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(54) **MINIMISING CARBON TRANSFER IN AN ELECTROLYTIC CELL**

MINIMIERUNG DES KOHLENSTOFFTRANSFERS IN EINER ELEKTROLYSEZELLE

MINIMISATION DU TRANSFERT DE CARBONE DANS UNE CELLULE ELECTROLYTIQUE

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- **CHEN G Z ET AL: "Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride" NATURE, NATURE PUBLISHING GROUP, LONDON, GB, vol. 407, 21 September 2000 (2000-09-21), pages 361-364, XP002968414 ISSN: 0028-0836**
- **SADOWAY D R ET AL: "Electrochemical deoxidation of yttrium-oxygen solid solutions" JOURNAL OF ALLOYS AND COMPOUNDS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 237, 15 April 1996 (1996-04-15), pages 150-154, XP004077077 ISSN: 0925-8388**
- **OKABE T H ET AL: "ELECTROCHEMICAL DEOXIDATION OF TITANIUM" METALLURGICAL TRANSACTIONS B. PROCESS METALLURGY, METALLURGICAL SOCIETY OF AIME. NEW YORK, US, vol. 24B, June 1993 (1993-06), pages 449-455, XP000381332**

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EP 1 483 431 B1

Description

[0001] The present invention relates to reduction of metal oxides in a solid state in an electrolytic cell.

[0002] The present invention was made during the course of an on-going research project on solid state reduction of titania (TiO_2) carried out by the applicant.

[0003] During the course of the research project the applicant carried out experimental work on the reduction of titania using an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten CaCl_2 -based electrolyte in the crucible, and a range of cathodes that included solid titania.

[0004] The CaCl_2 -based electrolyte was a commercially available source of CaCl_2 , namely calcium chloride dihydrate, that partially decomposed on heating and produced CaO .

[0005] The applicant operated the electrolytic cell at a potential above the decomposition potential of CaO and below the decomposition potential of CaCl_2 .

[0006] The applicant found that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen.

[0007] The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage. Nevertheless, whilst not wishing to be bound by the comments in this and the following paragraphs, the applicant offers the following comments by way of an outline of a possible cell mechanism.

[0008] The experimental work carried out by the applicant produced evidence of Ca metal dissolved in the electrolyte. The applicant believes that, at least during the early stages of operation of the cell, the Ca metal was the result of electrodeposition of Ca^{++} cations as Ca metal on electrically conductive sections of the cathode.

[0009] The experimental work was carried out using a CaCl_2 -based electrolyte at a cell potential below the decomposition potential of CaCl_2 . The applicant believes that the initial deposition of Ca metal on the cathode was due to the presence of Ca^{++} cations and O^- anions derived from CaO in the electrolyte. The decomposition potential of CaO is less than the decomposition potential of CaCl_2 . In this cell mechanism the-cell operation is dependent, at least during the early stages of cell operation, on decomposition of CaO , with Ca^{++} cations migrating to the cathode and depositing as Ca metal and O^- anions migrating to the anode and forming CO and/or CO_2 (in a situation in which the anode is a graphite anode).

[0010] The applicant believes that the Ca metal that deposited on electrically conductive sections of the cathode was deposited predominantly as a separate phase in the early stages of cell operation and thereafter dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of titania.

[0011] The applicant also believes that at later stages of the cell operation part of the Ca metal that deposited on the cathode was deposited directly on partially deox-

idised titanium and thereafter participated in chemical reduction of titanium.

[0012] The applicant also believes that the O^- anions, once extracted from the titania, migrated to the anode and reacted with anode carbon and produced CO and/or CO_2 (and in some instances CaO) and released electrons that facilitated electrolytic deposition of Ca metal on the cathode.

[0013] However, notwithstanding that the cell could electrochemically reduce titania to titanium with very low concentrations of oxygen, the applicant also found that there were relatively significant amounts of carbon transferred from the anode to the electrolyte and to the titanium produced at the cathode under a wide range of cell operating conditions.

[0014] Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was partially responsible for low energy efficiency of the cell. Both problems are significant barriers to commercialisation of electrolytic reduction technology.

[0015] The applicant carried out experimental work to identify the mechanism for carbon transfer and to determine how to minimise carbon transfer and/or to minimise the adverse effects of carbon transfer.

