CHEMIJA. 2014. Vol. 25. No. 1. P. 20–28

Electrochemical evaluation of the influence of low water contents on corrosion in ethanol and hydrocarbon mixtures

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Many studies investigated corrosion mechanisms in ethanol but their findings might not always be extended to bioethanol-based fuels, where dehydrated ethanol is mixed with 15% or larger amounts of conventional gasoline. This report describes how a 3-electrode electrolytic cell was used to study the effect of water on low carbon steel corrosion in fuel-like ethanol mixtures with hydrocarbons. The electrolyte EHX was prepared by mixing dehydrated ethanol with n-heptane and xylenes at a ratio, which addressed the octane number of retail fuels. Open Circuit Potential (OCP) and Electrochemical Impedance Spectroscopy (EIS) results revealed that addition of water to EHX reduced the solution resistance in general. However, 1% or less water did not accelerate corrosion, despite significant changes in EIS patterns throughout the course of immersion up to 172 h. Addition of 4% water dramatically increased steel corrosion, justifying the need for tight control of water contents in bioethanol fuels. Electrochemical data after 6 h immersion correlated quite well with the EIS, OCP and visual observations performed after 172 h. This suggests that the employed technique is capable of rapid screening of various formulations for biofuels like E85, which might greatly assist industrial research.

Key words: corrosion, ethanol, electrochemistry, fuel

INTRODUCTION

Ethanol based fuels have already firmly established themselves as a renewable alternative to petroleum-based gasoline due to numerous advantages in both technical and environmental aspects. However, a number of disadvantages still create major hurdles to further spread of alcohol fuels and high risk of corrosion is one of the most serious issues. Fuel system components in automobiles, gasoline reservoirs, fuel pipelines and other metal surfaces, which were designed to handle conventional gasoline, exhibited high susceptibility to corrosion in ethanol and its blends with gasoline [1–4]. Poor corrosion resistance was even further aggravated by water, which is present in fuel-grade ethanol, and affects its reactivity and corrosiveness towards steel [5–7].

Influence of water on corrosion processes in methanol and ethanol has been widely studied [8–10]. It has been suggested that very often water determines the mechanism and rate of corrosion. The presence of water, even at low concentrations, strongly influences the passivation of iron in protic alcoholic solutions. Corrosion usually accelerates in the presence of water, but in some cases water might act as an inhibitor. Research [4] showed that water reduced the rate of iron corrosion in methanol, while its addition to anhydrous ethanol inhibited corrosion at less than 1 vol.% and then again accelerated corrosion at higher water concentrations.

Presence of water in alcohol also plays a role in changing the solvent structure and its physical properties, such as

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dielectric constant, oxygen content [11] and proton activity [8]. Shchukarev et al. [11] reported that the concentration of dissolved oxygen decreased as the water content increased in an ethanol-water mixture. Lou et al. [5] also observed an increase of acidity with higher water contents in ethanol. A combination of all these effects due to the presence of water in ethanol leads to a significant change in reaction rates and overall corrosion and passivation mechanism [12–13]. So, excessive ageing or inadequate transportation and storage of alcohol fuel can increase the likelihood of corrosion.

The major difficulty in studying the electrochemical behavior of metals in ethanol media is high solution resistance [14–15]. Commercial fuel-grade ethanol also contains only some impurities and its ionic strength is very low. Supporting electrolytes or addition of various salts are often used to increase the conductivity of ethanol. However, supporting electrolytes could also affect the metal passivation in ethanol solutions [15]. Literature review did not identify any citeable voltammetric or potentiodynamic studies on corrosion of metals in ethanol blends with gasoline without any supporting additives.

The initial aim of this study was to set up an electrochemical technique for evaluation of corrosion mechanisms in medium, which is composed of ethanol and hydrocarbons without any salts or supporting electrolytes. This technique was then used to examine the electrochemical behavior of steel in the electrolyte, which simulated a bioethanol-based retail fuel with 4% or less water as a contaminant.

EXPERIMENTAL

The electrochemical measurements in a three-electrode cell were performed using a Potentiostat / Galvanostat / Frequency Analyzer AUTOLAB302 (Eco Chemie, B. V., the Netherlands). The working electrode represented a disc of 15 mm diameter, which was cut from panels of the commercially available cold rolled low carbon steel. Before measurements the disc surface was carefully polished with 2500 grit SiC abrasive paper to near-mirror quality, then cleaned / degreased with acetone and dried in blowing air. The area of the electrode surface exposed to the electrolyte was 0.5 cm^2. A Pt plate of ~8 cm^2 area was used as a counter electrode. A silver-silver chloride reference electrode for ethanol (Ag|AgCl|1 M LiCl, EtOH) was used in this study [14]. The distance between the counter electrode and the working electrode was fixed at 10 mm, and the distance between the reference electrode and the working electrode was fixed at 2 mm for every test. The impedance was measured with an applied AC voltage of 5 mV in the frequency range from 100 Hz to 0.001 Hz. Solutions were used under ambient conditions without aeration, i. e. "static air".

Optical inspection and images of the steel samples were performed by a B-353 Met microscope (Optika Microscopes, Italy), equipped with a digital camera OPTIKAM B 2.0. Except where indicated otherwise, all % represent the concentrations on the basis of volume-per-volume of individual components.

The test fluids were purchased from Alfa-Aesar (via UAB Bioeksma, Lithuania). Dehydrated ethanol was specified to contain less than 0.1% water, n-heptane had less than 1% isomers and xylenes represented a 99% pure technical mixture of o-, m- and p-isomers. Cold roll low carbon steel of SAE 1008/1010 grade was purchased from Q-panel / Q-Lab Products (via UAB Labostera, Lithuania). It contained more than 99% Fe with metallurgic additives (wt.%): C ~ 0.13, Mn ~ 0.25–0.6, P ~ 0.04, and S ~ 0.050.

RESULTS AND DISCUSSION

This investigation can be subdivided into four distinct stages: 1) development of the electrolyte to simulate the retail fuel, 2) establishment of electrochemical testing conditions for the steel electrode, 3) electrochemical comparison of corrosion-related processes in the fuel with various water contents, and 4) examination of the steel electrode corrosion patterns visually and by a microscope.

