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THE INFLUENCE OF LOW CURRENT DENSITIES ON ANODE PERFORMANCE

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ABSTRACT

While the dominant amount of electrolysis occurs on the bottom surface of aluminium smelting anodes, the sides of the anodes contribute up to one-third of the electro-active area. This zone contributes to the electrolytic process, but has an ever decreasing current density, also it is subjected to more vigorous agitation as the waves of anode gas bubbles rise near the vertically oriented surfaces. Some studies have suggested that most of the dusting of anodes occurs on this face, although the explanations are based on carboxy reaction. By performing a laboratory scaled investigation of the consumption rate of different quality carbon anodes, it is evident that low current density contributes significantly to the development of a roughened surface profile. The consumption rate simultaneously accelerates although its extent is clearly dependent on carbon quality. The differential reactivity was greater for some coke types and low baking temperatures.

Several methods for assessing anode performance have been developed and correlated with standard tests especially the carboxy reactivity test. The correlations show the tests are sensitive methods of assessing the total performance of an electrode, including its tendency to dusting.

INTRODUCTION

In recent years there have been considerable advances in the understanding of reactions contributing to the overall consumption of anodes, and how these relate to typical operating parameters and performance of cells[1-4]. In developing the various models that quantify the extent of reaction, it has become obvious that carbon quality is an important parameter - both in purity, the nature of the raw material used, and the manufacturing process for the anodes[4,5].

Consequently a range of tests have been developed which are valuable indicators of likely performance of anodes in operating cells[6,7]. Until recently, however, there have been no tests available for correlating the tendency of an anode and cell operating conditions to generate dust within the cell. Indeed quantifying dust formation has usually been done by its material balance differences (or unaccounted losses) and the quoted importance has varied considerably. It is generally considered the dust generating reactions occur on the sides of the anodes but it is less clear whether this has been initiated in the zone beneath the electrolyte or in the air burn zone of the emergent hot section of the electrode.

Dusting is due to differential reactivity of carbons resulting in poor adhesion of articulate material and subsequent detachment.

Barillion[8] showed that carbon dioxide evolved at the anode interface could permeate through the anode and react preferentially in pores. Subsequent work by Farr-Wharton et al[9] quantified the extent of this and the procedures have been adapted by others in studying anode consumption and dusting tendencies. Cutshall[10] found pore-reaction occurred both on the anode under-surface and on sides of anodes. He concluded that the majority of carbon sloughed from the anodes originated at the sides where the current densities were lower. While his work was technically sound, it could not rigorously eliminate the alternative cause, that being differential reaction occurring above the electrolyte interface through air burn. Accordingly a laboratory scale investigation has been undertaken whereby the latter cause can be eliminated.

EXPERIMENTAL DESIGN

Despite severe limitations of laboratory scale electrolytic testing, this approach enables the elimination of air burn reactions by control of atmosphere, and provides design flexibility for continuously monitoring process changes so that both dynamic and integral material balances can be performed. A laboratory scale study also has the advantage that a range of anodes that can be manufactured in a controlled manner and fully characterised with respect to traditional testing and properties are available and this enables direct correlation between properties and performance.

The totally enclosed electrolytic cell developed is illustrated in Figure 1. The dimensions of the crucible (cathode) were such that the current flow path between anodic and cathodic surface could be maintained constant for all immersed surfaces of the 50 mm diameter cylindrical anode specimens. The inter-electrode distance was similar to that applicable in operating cells. A similarity in scale (height versus depth of immersion) with real anodes was maintained and all electrolytic tests were performed in an electrolyte containing 12 wt% aluminium fluoride and 5 wt% calcium fluoride. The average alumina concentration was maintained at 4 ±1 wt%. Special features of the design apparatus were as follows:

- A nitrogen cover gas to minimise the concentration of oxidising (CO_2) gases above the surface

- Uniform current density at the sides and bottoms of anode specimens

- Continuous monitoring of the exit gas analysis

- Continuous monitoring of cell voltage and applied current

- Near constant current density being maintained

- Constant temperature electrolysis (975°C)

One of the disadvantages of the apparatus was the use of a carbonaceous cathode surface (the crucible) which had a much higher surface area than that of the anode specimen (ratio approximately 3.5:1). However, countering this disadvantage, approximately 2.0 kg of fresh electrolyte was used for each experiment thus ensuring that the degree of saturation of electrolyte with dissolved metal was repeatable at any equivalent stage of the experiment.

