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THE CORROSION OF CARBON BLACK ANODES IN ALKALINE ELECTROLYTE: II. ACETYLENE BLACK AND THE EFFECT OF OXYGEN EVOLUTION CATALYSTS ON CORROSION

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ABSTRACT

The effect of five different metal oxides on the corrosion rate of acetylene black during oxygen evolution in alkaline electrolyte was determined using the analytical methods described in Part I. All five metal oxides (Fe₂O₃, Cr₂O₃, NiO, Co₃O₄ and Ru) catalyzed the corrosion processes of the acetylene black, resulting in corrosion rates accelerated by factors of 3 to 50. The mechanism of this catalytic effect remains unclear. Some results with Co₃O₄ have indicated direct contact between the oxide and the carbon is not required to accelerate the corrosion, suggesting a redox mechanism involving dissolved species. However, the effects of Fe₃O₄ and Cr₂O₃, which were significantly greater than with Co₃O₄, are difficult to rationalize on this basis, as their redox potentials lie well below the oxygen evolution potential range.
INTRODUCTION

A review of the electrochemical literature for carbon black corrosion together with the results for uncatalyzed acetylene black and the effect of Co$_3$O$_4$ catalyzation was presented in Part I of this work (1). Three major anodic processes were found to occur in uncatalyzed carbon black electrodes at 450-600 mV vs. Hg/HgO in concentrated KOH: carbon dissolution to carbonate ion, gasification of the carbon to carbon monoxide, and oxygen evolution. Due to different potential and temperature dependence of these three processes, the current efficiency for oxygen evolution is very small below 500 mV and 50°C (13% at 480 mV and 45°C) so that the total anodic current is essentially the corrosion current. Above ca. 600 mV or above 60°C at any potential above 450 mV, oxygen evolution is the dominant anodic process (80% current efficiency at 600 mV and 45°C). Catalyzation of the carbon with Co$_3$O$_4$ increased both the oxygen current efficiency and the rate of the corrosion processes severalfold. Furthermore, the presence of cobalt oxide produced organic molecules (ca. 5% current efficiency) at conditions where none were found for uncatalyzed carbon black.

In this work, five different metal oxide catalysts on acetylene black were investigated with regard to their corrosion behavior. $^{14}$C labeling was not
used in this study, as the large amount of labeled carbon required for the investigation of this many metal oxide catalysts would have been very costly. The advantage of $^{14}\text{C}$ labeling is that it provides the most accurate quantitative analysis of the corrosion product distribution. Our interest in this study was to determine the effect of different metal oxides on the total anodic current and on the total corrosion current, and not on the product distribution. Quantitative mass spectrometer analysis of the gas evolved was used to determine current efficiencies for oxygen evolution and gasification of the carbon to carbon monoxide. Because of some experimental improvements after Part I of this work and in order to compare the results directly, the Co$_3$O$_4$ was included again among the other catalysts, NiO, Fe$_2$O$_3$, Cr$_2$O$_3$ and metallic ruthenium.

EXPERIMENTAL

Catalyzation and Electrode Preparation - The principles of the catalyzation procedure, the particular electrochemical cell for the corrosion measurements and the quantitative analysis of the evolved gas during oxygen evolution were described previously (1), so we report here only the changes. Except for ruthenium, the metal content was prepared at a 20 weight percent (w/o) level assuming Co$_3$O$_4$, NiO, Cr$_2$O$_3$ and Fe$_2$O$_3$ as final form using the impregnation procedure. The impregnated acetylene black were air dried at 320°C for 24 h, and the conversion of the metal hydroxides to the above oxide phases during this process were confirmed by x-ray diffraction analysis.

