United States Patent Office 3,558,452 Patented Jan. 26, 1971

3,558,452

ELECTROLYSIS CELL CURRENT EFFICIENCY WITH SOLID OXIDIZING AGENTS

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No Drawing. Filed Aug. 29, 1967, Ser. No. 663,978
Int. Cl. C22d 3/06
U.S. Cl. 204—68 5 Claims

ABSTRACT OF THE DISCLOSURE

A fused salt electrolysis cell bath is treated with a solid oxidizing agent, such as sodium chlorate, to improve current efficiency of the fused salt electrolysis cell.

BACKGROUND OF THE INVENTION

In the operation of alkali metal fused salt cells, a fused salt mixture is electrolyzed to produce alkali metal at the cathode and halogen gas at the anode. The anode is conventionally a cylindrical graphite or carbon anode surrounded by an annular metallic cathode. A porous diaphragm is provided in the anode-cathode annular space to assist in the separation of the products of electrolysis.

Metallic sodium is produced generally from a molten mixture of the chlorides of calcium and sodium in electrolytic cells of the Downs type (U.S. Pat. No. 1,501,756) or in modifications of these cells. These cells are characterized by having one or more bottom mounted vertically aligned cylindrical graphite anodes each of which is projected upwardly into a separate cylindrical opening within a unitary cathode assembly. The sodium is produced at the cathode surfaces and the chlorine at the anode surfaces. Due to the difference in densities between these products, and that of the molten bath, the products rise to the surface of the bath and are then collected.

The aforementioned cells of prior practice have given good results, but unfortunately cells of this type rarely ever achieve current efficiencies greater than 80–85% (cf. "Sodium," A.C.S. monograph 133, p. 31, M Sittig, Reinhold Publishing Corporation, 1956). The current efficiency of these cells increases as the operating temperature is reduced. However, crust formation or any bath solidification interferes seriously with economical operation so that satisfactory results can be secured only when the baths are maintained at temperatures above the melting point.

Alternate salt mixtures for use as electrolyte baths have been described in the prior art and, although some of these mixtures have shown improved current efficiencies, this advantage has been offset by high material costs or production of sodium whose quality does not meet present high purity requirements and is not readily purified. Grabau, U.S. Pat. 464,097 (Dec. 1, 1891), disclosed a ternary mixture consisting of sodium chloride, another alkali metal halide and alkaline earth halides. This mixture was stated to have a current efficiency of 95% but yielded sodium containing another alkali metal as an impurity. With the preferred other alkali metal salt, potassium chloride, the sodium was stated to contain 3% potassium. Seward et al., U.S. Pat. 841,724 (Jan. 22, 1907), described a mixed salt bath containing sodium chloride, sodium fluoride and an alkali earth chloride. This bath gave sodium free of other alkali metals but its current efficiency was not disclosed. However, neither of these baths appeared to have found commercial acceptance. More recently, Cathcart et al., U.S. Pat. 2,850,442, have devised a mixture consisting of sodium chloride, barium chloride and strontium chloride.

This electrolyte yields sodium containing less than 0.1% impurities and shows current efficiencies of 85–89% which can be raised to 90–95% by addition of 1–2% sodium fluoride. However, this mixture is expensive because of its strontium compound in that the original investment and maintenance are of a relatively high order. Wood, U.S. Pat. 2,876,181, obtains high current efficiency with a lithium chloride-sodium chloride electrolyte but the sodium is stated to contain 4% lithium under exemplary operating conditions and a lithium electrolyte is expensive.

It is aapparent that a tremendous effort has been exerted over the past years to achieve greater current efficiency. In view of the magnitude of the sodium industry coupled with the importance of sodium as a chemical intermediate and the rising power costs, the development of a relatively low cost, readily operable bath of improved current efficiency is of outstanding industrial importance.

SUMMARY OF THE INVENTION

This invention relates to a novel process for improving the current efficiency of an alkali metal fused salt electrolysis cell comprising treating the molten cell bath with a solid oxidizing agent.

