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(54) Title: ELECTRODE COMPOSITION

(57) Abstract

Electrodes suitable for the electrolysis of solutions, in particular for the production of aluminum in Hall-Heroult reduction cells, are composed of SnO_2 with various amounts of conductive agents and sintering promoters principally GeO_2, Co_3O_4, Bi_2O_3, Sb_2O_3, MnO_2, CuO, Pr_2O_3, In_2O_3, and MoO_3.

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Description

ELECTRODE COMPOSITION

BACKGROUND OF THE INVENTION

Aluminum is produced in Hall-Heroult cells by the electrolysis of alumina in molten cryolite, using conductive carbon electrodes. During the reaction the carbon anode is consumed at the rate of approximately 450 kg/mT of aluminum produced under the overall reaction $2Al_2O_3 + 3C \xrightarrow[Na_3AlF_6]{940^\circ-1000^\circ C} 4Al + 3CO_2$.

The problems caused by the consumption of the anode carbon are related to the cost of the anode consumed in the reaction above and to the impurities introduced to the melt from the carbon source. The petroleum cokes used in the anodes generally have significant quantities of impurities, principally sulfur, silicon, vanadium, titanium, iron and nickel. Sulfur is oxidized to its oxides, causing particularly troublesome workplace and environmental pollution. The metals, particularly vanadium, are undesirable as contaminants in the aluminum metal produced. Removal of excess quantities of the impurities requires extra and costly steps when high purity aluminum is to be produced.

If no carbon is consumed in the reduction the overall reaction would be $2Al_2O_3 \longrightarrow 4Al + 3O_2$ and the oxygen produced could theoretically be recovered, but more importantly with no carbon consumed at the anode and no contamination of the atmosphere or the product would occur from the impurities present in the coke.

Attempts have been made in the past to use non-consumable anodes with little apparent success. Metals either melt at the temperature of operation, or are attacked by oxygen or by the cryolite bath. Ceramic compounds such as oxides, with perovskite and spinel crystal structures usually have too high electrical resistance or are attacked by the cryolite bath.

Previous efforts in the field have resulted in U.S. 3,718,550, Klein, Feb. 27, 1973, Cl. 204/67; U.S. 4,039,401, Yamada et al., Aug. 2, 1977, Cl. 204/67; U.S. 3,960,678, Alder, June 1, 1976, Cl. 204/67; U.S. 2,467,144, Mochel, April 12, 1949, Cl. 106-55; U.S. 2,490,825, Mochel, Feb. 1, 1946, Cl. 106-55; U.S. 4,098,669, de Nora et al., July 4, 1978, Cl. 204/252; Belyaev + Studentsov, Legkie Metal 6, No. 3, 17-24 (1937), (C.A. 31 [1937], 8384); Belyaev, Legkie Metal 7, No. 1, 7-20 (1938) (C.A. 32 [1938], 6553).

Of the above references Klein discloses an anode of at least 80% SnO_2, with additions of Fe_2O_3, ZnO, Cr_2O_3, Sb_2O_3, Bi_2O_3, V_2O_5, Ta_2O_5, Nb_2O_5 or WO_3; Yamada discloses spinel structure oxides of the general formula $XYY'O_4$, and perovskite structure oxides of the general formula RMO_3, including the compounds $CoCr_2O_4$, $TiFe_2O_4$, $NiCr_2O_4$, $NiCo_2O_4$, $LaCrO_3$, and $LaNiO_3$; Alder discloses SnO_2, Fe_2O_3, Cr_2O_3, Co_2O_4, NiO, and ZnO; Mochel discloses SnO_2 plus oxides of Ni, Co, Fe, Mn, Cu, Ag, Au, Zn, As, Sb, Ta, Bi & U; Belyaev discloses anodes of Fe_2O_3, SnO_2, Co_2O_4, NiO, ZnO, CuO, Cr_2O_3 and mixtures thereof as ferrites, de Nora discloses Y_2O_3 with Y, Zr, Sn, Cr, Mo, Ta, W, Co, Ni, Pa, Ag, and oxides of Mn, Rh, Ir, & Ru.

