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(12) # EUROPEAN PATENT APPLICATION

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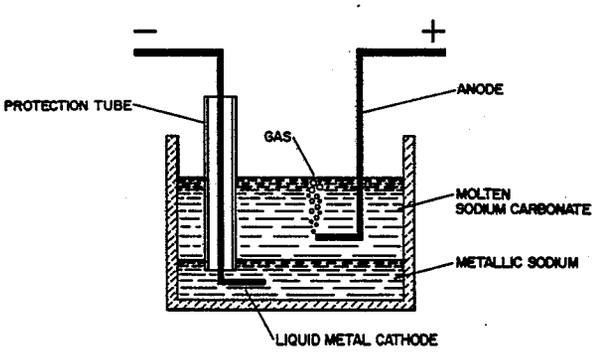
(54) **Production of metallic sodium from sodium carbonate by fused salt electrolysis.**

(57) A process for producing metallic sodium from molten sodium carbonate in an electrolytic cell comprising:

(a) placing molten sodium carbonate in an electrolytic cell containing a liquid metal cathode and an anode;

(b) electrolyzing the molten sodium carbonate so that the sodium ion is reduced into the liquid metal cathode as metallic sodium and the carbonate ion reacts to form a gas at the anode; and,

(c) recovering the metallic sodium from the liquid metal cathode.



EP 0 109 164 A1

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PRODUCTION OF METALLIC SODIUM FROM SODIUM CARBONATE BY FUSED SALT ELECTROLYSIS

This invention relates to the production of sodium hydroxide from sodium carbonate by fused salt electrolysis, and, more particularly, to the electrolysis of molten sodium carbonate to reduce sodium into a molten metal cathode.

Sodium hydroxide, commonly referred to as caustic soda, is commercially produced by electrolysis of sodium chloride solutions to yield aqueous sodium hydroxide. Caustic soda produced in a diaphram cell typically contains less than fifteen precent (15%) by weight sodium hydroxide, and caustic soda produced in a membrane cell contains less than forty percent (40%) by weight sodium hydroxide. Commercial grades of caustic soda solution contain from fifty to seventy-five percent (50 to 75%) sodium hydroxide. Caustic soda is also marketed in several solid forms.

Sodium hydroxide is concentrated for marketing by evaporating the required amount of water from the solutions obtained from electrolysis. Water removal is

accomplished by use of either single-effect or multiple-effect evaporators, the choice depending upon the desired sodium hydroxide concentration. This is a relatively expensive process because of the large quantity of heat required to remove water from the caustic liquor. Elimination of the evaporation step would constitute a significant improvement in caustic production technology.

In addition to being expensive, the techniques currently used for caustic soda production yield a product that contains a considerable amount of the sodium chloride. The presence of this impurity is undesirable for some users of sodium hydroxide, such as manufacturers of synthetic fibers. Therefore, in some instances, sodium chloride must be removed from the sodium hydroxide before the caustic soda can be used commercially. Sodium chloride removal increases the cost of producing sodium hydroxide, and elimination of this step would also constitute a significant improvement in caustic soda production technology.

The present invention can be used to produce metallic sodium. The present invention can also be used to produce caustic soda as a relatively dry, molten salt,

and water removal by evaporation does not have to be carried out. Furthermore, since sodium chloride is not used as a reactant in the production of caustic soda, this material would not be present in the sodium hydroxide product. Finally, the raw material for metallic sodium production, sodium carbonate, is readily available in large quantities as a relatively pure material which can be obtained at a reasonable price.

In addition to metallic sodium and caustic soda, other valuable by-products can be obtained in this process. For example, hydrogen gas is produced when sodium hydroxide is generated from elemental sodium, and the electrolytic cell can be operated in such a manner that carbon monoxide is also obtained. Both gases can be used as fuels or as feedstocks in the chemical industry.

Another important feature of this invention is that it does not produce by-products which are difficult to market. In contrast, in the production of caustic soda by aqueous electrolysis, chlorine is produced concurrently with sodium hydroxide. Because the chlorine market has matured in recent years, this product can be difficult to dispose of. Under these

conditions, a sluggish chlorine market has a negative impact on the economics of sodium hydroxide production.