Known from earlier experience, the Ru(OH)$_3$ impregnated carbon black (precipitation from dissolved RuCl$_3$·H$_2$O with NH$_4$OH) is chemically too active
to be air dried at 320°C like the other catalysts. It was therefore heat treated at 350°C for 4 h under hydrogen flow and then at the same temperature for 16 h under nitrogen flow. Prepared at 20 w/o level, the final form was highly dispersed metallic ruthenium on the acetylene black according to the x-ray diffraction analysis. In this case, the conversion to some ruthenium oxide and/or hydroxide phase occurred during the electrochemical "aging period" at 400 mV vs. Hg/HgO, when also soluble RuO$_4^{2-}$ ions were produced (see below). A paste mixed from 40 mg catalyzed black and 12 mg PTFE solids (in duPont TFE-30B dispersion) was applied to a gold-plated tantalum mesh and air dried at ca. 60°C for 24 h. The loading of catalyzed carbon black in each tested working electrode was 10 mg/cm$^2$. All corrosion experiments were done in pure 30 w/o KOH (Mallinckrodt, AR) at a temperature of 55°C. The reference electrode was Hg/HgO, so all potentials in this paper are given vs. Hg/HgO in the same electrolyte at room temperature.

Gas Analysis- A UTI model 100C quadrupole mass spectrometer was used for the quantitative determinations of the composition of the sampled gas (argon as dilutent gas and oxygen and carbon monoxide evolved from the electrode). It was equipped with a special thoria-coated iridium filament which has very low oxygen consumption and carbon monoxide production. The mass spectrometer was run by an IBM PC-XT with software developed for the purpose of these investigations. The calibration procedure using definite oxygen evolution from a nickel Exmet electrode as well as calibrated mixtures of oxygen and carbon monoxide (Matheson) was the same as that described in Part I. In order to keep the background signal at AMU 28 (carbon monoxide) very low, mass analyses were done with the lowest possible filament emission current of 0.2 mA at a pressure
of $10^{-7}$ torr. Nonetheless, some background subtraction was necessary and was included in the calculation of the absolute partial pressure in the case of carbon monoxide.

RESULTS

Structure of Oxide Impregnated Carbon- The physical structure of the oxide impregnated acetylene black, and differences in structure between the different oxides, were investigated by x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD analysis indicated the oxides were single phase and crystalline; in the case of Ru catalyzed carbon, the XRD pattern for the hydrogen reduced state was identical to the standard pattern for metallic Ru. Line-broadening analysis using the Scherrer equation indicated significant differences in average crystallite size between the various catalysts. Qualitatively, the line-broadening analysis indicated the ordering of crystallite size was: $\text{Co}_3\text{O}_4 > \text{Cr}_2\text{O}_3 \approx \text{Fe}_2\text{O}_3 > \text{NiO} > \text{Ru}$. Quantitative determination of crystallite size by XRD was not made due to the large distribution of crystallite sizes observed in TEM analysis (the Scherrer equation does not apply when there is a wide distribution of crystallite sizes). The crystallite size, size distribution, and the uniformity of dispersion of the crystallites within the acetylene black matrix was determined by TEM analysis. The TEM micrograph in Fig. 1 is characteristic of the crystallite size and dispersion in the matrix of the oxides $\text{Co}_3\text{O}_4$, $\text{Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$. For these oxides, there are heavily oxide coated regions and regions of carbon where there is no oxide. Characteristic dimensions of these oxide crystallites were 10-40 nm, which means the specific surface area of the oxide
phase is typically 25-100 m²/g, much higher than can be easily achieved in the absence of the carbon matrix. The NiO phase and the metallic Ru were much more uniformly dispersed in the carbon matrix, and consisted of significantly smaller crystallites, typically 5-10 nm.

Although the Ru catalyst was initially in the metallic state, it is known from the electrochemistry of this element that conversion of a significant fraction of the Ru to an oxide would occur in-situ in the potential region of this study. XRD analysis of a corroded electrode indicated a significant fraction of the Ru was in fact converted to a new (non-metallic) phase, but we could not identify the phase as being related to the known crystalline oxide phases, e.g. RuO₂ or Ru₂O₃.