Prior to starting any electrolysis the dimensions and weight of the specimens were carefully recorded. Electrolysis was continued at constant current density with a fixed number of coulombs being passed in each experiment. During electrolysis the flow rate of the cover gas, and the exit gas composition (CO/CO_2 and Nitrogen) were continuously monitored and recorded in the data acquisition unit. After electrolysis the specimen was cleaned of adhering electrolyte and weighed to determine the weight loss. Because of inherent errors associated with incomplete cleaning or potential variations of carbon density within a specimen, other cross checks were made. One was to measure the volume change of the test electrode by mercury displacement in a specially designed apparatus and another was to perform a total carbon material balance from the recording of gas analysis. Separate experiments were performed to assess the impact of electronic conduction[11] (or direct electrochemical re-oxidation of

dissolved metal at the anode) in order to maximise the accuracy of measurements. Likewise the checks were made on the rate of reaction between CO_2 and the carbon crucible, at the concentration levels used. Thus extraneous sources of CO (other than from the anode specimen) were eliminated
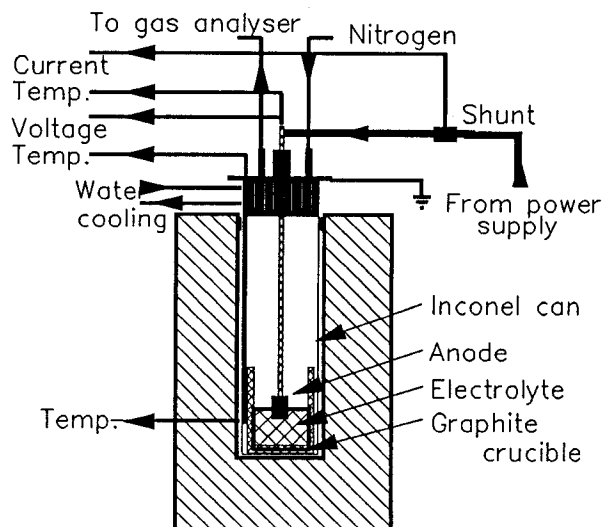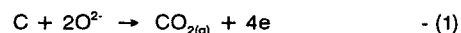

Figure 1: Overview of electrolytic cell and arrangement.

The basic performance of an anode is usually assessed against the minimum amount of carbon dioxide that is evolved according to the electrochemical reaction

$$C + 2O^{2-} \rightarrow CO_{2(g)} + 4e \qquad \text{- (1)}$$

and the theoretical amount of carbon consumed is related from the current passed and Faraday's law according to the equation

$$C \text{ weight lost (g)} = 3.11 \times 10^{-5} \int i dt \qquad \text{- (2)}$$

where t is the time in seconds at a total current i ampere.

The main cause of excess consumption is formation of carbon monoxide by direct reactions involving the carbon electrode. There are two reactions that contribute to this, these being electrochemical formations of carbon monoxide and the Boudouard reaction. As seen from equation (3) electrochemical formation of carbon monoxide doubles the rate of carbon consumption

$$2C + 2O^{2-} \rightarrow 2CO + 4e \qquad \text{- (3)}$$
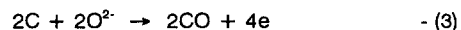
Formation of carbon monoxide by the carboxy reaction or the Boudouard reaction likewise doubles the consumption rate as seen by equation (4)

$$C + 2CO_2 \rightarrow 2CO \qquad \text{- (4)}$$
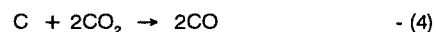
This reaction has been shown to occur within the anode pores due to the hydrostatic pressure of the electrolyte and the anode permeability.

TABLE I
Range of Electrodes and Properties Studies

COKE TYPE	BAKE TEMP (°C)	APPARENT DENSITY BAKED (kg/dm³)	AIR PERMEABILITY n/Pm	CO₂ REACTIVITY* %	DUST RATIO	SODIUM CONTENT (ppm)
A	950	1.537	1.31	16.7	1.32	176
A	1150	1.541	1.51	4.9	0.29	210
B	950	1.520	2.33	25.3	1.72	120
B	1150	1.526	2.69	12.0	0.75	128
S	950	1.542	1.76	20.8	1.29	239
S	1150	1.546	1.87	8.1	0.31	256
S+	950	1.531	3.50	42.9	2.00	484
S+	1150	1.544	2.12	19.0	0.78	475

