathode, wherein the cathode comprises an electrocatalyst; a plurality of ion exchange membranes disposed between the anode compartment and the cathode compartment; and at least one center compartment defined by a pair of said ion exchange membranes and comprising at least one element for removal or sequestering of copper ions that cross at least one of said membranes from the anode compartment.

[0010] In embodiments of the electrochemical cell, the plurality of ion exchange membranes may comprise anion exchange membranes, cation exchange membranes, or a combination thereof.

[0011] In further optional embodiments, the at least one center compartment comprises gas diffusion layers (GDLs) positioned adjacent the ion exchange membranes and defining sidewalls of the at least one center compartment.

[0012] The at least one center compartment may also comprise an inlet and an outlet to allow flow of an electrolyte therethrough. For instance, the inlet and the outlet may be connected to an electrolyte source to allow continuous flushing of the at least one center compartment with an electrolyte effective to remove copper ions. In certain non-limiting examples, the electrolyte may be water or hydrochloric acid. In the case of hydrochloric acid, the concentration may be in the range of about 1 M to about 12 M, for example within the range of about 4 M to about 11 M, such as about 6 M or about 11 M.

[0013] The selection flushing electrolyte would be effected by catholyte and anolyte compositions. In further embodiments, the electrolyte may comprise at least one material that can absorb, adsorb or react with the copper ions in the at least one center compartment.

[0014] The at least one center compartment may also be filled with a material to remove the copper ions in the at least one center compartment, by adsorption, chelation or other chemical reaction. In certain embodiments, the at least one center compartment may be filled with Reticulated Vitrious Carbon (RVC).

[0015] In yet further embodiments, the copper species can be removed from the center compartment *in-situ* by a deposition, absorption and/or chemical reaction, or *ex-situ* by a chemical separation process.

[0016] One or more of the plurality of ion exchange membranes may, as an example, be a cation exchange membrane, such as but not limited to a proton exchange membrane including those made from a resin of hydrated copolymers of polytetrafluoroethylene and poly-sulphonyl fluoride vinyl ether-containing pendent sulphonic acid groups. For instance, the proton exchange membrane may be a NAFION® N112, NAFION® N115, NAFION® N117, NAFION® N1110, NAFION® NRE-211, NAFION® NRE-212, NAFION® N324, NAFION® XL or NAFION® NE-1135 membrane. In other embodiments, the ion exchange membrane may be an anion exchange membrane, including membranes such as ACM, AMV, ASV, AXE or other anion exchange membranes used for desalination, electrodeionization, or any other such processes.

[0017] In certain embodiments of the anolyte, the hydrochloric acid concentration may be in the range of about 1 M to about 12 M, for instance within the range of about 4 M to about 11 M, or about 6 M, or alternatively about 11 M.

[0018] In other embodiments, the cathode may be for disposition, or disposed in a catholyte. For example, the catholyte may be water or hydrochloric acid. In the case of the latter, the hydrochloric acid concentration in the catholyte may be in the range of about 1 M to about 12 M, for example within the range of about 4 M to about 10 M, such as about 6 M or about 10 M.

[0019] In yet further embodiments, the electrocatalyst may be a metal such as platinum, ruthenium, palladium, iridium, osmium, and rhodium, for example platinum. Alternatively, the electrocatalyst may be a bimetallic alloy of platinum and a second metal such as ruthenium, tin, rhodium, molybdenum, nickel, cobalt, iron, or titanium, more particularly a bimetallic alloy of platinum and ruthenium. As another alternative, the electrocatalyst may comprise an alloy of platinum, ruthenium, and a third component such as tungsten, tungsten oxide ($W0_2$), tin, osmium, palladium, cobalt, iridium, manganese, chromium, gold, silver, rhodium, or tungsten carbide (W_2C). In addition, the electrocatalyst may comprise a thin film coating, or be dispersed on a high surface area carbon powder.

[0020] Also provided herein is a method for producing hydrogen gas, comprising:

(i) providing the electrochemical cell as described above; and

(ii) applying an electrical potential or current between the anode and cathode to produce hydrogen gas.

