Video Article

Metal Corrosion and the Efficiency of Corrosion Inhibitors in Less Conductive Media

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Abstract

Material corrosion can be a limiting factor for different materials in many applications. Thus, it is necessary to better understand corrosion processes, prevent them and minimize the damages associated with them. One of the most important characteristics of corrosion processes is the corrosion rate. The measurement of corrosion rates is often very difficult or even impossible especially in less conductive, non-aqueous environments such as biofuels. Here, we present five different methods for the determination of corrosion rates and the efficiency of anti-corrosion protection in biofuels: (i) a static test, (ii) a dynamic test, (iii) a static test with a reflux cooler and electrochemical measurements (iv) in a two-electrode arrangement and (v) in a three-electrode arrangement. The static test is advantageous due to its low demands on material and instrumental equipment. The dynamic test allows for the testing of corrosion rates of metallic materials at more severe conditions. The static test with a reflux cooler allows for the testing in environments with higher viscosity (*e.g.*, engine oils) at higher temperatures in the presence of oxidation or an inert atmosphere. The electrochemical measurements provide a more comprehensive view on corrosion processes. The presented cell geometries and arrangements (the two-electrode and three-electrode systems) make it possible to perform measurements in biofuel environments without base electrolytes that could have a negative impact on the results and load them with measurement errors. The presented methods make it possible to study the corrosion aggressiveness of an environment, the corrosion resistance of metallic materials, and the efficiency of corrosion inhibitors with representative and reproducible results. The results obtained using these methods can help to understand corrosion processes in more detail to minimize the damages caused by corrosion.

Video Link

The video component of this article can be found at https://www.jove.com/video/57757/

Introduction

Corrosion causes great material and economic damage around the world. It causes considerable material losses due to partial or complete material disintegration. The released particles can be understood as impurities; they can negatively change the composition of the surrounding environment or the functionality of various devices. Also, corrosion can cause negative visual changes of materials. Thus, there is a need to understand corrosion processes in more detail to develop measures to prevent corrosion and minimize its potential risks[1].

Considering environmental issues and the limited fossil fuel reserves, there is an increasing interest in alternative fuels, among which biofuels from renewable sources play an important role. There are a number of different potentially available biofuels, but bioethanol produced from biomass currently is the most suitable alternative for substituting (or blending with) gasolines. The use of bioethanol is regulated by the Directive 2009/28/EC in the European Union[2,3].

Ethanol (bioethanol) has substantially different properties in comparison with gasolines. It is highly polar, conductive, completely miscible with water, *etc.* These properties make ethanol (and fuel blends containing ethanol also) aggressive in terms of corrosion[4]. For fuels with low ethanol content, contamination by small amounts of water can cause separation of the water-ethanol phase from the hydrocarbon phase and this can be highly corrosive. Anhydrous ethanol itself can be aggressive for some less noble metals and cause "dry corrosion"[5]. With existing cars, corrosion can occur in some metallic parts (especially from copper, brass, aluminum or carbon steel) that come into contact with the fuel. Furthermore, polar contaminants (especially chlorides) may contribute to the corrosion as a source of contamination; oxygen solubility and oxidation reactions (that can occur in ethanol-gasoline blends (EGBs) and be a source of acidic substances) can also play an important role[6,7].

One of the possibilities on how to protect metals from corrosion is the use of so-called corrosion inhibitors that make it possible to substantially slow down (inhibit) corrosion processes[8]. The selection of corrosion inhibitors depends on the type of corrosive environment, the presence of corrosion stimulators, and particularly on the mechanism of a given inhibitor. Currently, there is no versatile database or classification available that would enable simple orientation in corrosion inhibitors.

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Corrosion environments can be divided into aqueous or non-aqueous, as the intensity and the nature of corrosion processes in these environments differ significantly. For non-aqueous environments, electrochemical corrosion connected with different chemical reactions is typical, whereas only electrochemical corrosion (without other chemical reactions) occurs in aqueous environments. Moreover, electrochemical corrosion is much more intensive in aqueous environments[9].