The Mochel patents are of electrodes for melting glass, while the remainder are intended for high temperature electrolysis such as Hall aluminum reduction. Problems with the materials above are related to the cost of the raw materials, the fragility of the electrodes, the difficulty of making a sufficiently large electrode for commercial usage, and the low electrical conductivity of many of the materials above when compared to carbon anodes.

U.S. 4,146,438 March 27, 1979, de Nora, Cl. 204/1.5 discloses electrodes of oxycompounds of metals, including Sn, Ti, Ta, Zr, V, Nb, Hf, Al, Si, Cr, Mo, W, Pb, Mn, Be, Fe, Co, Ni, Pt, Pa, Os, Ir, Rh, Te, Ru, Au, Ag, Cd, Cu, Sc, Ge, As, Sb, Bi and B, with an electroconductive agent and a surface electrocatalyst. Electroconductive agents include oxides of Zr, Sn, Ca, Mg, Sr, Ba, Zn, Cd, In, Tl, As, Sb, Bi, Sn, Cr, Mn, Ti; metals Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Pd & Ag; plus borides, silicides, carbides and sulfides of valve metals. Electrocatalysts include Ru, Rh, Pd, Ir, Pt, Fe, Co, Ni, Cu, Ag, MnO_2, Co_3O_4, Rh_2O_3, IrO_2, RuO_2, Ag_2O, Ag_2O_2, Ag_2O_3, As_2O_3, Bi_2O_3, $CoMnO_4$, $NiMn_2O_4$, $CoRh_2O_4$ & $NiCo_2O_4$.

Despite all of the above, preparation of usable electrodes for use in Hall cells still has not been fully realized in commercial practice. The raw materials are often expensive and production of the electrodes in the necessary sizes has been extremely difficult, due to the many difficulties inherent in fabricating large pieces of uniform quality.

Of the various systems disclosed above at this time no instance is known of any plant scale commercial usage. The spinel and pervoskite crystal structures shown above have displayed in general poor resistance to the molten cryolite bath, disintegrating in a relatively short time. Electrodes consisting of metals coated with ceramics have also shown poor performance, in that almost inevitably, even the smallest crack leads to attack on the metal substrate by the cryolite, resulting in spalling of the coating, and consequent destruction of the anode.

The most promising developments to date appear to be those using stannic oxide, which has a rutile crystal structure, as the basic matrix. Various conductive and catalytic compounds are added to raise the level of electrical conductivity and to promote the desired reactions at the surface of the electrode.

SUMMARY OF THE INVENTION

An electrode useful as the anode in Hall aluminum cells is manufactured by sintering a mixture of SnO_2 with various dopants. Ratios used are commonly less than 80% SnO_2 with approximately 20% GeO_2 or Co_3O_4 and 1-3% Sb_2O_3, CuO, Pr_2O_3, In_2O_3, MoO_3 or Bi_2O_3.

DETAILED DESCRIPTION OF THE INVENTION

Stannic oxide is sintered with additives to increase the electrical conductivity and to promote sintering. The resulting solid is a ceramic body with a rutile crystal structure.

Tin oxide falls into the class of materials denoted as having 'rutile' structures. Other compounds found in this class are TiO_2, GeO_2, PbO_2 and MnO_2. The structure is formed by a distorted cubic-close-packed array of oxygen anions with cations (Sn, Ge, etc.) filling half of the octahedral voids in the oxygen array. The cations occupy the octahedral positions because of the radius ratio (cation radius/anion radius) being ≥ 0.414 but <0.732. The large radius of the cations prevents them from occupying tetrahedral voids.