One can not differentiate between equations (3) and (4) if the reaction were occurring on the surface however. From these reactions it is evident that the carbon monoxide to carbon dioxide ratio is expected to be a good measure of the rate of consumption of the electrode. It should be noted, however, carbon monoxide alone is not a true measure since some carbon monoxide is formed by back reaction by carbon dioxide and dissolved metal in the electrolyte. This reaction (equation (5)) is usually considered to occur at the interface between the anode gas and electrolyte but is dependant on the degree of saturation of the electrolyte with the dissolved metal.

$$3CO_2 + 2Al_{(diss)} \rightarrow Al_2O_3 + 3CO \qquad - (5)$$
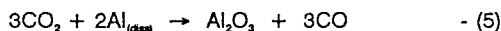
As noted above, since this reaction cannot be eliminated, the experimental procedure was to maintain it relatively uniform and repeatable.

The electrodes used in this study were made from

- 3 different sources of coke

- 2 different levels of sodium impurity

- at 2 different bake temperatures, these being 950°C and 1150°C.

Each of these specimens were made according to the recommended procedures for laboratory electrode testing and characterised by measurements of their physical properties and reactivities. Some of the more relevant properties are summarised in Table 1. (It should be noted that in this table, the CO_2 reactivity is equivalent to (100 - RR) where RR is the reactivity residue [6,7].) Several electrodes from each formulation were tested in the electrolytic cell, each being electrolysed at a constant current density. Practically, in order to account for the changed surface area with time, the current was stepped based on an assumed consumption performance. Cross checks showed this maintained the current density within 5% of the target value at all times. In some instances both at the beginning and end of an experiment the current density was stepped and resulting changes in anode gas composition monitored.

RESULTS OF INVESTIGATION

After applying the corrections determined from standardisation tests, the consumption rate measured is expressed as the fraction excess consumption based on the assumption that for no excess consumption the sole reaction at the anode is the production of pure carbon-dioxide according to Faraday's law.
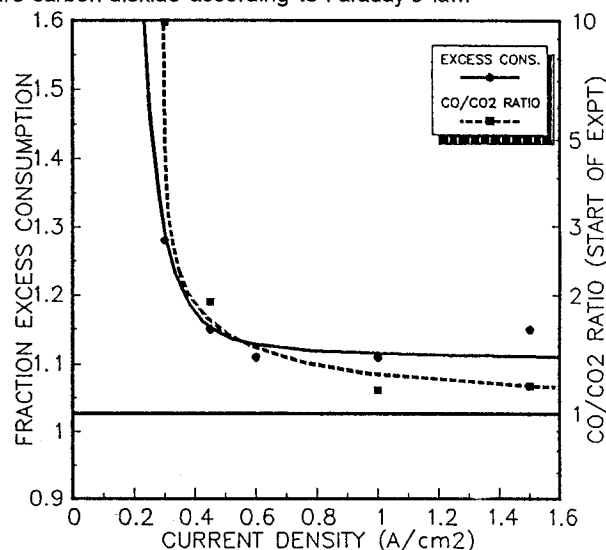

Figure 2: Influence of current density on both the consumption rate and anode gas composition.

Excess Consumption and Current Density

As seen in Figure 2, which is for a typical electrode baked at 1150 °C, there is an increase in consumption rate as the current density is lowered. The rate of increase accelerates as a current density is lowered below about 0.3 Amps/cm². This increase in consumption rate is associated with an increase in carbon-monoxide evolution as seen from the change in CO/CO_2. These changes occurred with all electrodes studied. The inflection and

acceleration in carbon-monoxide formation at low temperature is indicative of either a greater residence time or a changed reaction mechanism favouring either reactions 3 or 4 above.
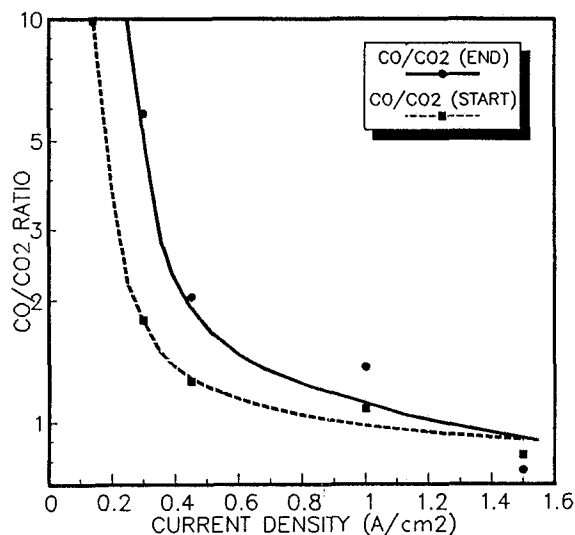

Figure 3: The change in CO/CO$_2$ ratio with current density through electrode roughening.