In non-aqueous, liquid organic environments, corrosion processes depend on the degree of polarity of the organic compounds. This is associated with the substitution of hydrogen in some functional groups by metals, which is connected with the change of the characteristics of the corrosion processes from electrochemical to chemical, for which lower corrosion rates are typical in comparison with electrochemical processes. Non-aqueous environments typically have low values of electrical conductivity[9]. To increase conductivity in organic environments, it is possible to add so called supporting electrolytes such as tetraalkylammonium tetrafluoroborates or perchlorates. Unfortunately, these substances can have inhibitive properties, or, on the contrary, increase corrosion rates[10].

There are several methods for short-term and long-term testing of corrosion rates of metallic materials or the efficiency of corrosion inhibitors, namely with or without environment circulation, *i.e.*, static and dynamic corrosion test, respectively[11,12,13,14,15]. For both methods, the calculation of the corrosion rates of metallic materials is based on weight losses of the tested materials over a certain time period. Recently, electrochemical methods are becoming more important in corrosion studies due to their high efficiency and short measurement times. Moreover, they can often provide more information and a more comprehensive view on corrosion processes. The most commonly used methods are electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and the measurement of the stabilization of the corrosion potential in time (in a planar, two-electrode or in a three electrode arrangement)[16,17,18,19,20,21,22,23].

Here, we present five methods for the short-term and long-term testing of the corrosion aggressiveness of an environment, the corrosion resistance of metallic materials and the efficiency of corrosion inhibitors. All of the methods are optimized for measurements in non-aqueous environments and are demonstrated on EGBs. The methods allow for obtaining representative and reproducible results, which can help to understand corrosion processes in more detail to prevent and minimize corrosion damages.

For the static immersion corrosion test in metal-liquid systems, static corrosion tests in metal-liquid systems can be performed in a simple apparatus consisting of a 250 mL bottle equipped with a hook for hanging an analyzed sample, see **Figure 1**.

For the dynamic corrosion test with liquid circulation, metal corrosion inhibitors or the aggressiveness of liquids (fuels) can be tested in a flow apparatus with the circulation of the liquid medium presented in **Figure 2**. The flow apparatus consists of a tempered part and a reservoir of the tested liquid. In the tempered part, the tested liquid is in contact with a metallic sample in the presence of air oxygen or in an inert atmosphere. The gas (air) supply is ensured by a frit with the tube reaching the bottom of the flask. The reservoir of the tested liquid containing about 400-500 mL of the tested liquid is connected with a reflux cooler that allows for the connection of the apparatus with the atmosphere. In the cooler, the evaporated portion of the liquid is frozen at -40 °C. The peristaltic pump allows for the pumping of the liquid at a suitable rate of about 0.5 Lh^{-1} via a closed circuit from chemically stable and inert materials (*e.g.*, Teflon, Viton, Tygon) from the storage part into the tempered part, from which the liquid returns via the overflow into the storage part.

For the static immersion corrosion test with a reflux cooler in the presence of gaseous medium, corrosion inhibitors, the resistance of metallic materials or the aggressiveness of a liquid environment can be tested in the apparatus presented in **Figure 3**. The apparatus contains two parts. The first part consists of a two-necked, tempered 500 mL flask with a thermometer. The flask contains a sufficient amount of a liquid environment. The second part consists of (i) a reflux cooler with a ground glass joint to achieve a tight connection with the flask, (ii) a hanger for placing the metallic samples and (iii) a frit with a tube for gas (air) supply reaching the bottom of the flask. The apparatus is connected to the atmosphere via the cooler that avoids liquid evaporation.