[0016] The experimental work indicated that the mechanism of carbon transfer is electrochemical rather than erosion and that one way of minimising carbon transfer and therefore contamination of titanium produced at the cathode by electrochemical reduction of titania at the cathode is to position a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms between the cathode and the anode and thereby prevent migration of carbon to the cathode.

[0017] Accordingly, the present invention provides an electrolytic cell for reducing a metal oxide in a solid state, which electrolytic cell includes an anode formed from carbon, a cathode formed at least in part from the metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

[0018] Preferably, the anode is formed from graphite.

[0019] The membrane may be formed from any suitable material.

[0020] Preferably, the membrane is formed from a solid electrolyte.

[0021] One suitable solid electrolyte tested by the applicant is yttria stabilised zirconia.

[0022] Preferably, the cathode also includes an electrical conductor.

[0023] The present invention also provides a method of reducing a metal oxide in a solid state using the above-described electrolytic cell.

[0024] Preferably, the method includes a step of operating the cell at a potential that is above a decomposition potential of at least one of the constituents of the electrolyte so that there are cations of a metal other than that of the metal oxide in the electrolyte.

[0025] In a situation in which the metal oxide is a titanium oxide, such as titania, it is preferred that the electrolyte be a CaCl_2 -based electrolyte that includes CaO as one of constituents.

[0026] In such a situation it is preferred that the cell potential be above the decomposition potential for CaO .

[0027] It is also preferred that the cell potential be below the decomposition potential for CaCl_2 .

[0028] It is preferred that the cell potential be less than or equal to 3.0 V.

[0029] It is preferred particularly that the cell potential be below 2.5 V.

[0030] It is preferred more particularly that the cell potential be below 2.0 V.

[0031] It is preferred that the cell potential be above 1.5 V.

[0032] The CaCl_2 -based electrolyte may be a commercially available source of CaCl_2 , such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO .

[0033] Alternatively, or in addition, the CaCl_2 -based electrolyte may include CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

[0034] The present invention is described further with reference to the following Example that relates to experimental work on the above-described electrolytic cell.

[0035] As indicated above, the cell included a high density graphite crucible that formed the anode of the cell, a pool of molten CaCl_2 electrolyte in the crucible, and a cathode that included solid titania. In the initial experimental set-up the solid titania was in the form of titania pellets connected to a lower end of a Kanthal or stainless steel electrically conductive wire.

[0036] As indicated above, experimental work on the cell identified carbon transfer as a significant issue in terms of contamination of cathode titanium and causing low energy efficiency of the cell. In addition, as indicated above, the experimental work established that carbon transfer was caused by an electrochemical reaction at the anode.

[0037] Thereafter the applicant carried out experimental work to investigate whether it was possible to prevent migration of carbon from the anode to the cathode.

[0038] One experiment investigated the impact of a solid ionic barrier on carbon migration.

[0039] The ionic barrier was in the form of a yttria stabilised zirconia membrane positioned between the anode and the cathode, thereby dividing the cell into an outer anode chamber and an inner cathode chamber.

[0040] Figure 1 is a schematic of the cell set-up for the experiment. With reference to the Figure, the cell included a graphite crucible 3 that formed the anode, a pool 19 of molten CaCl_2 electrolyte in the crucible, titania pellets 5 and an electrically conductive wire 7 that formed the cathode immersed in the electrolyte, and a yttria stabilised zirconia membrane 9 immersed in the electrolyte between the anode and the cathode. The cell was located in a resistance furnace 11 heated to a temperature to

maintain the electrolyte in a molten state. The experimental set-up also included gas monitoring, cleaning, and analysis equipment. The cell was operated at an applied potential of 3V for a period of 35 hours, during which time there was continuous monitoring of the off-gas from the furnace. At the conclusion of the experiment, the cell was cooled and the solidified electrolyte, the membrane, the anode and the cathode were analysed.

[0041] Figure 2 is a summary of the results of the experiment.

[0042] Figure 2 shows measured voltage, current, CO and CO_2 composition of the off-gas for the experiment.

[0043] Visual and analytical examination of the cathode and the cathode chamber indicated that there was no carbon on the cathode and in the cathode chamber.

