Electrochemical impedance spectroscopy (EIS) studies in ethanol

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Introduction

In mid-1970, Brazil developed technology for the adaptation of vehicular engines and for the production of ethanol fuel, achievements that have made the country the pioneer in the use of ethanol as a vehicle fuel. At that time, many researchers focused their works on metal corrosion by ethanol fuel studies [1-8]. As of 2003, with the development of a bi-fuel car technology (flex fuel), the country received new inputs for ethanol production with a significant increase in its consumption. Within this context, the studies of ethanol fuel began again to have relevance, mainly due to the need of carrying large volumes of the product through dedicated pipelines, called ethanol pipelines [9]. This work aims to study the behavior of AISI 1020 carbon steel in anhydrous ethanol from different sources as sugar cane and corn by means of the EIS technique, using reagent grade anhydrous ethanol as a reference.

Experimental

EIS measurements were conducted using the Solartron 1287/1260 system after the open circuit potential (OCP) stabilization which took place after about one hour. The scanned frequency range was from 50 kHz to 1 mHz and the amplitude was 10 mV peak-to-peak. Ten points were acquired for each frequency decade. A Tait type electrochemical cell was used with both counter electrode (CE) and quasi-reference electrode (QRE) made with Hastelloy. AISI 1020 carbon steel was used as a working electrode (WE). The Tait cell was kept in a Faraday cage during the experiments. In previous experiments, it was verified that EIS diagrams in this kind of experiments presented a strong noise due to environmental interferences which were completely eliminated by using a Faraday cage [10]. The distance (d) between the QRE and the WE was kept at 0.5 mm and between the CE and WE at 20 mm. Two commercial samples were studied: sugar cane ethanol and corn ethanol. Reagent grade anhydrous ethanol was used as a reference. The WE was ground with 1200-grit SiC paper, rinsed with distilled water followed by dipping in reagent grade ethanol, dried under hot air flow and then it was placed in the test cell. The ethanol samples were naturally aerated and the cell was kept closed throughout the period of the test. All tests were performed at room temperature ((23 ± 3)°C).

Results and Discussion

Figure 1 presents the OCP values as a function of immersion time of carbon steel in the three studied media. The obtained values after stabilization were: -0.135 V vs QRE for reagent grade ethanol; -0.186 V vs QRE for sugar cane ethanol and -0.183 V vs QRE for corn ethanol. It can be seen that the after-stabilization OCP value in the reagent grade ethanol was about 50 mV more positive than in the commercial samples. It can also be observed that the initial OCP value in sugar cane ethanol assumes a more positive value at the beginning of the immersion and increases with time. An opposite behavior is observed in corn ethanol: the initial OCP value is more negative and increases with the immersion time.

Figure 2 and Figure 3 present the Nyquist and Bode impedance diagrams for the three samples, respectively. From Figure 2, it can be observed that the Z' and the Z" obtained values for carbon steel in reagent grade ethanol are about one order of magnitude higher than those obtained in commercial ethanol samples. The Z' values obtained through the intersection between the first capacitive arc with real Z'-axis taken from Figure 2 are presented in Table 1. As these values are related to the capacitive/resistive behavior of the organic medium itself [10], the observed differences may be attributed to possible ionic contaminants present in the commercial samples. It is worth mentioning that the value obtained in sugar cane ethanol is slightly higher than the value obtained in corn ethanol.

Table 1 – Z' values obtained by the intersection between the first capacitive arc and the real Z'-axis (Figure 2).

Medium	**Frequency (Hz)**	**Z' (Ω cm^2)**
Reagent grade anhydrous ethanol	125	$1{,}37\text{x}10^6$
Sugar cane fuel ethanol	200	$6{,}73\text{x}10^5$
Corn fuel ethanol	250	$6{,}26\text{x}10^5$

Another important point in Figure 2 is related to the second arc: the reagent grade ethanol presented more capacitive behavior than the commercial ethanol samples. Here again, there is a slight difference between sugar cane ethanol and corn ethanol: the former presents a slightly more capacitive behavior. This may be an indication of more aggressive characteristics of the commercial ethanol due to the presence of contaminants, the aggressiveness of the sugar cane ethanol being slightly less than the corn ethanol. These contaminants can be one or more compounds which were within the established limits of commercial ethanol fuel standards [11, 12]. In order to confirm the higher aggressiveness of the commercial ethanol samples, immersion tests were conducted in naturally aerated and deaerated ethanol samples using crevice-former assemblies. This was done because, in a previous study [13], it was verified that crevice corrosion is the main corrosion mechanism of carbon steel in anhydrous contaminated ethanol, which is accelerated in a deaerated condition. Table 2 shows the carbon steel coupons after 21 days of immersion. It can be clearly seen that the commercial ethanol samples are more aggressive than the reagent grade ethanol. Additionally, it was observed that the sugar cane ethanol is less aggressive than the corn ethanol.