Corrosion Rates in Presence of NiO and Co₃O₄ - Before running the corrosion rate measurements, every new electrode underwent an "aging period" of 48 h at 400 mV and 55°C. The charge of about 250-280 C passed during this time is used almost entirely for carbon corrosion with relatively high production of organic compounds resulting in a dark brown electrolyte; the formation of "surface oxides" on the fresh carbon surface takes place during this "aging period" (see Part I). Corrosion rate measurements were conducted after this aging period with fresh electrolyte, i.e. cell drained and refilled. Because of the large double-layer capacitance of the porous electrodes and the related high currents during the first 30 seconds after switching from the open circuit potential to the measuring potential, the total current densities (i_{total}) were calculated from the slopes of the straight line of the recorded charge vs. time curves, omitting this initial region. In order to get reproducible results, the gas sampling at every potential (in fresh KOH solution) was stopped after the
charge of 25 C had passed with sampling times from 20 mins. to several hours. The total corrosion currents $i_{\text{corr}}$ were calculated by subtraction of the measured partial anodic currents for oxygen evolution $i_{O_2}$ from the overall anodic currents $i_{\text{total}}$:

$$i_{\text{total}} = i_{O_2} + i_{\text{corr}}$$

As shown in Part I, the corrosion processes are primarily carbon gasification to carbon monoxide (quantitatively determined) and the dissolution to carbonate, i.e. $i_{\text{corr}} \approx i_{\text{CO}} + i_{\text{CO}_3^{2-}}$. The results for the NiO and Co$_3$O$_4$ catalyzed acetylene black are shown in Fig. 2.

Both catalysts, NiO and Co$_3$O$_4$, reveal similar trends in their corrosion behavior. At lower potentials the total corrosion currents are predominant and greater than the oxygen evolution currents, then reach a maximum at 550 mV and drop again, in the case of NiO very sharply. In the potential region investigated, the partial currents for $O_2$ evolution show Tafel behavior with slopes of 145 mV per decade for NiO and 110 mV per decade for Co$_3$O$_4$, respectively. The most significant differences between the two catalysts according to Fig. 2 are the absolute current values, which are greater by a factor of about two for the NiO catalyzed electrode. This difference is qualitatively consistent with the result of the TEM analysis, where the particle size of the NiO-cluster was found to be smaller than that of the Co$_3$O$_4$-cluster and hence the effective catalytic area of the NiO is much higher than the Co$_3$O$_4$ area.

Table 1 summarizes the results including the current efficiencies for oxygen and carbon monoxide evolution and the total weight losses of the
catalyzed blacks. In order to see the catalytic effect, the results for uncatalyzed acetylene black are also listed. The rate of weight loss \( k (\% \text{ hr}^{-1}) \) is calculated from the expression

\[
k = \left( \frac{M}{4F} \cdot i_{\text{CO}_3}^{2-} + \frac{M}{2F} i_{\text{CO}} \right) \cdot 3600 \cdot 100
\]

where \( M = \text{g carbon per mol CO}_3^{2-} \) or \( \text{g carbon per mol CO} \) respectively, so \( M = 12 \). Substituting \( i_{\text{CO}_3}^{2-} \) by the relation

\[
i_{\text{CO}_3}^{2-} = i_{\text{corr}} - i_{\text{CO}}
\]

yields

\[
k = \left( \frac{M}{4F} \right) \left( 3600 \cdot 100 \cdot i_{\text{corr}} + i_{\text{CO}} \right)
\]

\[
= 11.2 \left( i_{\text{corr}} + i_{\text{CO}} \right)
\]

Two results are striking with respect to the current efficiencies. (i) Except for 600 mV, the \( \text{O}_2 \) current efficiency is ca. 5-10% higher and the \( \text{CO} \) current efficiency is ca. 5-10% lower for the \( \text{NiO} \) catalyzed electrode compared to the \( \text{Co}_3\text{O}_4 \). The rate of carbon dissolution to carbonate is therefore in both cases equal and the \( \text{O}_2 \) evolution rate is increased only at the expense of the \( \text{CO} \) production with \( \text{NiO} \) as electrocatalyst. (ii) For both catalysts, a large increase of the \( \text{O}_2 \) current efficiencies takes place between 550 mV and 600 mV.
Corrosion Rates in Presence of Cr$_2$O$_3$, Fe$_2$O$_3$ and Ru- These three catalysts are distinguished from NiO and Co$_3$O$_4$ in that they are electrochemically not stable in the high potential region applied during oxygen evolution and dissolve partly to soluble ions. However, there is remaining a certain quantity inside the carbon electrode in the form of a higher oxidation state either as solid metal oxides (CrO$_2$, RuO$_2$) or as adsorbed ions like CrO$_4^{2-}$, FeO$_4^{2-}$, and RuO$_4^{2-}$ which may then be the actual catalysts for the oxygen evolution (or carbon corrosion). The formation of these species occurred primarily during the "aging period" at 400 mV for 48 h at 55°C, when the charge passed through the electrode was about 50-80 C greater than in the case of NiO or Co$_3$O$_4$. This amount of charge equals ca. 30-50% of the charge necessary for the oxidation of the entire fresh catalyst into the highest possible oxidation state. There was visible evidence of further dissolution during the corrosion rate measurements.