[0044] In addition, the visual and analytical examination of the cathode indicated that titania was reduced to titanium. It follows from this finding that the yttria stabilised zirconia membrane did not restrict migration of O^- anions from the cathode to the anode.

[0045] Many modifications may be made to the present invention as described above without departing from the spirit and scope of the invention.

[0046] By way of example, whilst the above description of the invention focuses on reduction of titania, the invention is not so limited and extends to electrolytic reduction of other titanium oxides and to oxides of other metals and alloys.

[0047] Examples of other potentially important metals are aluminium, silicon, germanium, hafnium, magnesium, and molybdenum.

[0048] Furthermore, whilst the above description focuses on CaCl_2 -based electrolyte, the invention is not so limited and extends to any other suitable electrolytes.

[0049] Generally, suitable electrolytes will be salts and oxides that are soluble in salts. One example of a potentially suitable electrolyte is BaCl_2 .

Claims

1. An electrolytic cell for reducing a metal oxide in a solid state, which electrolytic cell includes an anode formed from carbon, a cathode formed at least in part from the metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.
2. The cell defined in claim 1 wherein the anode is formed from graphite.
3. The cell defined in claim 1 or claim 2 wherein the membrane is formed from a solid electrolyte.
4. The cell defined in claim 3 wherein the solid electrolyte is yttria stabilised zirconia.

5. The cell defined in any one of the preceding claims wherein the cathode also includes an electrical conductor.
6. A method of reducing a metal oxide in a solid state using an electrolytic cell that includes an anode formed from carbon, a cathode formed at least in part from the metal oxide, and a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode, which method includes operating the cell at a potential that electrolytically reduces the metal oxide.
7. The method defined in claim 6 includes operating the cell at a potential that is above a decomposition potential of at least one of the constituents of the electrolyte so that there are cations of a metal other than that of the metal oxide in the electrolyte.
8. The method defined in claim 6 or claim 7 wherein the metal oxide is a titanium oxide, such as titania and the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of constituents.
9. The method defined in claim 8 includes operating the cell at a potential that is above the decomposition potential for CaO .
10. The method defined in claim 8 or claim 9 includes operating the cell at a potential that is below the decomposition potential for CaCl_2 .
11. The method defined in any one of claims 6 to 10 wherein the cell potential is less than or equal to 3.0 V.
12. The method defined in claim 11 wherein the cell potential is below 2.5 V.
13. The method defined in claim 12 wherein the cell potential is below 2.0 V.
14. The method defined in any one of claims 6 to 13 wherein the cell potential is above 1.5 V.

Patentansprüche

1. Eine Elektrolysezelle zum Reduzieren eines Metalloxids in einen Festkörper, wobei die Elektrolysezelle eine aus Kohlenstoff gebildete Anode, eine wenigstens teilweise aus dem Metalloxid gebildete Kathode und eine Membran aufweist, die für Sauerstoff-Anionen durchlässig und für Kohlenstoff in ionischen und nicht-ionischen Formen undurchlässig zwischen der Kathode und Anode angeordnet ist,

um **dadurch** das Wandern von Kohlenstoff zu der Kathode zu verhindern.