Unlike most oxides, SnO_2 is primarily a covalent compound and not ionic. This is accounted for by the high electronegativity of elemental tin. The greater the differences in electronegativities of two elements, the greater the likelihood of an ionic compound. However Sn and O_2 are of relatively comparable electronegativities. This results in a sharing of electrons (covalent bonding) instead of a loss or gain (ionic). An empirical equation for calculating the percent ionic character of a compound is given as:

$$p = 16\,(X_A - X_B) + 3.51\,(X_A - X_B)^2$$

where: p = percent ionic character.
X_A = electronegativity of element A
X_B = electronegativity of element B.

By inserting electronegativity values for tin and oxygen (1.8 and 3.5 respectively) it is found that the structure is approximately 40% ionic with the remainder covalent. Evidence has been found that structures of this nature will have fluctuations in bonding which could attribute for the electrical conductivity being high.

Like most covalent compounds, SnO_2 is difficult to sinter. Research has shown that small additions of Sb_2O_3, MnO_2 or Bi_2O_3 enhance sintering. The mechanism is believed to be the presence of a liquid phase above 800°C. During the reaction, the Sb, Mn or Bi ions probably migrate to available octahedral positions (suitable radius ratio). Due to the presence of covalent bonding in the SnO_2 matrix (60%) it is possible that Sn-Sb, Sn-Mn or Sn-Bi covalent bonds occur in the array. These compounds are strongly covalent and conductive which would explain the tremendous increase in electrical conductivity when Sb_2O_3, MnO_2 or Bi_2O_3 are added for sintering. Conductivity also increases due to the shifting valency of tin (+4 to +2 and vice versa).

A reason for the increase in electrical conductivity is also apparent when the electronic configurations of SnO_2, MnO_2 and Sb_2O_3 are examined. SnO_2 is classed as an n-type semi-conductor. Higher conductivity can be induced by doping with a cation having more electrons in its external shell than does Sn. The outer electronic configuration of Sn is $5s^2 5p^3$. Therefore each added atom of Sb donates an extra electron to the conduction band of SnO_2. This reasoning also holds true for other doping agents.

EXAMPLE 1

An anode was prepared for comparison of properties and compared to a standard carbon anode as the control in a Hall aluminum reduction cell as follows:

The sample anodes were made by milling the powders, pressing them into pellets 0.8 in. (2 cm) diam. by 1 in. (2.54 cm) length at 2000 psi (140.6 kg/cm^2), then sintering them with the temperature rising to a maximum of 1250°C in 16 hrs. The power leads were attached by a threaded rod with melted copper powder.

	Cell Resistance at $1A/cm.^2$
a) Carbon-100%	0.03 Ω
b) SnO_2 - 77%	
GeO_2 - 21%	0.0085-0.018 Ω
Sb_2O_3 - 2%	
100%	

Sample (a) above is a standard carbon anode run as a control. After 4 hrs. the normal loss of carbon as a fraction of the aluminum produced was found.

Sample (b) above, SnO_2, GeO_2 & Sb_2O_3, was run at $1A/cm.^2$ with 11.2A total current at 0.2V, giving a resistance of 0.017 Ω a very favorable value. During the test the resistance fluctuated between 0.0085-0.018 Ω. After four hours the sample showed no attack, but had several thermal shock cracks.

EXAMPLE 2

An anode was prepared in the same manner as in Example 1 from:

SnO_2 - 96%
Bi_2O_3 - 4%
100%

At a current density of $1A/cm^2$ the resistance in the Hall cell of the anode was 0.13 Ω. After 4 hrs. at this current, the current was increased to $2A/cm^2$ for an additional 4 hrs. At the higher current the resistance dropped to 0.10 Ω, showing improved efficiency. At the end of the run, the electrode was in excellent condition showing no attack.

The higher resistance of this anode compared to the resistance of the anode in Example 1 shows that 2% Bi_2O_3 is very likely to be at or near the optimum value, and that 4% Bi_2O_3 is higher than the optimum. The increase in resistance with increased dopant content is probably due to exceeding the solubility limit of Bi_2O_3 in SnO_2, with the formation of a second phase of higher resistance.