Development of the fuel-like electrolyte

Bioethanol-based retail fuels, e. g. E85, which are the most widespread in European Union, often contain some conventional gasoline for a number of purposes, such as better ignition, improved longevity of fuel injectors, lower surface tension, denaturation, etc. However, the octane number is often considered more important than other parameters, which could be affected by introduction of gasoline components into the fuel. Therefore, in order to produce a simulation mixture, which could resemble the E85 fuel, the octane number was selected as a target in this study. Ethanol itself has a reportedly high value of 108.6 per the Research Octane Number determination protocol (Table), so other components had to be introduced for its reduction.

Conventional gasoline is composed almost exclusively from hydrocarbons, primarily alkanes, naphthenes and aromatic hydrocarbons, n-heptane was considered for inclusion into the electrolyte as a representative of alkanes. By definition, n-heptane has the octane number of 0. During the last

Table. **Composition and properties of individual components in the mixture EHX, which simulates the bioethanol-based retail fuel. Density is reported at 20 °C**

Component	Octane number	Density, g/ml	wt.% in EHX	vol.% in EHX
Ethanol (dehydrated)	108.6 [16]	0.789	85	83.5
n-Heptane	0	0.679	11	12.8
Xylene	120 [17]	0.864	4	3.7
Water	n. a.	0.998	<0.1%	<0.1%
EHX (i. e. final mixture)	97	0.78	100	100

several decades, petroleum refining technologies shifted towards conversion of paraffins and naphthenes into aromatic compounds. Therefore, xylene was also introduced as the electrolyte component. Abbreviation "EHX" was assigned to the electrolyte to represent its three components: Ethanol, Heptane and Xylene. Except water, inclusion of additional materials for improved electrical conductivity, such as salts or ions, was not considered in this study. It must be pointed out that fuel-grade ethanol specifications permit some presence of contaminants, which might accelerate corrosion. The standards EN 15376 and ASTM D 4806 limit not only the max. water contents to 0.3 and 1.25 wt.%, respectively, but also the presence of other contaminants, such as chloride ions to 20 and 40 ppm, respectively, acetic acid to 70 ppm and dissolved Cu to 0.1 ppm. Evidently, actual fuels might contain more materials, whose influence on corrosion process is very significant. However, in this study effects of such contaminants were not investigated and EHX was employed as the test electrolyte.

The octane number of the proposed EHX electrolyte is calculated at 97 on the weight-to-weight basis (Table). This is sufficiently similar to the octane numbers of 95 and 98, which are specified by the most popular brands of retail gasoline. Therefore, the resemblance of the EHX electrolyte to the actual E85 retail fuel can be considered quite high. The Table also shows the volume fractions of EHX for the ease of its preparation.

Determination of electrochemical testing conditions

Since the inclusion of aromatic and saturated hydrocarbons could make electrochemical properties of EHX different from those of ethanol, open circuit potential (OCP) tendencies were initially investigated. Steel electrodes were used in all experiments of this report. Figure 1 shows that electrodes, which were immersed in EHX without addition of water, achieved the highest OCP values. They also exhibited a rapid increase in OCP from –0.26 V to 0.1 V during initial 6 h of immersion before reaching equilibrium. Similar tendencies were observed in EHX with 0.4% and 1% H_2O addition as well. Increase in OCP of steel electrodes in ethanol and simulated fuel grade ethanol (SFGE) has been also reported elsewhere [6, 18]. This substantiates the expectation that surface layers are formed on steel during the immersion into EHX, in agreement to the observations by above researchers.

In EHX blends with 0% to 1% H_2O, the equilibrium of OCP was reached approximately after 30 h of immersion. This suggests that the process of surface layer buildup became less intensive or possibly stopped completely. In EHX + 4% H_2O the OCP tendencies were very different. Initially, OCP decreased rapidly and then seemed to stabilize until a sudden spike in OCP after 50 h. It is premature to draw any conclusions from the observed OCP tendencies in EHX + 4% H_2O. However, it is obvious that the surface reactions and oxide film characteristics in EHX environment are strongly affected by water addition, as reported by the research groups, who studied OCP in ethanol [6].

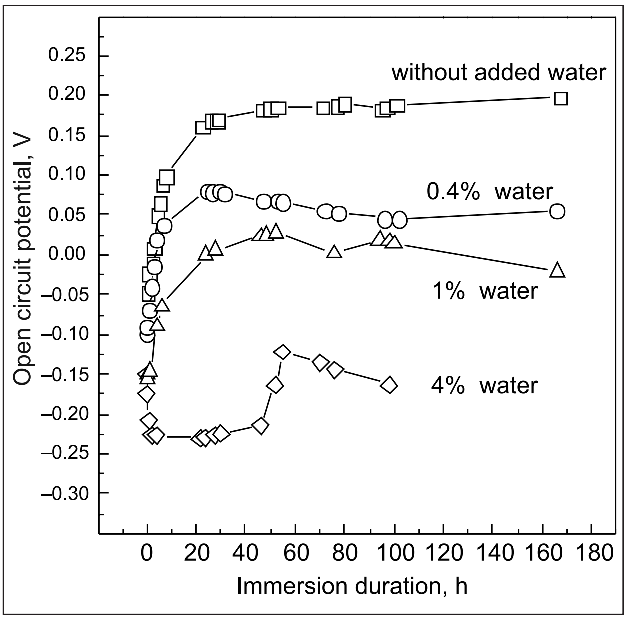

Fig. 1. Variation of OCP for steel immersed in Ethanol-Heptane-Xylene (EHX) with different water contents

As mentioned, after 30 h immersion EHX blends with 0% to 1% water appeared to have reached a steady state. Although EHX + 4% H_2O did not show the tendency to equilibrate, it was reasonable to expect that after 70 h or longer immersions the electrochemical characteristics of this blend were not likely to change dramatically. Therefore, immersion times of approx. 70 h could be sufficient for detailed studies, such as Electrochemical Impedance Spectroscopy (EIS), of the steady-state conditions in these blends.