The total anodic currents and the partial currents due to the different anodic processes are shown in Fig. 3. Comparison of the partial currents for oxygen evolution $i_{O_2}$ with the total corrosion currents $i_{corr}$ reveals three distinct situations. In case of the Fe$_2$O$_3$ catalyzed black, $i_{corr}$ is always greater than $i_{O_2}$ and is about 60% of the total current. For the Ru doped electrode the oxygen evolution rate was slightly greater than the corrosion rate, even at the lowest potential at 450 mV. The Cr$_2$O$_3$ as catalyst shows behavior similar to NiO and Co$_3$O$_4$, i.e. the Tafel slope for $i_{O_2}$ is much steeper than for $i_{corr}$ and the oxygen evolution prevails therefore only at potentials higher than 500 mV. The current efficiencies for oxygen listed in Table 2 reflect these different corrosion characteristics directly. They are constant within the accuracy of measurements for Fe$_2$O$_3$ and Ru and increase only in the case of the Cr$_2$O$_3$ catalyzed black. It is an interesting observation that for
the "Ru" electrode there is obviously no change in the product distribution for oxygen, carbon monoxide and carbonate in the potential region investigated.

**DISCUSSION**

In order to get a greater understanding of the catalyzed corrosion process, five potential oxygen evolution catalysts were investigated with regard to their corrosion behavior with acetylene black during oxygen evolution in 30 w/o KOH. Included were three catalysts that dissolve partly under these extreme conditions and it is clear that for practical applications, e.g. in a rechargeable metal-air battery, particular precautions must be taken to prevent diffusion and fatal action of these ions at the negative electrode (hydrogen evolution), e.g. use of cation excluding membranes. Similar precautions may be necessary in the case of the production of organic products which are formed with the stable catalysts NiO and Co$_3$O$_4$ at evolution potentials.

Although many different properties have to be considered in addressing the issue of the most suitable evolution catalyst, two main features are predominant. (i) The current efficiency for oxygen evolution, which is shown in Fig. 4 for each catalyst considered here. High efficiency at low potential is desirable in practice, but as these results indicate none of these catalysts exceeds 65% efficiency below 550 mV and ruthenium had the best efficiency of only 54% at the lowest potentials. (ii) The total carbon weight loss of the electrode, in combination with the oxygen current efficiency, reflects directly the corrosion resistance. As seen from Fig. 5, Fe$_2$O$_3$ as catalyst causes weight losses as high as 5% h$^{-1}$, followed by Cr$_2$O$_3$ with up to 2% h$^{-1}$. These values are much too high with respect to practical applications, where as a rule of
thumb, the total weight loss should not exceed ca. 0.01% h$^{-1}$ at most. Figure 4 also illustrates the catalytic effect of the metal oxides on the rate of carbon weight loss, which is seen by comparison of the rates for uncatalyzed acetylene black with those for the catalyzed material. At potentials below 550 mV, the effect varied from nearly an order of magnitude (in the case of Fe$_2$O$_3$) to about a factor of three (in the case of Co$_3$O$_4$). The latter factor is about the same as that reported in Part I using $^{14}$C doped acetylene black and the $^{14}$C detection method for weight loss measurement. Overall, NiO appears to have the best catalytic properties, with the highest absolute rate of oxygen evolution catalysis in combination with relatively low carbon corrosion catalysis. However, for practical purposes, the acetylene black corrosion rate, even with NiO catalyst, is at least an order of magnitude too high for practical use in a bifunctional air electrode.