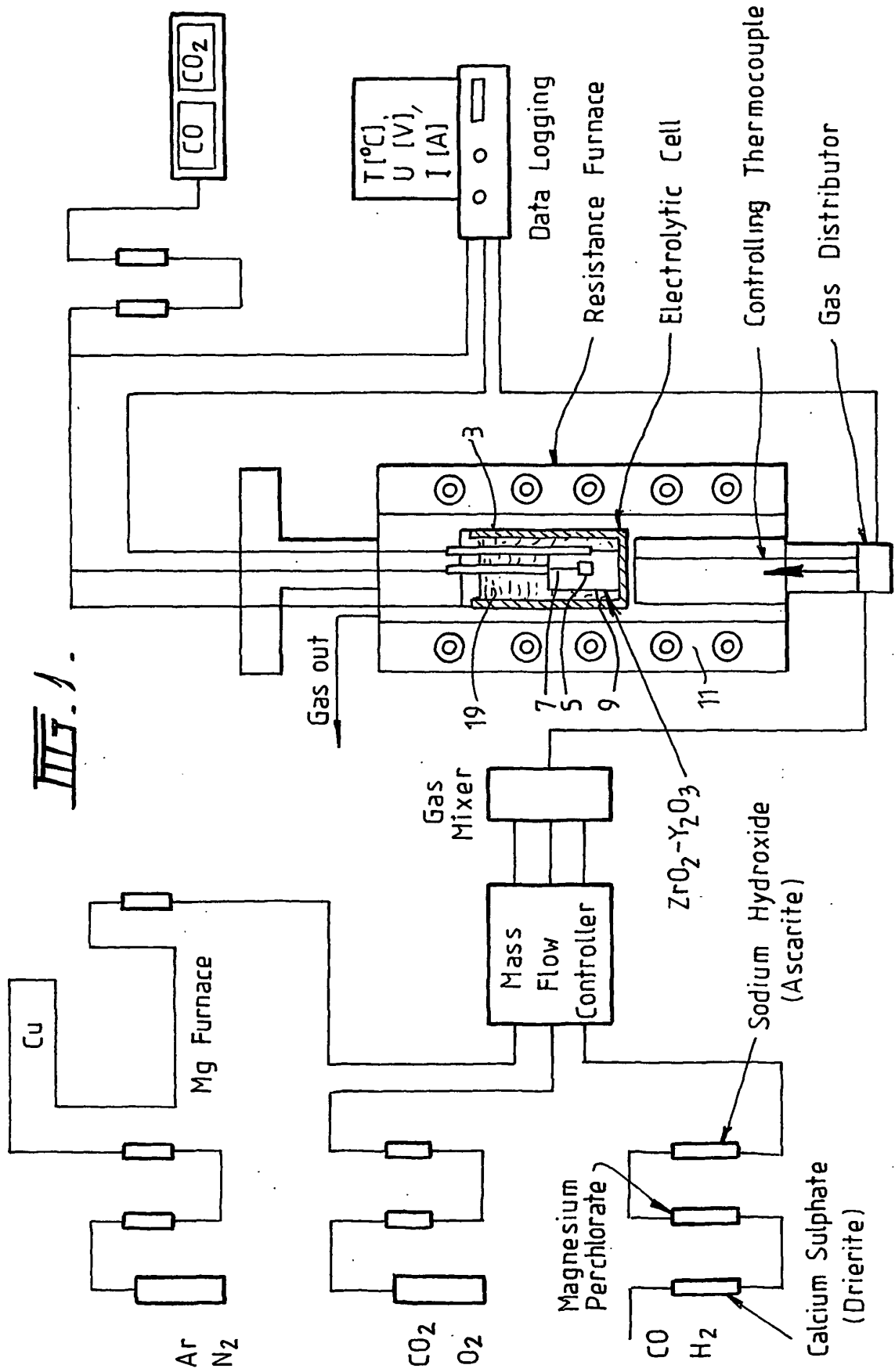
2. Die Zelle gemäß Anspruch 1, **dadurch gekennzeichnet, dass** die Anode aus Grafit gebildet ist.
3. Die Zelle gemäß Anspruch 1 oder Anspruch 2, **dadurch gekennzeichnet, dass** die Membran aus einem festen Elektrolyten gebildet ist.
4. Die Zelle gemäß Anspruch 3, **dadurch gekennzeichnet, dass** der feste Elektrolyt Yttrium-stabilisiertes Zirkoniumoxid ist.
5. Die Zelle gemäß einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, dass** die Kathode auch einen elektrischen Leiter aufweist.
6. Ein Verfahren zum Reduzieren eines Metalloxids in einen Festkörper unter Verwendung einer Elektrolysezelle, die eine aus Kohlenstoff gebildete Anode, eine wenigstens teilweise aus dem Metalloxid gebildete Kathode und eine Membran aufweist, die für Sauerstoff-Anionen durchlässig und für Kohlenstoff in ionischen und nicht-ionischen Formen undurchlässig zwischen der Kathode und der Anode angeordnet ist, um **dadurch** das Wandern von Kohlenstoff zu der Kathode zu verhindern, wobei das Verfahren das Betreiben der Zelle bei einem Potenzial beinhaltet, das das Metalloxid elektrolytisch reduziert.
7. Das Verfahren gemäß Anspruch 6 beinhaltet das Betreiben der Zelle bei einem Potenzial, das oberhalb eines Zerlegungspotenzials wenigstens eines der Bestandteile des Elektrolyten liegt, so dass Kationen eines Metalls vorhanden sind, die sich von denen des Metalloxids in dem Elektrolyten unterscheiden.
8. Das Verfahren gemäß Anspruch 6 oder Anspruch 7, **dadurch gekennzeichnet, dass** das Metalloxid ein Titanoxid, beispielsweise Titandioxid, ist und der Elektrolyt ein auf CaCl_2 basierender Elektrolyt ist, der CaO als einen seiner Bestandteile aufweist.
9. Das Verfahren gemäß Anspruch 8 beinhaltet das Betreiben der Zelle bei einem Potenzial, das oberhalb des Zerlegungspotenzials für CaO liegt.
10. Das Verfahren gemäß Anspruch 8 oder Anspruch 9 beinhaltet das Betreiben der Zelle bei einem Potenzial, das unterhalb des Zerlegungspotenzials für CaCl_2 liegt.
11. Das Verfahren gemäß einem der Ansprüche 6 bis 10, **dadurch gekennzeichnet, dass** das Zellpotential kleiner oder gleich 3.0 V ist.