On the other hand, during the first several hours of steel immersion rapid changes take place in all studied EHX blends. It is obvious that electrochemical measurements might be vulnerable to the transitional nature of the processes. However, these measurements can still provide more information about the changes on the electrode surface, which take place until a steady state is achieved.

In order to observe the evolution of surface processes, EIS was recorded after 2 h and 4 h immersion in EHX without any added water (Fig. 2). After 2 h immersion quite pronounced fluctuations in both impedance and phase angle diagrams were evident. The whole interval of scanned frequencies was affected. In the meanwhile, after 4 h immersion a much more uniform character of the measurement relation to the frequency was observed, especially in the range below 100 Hz. The transitional nature of the process can still be visible because some minor peaks or shoulders do not have an apparent explanation. However, the qualitative trends of impedance and phase angle behavior are already evident after 4 h immersion.

It was decided to use Bode plots in EIS measurements for more evident interpretation of the surface processes [19]. It must be noted that during the EIS measurements in low conductivity media, higher frequencies usually exhibit

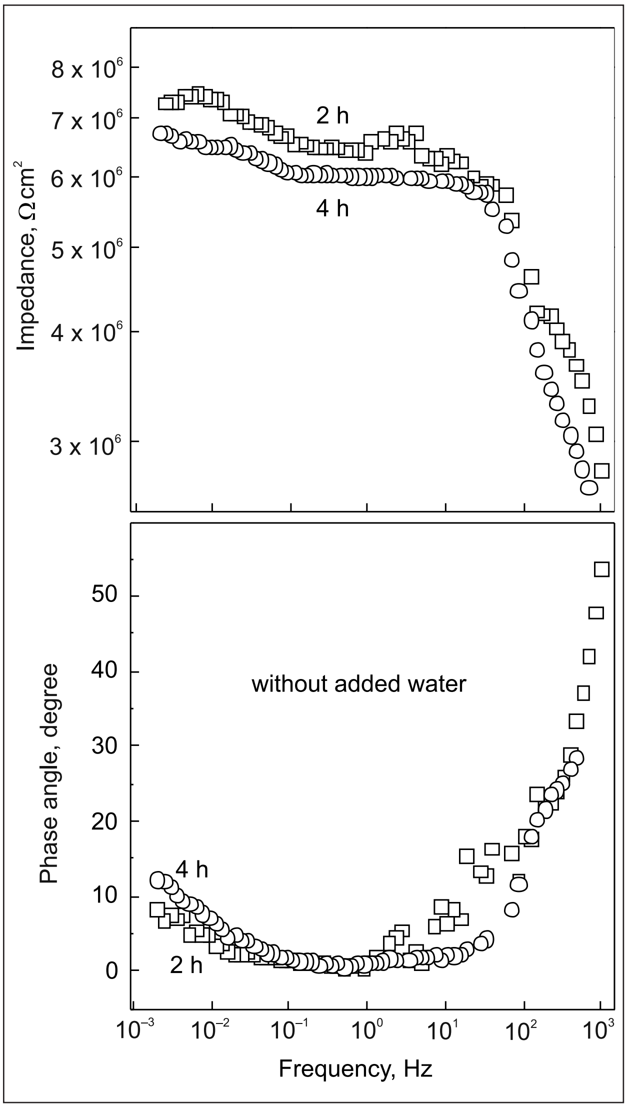

Fig. 2. EIS Bode plots on steel electrodes immersed for 2 and 4 h in EHX without added water

artifacts, which may take a form of capacitive or inductive arcs connected with loops [1]. These artifacts may be misinterpreted as interfacial properties. Investigators have attributed these artifacts to parasitic conduction paths within the electrochemical cell and the measurement system due to the interference caused by measurement electronics [18, 20–21]. Therefore, the EIS values above 100 Hz were considered as caused by the artifacts of low conductivity media (Fig. 2), and only the data within the frequency range from 0.01 to 100 Hz were used for the kinetic investigations. The impedance value, which corresponds to the frequency range where phase angle remains close to 0° over a substantial frequency range, was considered to represent the solution resistance (R_{SOL}). Polarization resistance (R_p) was also determined from EIS measurements as the difference between the total resistance at 10 mHz frequency and the solution resistance. In order to perform EIS during the transitional stage, 6 h immersion times were selected, because after 4 h immersion the measurements were still visibly affected by the non-equilibrium fluctuations (Fig. 2). Investigations at relatively steady-state conditions were based on immersions, whose durations were 72 h or longer.

Effect of water on corrosion processes

After recording OCP it became apparent that the course of corrosion in ethanol based fuels is strongly affected by the presence of water. Therefore, the kinetic trends were evaluated in more detail by performing EIS on steel electrodes, immersed in EHX electrolyte with 0% to 4% water added. Immersion durations were selected at either 6 h or 72 h for the transitional regime and steady-state conditions, respectively.

The dependence of EIS trends on the amounts of water in EHX after 6 h immersion is shown in Fig. 3. As evident from Curve 1, the solution resistance R_{SOL} of the electrolyte without added water is high and the kinetic processes are slow. Some minor activity can be observed in the low frequency region after 6 h immersion, but when EIS was performed after 10 min immersion (not shown here), only straight lines were recorded which were parallel to X-axis. This agrees with the assumption that reaction rates are slow and high R_{SOL} makes it difficult to identify any possible corrosion effects on the surface of metals. However, the addition of just 0.4% water reduced R_{SOL} appreciably and much more electrochemical activity could be observed, see Curve 2. This sample showed a distinct increase in the phase angle in the medium frequency range, as did the EHX + 1% H_2O sample. However, with the addition of 4% water there was a big change in electrochemical patterns, which was not less dramatic as in the case of OCP measurements. A major drop of the phase angle from 63° to 14° could be observed, while its maximum shifted towards higher frequencies significantly. Some increase of the impedance in lower frequencies was evident, but its magnitude was much lower than those of samples with 0.4% or 1% water. Nevertheless, the patterns demonstrated a clearly quantifiable character with little perturbations, despite OCP remaining still far away from any equilibrium (Fig. 1).