In Part I, we postulated that the mechanism of catalyzation of the carbon corrosion reaction may involve a redox sequence involving cobalt species in solution within the pores of the electrode matrix. Figure 6 shows schematically what we postulated this mechanism to be, using Co(II)/Co(III) as an example. Using the $^{14}$C tracer method, we were able to show previously that the Co$_3$O$_4$ particles did not have to be in physical contact with the carbon particles to catalyze the corrosion of the carbon. Solvated Co(II)/Co(III) species can act as a shuttle of charge (and current) between oxide particles and carbon particles. Because the oxide phase has a relatively high resistivity compared to the acetylene black, within the electrode structure the surface of oxide particles can be at a higher potential than carbon particles 10-100 nm away, creating an internal potential gradient which drives the redox shuttle. In effect, the carbon surface experiences the higher potential of the
nearby oxide particles due to this ionic coupling, thus corroding at a higher rate than in the absence of the oxide phase.

It is difficult to rationalize the catalytic effect of the iron and chromium oxides even though these catalysts clearly produced more solvated ions than the cobalt catalyst, and the catalytic effect with these oxides was approximately three times higher. A catalytic effect of solvated iron species on graphite oxidation in acid has been noted before (2), and was postulated to arise from a redox mechanism. The difficulty here in applying a redox mechanism for Fe(II)/Fe(III) redox is the potential region in which the effect is observed, which is a few hundred millivolts above (anodic) the limits of predominance for Fe(III), i.e. there is little driving force for the formation of Fe(II) species at these potentials. One would be forced to invoke Fe(III) as the reduced state in the redox shuttle, and invoke the formation of higher valent iron states, e.g. FeO_4^{2-} ferrate ion, whose existence is uncertain (3).

The situation for chromium is even more problematic. In this case, the applicable redox couple would be Cr(VI)/Cr(III), but the reduction potential for Cr(VI) lies well below the oxygen evolution potential in alkali medium (4). It is difficult, therefore, to account for the catalytic action of those oxides on carbon corrosion via a redox mechanism, and viable alternative mechanisms are not clearly available.

The dramatic decrease in the rate of carbon corrosion above 550 mV in the case of NiO and Co_{3}O_{4} catalyzed acetylene black has important technological consequences for bifunctional air electrodes. One explanation of this effect follows the conventional wisdom of gas evolution from porous materials (see, for example, the review by Hall (5) and references therein). Above a certain critical rate of gas evolution from the interior wetted surface of a porous
electrode, the rate of transport of dissolved gas by molecular diffusion is less than the rate of gas formation, resulting in bubble nucleation within pores. Gas bubble formation within pores is problematic for gas evolution, since bubble growth forces electrolyte out of the pores, and restricts ionic transport into the interior surface. The zone for gas evolution at high rate is, therefore, only the exterior macroporous region of the electrode, with the interior microporous surface either "dry" or ionically isolated from the bulk electrolyte. Gas bubble formation inside the catalyzed carbon electrode would, in this physical scheme, protect the microporous interior of the carbon from anodic dissolution, accounting for the sharp decrease in corrosion rate above a critical potential. The difficulty with this explanation, however, is that this "area effect" due to gas bubble formation would produce a decrease on both the oxygen evolution rate and the corrosion rate, unless gas evolution occurs predominantly from the exterior surface of the electrode at all potentials. Experimentally, the oxygen evolution rate was observed to increase monotonically with potential over the range where the corrosion rate dropped dramatically. It seems unlikely that gas evolution would occur nearly exclusively from the exterior surface at all potentials (and rates) so that this explanation seems unlikely.

There are two alternative mechanisms we can advance to explain the sharp maximum in the carbon corrosion rate. The first, which we consider the most likely, is related to the redox mechanism for the catalytic effect of NiO and Co$_3$O$_4$ on carbon corrosion (shown in Fig. 6 for the case of Co$_3$O$_4$). The redox mechanism can function only when the local (carbon sites) potential is below the reduction potential for the higher valent state of the metal ion, Co(III) or Ni(III). There will be an anodic limit to this process, above which the
ionic shuttle will stop and the carbon corrosion rate will drop towards the rate for uncatalyzed carbon. The second alternative mechanism is also related to the valence state of the oxide. It may be that the catalytic effect of the NiO and/or Co₃O₄ occurs when the oxide is in a certain characteristic valence state, probably the divalent state, and that the catalysis is turned off when the oxide reverts to the higher valent state at a critical anodic potential, i.e. the oxide is "passivated" for this particular reaction.