12. Das Verfahren gemäß Anspruch 11, **dadurch gekennzeichnet, dass** das Zellpotenzial unter 2,5 V liegt.
13. Das Verfahren gemäß Anspruch 12, **dadurch gekennzeichnet, dass** das Zellpotenzial unter 2,0 V liegt.
14. Das Verfahren gemäß einem der Ansprüche 6 bis 13, **dadurch gekennzeichnet, dass** das Zellpotenzial oberhalb von 1,5 V liegt.

Revendications

1. Cellule électrolytique pour réduire un oxyde de métal à l'état solide, ladite cellule électrolytique comprenant une anode formée de carbone, une cathode Formée au moins en partie de l'oxyde de métal, et une membrane qui est perméable aux anions d'oxygène et est imperméable au carbone sous des formes ionique et non ionique positionnée entre la cathode et l'anode de manière à prévenir la migration de carbone vers la cathode. 20
2. Cellule définie dans la revendication 1 dans laquelle l'anode est formée de graphite. 25
3. Cellule définie dans la revendication 1 ou la revendication 2 dans laquelle la membrane est formée d'un électrolyte solide. 30
4. Cellule définie dans la revendication 3 dans laquelle l'électrolyte solide est de la zircone stabilisée par de l'oxyde d'yttrium. 35
5. Cellule définie dans l'une quelconque des revendications précédentes dans laquelle la cathode comprend en outre un conducteur électrique. 40
6. Procédé de réduction d'un oxyde de métal à l'état solide en utilisant une cellule électrolytique qui comprend une anode formée de carbone, une cathode formée au moins en partie de l'oxyde de métal, et une membrane qui est perméable aux anions d'oxygène et est imperméable au carbone sous des formes ionique et non ionique positionnée entre la cathode et l'anode de manière à prévenir la migration de carbone vers la cathode, ledit procédé comprenant le fonctionnement de la cellule à un potentiel qui réduit électrolytiquement l'oxyde de métal. 45 50
7. Procédé défini dans la revendication 6, qui comprend le fonctionnement de la cellule à un potentiel qui est supérieur à un potentiel de décomposition d'au moins un des constituants de l'électrolyte de sorte qu'il y ait des cations d'un métal autre que celui de l'oxyde de métal dans l'électrolyte. 55

8. Procédé défini dans la revendication 6 ou la revendication 7 dans lequel l'oxyde de métal est un oxyde de titane, tel que l'oxyde de titane et l'électrolyte est un électrolyte à base de CaCl_2 qui comprend CaO en tant qu'un des constituants. 5
9. Procédé défini dans la revendication 8, qui comprend le fonctionnement de la cellule à un potentiel qui est supérieur au potentiel de décomposition pour CaO . 10
10. Procédé défini dans la revendication 8 ou la revendication 9, qui comprend le fonctionnement de la cellule à un potentiel qui est au-dessous du potentiel de décomposition pour CaCl_2 . 15
11. Procédé défini dans l'une quelconque des revendications 6 à 10 dans lequel le potentiel de cellule est inférieur ou égal à 3,0 V. 20
12. Procédé défini dans la revendication 11 dans lequel le potentiel de cellule est inférieur à 2,5 V. 25
13. Procédé défini dans la revendication 12 dans lequel le potentiel de cellule est inférieur à 2,0 V. 30
14. Procédé défini dans l'une quelconque des revendications 6 à 13 dans lequel le potentiel de cellule est supérieur à 1,5 V. 35