When considering the data from samples at longer immersion durations it must be noted that the electrolytic cell was not hermetically sealed during the course of immersions. Since EHX itself is relatively hygroscopic, ambient humidity could have contributed to the water contents, with this effect being more evident after longer immersion times. It must be noted that some commonplace measures were undertaken to limit the moisture increase in the electrolyte, such as keeping the cell covered with a frit-glass lid during the measurements and storage. EIS data from various immersion durations was processed to extract the solution resistance R_{SOL} values, as shown in Fig. 4.

The observations demonstrate that the conductivity of low-water samples EHX and EHX + 0.4%H_2O increases noticeably during the course of immersion. Evidently, some additional carriers of electrical charges were supplied during the process. At least two sources are available with a capability of generating the charge carriers: 1) absorption of the am-

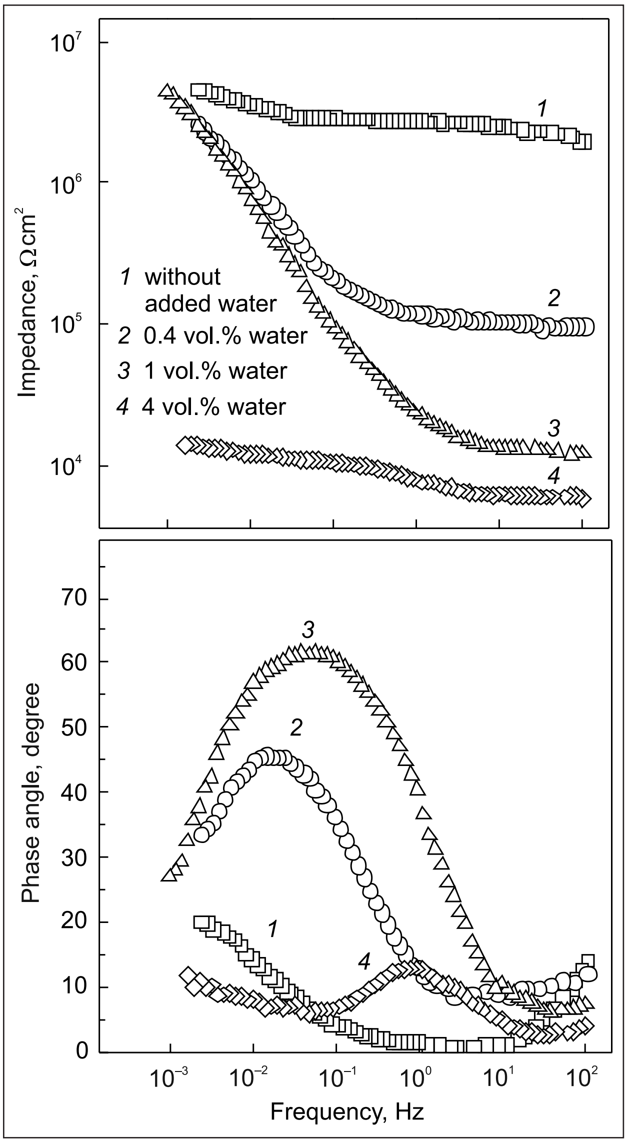

Fig. 3. Effect of water on phase angles and impedance after 6 h immersion of steel electrodes into EHX electrolyte

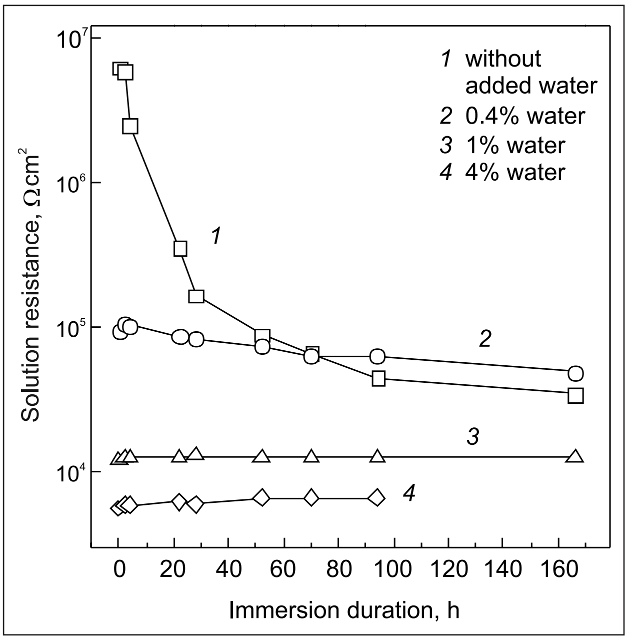

Fig. 4. Effects of water on decrease in solution resistance (R_{SOL}) with longer immersion durations

bient humidity and 2) dissolution of the steel electrode. The latter process is likely to produce dissolved metal ions such as Fe^{3+} or Fe^{2+}, which would make the solution coloured. In fact, a tone of brown color was observed in the EXH + 4% H_2O sample within a 1–2 mm distance from the steel electrode after 20 h immersion, while other electrolytes remained colorless. However, observed discoloration did not coincide with any change in R_{SOL} of EHX + 4% H_2O. This implies that metal dissolution might not be the dominant driving force in the increase of solution conductivity. Also, samples with higher water contents EHX + 0.4% H_2O and EHX + 1% H_2O do not show any tendency of the solution conductivity increase during the course of immersion. Their R_{SOL} remains nearly constant, which suggests that the water contents in the electrolyte are by far more important than the amounts of dissolved metals. It must be noted that EHX did not contain any significant amount of acetic acid, which can form relatively easily in ethanol if it is exposed to ambient conditions for longer durations. The presence of acetic acid can highly accelerate the metal dissolution.

Despite ageing effects such as humidity absorption or metal dissolution, the EIS patterns, which were observed after 6 h immersion, were even more clearly expressed after 72 h immersion (Fig. 5). Qualitatively, they demonstrated the same effects of water addition to the EHX electrolyte, except for the sample without any added water. Due to the ageing effects, Curve 1 should not be considered to represent a completely dehydrated EHX sample. Therefore, the observed convergence of Curves 1 and 2 in Fig. 5 might have occurred because of humidity, which was gradually absorbed by EHX and not because of the similarity between the processes in the EHX + 0.4% H_2O sample and the EHX sample without water.

