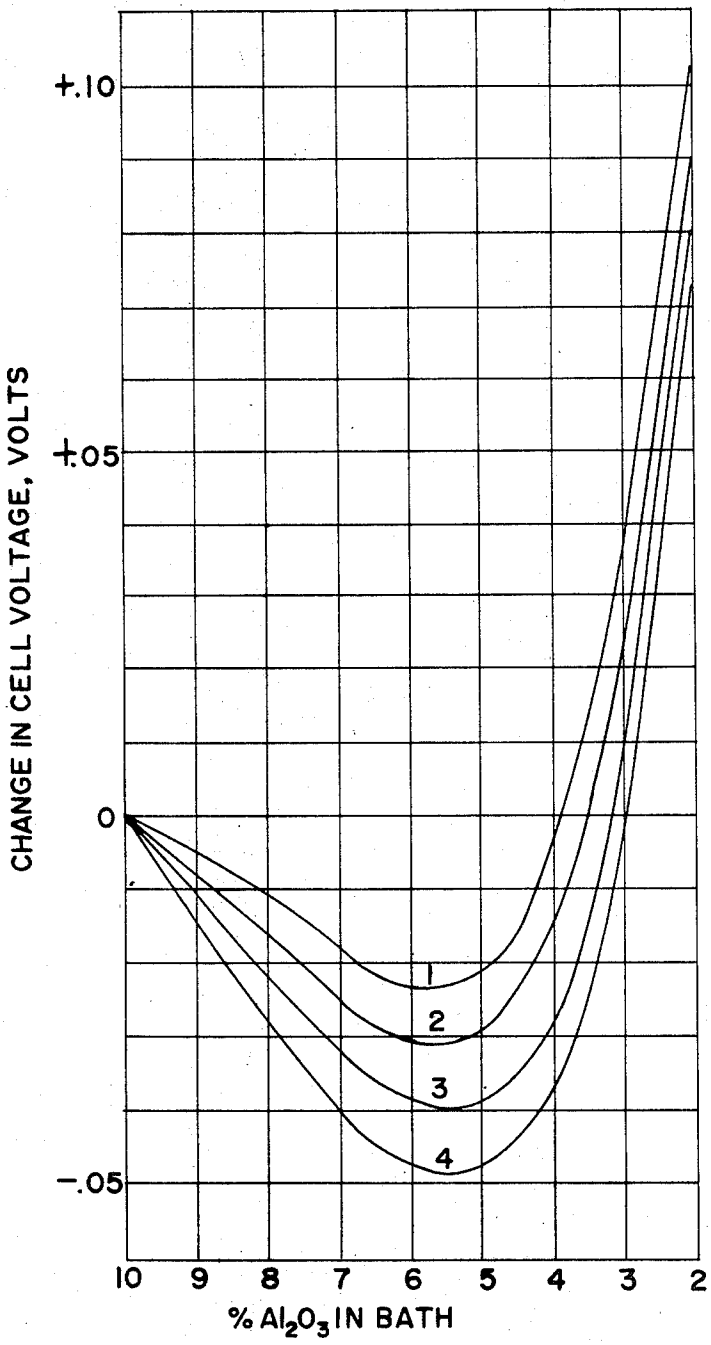
May 11, 1971 R. A. LEWIS 3,578,569

ANODE POLARIZATION DETECTOR

Filed Sept. 18, 1967 4 Sheets-Sheet 1



1. ANODE C.D. = 1.2 A/sq. cm.
2. ANODE C.D. = 1.0 A/sq. cm.
3. ANODE C.D. = 0.8 A/sq. cm.
4. ANODE C.D. = 0.6 A/sq. c.m.

Fig-1

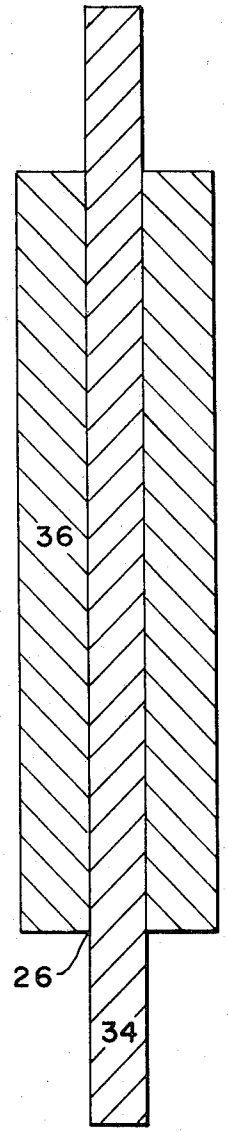


Fig-6

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ANODE POLARIZATION DETECTOR

Filed Sept. 18, 1967 4 Sheets-Sheet 2

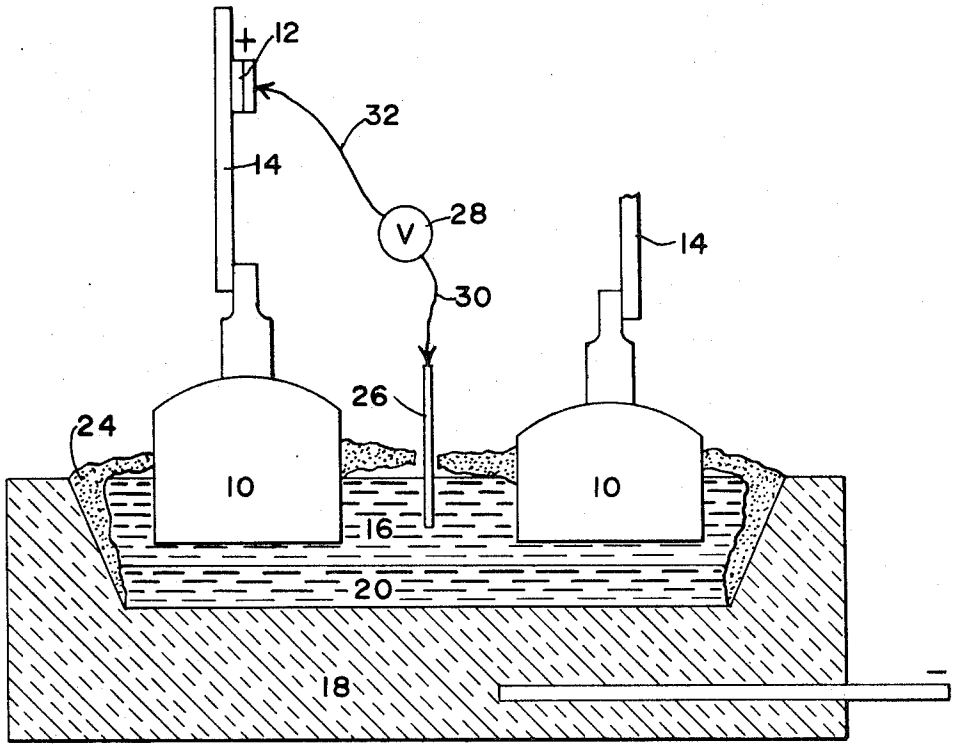

Fig-2

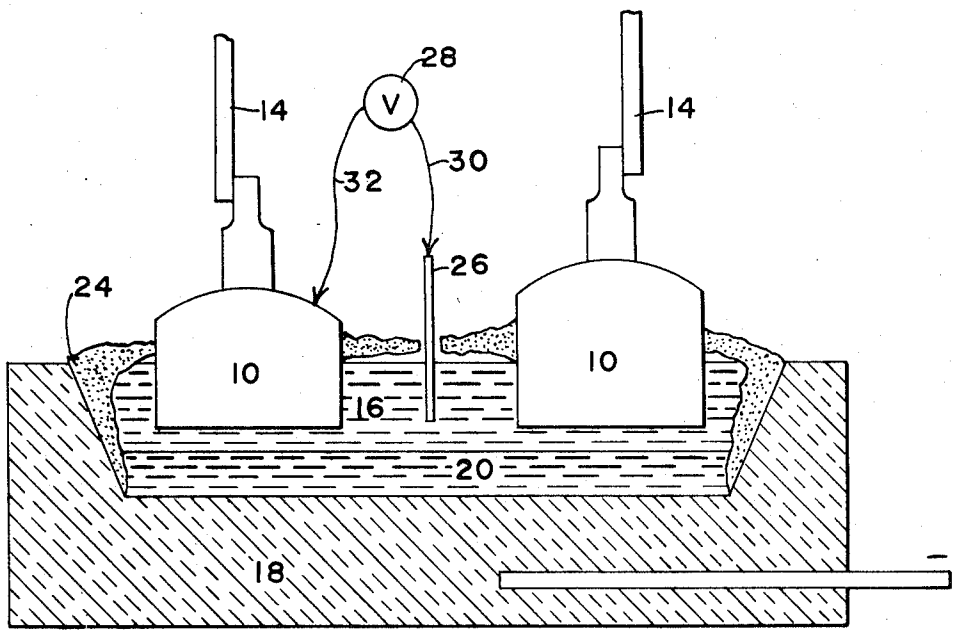