The apparatus for the electrochemical measurements in the two-electrode arrangement is presented in **Figure 4**. The electrodes are made from metal sheets (3 x 4 cm, from mild steel), which are completely embedded in epoxide resin on one side to protect them from the surrounding corrosive environment. Both electrodes are screwed to the matrix so that the distance between them is about 1 mm[22].

The electrochemical measurements in the three-electrode arrangement consist of working, reference and auxiliary electrodes placed in the measuring cell so that a small distance between the electrodes is ensured; see **Figure 5**. As the reference electrode, calomel or argent-chloride electrodes with a salt bridge containing either (i) a 3 $molL^{-1}$solution of potassium nitrate (KNO_3) or (ii) a 1 $molL^{-1}$solution of lithium chloride (LiCl) in ethanol can be used. A platinum wire, mesh or plate can be used as the auxiliary electrode. The working electrode consists of (i) a measuring part (tested material with a screw thread) and (ii) a screw attachment isolated from the corrosion environment, see **Figure 6**. The electrode must be sufficiently isolated by an anti-underflow seal.

Protocol

1. The Static Immersion Corrosion Test in Metal-Liquid Systems

1. Add 100–150 mL of the tested liquid corrosion environment for testing the resistance of metallic materials or the efficiency of corrosion inhibitors *(i.e.*, aggressive EGB contaminated with water and trace amounts of chlorides, sulfates and acetic acid) into a 250 mL bottle equipped with a hook for hanging an analyzed sample (**Figure 1**).
2. Adjust the surface of the metallic samples by grinding using sandpaper (1200 mesh) and polishing under running water so that the surface is adjusted evenly. Then, degrease the sample surface thoroughly with about 25 mL of acetone and about 25 mL of ethanol, dry it freely or using pulp tissue, and weigh the sample on an analytical balance with an accuracy of four decimal places.
NOTE: The sample treatment must always be performed in the same manner, otherwise measurements can be loaded by an error. It is crucial to always use sandpaper with the same grain size and the used sandpapers must be disposable, *i.e.*, one piece of sandpaper for each sample and measurement. The surface must be adjusted evenly, it cannot contain any surface defects such as scratches, pits, *etc.*

3. After the surface treatment, hang the metallic sample into the liquid in the bottle so that it does not lie on the bottom of the bottle, see **Figure 1**. Close the bottle tightly enough to prevent liquid evaporation and air entry.
4. Choose the volume of the tested liquid so that the liquid/metal surface ratio is about 10 cm^3/1 cm^2 minimally.
5. At regular intervals, remove the metallic sample from the bottle, rinse it with about 25 mL of acetone, and use pulp tissue to dry it and remove the surface layer of excess corrosion products. Then, weigh the sample on an analytical balance with an accuracy of four decimal places. After weighing, return the sample back into the bottle.
   NOTE: The intervals for removing and weighing the samples should be chosen individually for each tested sample based on a visual evaluation of the changes in the sample surface during the test. Shorter intervals (*e.g.*, 8 h or less) should be applied when intensive surface changes are observed and the intervals can become longer (*e.g.*, 24 h, 48 h) when less intensive or no surface changes are visible. When comparison between the samples is required, the test duration must be the same.
6. From the weight of the metallic sample, calculate the weight loss from the beginning of the experiment related to the sample surface for the given exposure time. After steady state in the metal-liquid system occurs (no increase in the weight loss over time has been observed), terminate the experiment.
7. Calculate the corrosion rate according to the procedure presented in **Step 4** (before pickling) or in **Step 5** (after pickling of the surface corrosion products).
   NOTE: Corrosion rates obtained after pickling of the surface corrosion products are used for the evaluation of the efficiencies of corrosion inhibitors, for more details, see **Representative Results**.