Regarding the three electrolytes with added water, the effects of water contents after 72 h immersions were qualitatively very similar to those after 6 h immersions. In EHX + 4% H_2O a major decrease of both phase angle and impedance could be observed, in comparison to others. The sample EHX + 1% H_2O again produces the largest magnitude of the maximum phase angle. This maximum also demonstrates a shift towards higher frequencies with increasing water contents, as it did after 6 h immersions. The actual recorded values are clearly different, but the established qualitative tendencies are very similar. This conclusion implies a supposition that in cases where a qualitative comparison is sufficient, such as evaluation of biofuel corrosion inhibitors, a shorter test under non-equilibrium conditions with 6 h immersion duration can be used rather than 72 h or longer immersions.

The electrochemical tendencies of the processes in EHX, EHX + 0.4% H_2O and EHX + 1% H_2O are even more similar

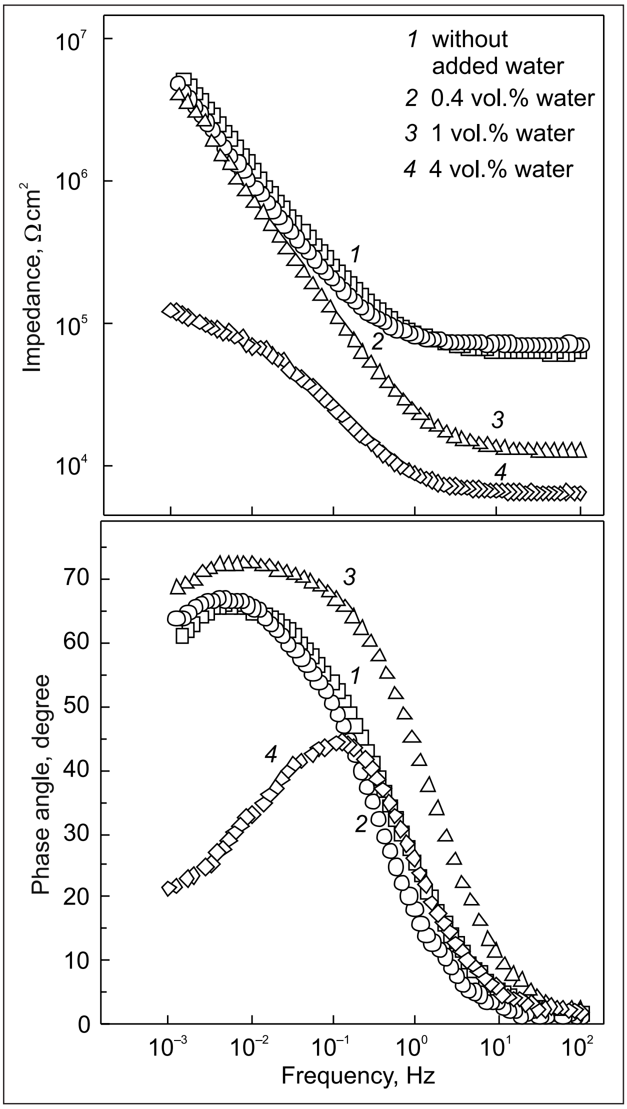

Fig. 5. Effect of water on phase angles and impedance after 72 h immersion of steel electrodes into EHX

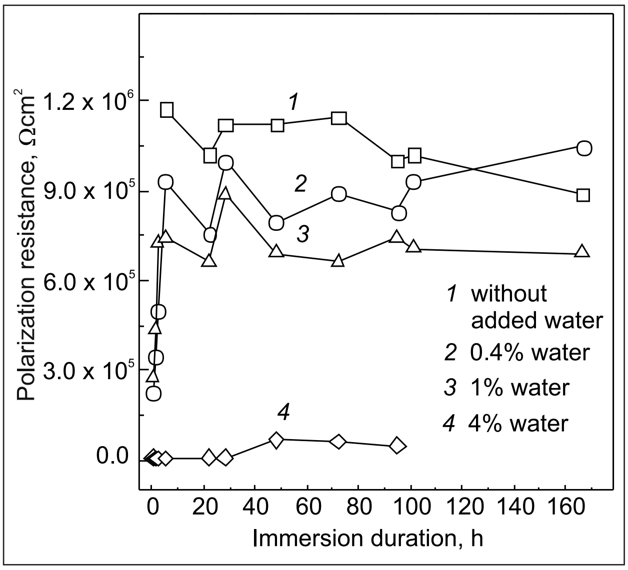

Fig. 6. Effects of water contents on the dependence of polarization resistance R_p on immersion duration, as shown using a linear scale to highlight the differences

qualitatively than it might appear from EIS data at 6 h and 72 h. Data, collected at other immersion durations, showed that all the trends of phase angle shifting were retained. The sample ranking in terms of the phase angle maximum also remained the same. The similarity of these tendencies is particularly evident, when R_p at different immersion durations is compared (Fig. 6).

It is obvious that R_p does not stay constant during the immersion, but it varies with time, also depending on the water contents in the electrolyte. The numeric values of R_p are different in all cases, but qualitatively the variation trends are mostly the same for EHX, EHX + 0.4% H_2O and EHX + 1% H_2O. Only EHX + 4% H_2O stands out, showing a distinctly different character of electrochemical tendencies.