However, none of the three explanations we have suggested for the corrosion rate maxima in NiO and/or Co₃O₄ catalyzed acetylene black have any independent evidence to support their validity. Also, we were unable to determine the mechanism by which the other oxides catalyze the corrosion processes of this carbon black.

CONCLUSIONS

1.) All five oxygen evolution catalysts also catalyzed the corrosion processes of the acetylene black, resulting in corrosion rates accelerated by factors of 3 to 50. The mechanism of this catalytic effect is unclear. Some results with Co₃O₄ have indicated direct contact between the oxide and the carbon is not essential, suggesting a redox mechanism involving dissolved species. However, the effects of Fe₂O₃ and Cr₂O₃, which are significantly greater than the effect with Co₃O₄, are difficult to rationalize on this basis, as their redox potentials lie well below the oxygen evolution potential range.

2.) NiO catalyzed acetylene black exhibited the best overall catalytic properties for oxygen evolution, but a relatively high anodic potential of 600 mV (vs. Hg/HgO) was required to increase the current efficiency for oxygen
above 90%. However, the carbon corrosion rate at this potential is at least an order of magnitude too high for technological application of this catalyzed carbon in a bifunctional air electrode.

ACKNOWLEDGMENTS

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REFERENCES

Table 1. Current Densities, Current Efficiencies and Weight Losses for Uncatalyzed and NiO and Co$_3$O$_4$ Catalyzed Shawinigan Black at 55°C.

<table>
<thead>
<tr>
<th>E (mV)</th>
<th>$I_{\text{total}}$ (mA/mg)</th>
<th>$I_{O_2}$ (mA/mg)</th>
<th>$%O_2$</th>
<th>$I_{CO}$ (mA/mg)</th>
<th>$%CO$</th>
<th>$I_{\text{corr}}$ (mA/mg)</th>
<th>Weight Loss (% hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncatalyzed Shawinigan Black</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.040</td>
<td>0.006</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>0.034</td>
<td>0.38</td>
</tr>
<tr>
<td>600</td>
<td>0.120</td>
<td>0.050</td>
<td>42</td>
<td>-</td>
<td>-</td>
<td>0.070</td>
<td>0.78</td>
</tr>
<tr>
<td>650</td>
<td>0.285</td>
<td>0.173</td>
<td>62</td>
<td>-</td>
<td>-</td>
<td>0.112</td>
<td>1.25</td>
</tr>
</tbody>
</table>

| 20 w/o NiO on Shawinigan Black |
| 450    | 0.085           | 0.035           | 41    | 0.016          | 19    | 0.050           | 0.74            |
| 500    | 0.190           | 0.093           | 49    | 0.027          | 14    | 0.097           | 1.39            |
| 550    | 0.288           | 0.178           | 62    | 0.023          | 8     | 0.110           | 1.49            |
| 600    | 0.420           | 0.394           | 94    | 0.021          | 5     | 0.026           | 0.53            |

| 20 w/o Co$_3$O$_4$ on Shawinigan Black |
| 450    | 0.040           | 0.014           | 35    | 0.011          | 26    | 0.026           | 0.41            |
| 500    | 0.082           | 0.034           | 41    | 0.018          | 22    | 0.048           | 0.74            |
| 550    | 0.154           | 0.085           | 55    | 0.020          | 13    | 0.069           | 1.01            |
| 600    | 0.361           | 0.307           | 85    | 0.018          | 5     | 0.054           | 0.81            |
Table 2. Correspondent Data as in Table 1 for Cr$_2$O$_3$, Fe$_2$O$_3$ and Ru as Oxygen Evolution Catalysts.

