United States Patent Office 3,716,471 Patented Feb. 13, 1973

3,716,471

ELECTRODE OF PETROLEUM COKE AND BROWN COAL CHAR

Geoffrey Victor Cullen, North Balwyn, John William Graham, Essendon, and Neil Graham Siviour, East Kew, Victoria, Australia, assignors to University of Melbourne, Victoria, Australia

No Drawing. Filed Sept. 9, 1970, Ser. No. 70,874
Int. Cl. B01r 3/08
U.S. Cl. 204—294 4 Claims

ABSTRACT OF THE DISCLOSURE

A material for use in electrodes of the kind employed in electrolytic cells and comprising a mixture of petroleum coke and brown coal char.

Field of the invention

The present invention relates to carbon containing electrodes of the kind used in electrolytic cells for the electrolytic reduction of aluminium oxide to aluminium.

Description of prior art

Aluminium metal is produced from aluminium oxide (Al_2O_3) by passing direct current electricity through an electrolyte comprising a molten solution of the aluminium oxide which is dissolved in cryolite (Na_3AlF_6) to which may be added certain other minor materials. The electrolyte is held in a cell which comprises a container lined with baked carbon paste or baked carbon blocks bonded by pitch, and this container serves also as the negative electrode (cathode) of the electrolytic cell. There are two main types of arrangement for the positive (anode) electrode. In one type, known as "pre-baked electrodes," blocks are prepared from particles of carbon, the filler material, bonded together by pitch, the blocks being formed by compacting the constituents under pressure, and subsequently firing at high temperatures. In the other type of electrode, known as a "Soderberg" electrode, the mixture of filler and pitch is fed as a continuous column in an open ended container the material being baked to a solid as it reaches the electrolyte in the cell.

The filler material employed in the anode electrode, in both of the commonly used anode electrode arrangements has a direct bearing upon the over-all efficiency of the process. For example, factors such as current efficiency (a measure of the quantity of electrical energy required to produce a given quantity of aluminium) and the comparative rate of anode consumption are dependent upon the characteristics of the filler material. It has been found that the filler material must comprise a relatively pure form of carbon and petroleum coke is widely used in industry as the filler material. Whilst this filler material is generally satisfactory, we have found that the addition of brown coal char can improve the electrode performance. Accordingly the invention provides an electrode filler material comprising a mixture of petroleum coke and brown coal char.

BRIEF SUMMARY OF THE INVENTION

The invention also provides a method of preparing electrode filler material comprising mixing petroleum coke and brown coal char.

DETAILED DESCRIPTION

The invention may be more fully understood from the following detailed description.

Anode electrodes formed from brown coal char filler together with pitch and from various mixtures of brown coal char and petroleum coke together with pitch were prepared and compared with electrodes formed in an

analogous manner from petroleum coke together with pitch. Test samples for each of the three filler materials were made with a range of proportions of pitch, and in the case of those employing mixtures, also having a range of proportions of brown coal char and petroleum coke. The brown coal used was purified by acid leaching, washing and drying and the brown coal char was produced by pressure briquetting the purified brown coal, charring at high temperatures (approximately 1150° C.) and crushing. All of the electrodes were prepared in a manner essentially similar to the normal commercial method.

The relevant mechanical and electrical properties of the test electrodes were then measured, and the performance of each tested in a small electrolytic cell. The characteristics which were measured are indicated below together with an indication of values which have been reported as obtaining to industrial electrodes.

(1) Compression strength, high values being desirable. Values in the range 4000–8000 p.s.i. are reported for industrial electrodes.

(2) Apparent (bulk) density, higher values indicating better quality. Values in the range 1.55–1.60 g./cc. are reported for industrial electrodes.

(3) Electrical conductivity, usually expressed in terms of resistivity, lower value indicating better quality. Values of about 0.0056 to 0.0066 ohm-cms. being reported for industrial electrodes.

(4) Carbon consumed for a given amount of electrical energy consumed, compared to a theoretical value and usually expressed as a percentage greater than 100. Values of 140–165% have been reported as a typical range for industrial conditions, the lower the values being better.

(5) Ratio of weight of carbon consumed to weight of aluminium produced, the lower the value the better the performance. The theoretical minimum is reported as 0.33, but values from 0.4–0.5 are reported as the usual range in industry, and reports of much higher values are found.

(6) Current efficiency, expressed in values up to the best possible of 100 percent, 75–90% being reported as the normal range in industry.

Of the above, the performance characteristics indicated in paragraphs 4 to 6, are the most significant since they are measures of the process efficiency of the electrode material. The properties mentioned in paragraphs 1 to 3 are of somewhat lesser importance since deficiencies in these properties may be to some extent allowed for in industrial use.

Table 1 shows the measured values for the properties and performance characteristics which were found to obtain to the test electrodes during one series of tests.