Such similarities imply that with water contents of 1% or less, corrosion processes in ethanol-based fuels follow the same general mechanism. Obviously, the rates of individual reactions or processes in this general mechanism might depend on the water contents. But it is very likely that the overall sequence of the processes and the mechanism stages probably remains the same. In general, this agrees with the qualitative observations from the studies of other research groups. Very similar trends had been presented [18] on steel in ethanol with 1% and 3% water when R_p rapidly increased for the first 5 h of immersion and then stabilized. With 5% or more water the drop in R_p during the first several hours of immersion with subsequent stabilization had been reported. It must be pointed out that NaCl had been used at 19.2 mg/L in that study. The trend of R_p increase had been confirmed in the SFGE study [19] as well, which also utilized NaCl (53 mg/L) in addition to 1% water, 0.5% methanol and 56 mg/L acetic acid. Even with high portion of hydrocarbons the stage of R_p increase lasted for 5 h, as demonstrated by the gasoline blend with just 20% ethanol [1]. Evidently, the differences in electrolyte compositions, such as addition of up to 50 ppm chlorides or acetic acid, do not lead to significant variation of corrosion mechanisms. In agreement with the above reports, Curves 2 and 3 in Fig. 6 show a very rapid increase in R_p values during the first ~5 hours of immersion, reaching values of ~1 MΩ cm². Since EHX without added water recorded R_p of 1.2 MΩ cm² from the very beginning, the trend of rapid acquisition of high polarization resistance can probably be extended to all 3 electrolytes with 1% added water or less. Even 3% water addition to EHX, based on the report from ethanol studies [18], would probably follow this trend of rapid R_p increase.

Possible existence of the same general mechanism suggests that the employed technique, which utilizes a conventional 3-electrode cell, is capable of relatively rapid screening of different steel alloys and alcohol-based electrolytes. In 6 h or less some qualitative understanding might be gained on the alloy or fuel susceptibility towards corrosion, i. e. much faster than humidity cabinet and similar tests. Industrially, this method can also be used to screen various bioethanol fuel formulations, which might greatly assist the development of the corrosion inhibitors for E85 gasoline.

EIS data for longer immersions is less conclusive in the reports from other authors, so it is more difficult to find similarities between the investigations in EHX and those in ethanol. Thus, further discussion is limited to the EHX study only. Within the 10–24 h immersion interval a transition through the stage of reduced polarization resistance with subsequent R_p recovery is evident for all three samples. Such a remarkable coincidence suggests that the interaction between steel and EHX proceeds via the same electrochemical mechanism independently of water contents, as long as it does not exceed 1%. After the stage of R_p recovery some reduction of the polarization resistance can be observed, which is more rapid for EHX + 0.4% H_2O and EHX + 1% H_2O, showing some variation from sample to sample. Unexpectedly, after 170 h immersion the highest R_p value was recorded for EHX + 0.4% H_2O and not for the EHX without any added water. Nevertheless, these observations and their relatively close conformance with the reports on ethanol studies imply the existence of a general mechanism, describing the interactions between low-water-content EHX electrolytes and steel.

If such mechanism does exist in fact, it might not be applicable to the electrolytes with 4% or higher amounts of water. The values of R_p in EHX + 4% H_2O remained very low throughout the immersion, again showing that this sample behaves differently. Again, this confirms the findings of other researchers [19], who report very different R_p variation tendencies between ethanol with 3% water and ethanol with 5% water. Low R_p suggests that passivating layers might not form on steel in EHX + 4% H_2O and if they do, their anticorrosion characteristics are much poorer than those formed in low water electrolytes, where R_p often exceeds 1 MΩ cm^2. The highest R_p attained in EHX + 4% H_2O comprised only 0.09 MΩ cm^2 and even then showed some tendency to drop after longer than 50 h immersion.

Recorded EIS data also provides a wealth of information, which might be useful in learning more about the corrosion mechanisms in ethanol-based electrolytes. However, the scope of this study was to compare the main kinetic trends of corrosion processes in the EHX electrolyte with those in ethanol. No major disagreements with investigations in ethanol by other researchers were found. It is somewhat premature to claim that addition of 15% hydrocarbons does not affect the general mechanism of corrosion processes in ethanol, however, the abundance of similar findings in the reports of other authors gives some ground to the validity of such supposition. One more conclusion can be drawn with probably even more viability. The observations show that corrosion processes in ethanol-based fuels with low water contents such as 1% (and probably 3%, as reported by other researchers [18]) follow a different mechanism than those in fuels with 4% water or more. However, more investigations would be needed to explain the reasons of the mechanism change.

Evaluation of corrosion spots

Based on the obtained results from the EIS measurements, it is evident that corrosion processes must proceed faster in EHX + 4% H_2O than in the electrolytes with 1% water or less. During the study, some spent steel electrodes were also evaluated visually and by a microscope after completing the immersion tests. Visual observation showed that corrosion proceeds much more rapidly in EHX + 4% H_2O (Fig. 7).

After 90 h immersion the electrode in EHX + 4% H_2O was much more severely corroded than those in the electrolytes with lower water content after nearly twice as long immersion of 170 h. The extent of corrosion in EHX + 4% H_2O is a clear confirmation that qualitative ranking of R_p, which was determined from EIS results as early as after 2 h immersion, correlates well with the experimental observations after 90 h. R_p values of the samples during the tests with 1% water or less were much higher than those of EHX + 4% H_2O. Such retention of the ranking order again supports the supposition that EIS results from 6 h immersion tests can be successfully used to predict long term corrosion results.

Electrodes from the remaining three EHX blends looked much more similar to each other, all of them showing some corrosion on the surface. The electrode from EHX + 1% H_2O was a bit more corroded than the other two. The electrode from EHX + 0.4% H_2O showed somewhat less corrosion than EHX without added water. This is even more obvious in photomicrographs of the corrosion spots (Fig. 8).