EXAMPLE 3

An anode of the composition:

SnO_2 75%
Co_3O_4 23%
Sb_2O_3 2%
100%

was made as in Example 1, and run in the Hall cell at $1A/cm^2$, showing a resistance of 0.048 Ω. After 8 hrs, the current was increased to $2A/cm^2$, the resistance dropping to 0.041 Ω, for another 8 hrs. At the end of this period, the anode showed a crack due to the expansion of the metal lead, and the run was discontinued. No attack on the body of the anode was seen.

EXAMPLE 4

The anode composed of the following compounds was prepared as in Example 1:

SnO_2	60%
GeO_2	38%
Sb_2O_3	2%
	100%

It was run in the Hall cell at $1A/cm^2$. As soon as the power was applied, material started to erode from the surface of the anode in a rapid attack. The failure was probably due to exceeding the solubility limits of GeO_2 in the SnO_2-GeO_2 system.

EXAMPLE 5

A conductive phase (SnO_2 & Sb_2O_3) was dispersed in a non-conductive phase (ZrO_2) at two levels in order to determine their utility as electrodes in Hall cells, and prepared as in Example 1. These were of the following compositions:

	(a)	(b)
SnO_2	77%	23%
ZrO_2	21%	75%
Sb_2O_3	2%	2%
	100%	100%

Sample (a) at $1A/cm^2$ had a resistance of 0.2 Ω, higher by an order of magnitude than desired, and Sample (b) at $1A/cm^2$ had a resistance of 2.5 Ω, higher by two orders of magnitude than desired. It was concluded that this system in its present form was not feasible for use as Hall cell anodes.

EXAMPLE 6

Samples of the SnO_2-Sb_2O_3 system in an Al_2O_3 matrix were made at the following levels, as in Example 1 with firing carried up to 1500°C.:

	(a)	(b)
SnO_2	77%	23%
Al_2O_3	21%	75%
Sb_2O_3	2%	2%
	100%	100%
Resistance @ 1A/cm^2	0.3 Ω	3.1 Ω

No attack was noted in runs using these samples as anodes in the Hall cell, but their high resistances eliminated these from consideration.

EXAMPLE 7

An anode of the following composition prepared as in Example 1 was sintered in a 16 hr. cycle of rising temperature with the temperature reaching 1250°C.:

SnO_2 - 49%
Co_3O_4 - 49%
Sb_2O_3 - 2%
100%

In the Hall cell at a current density of 1A/cm^2 the resistance was 0.08 Ω. An 8 hr. run was completed without anode degradation.

EXAMPLE 8

Two compositions incorporating PbO_2 were prepared by mixing and pressing at 10,000 psi (703 kg/cm^2), as in Example 1, then fired in a cycle rising to 1050°C. They were tested for weight loss with the following results:

	(a)	(b)
PbO_2	50%	20%
SnO_2	48%	78%
Sb_2O_3	2%	2%
	100%	100%
Weight loss	18%	7%

The high weight loss of sample (a) indicates a solubility limit of the system PbO_2-SnO_2 of below 50% PbO_2 at the 1050°C. firing temperature. PbO_2 melted and noticeably stained the support brick.

EXAMPLE 9

Two formulations containing GeO_2 were prepared by ball milling the mixed powders, cold pressing at 5000 psi (352 kg/cm^2), firing at 1200°C, and testing as in Example 1 as follows:

	(a)	(b)
SnO_2	56%	78%
GeO_2	21%	10%
Co_3O_4	21%	10%
Sb_2O_3	2%	2%
	100%	100%
Current	1 A/cm^2	1 A/cm^2
Cell resistance	0.10 Ω	0.07 Ω
Test duration	6 hrs.	6 hrs.
	Sl. attack	no attack

EXAMPLE 10

A series of anodes was prepared and tested as in Example 1 as follows:

	(a)	(b)	(c)
SnO_2	78%	78%	78%
GeO_2	18%	18%	18%
CuO	2%	2%	2%
Pr_2O_3	2%	---	---
In_2O_3	---	2%	---
MoO_3	---	---	2%
Current	$1A/cm^2$	$1A/cm^2$	---
Cell resistance	0.3 Ω	0.2 Ω	not tested
Test Duration	6 hrs.	6 hrs.	
	No Attack	No Attack	

The resistance of anodes (a) and (b) was higher than desired, but their good qualities in other properties and potential for improvement counterbalanced this deficiency.