According to the present invention there is provided a process for producing metallic sodium from molten sodium carbonate in an electrolytic cell which comprises placing molten sodium carbonate (e.g. soda ash) in an electrolytic cell containing a liquid metal (e.g., lead, tin, silver or an alloy) cathode and an anode (consumable or non-consumable), electrolyzing the molten sodium carbonate so that the sodium ion is reduced into the liquid metal cathode as metallic sodium and the carbonate ion reacts at the anode to form a gas (either carbon monoxide or carbon dioxide and oxygen, depending on whether the anode is consumable or non-consumable), and recovering the metallic sodium from the liquid metal cathode.

The single Figure is a schematic diagram illustrating an apparatus useful in carrying out the invention.

Previous work on molten carbonate melts has indicated that carbonate ion can be removed from sodium carbonate by oxidation of this species to carbon dioxide and oxygen at an insoluble anode in a molten salt electrolytic cell.

Selman, J.R. and Maru, H.C., "Physical Chemistry and Electrochemistry of Alkali Carbonate Melts, with special reference to the molten carbonate fuel cell", Advances in Molten Salt Chemistry, Mamantov, G. and Braunstein, J., editors, Plenum Press, N.Y., N.Y., vol. 4, pp. 159-389 (1981).

The present invention is a process for producing metallic sodium from molten sodium carbonate in an electrolytic call containing a molten metal cathode and an anode.

The electrolyte for the electrolytic cell consists of molten (fused) sodium carbonate. The electrolyte may also contain other salts, such as barium carbonate or lithium carbonate, which are added for the purpose of depressing the melting point of the sodium carbonate. In general, if the salt or salts added to the electrolyte contain cations other than sodium, those cations must be sufficiently difficult to reduce so that they would not be co-reduced to a significant extent with sodium. If the salts or salts contain anions other than carbonate, those anions must be sufficiently difficult to oxidize so that the carbonate ion reacts preferentially at the anode.

Insofar as the electrochemical stability of carbonate melts is concerned, it is well known that carbonate ion can be reduced to elemental carbon at sufficiently high potentials. Selman, J.R. and Maru, H.C., ibid. The electrolytic cell potential of the present invention must be low enough so that the foregoing reaction does not occur at an appreciable rate on the surface of the material which is chosen for the cathode.

During electrolysis of the molten sodium carbonate, sodium is reduced into the cathode as follows:

$$2Na^{+}\ (l) + 2e^{-} \rightarrow 2Na\ (alloy).$$

The liquid metal cathode must be an electrical conductor in which sodium exhibits appreciable solubility (i.e., greater than about 0.1 percent by weight). A pure metal such as lead, tin or silver, or an alloy of these metals which is liquid at the operating temperature of the cell would be useful for this purpose.

Another important consideration in the selection of the cathode material is that it must be capable of passing through the sodium removal step without excessive

degradation. In the case of caustic formation by the reaction of steam with sodium dissolved in the cathode, the metal in the cathode must not be oxidized extensively by steam under the conditions involved. Alternatively, if the sodium is removed from the cathode by vacuum distillation, the metal or alloy used as the cathode must exhibit a significantly lower vapor pressure than the sodium.

The anode can be either a consumable or non-consumable material. A consumable anode reacts electrochemically with the molten sodium carbonate and could be made of carbon or graphite. A non-consumable anode would be constructed of a material (e.g. a cermet or a metal such as nickel or Inconel 625) which exhibits low reactivity with the molten sodium carbonate. See, for example: U.S. 4,187,155, and United Kingdom Patent Nos. 2,069,529 and 2,078,259. Previous investigations (Selman J.R. and Maru, H.C., ibid.) have demonstrated that the carbonate ion is oxidized to carbon dioxide and oxygen at the anode as follows :

$$CO_3^{=}(1) \rightarrow CO_2(g) + 1/2\ O_2(g) + 2e^{-}.$$

When a consumable carbon anode is used, carbon monoxide is generated as follows :

$$2C_{(s)} + CO_3^{=}\ (l) \rightarrow 3CO_{(g)} + 2e^{-}.$$

The metallic sodium can be recovered from the metal cathode by a number of well-known techniques. The metallic sodium can be oxidized by contacting the molten cathode material with water dissolved in sodium hydroxide. Under the foregoing conditions, sodium hydroxide formation occurs as follows :

$$xNa_{(alloy)} + NaOH.xH_2O_{(l)} \rightarrow (1+x)\ NaOH_{(l)} + x/2\ H_{2(g)}.$$