[0021] The above-described method may additionally comprise the steps of collecting and storing the hydrogen gas produced in step (ii).

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] These and other features of the invention will become more apparent from the following description in which reference is made to the appended drawings, wherein:

[0023] Figure 1 illustrates the single-cell wide gap configuration of an electrolysis cell according to U.S. 2010/0051469 (Stolberg);

[0024] Figure 2 illustrates the results of testing CuCl/HCl electrolysis cell performance in single and double membrane embodiments, in which voltage is measured as a function of time at a constant current;

[0025] Figure 3 illustrates a double membrane electrolysis cell according to an example of an embodiment of the present invention, in wide gap configuration; and

[0026] Figure 4 illustrates the results of comparing between total catholyte copper species data for a single membrane cell (SMC) and a double membrane cell (DMC) using an N1110 ion exchange membrane; T = 45°C.

DETAILED DESCRIPTION

[0027] The present inventors have analyzed the electrolysis efficiency of electrolysis cells such as that described by Stolberg (U.S. 2010/0051469) in the Cu-Cl cycle. In carrying out these studies, it was found that copper ions cross the ion-exchange membrane that separates the anode and cathode compartments in the cell, and compromise electrolysis efficiency over short or long periods.

[0028] The Cu^{2+} species that form when Cu^+ is oxidized can be neutral ($CuCl_2$) or cationic ($CuCl^+$), depending on the HCl concentration used. Thus, during CuCl/HCl electrolysis, copper species can cross the membrane by diffusion ($CuCl_2$) or by an ion-exchange ($CuCl^+$) transport process in addition to diffusion.

[0029] The transfer of copper ions from the anode to the cathode during CuCl/HCl electrolysis cannot be prevented when a single layer of membrane is used. In a configuration like the one shown in Figure 1, increasing the catholyte flow rate may help to prevent copper from reaching the cathode. However, maintaining electrolysis efficiency and high performance of the cell over long periods is important for economical production of hydrogen from the Cu-Cl process. Accordingly, an improved cell design was needed.

[0030] In an effort to reduce copper species crossover, including neutral and charged species, and hence the concentration of copper in the cathode compartment, an electrolysis cell comprising more than one layer of ion-exchange membrane separating the anode and cathode compartments was designed and tested using the Stolberg electrolysis cell as a comparison.

[0031] One example of the electrolysis cell of Stolberg is shown in Figure 1, and includes a cathode side catalyst (1), an anode side catalyst (2), cathode and anode side graphite blocks (3,4), a membrane (5), cathode and anode side solution inlet ports (6,7), and cathode and anode side solution outlet ports (8,9). In Figure 2, the curve shown as "Single Membrane Cell One Nafion 212" demonstrates the performance characteristic of a cell designed according to Stolberg, using one proton exchange membrane (PEM).

[0032] Referring to Figure 3, which is one example of an electrolysis cell according to the present invention, two ion-exchange membranes are used to form an isolated compartment in the middle of the two membranes. The cell comprises a cathode side catalyst layer (1'), an anode side catalyst layer (2'), cathode and anode side graphite blocks (3',4'), cation and/or anion-exchange membranes (5a and 5b), cathode and anode side solution inlet ports (6',7'), cathode and anode side solution outlet ports (8',9'), and a center compartment (10) formed between the first (5a) and the second (5b) ion exchange membrane layers. In the embodiment shown, the center compartment (10) comprises gas diffusion layers (15) positioned adjacent the membrane layers (5a) and (5b), as well as inlet (20) and outlet (21) ports. The center compartment (10) as shown contains a porous layer of RVC. Several variations of the embodiment shown in Figure 3 are envisioned, including an embodiment in which there is a zero gap between the catalyst and the membranes. In this example RVC or some other suitable electronic conductor is placed between the graphite block and the gas diffusion layer. Another example of a zero gap configuration is achieved using graphite blocks or any other suitable material with flow fields. In this case, flow fields are used to direct the flow of the electrolytes through their respective compartments.