2. The Dynamic Corrosion Test with Liquid Circulation

1. Add 500 mL of the tested liquid corrosion environment into the four-necked flask of the storage part of the apparatus. Lubricate the ground glass joints of the flask with a silicone grease and fix (i) a reflux cooler, (ii) a thermometer, (iii) a suction capillary connected to a pump and (iv) the overflow connected to the tempered part on the necks of the flask according to **Figure 2**.
2. Turn on the cryostat connected to the cooler and set the temperature to -40 °C. Fill the closed cooling circuit with ethanol.
3. Use the capillary for fuel pumping to connect the pump to the preheating spiral of the tempered part, which brings a preheated fuel via the bottom of the measuring cell. Turn on the pump and set the desired fuel flow rate (500 $mL \times h^{-1}$). Turn on the thermostat of the tempered part and set the temperature to the desired value (40 °C).
4. Once the tempered part is filled with fuel and the fuel starts to flow via the overflow part back into the storage flask, open the measuring cell that consists of two parts connected via a ground glass joint and hang the ground, polished, degreased and weighed sample (metal sheet with appropriate proportions) on the hanger.
   NOTE: The sample treatment is performed according to the procedure presented in **Step 1.2**.
5. Connect the frit to the tube for air supply with a pressure vessel via a pressure regulator and a flowmeter and set the desired gas flow rate on the flowmeter (20–30 $mL \times min^{-1}$).
6. At regular intervals, remove the metallic sample from the tempered part and follow the instructions presented in **Step 1.5**.
7. Follow the instructions presented in **Steps 1.6** and **1.7**.

3. The Static Immersion Corrosion Test with a Reflux Cooler in the Presence of Gaseous Medium

1. Add 200–300 mL of the tested sample (*e.g.*, tested engine oil containing an aggressive E100 fuel) into the tempered flask.
2. Hang a ground, polished, degreased and weighed sample on the hook of the cooler. Lubricate the ground glass joint of the cooler with a silicone grease and fix the cooler into the flask.
   NOTE: The sample treatment is performed according to the procedure presented in **Step 1.2**.
3. Connect the frit to the tube for the air supply with a pressure vessel via a pressure regulator and a flowmeter and set the desired gas flow rate (80 $mL \times min^{-1}$) on the flowmeter.
4. Set the temperature to 80 °C on the thermostat for flask tempering and to -40 °C on the cryostat connected to the cooler.
5. After an appropriate period (*e.g.*, 14 days), remove the metallic sample from the apparatus and follow the instructions presented in **Step 1.5**.
6. Follow the instructions presented in **Steps 1.6** and **1.7**.

4. Calculation of the Corrosion Rate from Weight Losses

1. From the corrosion losses obtained according to the methods presented in **Steps 1-3**, calculate the value of the corrosion rate according to **Equations 1** and **2**.

$$v_{Lr} = 8{,}76 \cdot \frac{v_{Pm}}{\rho} \qquad (1)$$

$$v_{Pm} = \frac{\Delta m}{T \cdot S} \qquad (2)$$

where n_{Pm} is the corrosion rate in $g \cdot m^{-2} \cdot h^{-1}$, ρ is the density of the metallic material in $g \cdot cm^{-3}$, Δm is the average weight loss in g, S is the surface area of the metallic material in m^2, and T is the time (in hours) from the beginning of the test to the removal of the metal plate for measurement.

5. Pickling of the Corrosion Products on the Metal Surface

1. Pickle the corroded samples of mild steel in a 10 wt. % solution of chelaton III at 50 °C for 5 min. Then, remove the sample from the solution, clean it using a brush under running water, rinse it with acetone, dry and weigh it. After that, put the sample back into the chelaton solution and repeat the procedure until a constant weight is obtained.
2. Pickle the corroded samples from brass, bronze or copper in a 10 vol. % solution of sulfuric acid under nitrogen bubbling (to remove dissolved air oxygen) for 1 min. Then, remove the sample from the solution, clean it using a brush under running water, rinse it with acetone, dry and weigh it. After that, put the sample back into the acid solution and repeat the procedure until a constant weight is obtained.