Caustic soda can also be produced by contacting the sodium alloy directly with steam as follows :

$$Na_{(alloy)} + H_2O_{(g)} \rightarrow NaOH_{(l)} + 1/2\ H_2(g).$$

The metallic sodium can also be removed from the metal cathode by vacuum distillation. The sodium vapor obtained by this technique can be condensed directly to metallic sodium. Altetnatively, the sodium metal can be reacted with steam in either the solid or gas phase to produce sodium hydroxide. See, for example: United Kingdom Patent Nos. 1,009,113 and 1,013,004 (1965); Ito, Y. and Yoshizawa, S., "Some New Molten Salt Electrolytic Processes", Advances in Molten Salt Chemistry, Mamantov,

G., and Braunstein, J., editors, Plenum Press, N.Y., N.Y., vol 4, pp. 403-404 (1981); Applied Electrochemistry and Welding, Part I, Burgess, G.W., American Technical Society, Chicago, IL, pp. 42-43 (1914); The Principles of Applied Electrochemistry, 2nd edition, Allmand, A.J. and Ellingham, H. J. T., Longmans, Green, and Co., N.Y., pp. 582-530 (1924); and, Kuhn, A. T., "The Chlor-Alkali Industry", in Industrial Electrochemical Processes, Kuhn, A.T., editor Elsevier Publishing Co., N.Y., N.Y., pp. 103-104 (1971).

If sodium hydroxide is produced by the foregoing methods, any contained metallic impurities can be eliminated by the addition of suitable oxidizing agents, reducing agents or fluxes. The elimination of iron from fused caustic soda is a well known technique. Faith, Keys, and Clark's Industrial Chemicals, 4th edition, Lowenheim, F.A. and Moran, M. K., editors, John Wiley & Sons, N.Y., N.Y. p. 741 (1975).

The process of the present invention is further illustrated by the following non-limiting examples.

EXAMPLE ONE

Approximately 200 gm of reagent-grade sodium carbonate was electrolyzed in a 250 ml (5.7 cm diameter)

alumina crucible. An Inconel 625 anode was used, and sodium was collected in a 150 gm liquid lead cathode. The temperature was maintained at 960°C which is well above the melting point of sodium carbonate, 856°C.

Electrolysis was conducted at a cell potential of 1.35 volts and a current of 2.0 amps for 3.0 hr (this current corresponds to a cathodic current density of 7.8 amps/dm^2). The sodium content of the lead cathode was 3.4 percent by weight which is also the theoretical sodium content of the cathode calculated from Faraday's law assuming a current efficiency of 100 percent. The decomposition potential of the cell was 0.95 volts, and the cell resistance was 0.20 ohm.

EXAMPLE TWO

The Inconel anode of EXAMPLE ONE was replaced with a 0.64 cm-diameter carbon rod. The lower end was located approximately 1.5 cm from the top of the liquid lead cathode. The reagents and amounts used were the same as in EXAMPLE ONE.

Electrolysis was carried out for 3.0 hr. The potential was 1.8 volts, and the current was 1.3 amps. The theoretical sodium content of the lead in the cell

is 2.2 percent by weight. The measured sodium content was also 2.2 percent.

The decomposition potential and cell resistance in this instance were 0.2 volts and 1.3 ohms, respectively. The decomposition potential in this case is significantly lower than that in the case where the non-consumable electrode was involved. However, the operating potential of the cell with the carbon anode was relatively high because of the high resistance of the electrolytic cell. The high resistance is due to the unfavourable shape of the anode used in this experiment.

EXAMPLE THREE

The sodium present in a cathode was removed by oxidation with steam. The cathode was prepared by the method described in EXAMPLE ONE and contained 1.5 percent sodium by weight. The mass of alloy involved was 43.5 gm. The alloy was combined with 43.0 gm of sodium hydroxide in a nickel crucible, and this material was heated to 425°C in a muffle furnace. The molten sodium hydroxide, present on top of the molten sodium-lead alloy, was then contacted with steam at atmospheric

pressure for two hours. The crucible was removed from the furnace and cooled to ambient temperature. The sodium content of the lead was reduced to 0.005 percent by weight in this experiment indicating that steam oxidized the sodium present in the alloy.