[0033] Copper ions from the anode compartment that cross the first membrane (5a) can be removed from the cell by continuously flushing the center compartment (10) with an electrolyte containing a minimum copper ion concentration. Alternatively, a suitable material may be inserted into the center compartment (10) between the two membranes to remove the copper species by adsorption or by other chemical reaction processes (e.g. chelation). The electrolyte used for flushing the centre compartment may also contain, as suspension or dissolved, materials that can absorb/adsorb or react with the copper species entering the middle compartment from the anode compartment.

[0034] Referring again to Figure 2, the curve identified as “Double Membrane Cell Two Nafion 212” illustrates that the negative effects of the copper species is minimized and the cell performance is maintained at the desired level, especially as compared to the single membrane version of the electrolysis cell. In addition, the copper transfer from anode to cathode is greatly reduced, as can be seen in Figure 4 which provides one example of an experiment carried out for more than 70 hours with very little copper observed in the catholyte when using two N1110 membranes in an electrolysis cell according to the present invention. In another test that ran 96 h, copper species were not found to be present in the catholyte (data not shown).

[0035] In further embodiments of the invention, the electrolysis cell may contain multiple central compartments between the two electrodes to accomplish the effect described above. Also, unlike Stolberg which describes the use of cation-exchange membranes in the cell, anion-exchange membranes may be used in the current invention. In other configurations, both anion- and cation- exchange membranes may be used, in any combination, in the same multiple-membrane cell in a strategic way.

[0036] The present invention reduces the net amount of copper transferred from the anode to the cathode compartment by using multiple membranes in a CuCl/HCl electrolysis cell. The compartment formed between two membranes provides a means to removing copper species *in-situ* (e.g. by adsorption or chemical reaction) or *ex-situ* (e.g. by flushing the compartment with clean electrolyte solution), thus reducing the amount of copper species reaching the cathode and improving the long-term performance of the CuCl/HCl electrolysis cell.

[0037] All publications, patent applications and patents mentioned in this specification are herein incorporated by reference.

[0038] While the invention has been described in connection with specific embodiments, it will be understood that it is capable of further modifications. Therefore, this application is intended to cover any variations, uses, or adaptations of the invention that follow, in general, the principles of the invention, including departures from the present disclosure that come within known or customary practice within the art.

WHAT IS CLAIMED IS:

1. An electrochemical cell for producing hydrogen gas and cupric chloride, comprising:

   an anode compartment comprising an anode for disposition in an anolyte, wherein the anolyte is cuprous chloride in hydrochloric acid;

   a cathode compartment comprising a cathode, wherein the cathode comprises an electrocatalyst;

   a plurality of ion exchange membranes disposed between the anode compartment and the cathode compartment; and

   at least one center compartment defined by a pair of said ion exchange membranes and comprising at least one element for removal or sequestering of copper ions that cross at least one of said membranes from the anode compartment.

2. The electrochemical cell of claim 1, wherein the plurality of ion exchange membranes comprise anion exchange membranes, cation exchange membranes, or a combination thereof.

3. The electrochemical cell of claim 1, wherein the at least one center compartment comprises gas diffusion layers positioned adjacent the ion exchange membranes of the at least one center compartment.

4. The electrochemical cell of claim 1, wherein the at least one center compartment comprises an inlet and an outlet to allow flow of an electrolyte therethrough.

5. The electrochemical cell of claim 4, wherein the inlet and the outlet are connected to an electrolyte source to allow continuous flushing of the at least one center compartment with an electrolyte effective to remove copper ions.

6. The electrochemical cell of claim 4, wherein the electrolyte further comprises at least one material that can absorb, adsorb or react with the copper ions in the at least one center compartment.

7. The electrochemical cell of claim 1, wherein the at least one center compartment is filled with a material to remove the copper ions in the at least one center compartment by adsorption, chelation or other chemical reaction.

8. The electrochemical cell of claim 1, wherein the at least one center compartment is filled with reticulated vitrious carbon.