Fig-3

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ANODE POLARIZATION DETECTOR

Filed Sept. 18, 1967 4 Sheets-Sheet 3

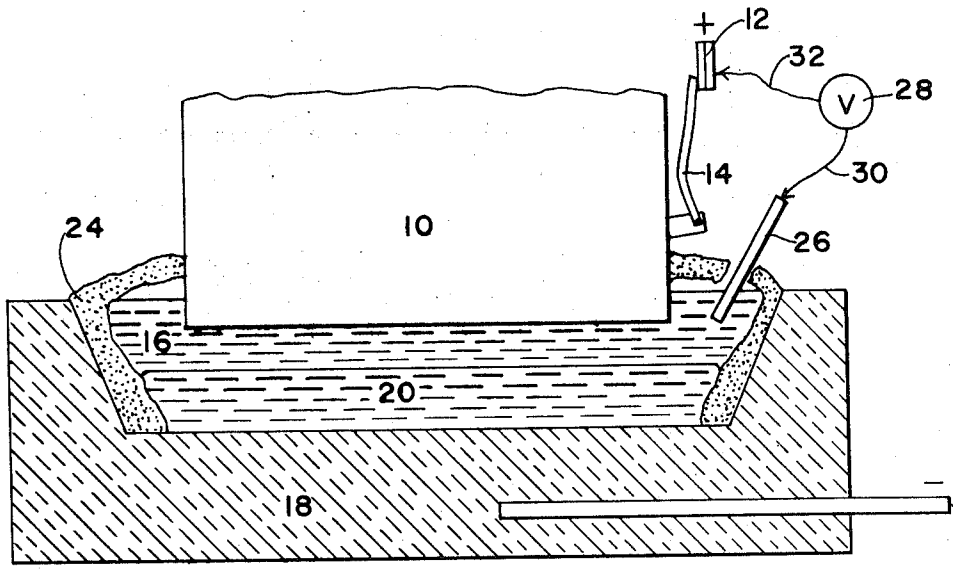

Fig-4

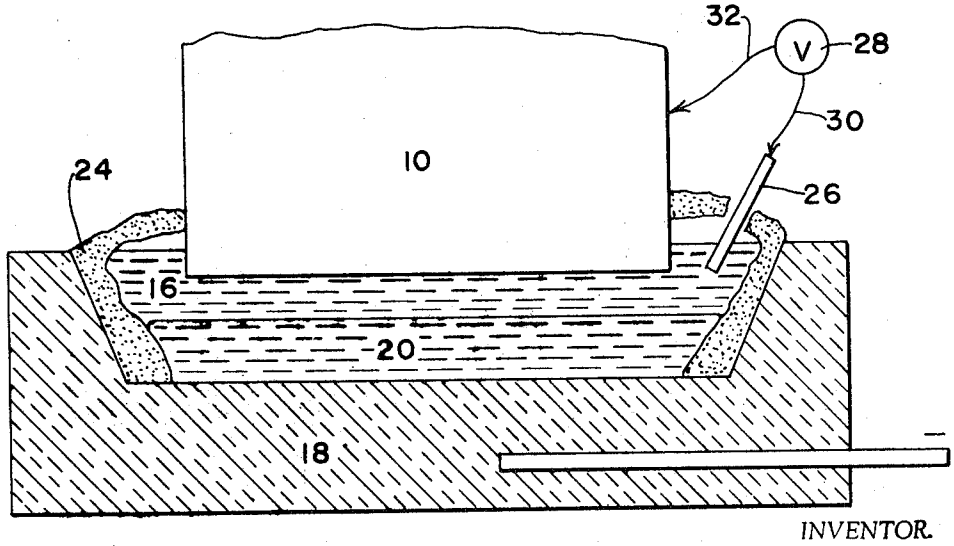

Fig-5

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ANODE POLARIZATION DETECTOR

Filed Sept. 18, 1967 4 Sheets-Sheet 4

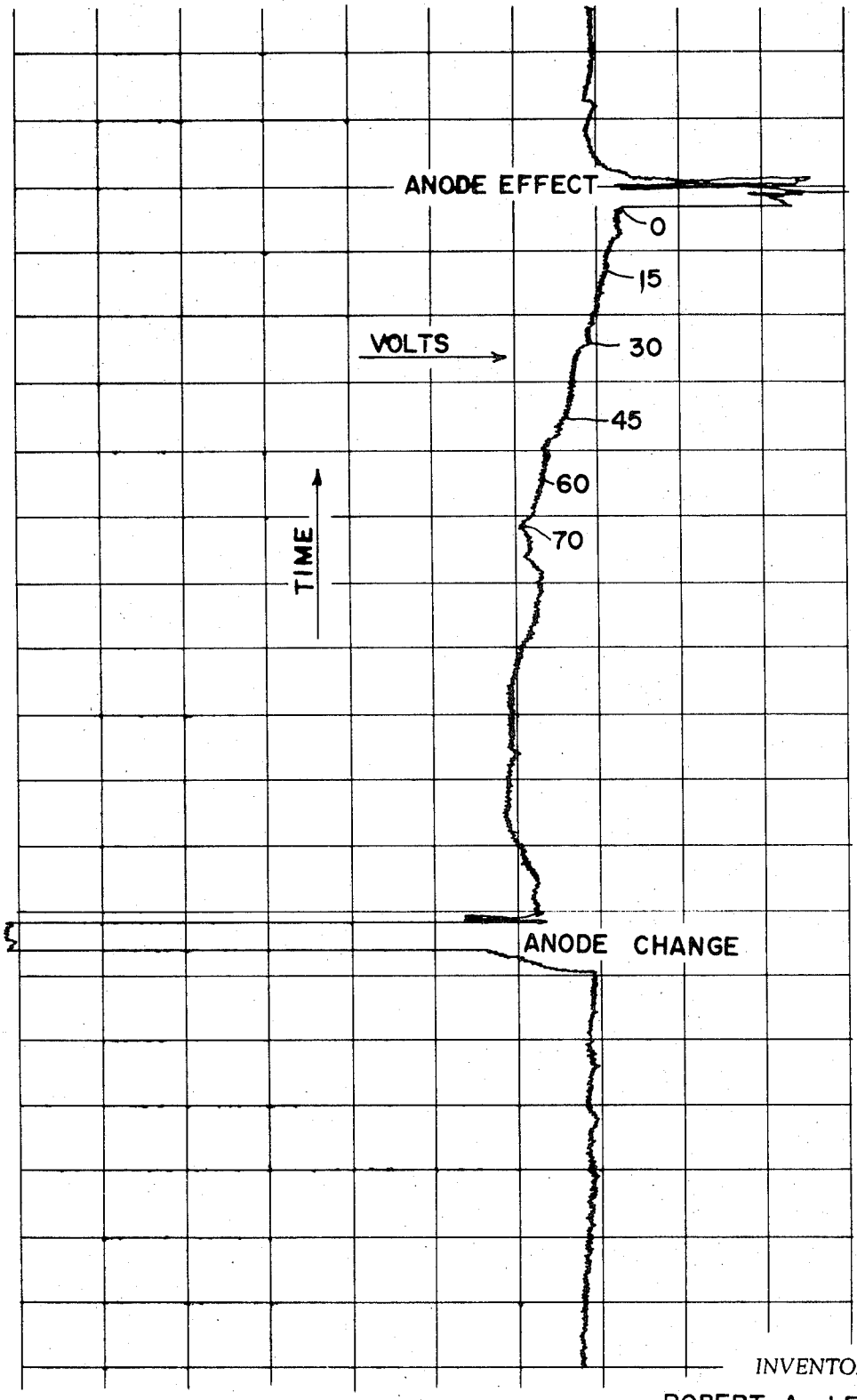

Fig-7

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3,578,569

ANODE POLARIZATION DETECTOR

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Int. Cl. B01k 1/00; C22d 3/12
U.S. Cl. 204—1 6 Claims

ABSTRACT OF THE DISCLOSURE

This invention describes a method and a system for indicating the alumina requirements of the molten bath in an electrolytic cell for the production of aluminum so as to maintain stable operation. A reference electrode is inserted into the molten bath of the cell and an instrument for measuring potential is connected between the reference electrode and the operating anode system of the cell so as to measure the potential difference between the reference electrode and the operating system of the cell. Increasing potential difference indicates increasing polarization of the operating anode system and decreasing alumina content in the molten bath. Decreasing potential difference indicates decreasing polarization of the operating anode system and increasing alumina content of the bath. In accordance with the indication received, the alumina content in the bath is adjusted as needed to maintain stable operation of the electrolytic reduction cell.