CLAIMS:

1. A process for producing metallic sodium from molten sodium carbonate in an electrolytic cell comprising:

(a) placing molten sodium carbonate in an electrolytic cell containing a liquid metal cathode and an anode;

(b) electrolyzing the molten sodium carbonate so that the sodium ion is reduced into the liquid metal cathode as metallic sodium and the carbonate ion reacts to form a gas at the anode; and,

(c) recovering the metallic sodium from the liquid metal cathode.

2. A process as claimed in Claim 1 wherein the liquid metal cathode is a metal alloy selected from lead, tin or silver.

3. A process as claimed in Claim 1 wherein the liquid metal cathode is lead.

4. A process as claimed in Claim 1 wherein the liquid metal cathode is capable of dissolving at least 0.1 percent by weight of metallic sodium.

5. A process as claimed in any one of the preceding Claims wherein the melting point of the molten sodium carbonate is depressed by the addition of at least one additional salt.

6. A process as claimed in any one of the preceding Claims wherein the electrolytic cell contains a liquid metal cathode and an anode that are electrically isolated from each other.

7. A process as claimed in any one of the preceding claims wherein the anode is a consumable anode that reacts electrochemically with the molten sodium carbonate.

8. A process as claimed in Claim 7 wherein the consumable anode is carbon or graphite.

9. A process as claimed in Claim 7 or Claim 8 wherein the anode is a consumable anode that electrochemically reacts with the carbonate ion and produces carbon monoxide gas.

10. A process as claimed in any one of Claims 1 to 6 wherein the anode is a non-consumable anode which is insoluble in or which exhibits low chemical reactivity

to the molten sodium carbonate.

11. A process as claimed in Claim 10, wherein the non-consumable anode is a metal, an alloy or a cermet.

12. A process as claimed in Claim 10 or Claim 11, wherein the anode is a non-consumable anode which is insoluble or which exhibits low chemical reactivity to the carbonate ion and produces carbon dioxide and oxygen gas.

13. A process for producing metallic sodium from molten sodium carbonate in an electrolytic cell comprising:

(a) placing molten sodium carbonate in an electrolytic cell containing a liquid lead cathode and an consumable carbon or graphite anode;

(b) electrolyzing the molten sodium carbonate so that the sodium ion is reduced into the liquid lead cathode as metallic sodium and the carbonate ion reacts electrochemically to form carbon monoxide gas at the consumable anode; and,

(c) recovering metallic sodium from the liquid lead cathode.

14. A process for producing metallic sodium from molten sodium carbonate in an electrolytic cell comprising:

(a) placing molten sodium carbonate in an electrolytic cell containing a liquid lead cathode and a non-consumable anode which is a metal or an alloy which is insoluble in or which exhibits low chemical reactivity to the molten sodium carbonate;

(b) electrolyzing the molten sodium carbonate so that the sodium ion is reduced into the liquid lead cathode as metallic sodium and the carbonate ion is oxidized to carbon dioxide and oxygen gas at the non-consumable anode; and,

(c) recovering the metallic sodium from the liquid lead cathode.