The CO/CO$_2$ ratio has been found to be an extremely sensitive indicator of the change in reactions for all samples tested. It has the advantage that it is less influenced by the electrochemical re-oxidation of metal at very low current densities and is therefore the preferred assessment method. However, the ratio measured when electrolyzing a freshly machined electrode compared to one that has had a roughened profile developed through more prolonged electrolysis is also apparent.
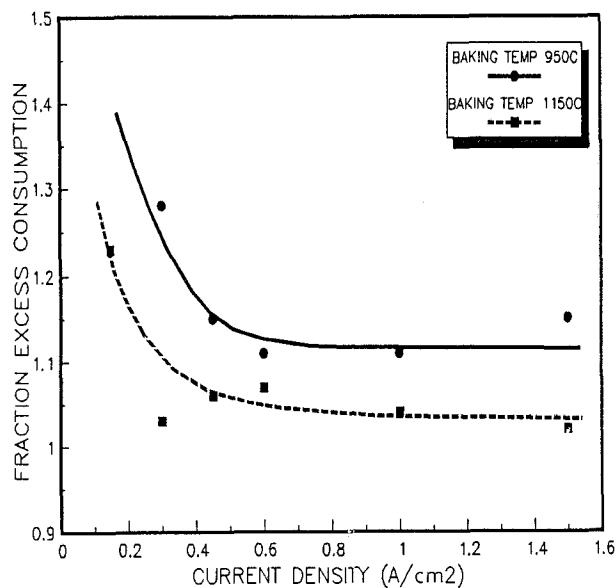

Figure 4: Influence of baking temperature on carbon consumption.

This is illustrated in Figure 3 but for a different electrode type. It is normal to observe the carbon monoxide content increasing as the surface area is increased by differential activity and roughening. Except when otherwise specifically mentioned, subsequent data presented in this investigation will be based on gas ratio evaluated at the start of the experiment. This is because the conditions are more precisely known.

Influence of Baking Temperature on Consumption

As illustrated in Figure 4, at any given current density the material baked at the higher temperature had the lower carbon consumption, all other things being equal. This also led to a lower CO/CO$_2$ ratio in the anodic gas (Figure 5) as the baking temperature rises. This change indicates that the reactivity of the carbon rather than increased residence time for carboxy reactivity plays an important role. Differences in reactivity become much more pronounced at the lower current densities. It is indicative of the important role played by binder and its resulting coke structure since it is that component of the heterogeneous materials that differs most structurally.
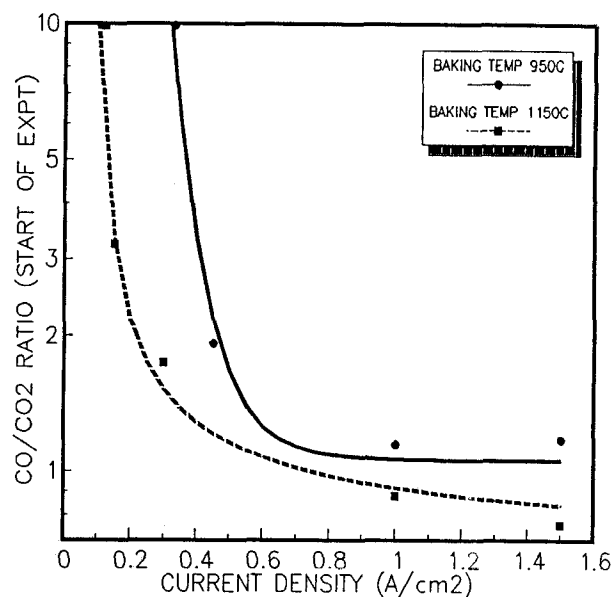

Figure 5: Influence of baking temperature on CO/CO$_2$ ratio.