EXAMPLE 11

An anode was prepared and tested as in Example 1 with the following composition:

SnO_2	78%
GeO_2	10%
ZnO	10%
Sb_2O_3	2%
Current	$1\ A/cm^2$
Cell resistance	0.08 Ω
Test Duration	28 hrs.
	Sl. beveling at edges.

Claims

Claim 1. An electrode suitable for the production of aluminum in a Hall cell comprising a homogeneous sintered ceramic body having the composition of 67 to 78% SnO_2, 19 to 30% GeO_2 and from 1 to 3% of an electroconductive oxide selected from the group consisting of Sb_2O_3, Bi_2O_3, and MnO_2.

Claim 2. The electrode of Claim 1 prepared by the method of mixing the ingredients in the powdered form, cold pressing the so-formed powdered mixture in a mold at a pressure of at least 5000 psi. (352 kg/cm^2), and sintering the cold pressed form at a temperature of at least 1200^oC.

Claim 3. The electrode of Claim 1 wherein the electroconductive oxide is Sb_2O_3.

Claim 4. The electrode of Claim 1 wherein the electroconductive oxide is Bi_2O_3.

Claim 5. the electrode of Claim 1 wherein the electroconductive oxide is MnO_2.

Claim 6. An electrode suitable for the production of aluminum in a Hall cell comprising a sintered ceramic body of homogeneous composition having a composition of from 47 to 79% SnO_2, from 20 to 50% Co_3O_4 and from 1 to 3% of an oxide selected from the group consisting of Sb_2O_3, Bi_2O_3, and MnO_2.

Claim 7. An electrode of homogeneous composition comprising a rutile crystalline ceramic body having a composition of from 47 to 79% SnO_2, from 8 to 25% Co_3O_4, from 8 to 25% GeO_2, and from 1 to 3% of an oxide selected from the group consisting of Sb_2O_3, Bi_2O_3, and MnO_2.

Claim 8. An electrode suitable for the production of aluminum in a Hall cell comprising a homogeneous sintered ceramic body having the composition of from 64 to 79% SnO_2, 15 to 30% GeO_2, 1 to 3% CuO, and from 1 to 3% of an oxide selected from the group consisting of Pr_2O_3, In_2O_3, and MoO_3.

Claim 9. An electrode suitable for the production of aluminum in a Hall cell comprising a homogeneous sintered ceramic body having the composition of from 57 to 79% SnO_2, from 9 to 20% GeO_2, from 9 to 20% ZnO, and from 1 to 3% of an oxide selected from the group consisting of Sb_2O_3, Bi_2O_3, and MnO_2.

Claim 10. The electrode of Claim 9 with from 1 to 3% Sb_2O_3.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 80/00475

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.^{3} C25C 7/02

US. CL. 204/67, 290R, 290F, 291

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	204/67, 290R, 290F, 291

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 3,882,002, Published, 06 May 1975, Cook	1-10
A	US, A, 3,960,678, Published, 01 June 1976, Alder	1-10
A	US, A, 4,146,438, Published, 27 March 1979, DeNora et al	1-10
A,P	US, A, 4,173,518, Published, 06 November 1979, Yamada et al	1-10
A	US, A, 3,701,724, Published, 31 October 1972, Entwisle et al	1-10

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"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 15 SEPTEMBER 1980	Date of Mailing of this International Search Report [2] 29 SEP 1980
International Searching Authority [1] ISA	Signature of Authorized Officer [20] F. C. Edmundson F. C. EDMUNDSON