It will be observed that whilst electrodes employing brown coal char as a filler are generally inferior to those employing petroleum coke, electrodes employing mixtures of brown coal char and petroleum coke are, in general, superior to either in a number of respects. Particularly, considering the average values for electrodes containing mixtures of brown coal char and petroleum coke fillers, and petroleum coke fillers alone, respectively, it may be seen that the mixture electrodes give approximately 12½% lower (better) carbon consumption, 22% lower (better) ratio of carbon consumed to aluminium produced, 13% higher (better) current efficiency, 17% higher (better) compression strength, 10% lower (worse) apparent density and 11% higher (worse) electrical resistivity. Although the mixture electrodes exhibit inferior densities and electrical resistivities the values for all the more important performance characteristics are superior.

Table 2 lists results obtained from a second series of tests made upon electrodes consisting of petroleum coke and of various mixtures of petroleum coke and brown coal char. The tested electrodes were prepared in the

same manner as described in relation to the electrodes of the first series of tests and were tested in the same manner as were those electrodes. There were no tests in the series upon electrodes utilizing only brown coal char filler.

The listed characteristics in Table 2 correspond to those listed in Table 1 but some additional information is incorporated. In particular, for each listed characteristic there is indicated the average of the test figures relating to the three listed electrodes utilizing petroleum coke as a filler. There is also listed, beside each listed result for the various mixture electrodes, a figure indicating the percentage difference between that result and the corresponding average figure for the three petroleum coke filled electrodes. These percentage differences are contained in the columns headed "rating" and positive figures indicate instances in which the result for the relevant mixture is superior to the corresponding average for the petroleum coke filler whilst negative results indicate instances in which the result for the relevant mixture is inferior to the corresponding average for the petroleum coke filled electrodes. Lastly, average ratings for the series of mixtures having 20%, 30%, 40%, and 50% brown coal char, and for the series of mixtures having 20%, 30%, 40%, 50% and 60% brown coal char are indicated.

It should be noted that the petroleum coke filled electrodes tested in the second series of tests generally possess superior characteristics to the petroleum coke filled electrodes tested in the first series of tests. Nevertheless the characteristics of the series 2 petroleum coke filled electrodes are still inferior to the second series mixture electrodes in several important respects. In particular the current efficiency of all of the tested mixture electrodes is superior.

Bearing in mind the relative importance in practice of each of the listed characteristics for the two series of tests it emerges that percentage additions of brown coal char of the order of 20% to 50% can be expected to produce the best overall results. However, in specific applications different emphases may be placed upon the various properties so that the optimum proportions for these applications may differ to the extent that the addition of 20% to 80% brown coal char can be expected to produce satisfactory results.

It is surprising to note that the performance of the mixture electrodes with each of the listed additions of brown coal char is comparable with those utilizing petroleum coke used alone even in those characteristics in which performance of the mixtures may be worse than that of petroleum coke alone, and satisfactory fillers are obtained with each of the specified mixtures.

Modifications may of course be made to the described method of preparing the filler material. In this regard, although the brown coal char was, in the described examples, prepared by charring at a temperature of approximately 1150° C., charring may be carried out over a wide range of temperatures but preferably in the range of 1100° C. to 1500° C.

Electrodes prepared from the filler material of the invention may utilize proportions of pitch which differ from the proportions indicated in the tables. In particular, a proportion of pitch in the range 13 to 23% is suitable for many industrial electrodes.

TABLE I

Properties and alumina reduction cell performance tests for electrodes prepared from brown coal char, petroleum coke and mixtures of both components

Electrode filler material	Pitch content, percent	Properties: Compression strength (p.s.i.) [1]	Properties: Apparent density (g./cc.) [1]	Properties: Electrical resistivity (ohm-cms.) [1]	Performance: Carbon consumed (percent of theoretical) [2]	Performance: Ratio of weights of carbon consumed to aluminium produced.	Performance: Current efficiency, percent [3]
Petroleum coke	17	3,740	1.49	0.0068	150	0.73	63
	17	3,740	1.49	0.0068	145	0.76	67
	19	6,370	1.50	0.0065	147	0.73	64
	19	6,270	1.50	0.0065	147	0.66	78
	21	5,610	1.46	0.0061	135	0.58	74
Brown Coal Char	23	5,440	1.21	0.01165	187	0.98	68
	27	6,770	1.15	0.01025	150	0.86	60
	31	5,650	1.21	0.0095	197	1.09	64
25% brown coal char, 75% petroleum coke	19	7,000	1.408	0.0069	129	0.51	80
50% brown coal char, 50% petroleum coke	23	6,940	1.306	0.00737	122	0.51	83
50% brown coal char, 50% petroleum coke	23	6,940	1.306	0.00735	128	0.59	7

[1] Value for a single specimen from batch of given pitch content.
[2] Based on CO_2 equivalent of carbon consumed for 40 amp-hours.
[3] Based on aluminium actually produced compared to theoretical amount for 40 amp-hours.