9. The electrochemical cell of claim 1, wherein copper species are removed from the center compartment *in-situ* by a deposition, absorption and/or chemical reaction, or *ex-situ* by a chemical separation process.

10. The electrochemical cell of claim 1, wherein one or more of the plurality of ion exchange membranes is a proton exchange membrane made from a resin of hydrated copolymers of polytetrafluoroethylene and poly-sulphonyl fluoride vinyl ether-containing pendent sulphonic acid groups.

11. The electrochemical cell of claim 10, wherein the proton exchange membrane is a NAFION® N112, NAFION® N115, NAFION® N117, NAFION® N1110, NAFION® NRE-211, NAFION® NRE-212, NAFION® N324, or NAFION® NE-1135 membrane.

12. The electrochemical cell of claim 11, wherein the proton exchange membrane is NAFION® N1110.

13. The electrochemical cell of claim 1, wherein one or more of the plurality of ion exchange membranes is an ion exchange membrane selected from ACM, AMV, ASV, AXE or another anion exchange membranes used for desalination or electrodeionization.

14. The electrochemical cell of claim 1, wherein the hydrochloric acid concentration is in the range of about 1 M to about 12 M.

15. The electrochemical cell of claim 14, wherein the hydrochloric acid concentration is within the range of about 4 M to about 11 M.

16. The electrochemical cell of claim 14, wherein the hydrochloric acid concentration is about 6 M.

17. The electrochemical cell of claim 14, wherein the hydrochloric acid concentration is about 11 M.

18. The electrochemical cell of claim 1, wherein the cathode is disposed in a catholyte.

19. The electrochemical cell of claim 18, wherein the catholyte is water.

20. The electrochemical cell of claim 18, wherein the catholyte is hydrochloric acid.

21. The electrochemical cell of claim 20, wherein the hydrochloric acid concentration in the catholyte is in the range of about 1 M to about 12 M.

22. The electrochemical cell of claim 20, wherein the hydrochloric acid concentration in the catholyte is within the range of about 4 M to about 10 M.

23. The electrochemical cell of claim 20, wherein the hydrochloric acid concentration in the catholyte is about 6 M.

24. The electrochemical cell of claim 20, wherein the hydrochloric acid concentration in the catholyte is about 10 M.

25. The electrochemical cell of claim 1, wherein the electrocatalyst is a metal selected from the group consisting of platinum, ruthenium, palladium, iridium, osmium, and rhodium.

26. The electrochemical cell of claim 25, wherein the electrocatalyst is platinum.

27. The electrochemical cell of claim 1, wherein the electrocatalyst is a bimetallic alloy of platinum and a metal selected from the group consisting of ruthenium, tin, rhodium, molybdenum, nickel, cobalt, iron, and titanium.

28. The electrochemical cell of claim 27, wherein the electrocatalyst comprises a bimetallic alloy of platinum and ruthenium.

29. The electrochemical cell of claim 1, wherein the electrocatalyst comprises an alloy of platinum, ruthenium, and a third component selected from the group comprising tungsten,

tungsten oxide (WO_2), tin, osmium, palladium, cobalt, iridium, manganese, chromium, gold, silver, rhodium, and tungsten carbide (W_2C).

30. The electrochemical cell of claim 1, wherein the electrocatalyst comprises a thin film coating.

31. The electrochemical cell of claim 1, wherein the electrocatalyst is dispersed on a high surface area carbon powder.

32. A method for producing hydrogen gas comprising the following steps:

(i) providing the electrochemical cell of claim 1; and

(ii) applying an electrical potential between the anode and cathode to produce hydrogen gas.

33. The method of claim 32, additionally comprising the steps of collecting and storing the hydrogen gas produced in step (ii).