BACKGROUND OF THE INVENTION

In the production of aluminum by the conventional electrolytic process, the electrolytic cell comprises in general a steel shell having disposed therein a carbon lining. The bottom of the carbon lining along with a layer of electrolytically produced molten aluminum which collects thereon during operation, serves as the cathode. One or more consumable carbon electrodes is disposed from the top of the cell and is immersed at its lower extremity into a layer of molten electrolyte which is disposed in the cell. In operation, the electrolyte or bath which is a mixture of alumina and cryolite is charged to the cell, and an electric current is passed through the cell, from the anode to the cathode via the layer of molten electrolyte while oxygen collects at the anode. A crust of solidified electrolyte and alumina forms on the surface of the bath, and this is usually covered over with additional alumina.

As the electrolysis continues, alumina is consumed in direct proportion to the metal production. As the alumina concentration in the electrolyte is reduced, a point is reached where a troublesome phenomenon known as "anode effect" occurs. The voltage drop across the cell can increase from around four volts to as much as 40 volts and even higher. This effect is generally attributed to too low a concentration of alumina in the reduction cell bath or electrolyte. The actual concentration of alumina at anode effect seems to depend upon the temperature, the composition of the electrolyte and the anode current density. The occurrence of the anode effect is the signal for the addition of more alumina. The attendant does this by breaking the frozen crust, on top of which he has previously distributed a layer of alumina. The addition of the alumina, as well as a vigorous stirring of the electrolyte, causes the anode effect to disappear, after which the electrolysis continues its normal course, until the next anode effect occurs.

There are several disadvantageous results of an anode effect such that minimizing or substantially eliminating their occurrence is desirable. During the normal course of electrolysis, the anode is surrounded by gas bubbles which are constantly escaping from it. They appear to

form on the anode, break away easily, and escape from the electrolyte. Smooth evolution of gas around the anode is a sign of normal operation. The moment the anode effect occurs, the electrode seems to be entirely surrounded by a film of gas. This covers the surface of the anode and pushes the fused electrolyte away, producing the so-called "nonwetting" of the anode. Small arcs form between the electrolyte and the anode. Complete interruption of the current does not occur, as some current is being carried by these continually shifting arcs. The arcs cause local heating, volatilizing some bath material or producing sufficient gas so that the individual arcs are almost immediately broken. New arcs form, as the bath film near the anode must necessarily be uneven in character, and momentary contacts take place between the anode and bath. This overheating causes excessive consumption of the anode, excessive consumption of electrolyte by volatilization, and results in a lowered yield of product. A very important result of the anode effect is a large unproductive power consumption.

In the conventional electrolytic process, use has been made of two types of electrolytic cells, namely, that commonly referred to as a "prebaked" cell and that commonly referred to as a Soderberg cell. With either cell, the reduction process involves precisely the same chemical reactions. The principal difference is one of structure. In the prebake cell the carbon anodes are prebaked before being installed in the cell, while in the Soderberg, or self-baking anode cell, the anode is baked in situ, that is, it is baked during operation of the electrolytic cell, thereby utilizing part of the heat generated by the reduction process.

With the developing trend toward automated cell operation, the control of alumina concentration in the bath or electrolyte through cell feeding has become quite important. In most cell control schemes, it is desired that the number of anode effects be minimized without overfeeding the cell. This involves either a measuring of the concentration of the alumina in the bath or electrolyte or the feed rate or in some other way receiving an indication of incipient anode effects so that the cells can be fed with additional alumina before anode effects occur. The prior art describes many methods which have been utilized in the past to determine the alumina concentration in the electrolyte or bath or to obtain some sort of a prewarning of an oncoming anode effect. These methods include chemical analysis for the alumina concentration, either by pyrotitration techniques, caustic leach methods, gravimetric methods of analysis, volumetric methods of analysis or by means of electrical conductivity measurements. Examination of physical properties of the electrolyte has also been utilized to some extent. The appearance of the electrolyte, both molten and solidified, has been compared with known samples; crystalline phases have been examined by microscope and X-ray diffraction as well as in other ways. None of these prior art methods have been truly satisfactory. Those methods with high accuracy and reliability take too long to yield the desired information. Techniques which produce an answer more rapidly tend to be rather inaccurate. The present invention was developed against this background in the art.