Sodium from Recycled Butts

The specimens that had a higher amount of sodium as a consequence of recycled bath material gave higher reactivities as illustrated by the CO/CO$_2$ ratios versus current density presented in Figure 6.

Whereas the difference due to carbon reactivity is greater at low current densities the catalytic effect leads to a more discernable difference at higher current densities. This may be due to the structure of the carbon influencing the limiting rate of CO formation according to equation 3, whereas the sodium acts to catalyse reaction according to equation 4.
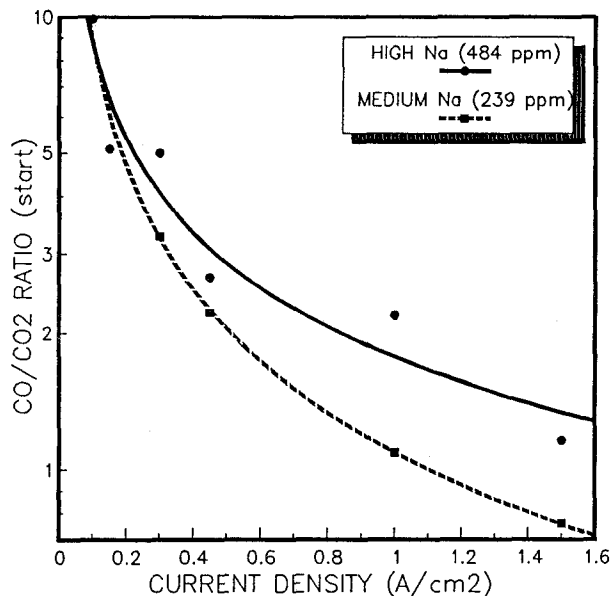
Figure 6: The change in CO formation rate through butt sodium as a function of current density.

Differences In Carbons

As seen in Figure 7, the CO/CO_2 ratio versus current density curves were different for different electrodes with the inflection occurring between 0.15 and 0.5 Amps $/cm^2$. Characterising different carbons is difficult, but as noted on the graphs the trend observed is consistent with the trends observed for the carboxy-reactivity according to one of the accepted standard tests[4,9]. The more electrochemically reactive electrodes had the higher reactivity to carbon dioxide whereas the least reactive electrode also had the lowest carboxy reactivity.
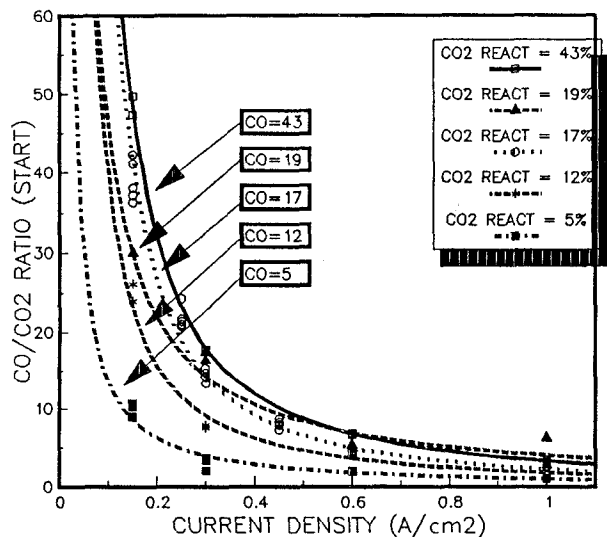

Figure 7: The influence of current density on electrolytic consumption for carbons of varying carboxy reactivity.
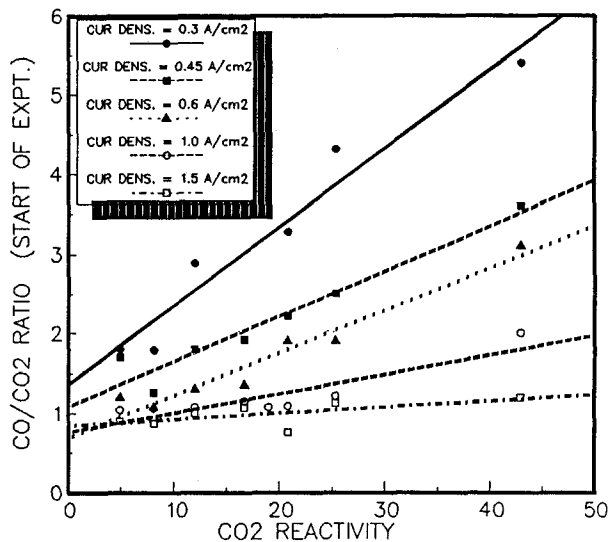

Figure 8: The correlation between observed anode electrochemical reactivity and measured carboxy reactivity.