6. Electrochemical Measurements in the Two-Electrode Arrangement

1. Remove the electrode system from the measuring cell, unscrew it, adjust the surface of the electrodes according to the procedure presented in **Step 1.2** (without weighing) and then complete the electrode system again.
2. Fill the measuring cell with 80 mL of the tested liquid corrosion environment and close it through the electrode system. Put the whole cell into a grounded Faraday cage. Connect the galvanostat and potentiostat to the electrode system so that one electrode of the system acts as a reference electrode and the second electrode acts as a working and an auxiliary electrode at the same time.
3. In the instrument software, set the sequence containing the open circuit potential measurements (OCP, stabilization of corrosion potential in an open circuit) and the electrochemical impedance spectroscopy (EIS) measurement. The stabilization perform for at least 30 min to minimize the potential change.
4. Undertake the EIS measurements at sufficiently high amplitude according to the conductivity of corrosion environment (fuel).
   NOTE: The lower the fuel conductivity is, the higher amplitude values are needed. For fuels containing more than 80 vol. % of ethanol, choose the amplitude values in the range of 5–10 mV. For fuels containing ethanol in the range of 10–80 vol. %, choose the amplitude values in the range of 10–50 mV. For fuels containing less than 10 vol. % of ethanol, choose the amplitude values in the range of 50–80 mV.
5. Undertake the impedance measurements in a sufficient range of frequencies (1–5 mHz) to be able to evaluate the low- and also high-frequency parts of the spectra.
6. Determine the cell constant K_s for each electrode by measurement in n-heptane, which has a permittivity of about 1.92 according to the following equation:
   $$K_s = \frac{\varepsilon_r \cdot \varepsilon_0}{C} \qquad (3)$$
   where C is the capacitance obtained from the high-frequency part of the impedance spectrum measured in a planar electrode arrangement in the n-heptane-metal system, ε_r is the relative permittivity of n-heptane, and ε_0 is the relative permittivity of the vacuum.
7. Use the obtained cell constant for the calculation of the fuel permittivity ε and for the recalculation of the resistivity R according to the following equations:
   $$\varepsilon = \frac{K_s \cdot C_v}{\varepsilon_0} \qquad (4)$$
   $$R_s = \frac{R_v}{K_s} \qquad (5)$$

7. Electrochemical Measurements in the Three-Electrode Arrangement

1. Adjust the measuring part of the working electrode from the tested metallic material according to the procedure presented in **Step 1.2** (without weighing) and screw it onto the electrode extension.
2. Fill the measuring cell with 100 mL of the tested liquid corrosion environment and close it with a cap through which the working electrode from the tested material and the auxiliary electrode from the platinum wire are led. Twist the wire, *i.e.*, auxiliary electrode, evenly around the working electrode. Through the side entry of the cell, insert the reference electrode with a bridge so that it is as close to the working electrode as possible.
   NOTE: Electrodes cannot touch each other.
3. Insert the cell into a grounded Faraday cell and connect the electrodes via a cable system to the galvanostat and potentiostat equipped with the appropriate software.
4. In the software of the used measuring devices, set the measuring sequence containing the measurement of (i) the OCP for a sufficiently long time period (at least 60 min), (ii) the EIS in the range of about 1 MHz–1 mHz at an amplitude value of 5–20 mV and (iii) the polarization characteristics (Tafel scan) in the range of 200–500 mV to the corrosion potential.
5. Calculate the current density j_{corr} according to the Stern-Geary equation:
   $$j_{corr} = \frac{B}{R_p} \qquad (6)$$

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$$B = \frac{b_a \cdot b_b}{2.3 \cdot (b_a + b_b)} \qquad (7)$$

where j_{corr} is the corrosion current density, b_a and b_k are Tafel constants, and R_p is the polarization resistance estimated from the EIS measurements. Furthermore, calculate the instantaneous corrosion rate from the material weight losses. Determine the material weight losses from the current density from Faraday´s law as follows:

$$m = A \cdot I \cdot t \qquad (8)$$

$$A = \frac{M}{z \cdot F} \qquad (9)$$

where m is the mass of the substance in g; I is the current; t is the time; A is the proportionality constant designated as the electrochemical equivalent of the substance, measured in kg·C^{-1}; F is the Faraday constant (9.6485 × 10^{4} C·mol^{-1}); and z is the number of electrons needed to exclude one molecule.[22]