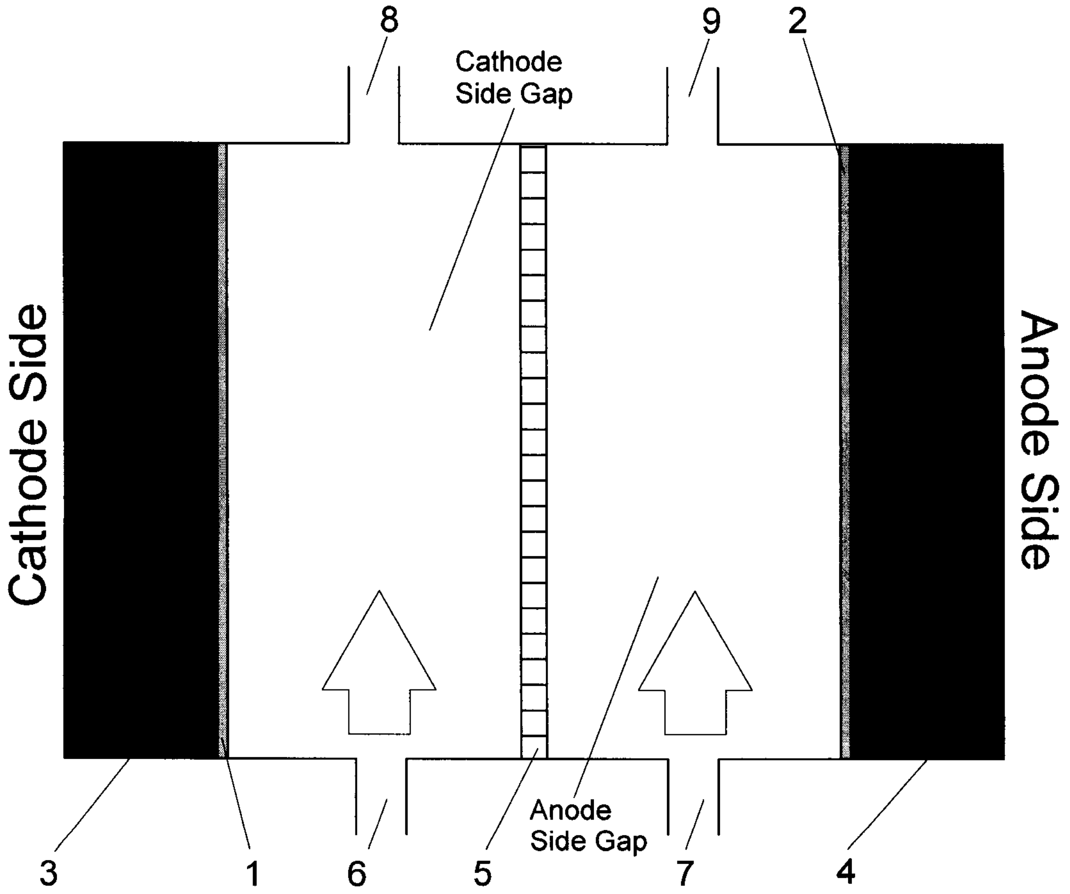
8
9
2
Cathode Side Gap
Cathode Side
Anode Side
Anode Side Gap
3
1
6
5
7
4