Only little rust was observed on the electrode from EHX + 0.4% H_2O, while the electrode from EHX without added water showed corrosion zones, which seemed visually to resemble uniform corrosion. EIS data demonstrated counter-intuitive readings (Fig. 6) when R_p of the sample in EHX without added water dropped below that of EHX + 0.4%H_2O after 170 h immersion. Since this was observed only at one immersion duration, the finding cannot be considered reliable enough. However, the microscopy also confirmed better

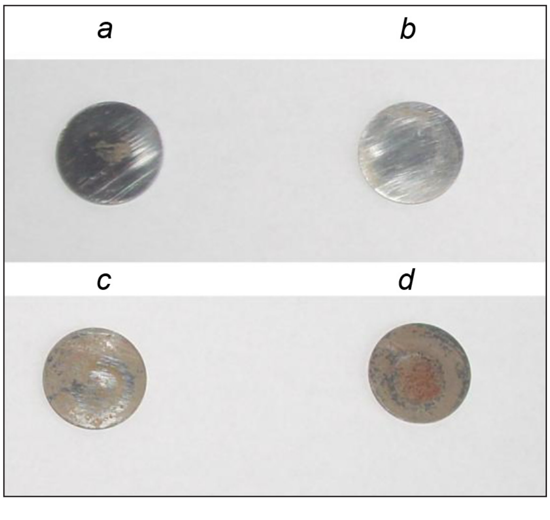

Fig. 7. Electrodes after immersion in EHX with no added water (*a*), 0.4% water (*b*), 1% water (*c*), 4% water (*d*). Immersion durations: *a, b, c* – 170 h, *d* – 90 h

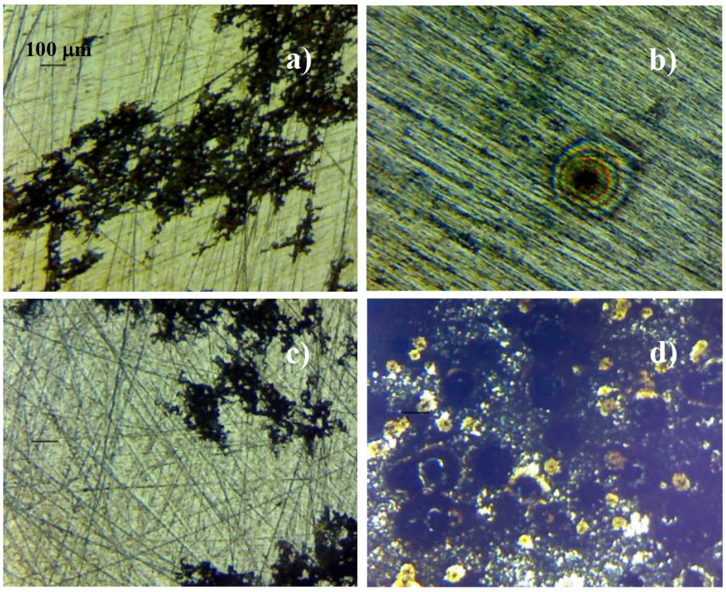

Fig. 8. Photomicrographs of corrosion zones on electrodes. See Fig. 7 for abbreviations

corrosion resistance of EHX + 0.4% H_2O. It has been known the water can act as an oxygen donor in the passivation process on the metal surface, which stabilizes the passive layer. In an anhydrous solution, a stable oxide film may not form to passivate the surface well, causing more rapid steel corrosion [9, 22].

Excluding water, EHX does not contain any significant levels of chlorides and other contaminants, which might have an appreciable impact on corrosion. Therefore, the only significant factor, which could be considered to make corrosion mechanisms in EHX different than those in ethanol, would be the presence of heptane and xylene. Ethanol belongs to protogenic solvents and undergoes auto-dissociation to the equilibrium:

$$2C_2H_5OH \leftrightarrow C_2H_5OH_2^+ + C_2H_5O^-.$$

From the first glance, it is not likely that heptane or xylene could significantly affect the ethanol auto-dissociation process. Compared to hydrocarbons, the $C_2H_5O^-$group plays a much more important role in the reactions of anodic dissolution and cathodic deposition (similarly to OH^- group). However, it cannot be assumed that heptane or xylene do not have any effect on the surface layers of steel electrodes in EHX because these layers might be quite complex, involving organometallic intermediates. Banas et al. [23] have shown that in anhydrous methanol the formation of oxide or hydroxide layers on the Fe surface does not represent a major electrochemical process. Instead, methoxy species dominate, which build an organometallic layer and the produced intermediates act as membrane inhibitors rather than a passive oxide layer. These researchers [23] also showed that the formation of such membrane type layer was most pronounced at lower potentials. In SFGE with little water the formation of an ethoxy-iron surface layer may be responsible for the decrease of corrosion-driven weight loss. Similar organometallic compounds have been reported to be present in an initial reaction layer on the Zn surface in pure methanol [24]. Ethoxy-iron might serve as a pseudo-passive layer, leading to an increase of OCP with time, however, such pseudo-passive layer is not likely to be stable. It is very uncertain whether hydrocarbons can or cannot be included into such organometallic layer, because compared to Fe oxides and hydroxides, the ethoxy moieties are much larger and more compatible with nonpolar organic molecules. Consequently, it would be too speculative to claim that heptane or xylene cannot participate in the formation of such pseudo-passive organometallic layers on steel surface in EHX.

On the other hand, the complexity of such pseudo-passive organometallic layers makes it possible to explain why the presence of some water in the electrolyte might contribute to the formation of a passive film. Water or hydroxy ions can react with the organometallic Fe and produce iron oxides and hydroxides, which would form a more densely packed layer, thus improving surface passivation. Such supposition is supported not only by the above observation of corrosion rate reduction in EHX + 0.4% H_2O. The viability of the beneficial effect of 0.4% water can also be strengthened by taking the solution resistance into account. As shown in Fig. 4, R_{SOL} went down with water addition in general. But after longer immersion in EHX + 0.4% H_2O the resistance became higher than R_{SOL} in EHX without added water. As discussed previously, it is not clear how much the resistance was affected by humidity absorption and metal dissolution. Nevertheless, R_{SOL} must also be considered when trying to explain why steel in EHX without added water corroded faster than in EHX + 0.4% H_2O.

These findings demonstrate that corrosion in ethanol fuels may have some differences from the corrosion process in pure ethanol. Although OCP and EIS results show many similarities between pure ethanol and EHX, many uncertainties still remain unsolved and further electrochemical research is necessary to find the answers.

CONCLUSIONS

An electrochemical technique was successfully employed to screen corrosion tendencies of ethanol and hydrocarbon mixtures. The method utilized a three electrode cell with the fuel media without additional electrolytes or supporting ions. Heptane and xylene were added to dehydrated ethanol at 11% and 4%, respectively, to make the EHX electrolyte, which approached the octane number of most retail fuels. Experiments on LCS electrodes revealed the following findings.