8. Calculation of the Efficiency of Corrosion Inhibitors

1. Use the obtained values of polarization resistance or corrosion rate to calculate the efficiency of the corrosion inhibitors according to the following equations:

$$E_f = \frac{100 \cdot (R_i - R_0)}{R_i} \qquad (10)$$

or

$$E_f = \frac{100 \cdot (\nu_i - \nu_0)}{\nu_i} \qquad (11)$$

where E_f is the efficiency of corrosion inhibitors in %; R_i is the polarization resistance of material; n_I is the corrosion rate of material in a metal-fuel system containing the corrosion inhibitor; R_0 is the polarization resistance; n_0 is the corrosion rate in the metal-fuel system without the corrosion inhibitor.

Representative Results

The above mentioned methods were used to measure the corrosion data of mild steel (consisting of 0.16 wt. % of C, 0.032 wt. % of P, 0.028 wt. % of S and balance F)[22] in the environment of ethanol-gasoline blends (EGBs) containing 10 and 85 vol. % of ethanol (E10 and E85), respectively. For the preparation of these EGBs, gasoline in compliance with the requirements of the EN 228 containing 57.4 vol. % of saturated hydrocarbons, 13.9 vol. % of olefins, 28.7 vol. % of aromatic hydrocarbons, and 1 mgkg^{-1} of sulfur was used. The aggressiveness of these fuels was increased by the addition of water and trace amounts of chlorides (3 mgkg^{-1}), sulfates (3 mgkg^{-1}) and acetic acid (50 mgkg^{-1}). The E10 fuel contained 0.5 vol. % of water so that no separation to aqueous-ethanol and hydrocarbon phases occurred. The E85 fuel was contaminated by 6 vol. % of water.[22] The tested corrosion inhibitor contained octadecylamin and the concentration of the inhibitor in the fuels was 200 mgL^{-1}. The obtained data is presented in **Table 1**.

The time course of the static and dynamic tests is presented in **Figure 7** and **Figure 8**. The dependences of weight loses presented in these figures are related to the surface area of the tested metallic sample. These weight losses can be recalculated to the course of corrosion rate according to the procedure presented in **step 4**. This is shown for the contaminated E85 fuel in **Figure 7** and **Figure 8**. From both figures, it is obvious that the time periods of 1200 h and 340 h were sufficient enough to achieve the stabilization of the mild steel-E10 (E85) fuel systems for static and dynamic tests, respectively. Also, the efficiency of the corrosion inhibitor is evident in both fuels, as substantially lower material losses were observed when the inhibitor was applied. The inhibitor efficiencies, see **Table 1**, were calculated after the experiment and after the pickling of the sample surface in the solution of chelaton III, see **step 5.1**. The removal of the surface corrosion products by pickling enables us to obtain real material losses that are important for the calculation of the efficiency of corrosion inhibitors. Pickling causes an increase of the real corrosion rate as documented by the results presented in **Table 1**. This can be observed especially for the dynamic test with the circulation of the corrosive environment, where the metal-environment system is much more stressed and the material resistance is significantly decreased. According to the conditions of the test and the corrosion environment, the metal is evenly coated by a thick layer of corrosion products, see **Figure 9**.