Conclusions

The EIS using quasi-reference electrode technique proved to be viable for qualitatively differencing anhydrous ethanol from different sources. It was possible to verify the differences between a reagent grade anhydrous ethanol and commercial ethanol samples which were attributed to the presence of contaminants in the commercial samples. Slight differences among commercial samples were also verified through the EIS technique.

Acknowledgements

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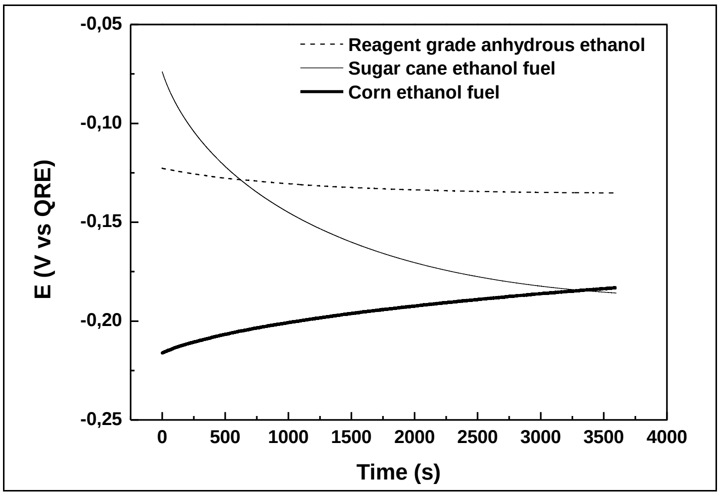

Figure 1 – OCP as a function of immersion time for the three studied anhydrous ethanol samples.

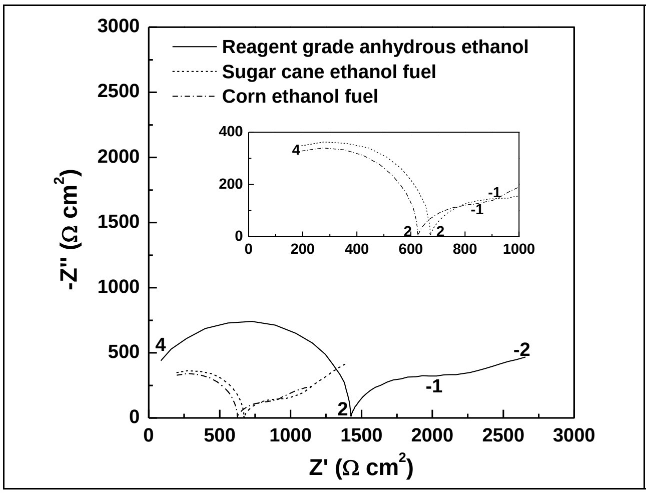

Figure 2 – Nyquist diagrams for carbon steel in three different ethanol samples. The numbers near the arcs represent the frequencies in decades.

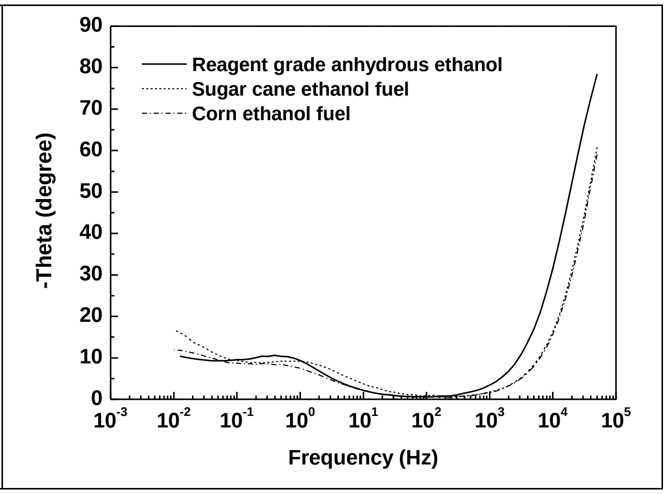

Figure 3 – Bode diagrams for carbon steel in three different ethanol samples.

Table 2 – Carbon steel coupons after 21 days of immersion

Ethanol	**Test Condition**	
	Aerated	**Deaerated**
Reagent grade anhydrous ethanol		
Sugar cane ethanol		
Corn ethanol