Figure 1

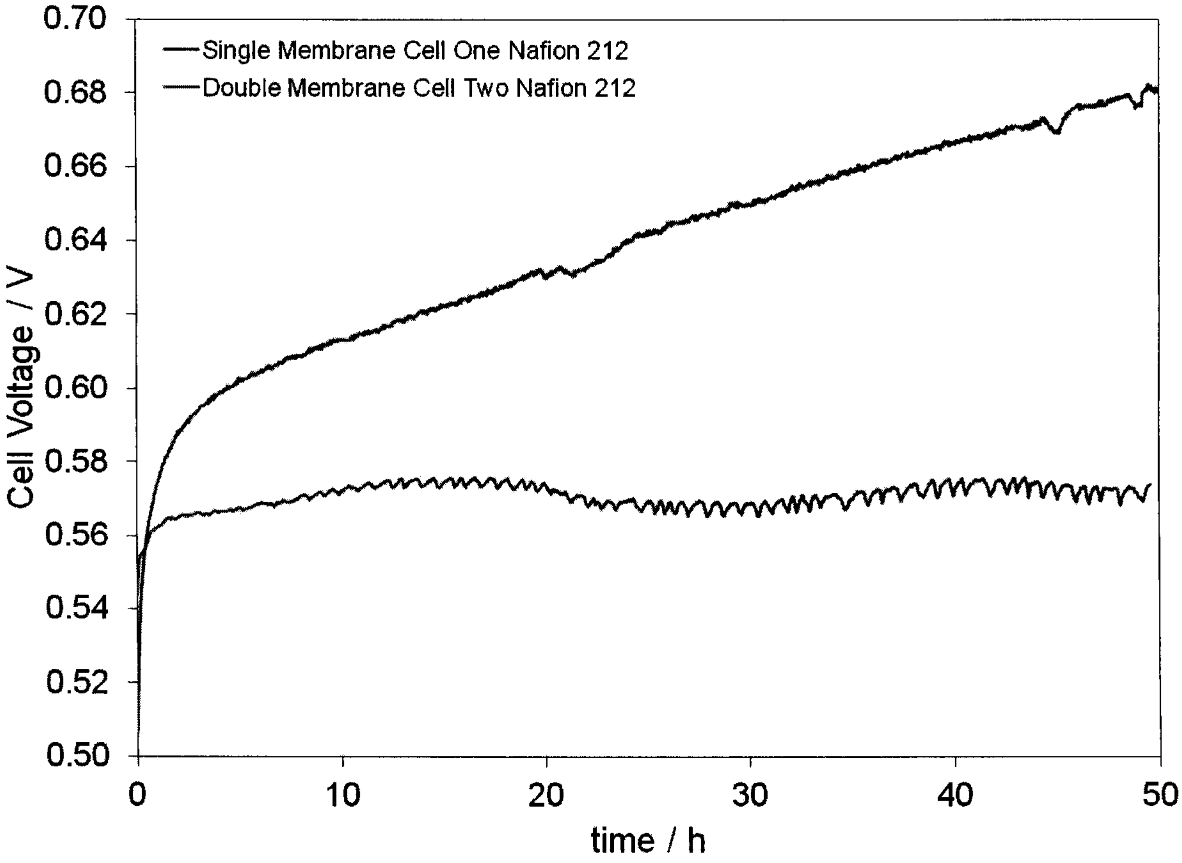
Single Membrane Cell One Nafion 212
Double Membrane Cell Two Nafion 212
Cell Voltage / V
0.70
0.68
0.66
0.64
0.62
0.60
0.58
0.56
0.54
0.52
0.50
0
10
20
30
40
50
time / h