SUMMARY OF THE INVENTION

It is an advantage of the anode polarization detection system of the instant invention and the method of use thereof that the system and the method isolates and measures directly the one voltage drop in the cell whose value is almost solely influenced by the alumina content of the bath in a given operating reduction cell in the polarization of the operating anodes. The other systems which have

been proposed are based on measuring the total reduction cell or pot voltage drop and calculating the resistance changes. While this total cell resistance is influenced by the change in anode polarization caused by changing alumina content, the total cell resistance includes other components of resistance which can change because of factors other than alumina content or approaching anode effect.

The invention relates to a method of, and a system for, determining the alumina requirements of the cell bath in an electrolytic reduction cell for the production of aluminum and adjusting the alumina content in the bath as needed to maintain stable operation of the electrolytic reduction cell. According to the invention, a reference electrode is inserted into the molten bath of the cell. An instrument for measuring potential between the reference electrode and the operating anode system of the cell is connected therebetween. Th potential difference between the reference electrode and the operating system of the cell is measured. Increasing potential difference indicates increasing polarization of the operating anode system and decreasing alumina content in the molten bath. Decreasing potential difference indicates decreasing polarization of the operating anode system and increasing alumina content in the molten bath. The alumina content in the bath may be adjusted as needed to maintain stable operation of the electrolytic reduction cell.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graph showing the change in cell voltage as a function of alumina concentration for different anode current densities.

FIG. 2 is a front elevation view, partly in cross section, showing one embodiment of the instant invention as applied to a prebaked anode reduction cell.

FIG. 3 is a front elevation view, partly in cross section, showing another embodiment of the instant invention.

FIG. 4 is a front elevation view, partly in cross section, showing another embodiment of the instant invention as applied to a Soderberg cell.

FIG. 5 is a front elevation view, partly in cross section, showing yet another embodiment of the instant invention as applied to a Soderberg cell.

FIG. 6 is a front sectional view showing a reference electrode used in the practice of the instant invention.

FIG. 7 is a typical reference electrode voltage chart showing the change in voltage with oncoming anode effect.

DETAILED DESCRIPTION

A series of tests were performed to determine the electrical conductivity of cryolite baths with various alumina contents. The tests showed the conductivity of the bath to increase as the alumina decreased. The voltage drop across the bath, due to ohmic bath resistance, thus would be least immediately prior to an anode effect. On the other hand, anode polarization is also dependent upon the alumina content of the bath. The polarization voltage increases as the alumina content decreases. The two opposing effects should result in a changing effective cell resistance, first decreasing as alumina is depleted, reaching a minimum, then rising as the anode effect is approached. These relationships are altered by current density and anode-cathode distance changes. However, the curve forms are similar over reasonable operating ranges. FIG. 1 shows a family of such curves. The instant invention eliminates some of the resistances normally included in cell resistance measurements, e.g., the cathode resistance and at least some of the bath resistance making it more sensitive to anode polarization.

Referring now more particularly to FIGS. 2–5, typical installations of the anode polarization detector according to the instant invention shall be described. As seen in these figures, an electrolytic reduction cell involves an anode (or anodes)**10** suspended from the incoming current source bus **12** by a suitable connector **14**, which in the case of a prebaked anode is an anode rod and stub and in the case of a Soderberg anode is a flexible lead and stud combination. For our purposes here, they shall both be referred to as connectors **14**. The anodes **10** are suspended in the molten bath, or electrolyte **16** of the cell. The electrolyte **16** is disposed in the carbon lining **18** of the cell. The bottom of carbon lining **18** along with a layer of electrolytically produced molten aluminum **20** which collects thereon serves as the cathode. Suitable collector bars, **22**, are disposed in carbon lining **18** and are connected to a cathode bus (not shown) to complete the electrical circuit. In operation, a crust **24** of solidified electrolyte and alumina forms on the surface of electrolyte bath **16**. An unpolarized reference electrode **26** is inserted in the molten electrolyte bath **16** of the cell to continuously or intermittently (as desired) measure the anode polarization voltage of the cell. This is done by measuring the potential difference between the unpolarized reference electrode **26** and the polarized operating anode **10** of the cell. Anode polarization increases fairly uniformly as electrolysis proceeds and bath alumina content decreases. As the anode effect approaches, the anode polarization increases more rapidly until the anode effect itself occurs, under which condition the anode polarization, of course, rises rapidly to very large values.