**20 w/o Cr$_2$O$_3$ on Shawinigan Black**

<table>
<thead>
<tr>
<th>E (mV)</th>
<th>$I_{\text{total}}$ (mA/mg)</th>
<th>$I_{O_2}$ (mA/mg)</th>
<th>% $O_2$</th>
<th>$I_{CO}$ (mA/mg)</th>
<th>% CO</th>
<th>$I_{\text{corr}}$ (mA/mg)</th>
<th>Weight Loss (% hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.086</td>
<td>0.029</td>
<td>34</td>
<td>0.019</td>
<td>22</td>
<td>0.057</td>
<td>0.85</td>
</tr>
<tr>
<td>500</td>
<td>0.183</td>
<td>0.099</td>
<td>54</td>
<td>0.032</td>
<td>18</td>
<td>0.084</td>
<td>1.30</td>
</tr>
<tr>
<td>550</td>
<td>0.335</td>
<td>0.201</td>
<td>64</td>
<td>0.037</td>
<td>11</td>
<td>0.134</td>
<td>1.91</td>
</tr>
</tbody>
</table>

**20 w/o Fe$_2$O$_3$ on Shawinigan Black**

<table>
<thead>
<tr>
<th>E (mV)</th>
<th>$I_{\text{total}}$ (mA/mg)</th>
<th>$I_{O_2}$ (mA/mg)</th>
<th>% $O_2$</th>
<th>$I_{CO}$ (mA/mg)</th>
<th>% CO</th>
<th>$I_{\text{corr}}$ (mA/mg)</th>
<th>Weight Loss (% hr$^{-1}$)</th>
</tr>
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<tr>
<td>450</td>
<td>0.093</td>
<td>0.033</td>
<td>35</td>
<td>0.023</td>
<td>22</td>
<td>0.060</td>
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<tr>
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<td>0.083</td>
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<tr>
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<td>0.249</td>
<td>41</td>
<td>0.085</td>
<td>14</td>
<td>0.359</td>
<td>4.97</td>
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**20 w/o Ru on Shawinigan Black**

<table>
<thead>
<tr>
<th>E (mV)</th>
<th>$I_{\text{total}}$ (mA/mg)</th>
<th>$I_{O_2}$ (mA/mg)</th>
<th>% $O_2$</th>
<th>$I_{CO}$ (mA/mg)</th>
<th>% CO</th>
<th>$I_{\text{corr}}$ (mA/mg)</th>
<th>Weight Loss (% hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.082</td>
<td>0.044</td>
<td>54</td>
<td>0.015</td>
<td>19</td>
<td>0.038</td>
<td>0.56</td>
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<tr>
<td>500</td>
<td>0.138</td>
<td>0.070</td>
<td>51</td>
<td>0.023</td>
<td>17</td>
<td>0.068</td>
<td>1.02</td>
</tr>
<tr>
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FIGURE CAPTIONS

Fig. 1. TEM of chromium oxide catalyzed acetylene black.

Fig. 2. Total anodic currents, partial anodic currents for oxygen and carbon monoxide and total corrosion currents for the NiO and Co₃O₄ catalyzed carbon.

Fig. 3. Same plots like Fig. 2 for Fe₂O₃, Cr₂O₃ and Ru as catalysts.

Fig. 4. Current efficiencies for oxygen evolution as a function of potential for the different catalyzed acetylene blacks at 55°C.

Fig. 5. Total weight losses of carbon, expressed as a percentage of carbon initially in the electrode.

Fig. 6. Possible reaction mechanism involving the soluble redox system Co(II)/Co(III) to explain the accelerated carbon corrosion in presence of a catalyst.
Electrode potential (mV vs Hg/HgO)

Current density (mA/mg)

20 w/o NiO
55°C

20 w/o Co$_3$O$_4$
55°C

- total
- O$_2$
- corr
- CO

Fig. 2
Fig. 3

Electrode potential (mV vs Hg/HgO)

Current density (mA/mg)

- total
- O₂
- corr
- CO

20 w/o α-Fe₂O₃ 55°C
20 w/o Ru 55°C
20 w/o Cr₂O₃ 55°C
Fig. 4
Fig. 5

Electrode potential (mV vs Hg/HgO)

Weight loss (% hr⁻¹)

- Ni
- Co
- Fe
- Ru
- Cr

Electrode potential vs Weight loss for different metals.
A: C + 4 Co (III) + 6 OH⁻ → CO₃²⁻ + 4 Co (II) + 3H₂O
B: 4 Co (II) → 4 Co (III) + 4 e⁻

C + 6 OH⁻ → CO₃²⁻ + 3 H₂O + 4 e⁻