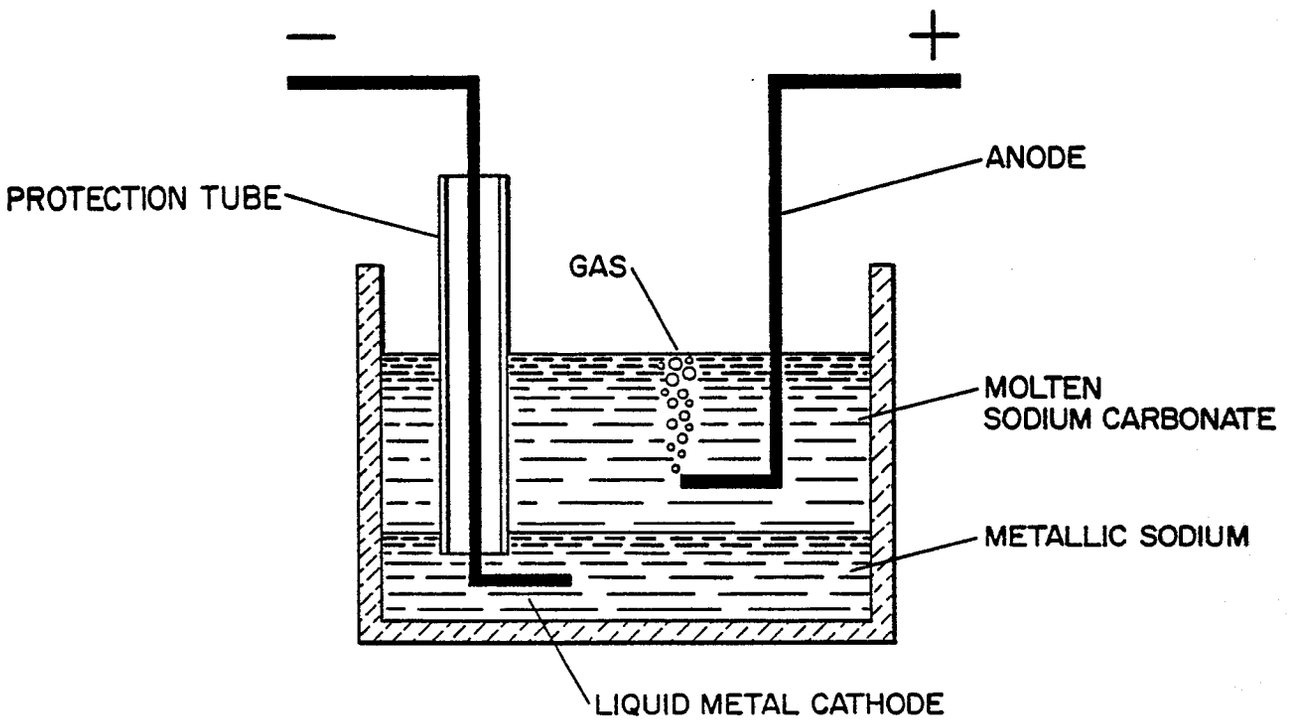
15. A process as claimed in any one of the preceding claims wherein the metallic sodium is recovered

from the liquid metal cathode by oxidizing the metallic sodium to sodium hydroxide.

16. A process as claimed in claim 15, wherein the metallic sodium is oxidized to sodium hydroxide by contacting the liquid metal cathode with steam or with water dissolved in sodium hyroxide.

17. A process as claimed in any one of Claims 1 to 14, wherein the metallic sodium is recovered from the liquid metal cathode by vacuum distillation.

18. A process as claimed in any one of the preceding claims wherein the cell potential is maintained at a sufficiently low value that carbonate ion is not reduced to carbon at the cathode.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PROTECTION TUBE
ANODE
GAS
MOLTEN
SODIUM CARBONATE
METALLIC SODIUM
LIQUID METAL CATHODE

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Application number

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

EP 83305984.3

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X	DR. ING. GEORG EGER "Handbuch der technischen Elektrochemie", 2nd edition, vol. 3, 1955, AKADEMISCHE VERLAGSGESELLSCHAFT, Leipzig, pages 494-496 * Page 495, line 23 - page 496, line 4; page 494, line 29 - page 495, line 12 *	1-9,13	C 25 C 3/02 C 25 B 1/16 C 25 C 3/36
X	DE - C - 269 712 (CHEMISCHE FABRIK VON HEYDEN) * Claims *	1-9,13	
A	DE - B - 1 200 553 (CHLORMETALS INCORPORATED) * Claims *	1,17	
A,D	US - A - 4 187 155 (DE NORA) * Claim 1; column 7, lines 22-28 *	1,10-12,14	C 25 C 3/00 C 25 B 1/00
A,D	GB - A 2 069 529 (DIAMOND SHAMROCK) * Abstract *	1,10-12,14	
A,D	GB - A - 2 078 259 (DIAMOND CHAMROCK) * Abstract *	1,10-12,14	

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	10-02-1984	ONDER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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Application number

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EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A,D	A.T. KUHN "Industrial electrochemical processes", 1971 ELSEVIER PUBLISHING COMPANY, Amsterdam-London-New York pages 103,104 --	
A,D	GB - A - 1 013 004 (PHILBLACK LIMITED) * Page 1, lines 61-81 * --	1-3,17
A,D	GB - A 1 009 113 (PHILBLACK LTD) * Page 1, lines 55-64 * --	1-3,17
A	ULLMANNS ENCYKLOPÄDIE DER TECHNISCHEN CHEMIE, 4th edition, vol. 17, 1979, VERLAG CHEMIE; Weinheim, pages 146-151 * Page 151, column 1, line 6 - column 2, line 11 * ----	1-3,17

CLASSIFICATION OF THE APPLICATION (Int. Cl.)

TECHNICAL FIELDS SEARCHED (Int. Cl.³)