1. Electrochemical processes do not achieve steady state conditions for at least 60 h after immersing steel electrodes into EHX with or without water.

2. Based on EIS results, addition of water at 1% or less does not show accelerating effects on steel corrosion. Increasing water content up to 4% reduces polarization resistance drastically and results in rapid corrosion.

3. Microscopy and EIS observations showed that the fuel with 0.4% water might produce somewhat higher corrosion resistance than the dehydrated fuel, although more investigations are necessary to explain the findings.

4. Many similarities exist between corrosion processes in EHX blends with 1% water or less and those in ethanol. Consequently, in many cases electrochemical testing after relatively short immersion, e. g. 6 h, can result in the same qualitative ranking of corrosion resistances as those after 170 h or longer immersions.

ACKNOWLEDGEMENTS

Budgetary funding was utilized to support the research investigations. COST action CM0901 "Detailed Chemical Models for Cleaner Combustion" was useful in gaining knowledge about technical properties of ethanol-based fuels.

Received 24 September 2013
Accepted 19 November 2013

References

1. L. M. Baena, M. Gómez, J. A. Calderón, *Fuel*, **95**, 320 (2012).
2. S. K. Hoekman, *Renew Energy*, **34**, 14 (2009).
3. Z. Szklarska-Smialowska, J. Mankowski, *Corr. Sci.*, **22**, 1105 (1982).
4. P. L. de Anna, *Corr. Sci.*, **25**, 43 (1985).
5. X. Y. Lou, D. Yang, P. M. Singh, *Corrosion*, **65**, 785 (2009).
6. X. Y. Lou, P. M. Singh, *Corr. Sci.*, **52**, 2303 (2010).
7. H. Jafari, M. H. Idris, A. Ourdjini, H. Rahimi, B. Ghobadian, *Fuel*, **90**, 1181 (2011).
8. C. S. Brossia, E. Gileadi, R. G. Kelly, *Corros. Sci.*, **37**, 1455 (1995).
9. J. Banas, *Electrochim. Acta*, **32**, 871 (1987).
10. F. Bellucci, G. Faita, C. A. Farina, F. Olivani, *J. Appl. Electrochem.*, **11**, 781 (1981).
11. S. A. Shchukarev, T. A. Tolmacheva, *J. Struct. Chem.*, **9**, 6 (1968).
12. T. Mussini, F. Mazza, *Electrochim. Acta*, **32**, 855 (1987).
13. S. Trasatti, *Electrochim. Acta*, **32**, 843 (1987).
14. N. Sridhar, K. Price, J. Buckingham, J. Dante, *Corrosion*, **62**, 687 (2006).
15. M. G. Athayde, O. R. Mattos, L. Sathler, *Electrochim. Acta*, **32**, 909 (1987).
16. M. Eyidogan, A. Necati Ozsezen, M. Canakci, A. Turkcan, *Fuel*, **89**, 2713 (2010).
17. Ch. S. Hsu, P. R. Robinson, *Practical Advances in Petroleum Processing*, Ch. 1, Springer (2006).
18. Sh. M. Bhola, R. Bhola, L. Jain, B. Mishra, D. L. Olson, *J. Mater. Eng. Perform.*, **20**, 409 (2011).
19. X. Lou, P. M. Singh, *Electrochim. Acta*, **56**, 1835 (2011).
20. G.-L. Song, M. Liu, *Corr. Sci.*, **72**, 73 (2013).
21. J. P. de Souza, O. R. Mattos, L. Sathler, H. Takenouti, *Corr. Sci.*, **27**, 1351 (1987).
22. M. Kabasakaloglu, I. Kalyoncu, T. Kiyak, *Appl. Surf. Sci.*, **135**, 188 (1998).
23. J. Banaś, B. Stypuła, K. Banaś, J. Światowska-Mrowiecka, M. Starowicz, U. Lelek-Borkowska, *J. Solid. State Electrochem.*, **13**, 1669 (2009).
24. M. Sakakibara, N. Saito, H. Nishihara, K. Aramaki, *Corros. Sci.*, **34**, 391 (1993).

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NEDIDELIŲ VANDENS KIEKIŲ ĮTAKOS KOROZIJAI ETANOLIO IR ANGLIAVANDENILIŲ MIŠINIUOSE ELEKTROCHEMINIS VERTINIMAS

Santrauka

Metalų korozijos mechanizmai etanolyje yra gana išsamiai ištirti, tačiau gautos išvados ne visada tinka bioetanolio degalams, kuriuose dehidratuotas etanolis būna maišomas su 15 % ar didesniais įprastinio benzino kiekiais. Šiame straipsnyje nagrinėjamas trijų elektrodų elektrolitinės celės pritaikymas mažaanglio plieno korozijos tyrimui etanolio ir angliavandenilių mišiniuose įvertinant nedidelių vandens kiekių įtaką. Elektrolitas EHX buvo gautas sumaišius dehidratuotą etanolį, n-heptaną ir ksilenus tokiu santykiu, kad elektrolito ir įprastinių degalų oktano skaičiai būtų panašūs. Atviros grandinės potencialo (OCP) ir elektrocheminio impedanso spektroskopijos (EIS) tyrimai parodė, kad vanduo mažina EHX mišinių varžą. 172 val. imersija pademonstravo, jog mažesni nei 1 % vandens kiekiai nepagreitina korozijos, nors EIS rezultatuose ir yra didelių pokyčių. EHX elektrolite su 4 % vandens labai pagreitėjo plieno korozija, tuo patvirtinamas poreikis griežtai kontroliuoti vandens kiekį bioetanolio degaluose. Elektrocheminiai rezultatai, gauti po 6 val. imersijos, neblogai atitiko EIS, OCP ir vizualinius stebėjimus po 172 val. imersijos. Tai rodo, kad pasirinktas tyrimų metodas gali padėti sparčiau įvertinti receptūras degalams, pvz., E85, ir iš esmės palengvinti pramoninius tyrimus.