TABLE II

Properties and alumina reduction cell performance tests for electrodes prepared from petroleum coke and mixtures of brown coal char with petroleum coke. (Series 2)

Electrode filler material	Pitch content, percent	Electrode properties: Compression strength (p.s.i.) Value	Rating [3]	Apparent density (g./cc.) Value	Rating [3]	Resistivity (ohm-cms.) Value	Rating [3]	Electrode performance: Carbon consumed (percent of theoretical) [1] Value	Rating [3]	Ratio of carbon aluminium produced Value	Rating [3]	Current efficiency, percent [2] Value	Rating [3]
Petroleum Coke	17	6,050		1.52		0.0058		117		0.55		70.5	
	19	4,960		1.49		0.0051		107		0.51		70.5	
	21	4,460		1.49		0.0052		111		0.45		81.5	
Averages		5,154		1.50		0.0054		112		0.50		74.1	
20% brown coal char, 80% petroleum coke	19	5,500	+6.7	1.44	−4.0	0.0054	0.0	110	+1.8	0.45	+10.0	81.5	+10.0
30% brown coal char, 70% petroleum coke	19	7,610	+47.5	1.39	−7.3	0.0057	−5.6	118	−5.4	0.53	−6.0	75.0	+1.2
40% brown coal char, 60% petroleum coke	19	6,150	+19.3	1.34	−10.7	0.0074	−37.0	112	0.0	0.49	+2.0	76.0	+2.6
50% brown coal char, 50% petroleum coke	19	6,140	+19.2	1.32	−12.0	0.0070	−29.6	132	−17.9	0.54	−8.0	81.5	+10.0
Averages for 20 to 50% brown coal char			+23.2		−8.5		−18.0		−5.4		−0.5		+6.0
60% brown coal char, 40% petroleum coke	19	5,350	+3.8	1.28	−14.7	0.0081	−50.0	124	−10.7	0.53	−6.0	78.5	+5.9
Averages for 20 to 60% brown coal char			+19.3		−9.5		−24.4		−6.4		−1.6		+5.9
70% brown coal char, 30% petroleum coke	19	6,170	+19.7	1.24	−17.3	0.0087	−61.2	120	−7.2	0.53	−6.0	75.0	+1.2
80% brown coal char, 20% petroleum coke	19	4,260	−17.4	1.19	−20.7	0.0085	−57.3	138	−26.0	0.58	−16.0	79.5	+7.3

[1] Based on CO_2 equivalent of carbon consumed for 40 amp-hours.
[2] Based on aluminium actually produced compared to theoretical amount for 40 amp-hours.
[3] Percentage difference between values for mixtures compared with petroleum coke alone (+better, −worse).

We claim:

1. An electrode for use in an electrolytic cell for electrolytic reduction of aluminium oxide to aluminium, said electrode comprising an intimate mixture of petroleum coke and brown coal char particles, and mixture comprising 20% to 80% by weight of brown coal char.

2. An electrode for use in an electrolytic cell for electrolytic reduction of aluminium oxide to aluminium, said electrode comprising an intimate mixture of petroleum coke and brown coal char particles, said mixture comprising 20% to 50% by weight of brown coal char.

3. An electrode for use in an electrolytic cell for electrolytic reduction of aluminium oxide to aluminium, said electrode comprising pitch together with an intimate mixture of petroleum coke and brown coal char, said pitch being present in proportions 13% to 23% by weight of the electrode and the balance comprising said mixture, said mixture comprising 20% to 80% by weight of brown coal char and the balance comprising petroleum coke.

4. An electrode for use in an electrolytic cell for electrolytic reduction of aluminium oxide to aluminium, said electrode comprising pitch together with an intimate mixture of petroleum coke and brown coal char, said

pitch being present in proportions 13% to 23% by weight of the electrode and the balance comprising said mixture, said mixture comprising 20% to 50% by weight of brown coal char and the balance comprising petroleum coke.

References Cited

UNITED STATES PATENTS

2,998,375	8/1961	Peterson et al.	204—294
1,733,866	10/1929	Crossley	204—294

OTHER REFERENCES

I & EC Prod. Res. and Dev., vol. 8, No. 2, June 1969, pp. 188–193.

Chem. Abs., vol. 73:27426n, July 27, 1970.

Chem. Abs., 65:5268d, 1966; 1964; 61:15889f; 1958, 52:19090d.

Chem. Abs., 1957, 51:14243f.

JOHN H. MACK, Primary Examiner

R. J. FAY, Assistant Examiner

U.S. Cl. X.R.

106—284; 204—67, 243 R