In the embodiment shown in FIG. 2, a potential measuring instrument **28**, for example, a volt meter or potentiometer is connected by suitable leads **30** and **32** between the reference electrode **26** and the operating anode system of the cell at the anode bus **12**. In effect, this measures a composite anode polarization voltage for the cell, but includes some ohmic potential drop in the anode bus **12** and rod and stub connector **14**. FIG. 3 shows the potential being measured in the same manner, but between the reference electrode **26** and the exposed carbon surface of a single anode **10** of a prebaked multianode cell. This, in effect, measures the anode polarization of this single anode and only includes the small ohmic potential drop in the carbon anode itself between its top surface and the active anode surface beneath the electrolyte. FIGS. 4 and 5 are similar to FIGS. 2 and 3, but show the application of the invention in Soderberg anode cells.

FIG. 6 shows a typical reference electrode **26**. As shown in FIG 6, the reference electrode consists of an unpolarized, carbonaceous, e.g., graphite or carbon, rod **34** protected by a sleeve **36** of suitable material such as boron nitride to prevent what is known as air burn, a type of oxidation, at the exposed surface of the rod **34** from occurring. One end of rod **34** is inserted into the the electrolyte bath **16** (FIGS. 2–5 inclusive) of the cell and the other end of rod **34** is connected by a suitable terminal, such as an alligator clip not shown, to lead **30** (as shown in FIGS. 2–5 inclusive).

The anode polarization potential will be measured as shown in FIGS. 2 through 5 inclusive by means of well-known potential measurement instruments **28**, either continuously or intermitently, to follow changes in the polarization as electrolysis proceeds. Decreasing polarization potential measured in this way would indicate increasing alumna content and conversely, increasing polarization would indicate decreasing alumina content. An abnormal increase in the polarization voltage would indicate approaching anode effect.

The carbonaceous reference electrode **26** should be immersed deep enough into the electroylte bath **16** so that its lowest end is free of frozen electrolyte crust **24** and is essentially at the operating bath temperature. It should not be immersed so deep or otherwise placed so that it conducts any of the cell current. In this way, the difference in potential between the carlon reference electrode and the operating anode is almost wholly that of the polarization or over-potential existing on the operating anodes. The measured potential difference between the operating anodes and the carbonaceous reference

electrode will not include any electrochemical decomposition potential.

FIG. 7 is a typical chart showing the practice of the instant invention. As shown in FIG. 7 the polarization potential on the anode increases as anode effect approaches resulting in an increased voltage on the meter. It will be noted that the change in the scope of the curve provides the indication of feed concentration.

Anode effects in a typical electrolytic cell were monitored for a two-month period using reference electrodes on a more or less continuous basis. The arrangement used was that shown in FIG. 2. In all, a total of twenty-one anode effects were monitored. In two cases, the slope of the voltage line showed no immediate change, in the other nineteen cases there was a slope change which could be considered indicative of an anode effect impending. Warning time was seven minutes to four hours. Table I summarizes these data.

These data are in good agreement with the theory upon which the instant invention is based. The data indicates that about 90% of the anode effects show prewarning and could therefore be prevented. Through the use of this process and system, one would be able to adjust the alumina content in the bath as needed to maintain stable operation of the electrolytic reduction cell and eliminate or, if desired, control the occurrence of anode effects.

The advantage of the method of detecting changes in alumina content and approaching anode effect according to the instant invention is that it isolates and measures directly the one voltage in the cell whose value is almost solely influenced by the alumina content of the bath in a given operating reduction cell. Other systems have been proposed that are based on measuring the total pot voltage and a calculating the resistance changes. While this total cell resistance is influenced by the change in anode polarization caused by changing alumina content, the total cell resistance includes other components of resistance which can change because of factors other than alumina content or aproaching anode effects.