CORRELATIONS BETWEEN CONSUMPTION AND REACTIVITY

The data presented in Figure 7 is clearly indicative of the important link between the carboxy reactivity test and the consumption rates observed in cells at low current densities. General correlations have been established with plant data earlier. The various tests applied to the materials (and summarised in Table 1) have been examined for correlations with the observed electrolytic consumption rates. Strong correlations existed between the carboxy reactivity test and the laboratory generated electrolytic consumption, as illustrated in Figure 8. This correlation is performed at several current densities with the data points on each curve represent the full range of carbons tested. Figure 8 demonstrates that the slope is a function of current density. (Linear regression gave adequate fits but the correlation is not necessarily expected to be linear.)

By performing similar data processing for a wider range of current densities and evaluating the slopes the correlation as presented in Figure 9 is clearly obtained. This indicates the importance of carbon reactivity at low current density. While air permeability was known to be important, the correlations were not as strong, but, the dimensions of the test specimens used were a poor simulation of operating environment in this instance.

Roughening and Dusting

Whenever the specimens showed a high excess carbon consumption, they were invariably associated with a marked increase in surface roughening. After performing a full range of tests, the specimens were arranged in order of increased surface roughness (as assessed visually) and assigned a numerical roughness index on a scale 1 to 10. Whilst this approach is quite qualitative, it was found that it gave extremely strong correlations with the dusting test that is used in conjunction with the air burn or carboxy reactivity tests. It demonstrates the importance of
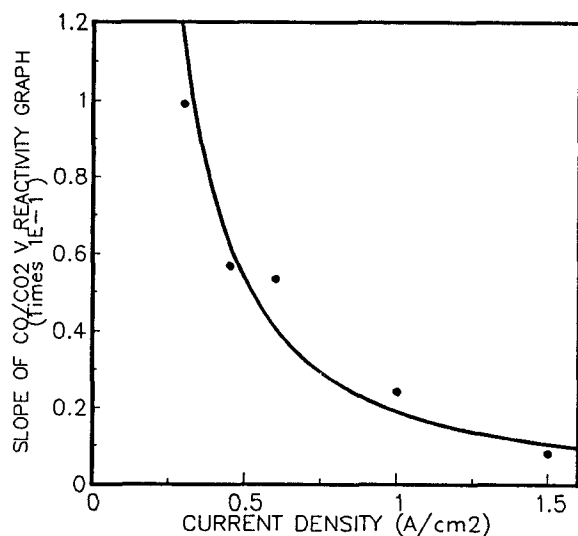
Figure 9: The interrelationship between carboxy reactivity and electrolytic consumption as a function of current density.

differential reactivity and the favoured oxidation of the binder carbon.

DISCUSSION AND CONCLUSIONS

The data presented in this paper, together with other results obtained during the investigation, demonstrate that when no metal can be directly re-oxidised at the anode surface, the carbon consumption rate tends to twice the theoretical at low current densities. Because of the simultaneous rapid acceleration in both the consumption rate and the rate of carbon monoxide formation, it is unlikely to be solely due to the Boudouard reaction. Thus direct electrochemical formation of carbon monoxide becomes an important mechanism at the low current densities. These conditions exist on sides of anodes, which, depending on depth of immersion of the electrodes, can carry more than 10% of the total anode current although at much lower current density.

The rate of increase in carbon consumption and carbon monoxide formation at low current densities differs with differing baking temperatures, carbon types and purity contents. This indicates that the coke source plays an important role. However, from the data presented (refer Figures 4,5 and 7) it is evident that the baking temperature is the most sensitive. This shows the important role of carbon structure and its modification during treatment. It is also evident that this reacting carbon arises from the binder phase since the parent coke has invariably been calcined to a higher temperature.

Sodium catalysis of the carboxy reaction is supported by this data. Because this reaction becomes more important at high current densities (through the higher rate of formation of carbon dioxide) the sodium sensitivity becomes more important in that region.

Correlations between the carbon consumption and the standard carboxy Reactivity Residue test are extremely good. While the Reactivity Residue test is a gaseous reaction, it is evident that it is

invaluable for assessing the dusting tendency and the overall electrochemical performance as well.

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