Figure 2

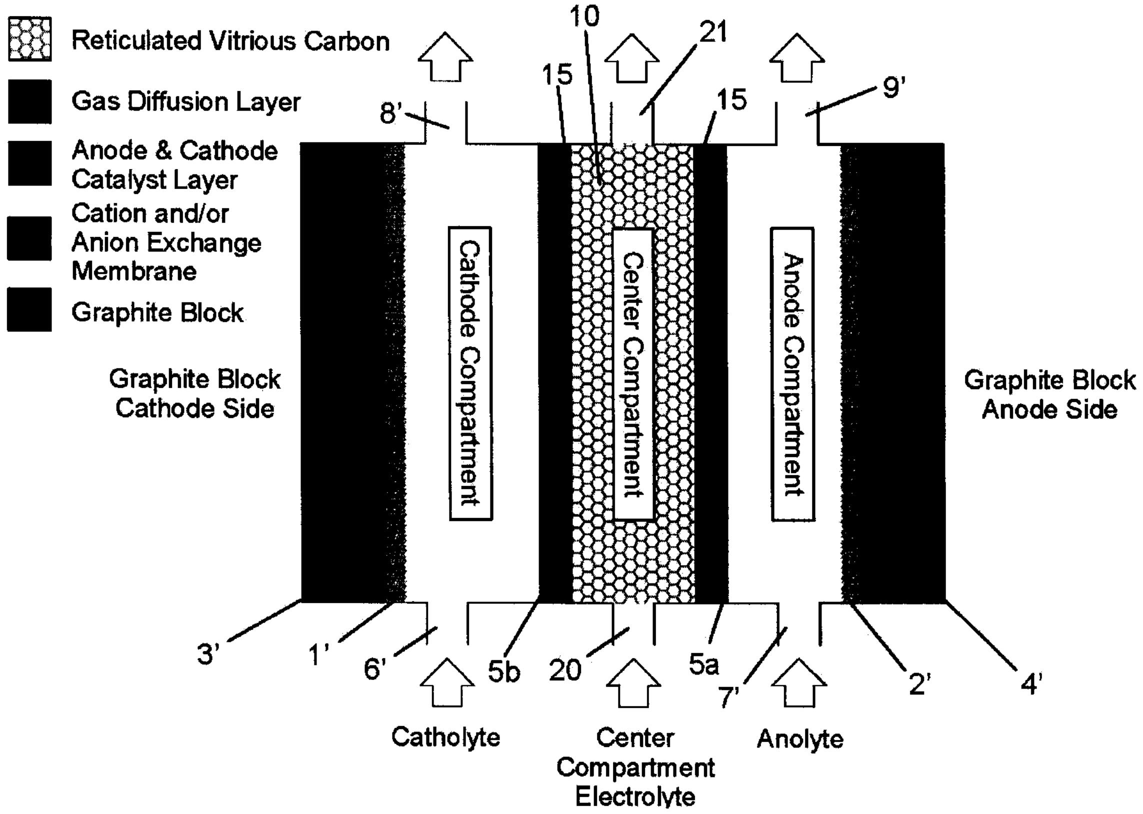
Reticulated Vitrious Carbon
Gas Diffusion Layer
Anode & Cathode Catalyst Layer
Cation and/or Anion Exchange Membrane
Graphite Block
Graphite Block Cathode Side
Graphite Block Anode Side
Cathode Compartment
Center Compartment
Anode Compartment
10
21
15
15
8'
9'
3'
1'
6'
5b
20
5a
7'
2'
4'
Catholyte
Center Compartment Electrolyte
Anolyte

Figure 3

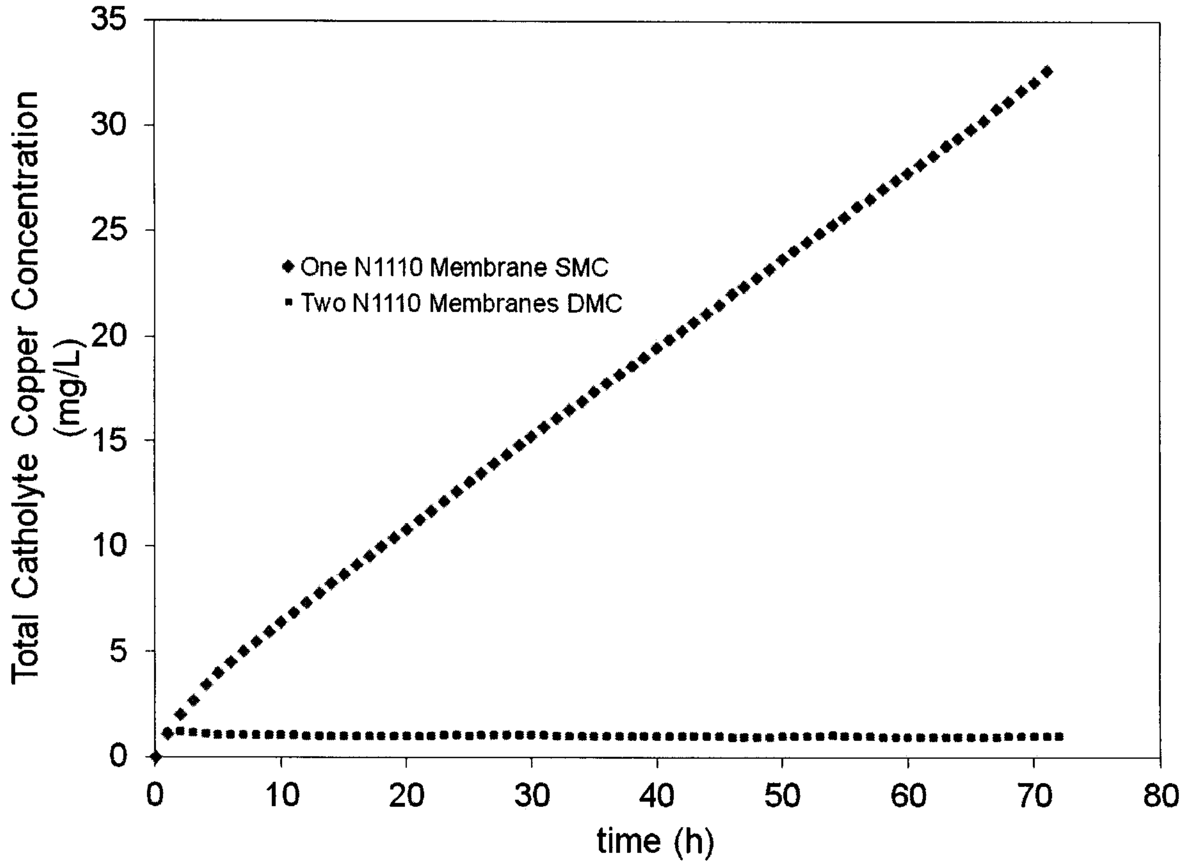
Total Catholyte Copper Concentration (mg/L)
35
30
25
20
15
10
5
0
time (h)
0
10
20
30
40
50
60
70
80
◆ One N1110 Membrane SMC
▪ Two N1110 Membranes DMC