It has been discovered that this oxidation treatment increases the current efficiency of a fused salt electrolysis cell in a cheap, efficient and commercially applicable manner.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novel process of this invention for improving the current efficiency of an alkali metal salt electrolysis cell comprises treating the molten salt bath of the cell with a solid oxidizing agent selected from the group consisting of chlorates, chlorites, nitrates, nitrites, hypochlorites and mixtures thereof. The treatment consists essentially of adding a given quantity of oxidant to a molten cell bath.

In normal commercial operations, a sodium cell may be operated for a period of several months before the current efficiency decreases significantly. At this point a solid oxidant such as sodium chlorate may be added to the operating cell bath. In the alternative, a portion or all of the cell bath may be removed from the electrolysis cell and placed in a separate container. The cell bath in the container is maintained in a molten state and the solid oxidizing agent is then added to this molten cell bath. In either situation, the oxidizing agent decomposes rapidly at the high temperature of the cell bath and the cell bath current efficiency is increased within a short period of time.

The oxidizing agents may be selected from any of the well-known solid oxidizing agents. The preferred oxidizing agents are selected from the group consisting of chlorates, chlorites, nitrates, nitrites, hypochlorites and mixtures thereof, and these include sodium chlorate, sodium chlorite, sodium hypochlorite, sodium nitrite, sodium nitrate and potassium chlorate. The preferred oxidizing agent is sodium chlorate.

The amount of oxidizing agent added to the cell bath may vary according to the condition of the cell bath, the desired degree of oxidation and speed of oxidation. Generally, the oxidizing agent can comprise from about 0.01–10% by weight of the cell bath. The preferred range of 0.5–5% by weight has been found to produce the desired degree of oxidation and improved current efficiency. Additionally, the oxidizing agent may be added to the cell bath in one lump portion or in incremental portions. For example, a total of 15 pounds sodium chlorate may be added in three 5 pound additions to the cell bath.

The reasons for a current efficiency recovery from the oxidation treatment are not fully understood. While this

invention is not intended to be based upon any particular theory, it is speculated that poor current efficiency may be due to the presence of small particulate electronic conductors in the bath which serve to transfer metallic sodium to the anolyte by a concentration cell mechanism. At the anolyte the sodium is destroyed by the direct combination with chlorine. The addition of an oxidizing agent serves to change the particulate electronic conductor to an inert oxide. Thus, current efficiency loss by a concentration cell mechanism cannot take place.

The following example is illustrative of the practice of this invention. The electrolyte composition is reported as percent by weight.

EXAMPLE

A substantially conventional Downs cell was charged with an electrolyte containing about 26% sodium chloride, 24% calcium chloride and the remainder barium chloride. This bath had a melting point of about 560° C. and was operated with a direct current for several months at an average of about 605° C. This cell was equipped with a mesh diaphragm between anode and cathode and the spacing between these electrodes was 1.5 inches. Electrolysis was carried out at about 38,000 amps. and at a cell voltage of about 7 volts.

A portion of the cell bath was transferred to a laboratory compartmental cell where the current efficiency was found to be 73%. An identical portion of the above described Downs cell bath was transferred to a beaker; the cell bath was maintained in the molten state. Then 0.5% by weight sodium chlorate was added to the molten cell bath. After a few minutes the cell bath was transferred to the laboratory compartmental cell where the current efficiency was measured and found to be 87%. This 14% increase in current efficiency is attributed to the treatment with the oxidizing agent.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

I claim:

1. In a process for producing alkali metal by electrolyzing a fused alkali metal salt bath and recovering said alkali metal which is liberated at the cathode, the improvement comprising regenerating a used alkali metal fused salt bath by adding a solid oxidizing agent to said bath.

2. In a process for producing alkali metal by electrolyzing a fused alkali metal salt bath and recovering said alkali metal which is liberated at the cathode, the improvement comprising regenerating a used alkali metal fused salt bath by adding 0.01–10% by weight of a solid oxidizing agent selected from the group consisting of chlorates, chlorites, nitrates, nitrites, hypochlorites and mixtures thereof to said bath.

3. A process in accordance with claim 2 wherein the oxidizing agent is selected from the group consisting of sodium chlorate, sodium nitrate, sodium chlorite, sodium hypochlorite, potassium chlorate, and mixtures thereof.

4. A process in accordance with claim 2 wherein the oxidizing agent is sodium chlorate.

5. A process in accordance with claim 2 wherein the oxidizing agent is added in incremental portions.

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