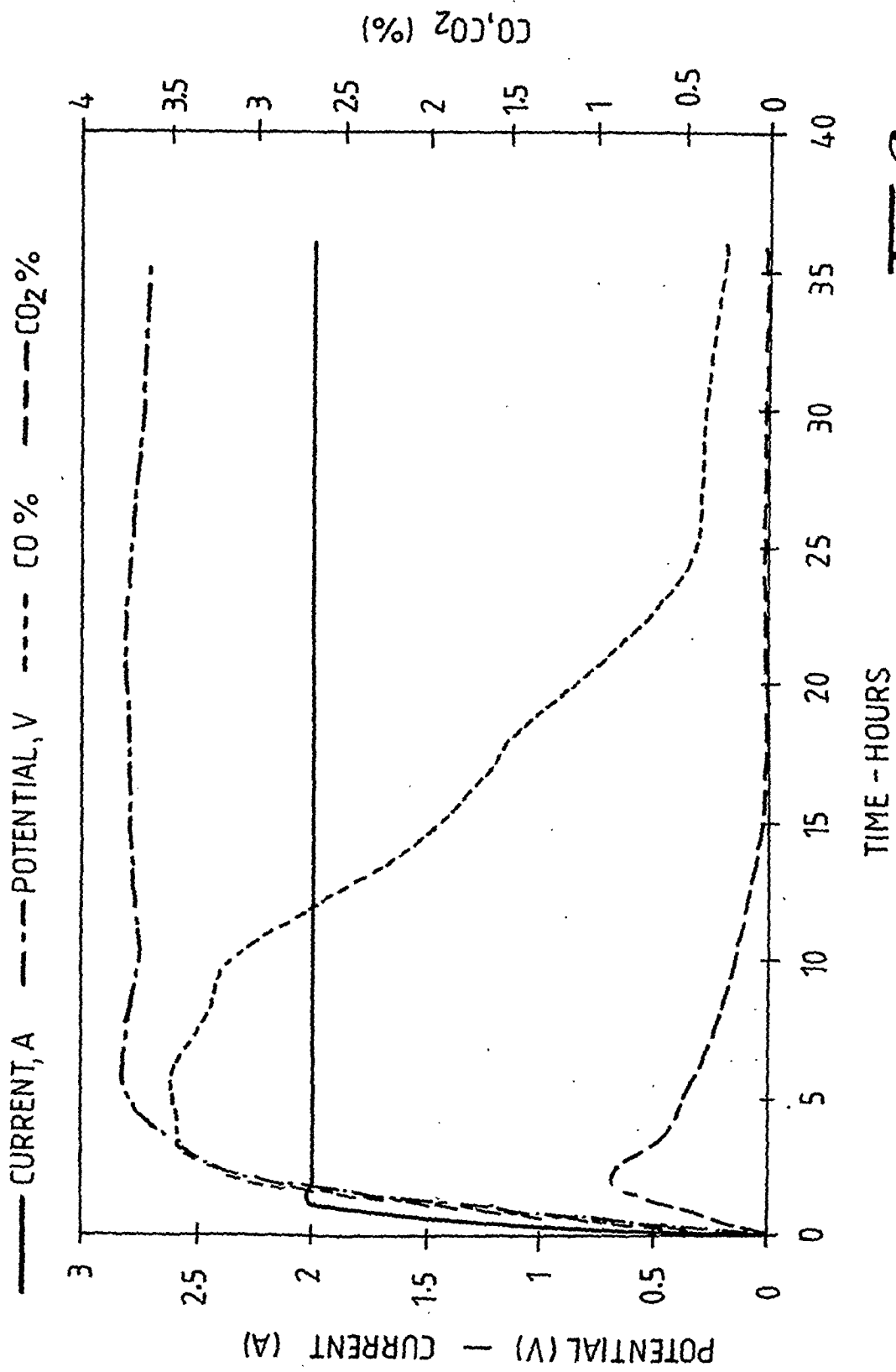


Fig. 2.