While there has been shown and described hereinabove possible embodiments of this invention, it is to be understood that the invention is not limited thereto and that various changes, alterations and modifications can be made thereto without departing from the spirit and scope thereof as defined in the appended claims wherein:

TABLE I.—REFERENCE ELECTRODE USED AS ANODE EFFECT PREDICTOR

[+ Terminal=Anode Bus, — Terminal=Reference Electrode]

	Approx. length warning, min.	Volts				
		Anode + A.E. start	—5 min.	—10 min.	—15 min.	30 min.
AE cause:						
Induced	15	1.97	1.94	1.86	1.83	1.84
do	7	1.70	1.61	1.59	1.60	1.64
do	120 (gradual)	2.09	2.08	2.07	2.07	2.06
do	45	1.95	1.92	1.91	1.90	1.86
do	None	1.97	1.97	2.01	1.98	1.96
After A.C.[a]	90	1.99	1.96	1.94	1.93	1.89
Low Al_2O_3	240	2.24	2.22	2.19	2.17	2.12
After A.C.	180	1.88	1.87	[b] 1.95	1.85	1.83
do	20	1.58	1.57	1.55	1.54	
do	90	1.41	1.40	1.39	1.38	1.35
do	90 total[c]	1.37	1.36	1.35	1.34	
do	20	2.13	2.08	2.04	2.02	2.01
do	90	2.27	2.24	2.21	2.20	2.13
do	100	1.70	1.68	1.67	1.65	1.64
Low Al_2O_3	([d])					
After A.C.	([e])					
do	120	1.68	1.67	1.65	1.64	1.63
do	20	1.52	1.48	1.47	1.46	
do	45	1.83	1.80	1.79	1.77	1.77
do	15	1.80	1.78	1.77	1.77	1.77
Low Al_2O_3	45	1.82	1.81	1.80	1.78	1.76
Low Al_2O_3	None	1.96	1.96	1.96	1.96	1.97
After A.C.	70	1.83	1.81	1.78	1.77	1.72

[a] A.C.=Anode change.
[b] Partial anode effect.
[c] 15 min. immediate.
[d] Meter off scale—equipment malfunction.
[e] Probe broken.

What is claimed is:

1. A method of detecting polarization of the anode of an aluminum reduction cell which is connected in a potline of cells through which a line current is conducted, comprising:
   (a) immersing an unpolarized reference electrode in the electrolytic bath of the cell,
   (b) positioning said reference electrode in the bath so that its lower end is below the crust over the bath but so that the electrode does not carry said line current, and
   (c) monitoring the potential difference between the reference electrode and the anode of the cell, such potential difference being almost wholly an indication of the polarization of the anode.

2. The method of claim 1 including the step of adjusting the alumina content of the bath when the potential difference monitored reaches a predetermined level.

3. The method of claim 1 wherein said potential difference is monitored between said electrode and the upper surface of the anode.

4. The method of claim 1 wherein the anode of each cell in the potline is electrically connected to an electrical connector which carries said line current, and wherein said potential difference is monitored between the electrode and the connector associated with the anode of the cell.

5. A system for detecting polarization of the anode of an aluminum reduction cell adapted to contain an electrolytic bath, said cell being connected in a potline of such cells through which a line current is conducted comprising:
   (a) an unpolarized reference electrode positioned to be immersed in the electrolytic bath of the cell, and
   (b) means for measuring the voltage between the reference electrode and the anode of the cell, said electrode being so positioned in the cell that the electrode does not carry said line current, said voltage measuring means thereby measuring a voltage substantially entirely representative of the polarization of the anode.

6. The system of claim 5 wherein said cells are either Soderberg or prebaked cells and wherein said reference electrode has a substantially smaller cross-sectional area than the total cross-sectional area of either the entire

anode, if a Soderberg cell, or an individual anode block, if a prebaked cell.

References Cited

UNITED STATES PATENTS

3,317,413	5/1967	Chambran.	
3,391,074	7/1968	Chambran	204—231
3,329,592	7/1967	Uhrenholdt	204—67
3,380,897	4/1968	Dewey	204—67X
3,400,062	9/1968	Bruno et al.	204—243X

FOREIGN PATENTS

1,012,790	12/1965	Great Britain	204—67

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U.S. Cl. X.R.

204—67, 195, 231, 243R