Figure 4

INTERNATIONAL SEARCH REPORT	International application No. PCT/CA2013/000294

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C25B 9/08*** (2006.01) , ***C25B 1/02*** (2006.01) , ***C25B 1/26*** (2006.01)
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)
IPC: ***C25B*** (2006.01) ,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Total Patent, Canadian Patent Database, ACS Publications Database, Scopus
cuprous chloride, cupric chloride, ion exchange, hydrogen, hydrochloric acid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 4,376,019 (GAMLEN et al) 8 March 1983 (08-03-1983) * columns 8-11, examples 8 and 9*	1, 2, 4, 5, 14, 18, 19, 25, 26, 32 and 33 11-13, 15-17, 20-24 and 27-31
Y	US 2010/0051469 (STOLBERG) 4 March 2010 (04-03-2010) *paragraphs 50-52, 55-6174-77, examples 2 and 3*	11-13, 15-17, 20-24 and 27-31

[ ] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 06 May 2013 (06-05-2013)	Date of mailing of the international search report 08 May 2013 (08-05-2013)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer Chris Bowen (819) 994-3555

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/000294

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US4376019A	08 March 1983 (08-03-1983)	AT8493T	15 August 1984 (15-08-1984)
		AU6968981A	05 November 1981 (05-11-1981)
		BE888652A1	30 October 1981 (30-10-1981)
		BR8102633A	26 January 1982 (26-01-1982)
		CA1155872A1	25 October 1983 (25-10-1983)
		DE3164837D1	23 August 1984 (23-08-1984)
		EP0039547A1	11 November 1981 (11-11-1981)
		EP0039547B1	18 July 1984 (18-07-1984)
		ES501818D0	01 October 1982 (01-10-1982)
		ES8300143A1	01 January 1983 (01-01-1983)
		IT8121329D0	22 April 1981 (22-04-1981)
		IT1137547B	10 September 1986 (10-09-1986)
		JPS56169631A	26 December 1981 (26-12-1981)
		JPH0238573B2	31 August 1990 (31-08-1990)
		JPH02290988A	30 November 1990 (30-11-1990)
US2010051469A1	04 March 2010 (04-03-2010)	CA2676755A1	26 February 2010 (26-02-2010)
		FR2935398A1	05 March 2010 (05-03-2010)