Some samples of the corrosion environments cannot be tested by the dynamic test due to their high viscosity. Such samples (*e.g.*, engine oil contaminated with an unburned E100 fuel) can be tested by a static test under a reflux cooler at elevated temperatures, see **Step 3**. **Table 2** presents the obtained results of the corrosion rates of mild steel and two samples of brass that were tested in the oxidized engine oil (artificially aged oil in an oxygen atmosphere at 650 kPa and 160 °C) with a total acid number (TAN) of 3.5 mg KOHg^{-1} containing 15 vol. % of an azeotropic, aggressive E100 fuel (containing 6 vol. % of water and trace amounts of contaminants, see the fuel aggressiveness above).

Nowadays, electrochemical methods like electrochemical impedance, measurements of polarization characteristics, corrosion potential, *etc.* have a great potential and can inform one not only about the properties of environments (permittivity, resistivity), but also about the electrode properties such as polarization resistance and the capacity of a double-layer. Also, electrochemical methods have a great importance for the measurements in non-aqueous environments. Due to low conductivity of non-aqueous environments, conductivity salts can be applied to reduce the resistivity and increase the conductivity of an environment so that electrode properties (corrosion data) can be measured also. However, conductivity salts do not often only change the properties of corrosion environments, but they can also have negative impacts on the obtained corrosion data, *e.g.*, they can have corrosive or inhibitive properties. These effects can be avoided by performing the measurements without these salts in special cells with a modified geometry, see **steps 6** and **7**, so that the distances between the electrodes are as small as possible.

Figure 10 and **Figure 11** show impedance spectra measured in the two-electrode arrangement. The shape of impedance spectra is dependent on the conductivity of a used environment (fuel). When the conductivity of an environment is low (gasoline, EGBs containing up to 10 vol. % of ethanol) the spectrum consists of only one half-circle (the high-frequency part). This half-circle makes it possible to evaluate the properties that characterize the used environment only (resistivity, high-frequency capacity for the calculation of permittivity). The low-frequency part characterizing the electrode properties is completely missing. When the conductivity of an environment is high enough, the spectra consist of both high- and low-frequency parts that form two relatively well separated half circles, see **Figure 11**. Again, the high-frequency part informs one about the properties of an environment, whereas the low-frequency capacitive loop is associated with the response of an electrical double layer on the phase interface and parallel polarization resistance, which is the main corrosion quantity and characterizes the instantaneous corrosion rate. The spectrum can be evaluated according to the equivalent circuit that is presented in **Figure 11**. The measured and evaluated results for mild steel in a planar electrode arrangement are presented in **Table 1**.

The three-electrode arrangement enables us to measure the polarization characteristics presented in **Table 1** (*i.e.*, polarization resistance, corrosion potential, corrosion current density and Tafel constants of the cathodic and anodic parts of the Tafel polarization curve). These characteristics can be used to calculate the instantaneous corrosion rate from Stern-Geary equation, see **step 7.5**. The measurement of the polarization characteristics is difficult, especially in environments with low conductivity, as the measured data is substantially loaded by a potential loss (*iR* drop) that is strongly dependent on the resistivity of an environment and the distance of the working and reference electrodes. This potential loss can be minimized, estimated and subtracted from the polarization data based on the impedance spectroscopy performed before the measurement of the polarization curve or from the impedance spectroscopy after the measurement of the polarization curve. The evaluated polarization resistance from the previous impedance spectrum is important for the calculation of the corrosion rate and the resistivity for the calculation of the *iR* drop. **Figure 12** presents the Tafel curve of mild steel in the environment of the aggressive E85 fuel without the inhibitor before and after the *iR* drop compensation (blue and red, respectively). Also, this figure shows the linear areas of the cathode and anode parts that are used to obtain the Tafel coefficients. **Figure 11** also compares the Tafel curve of the mild steel measured in the environment of the aggressive E85 fuel containing an amine-based inhibitor, where the entire curve is shifted more toward cathode potentials (to more negative values) and lower current densities that lead to a lower instantaneous corrosion rate of the mild steel.

Figure 1: Exposure of mild steel in the aggressive E85 fuel during the static test. Please click here to view a larger version of this figure.

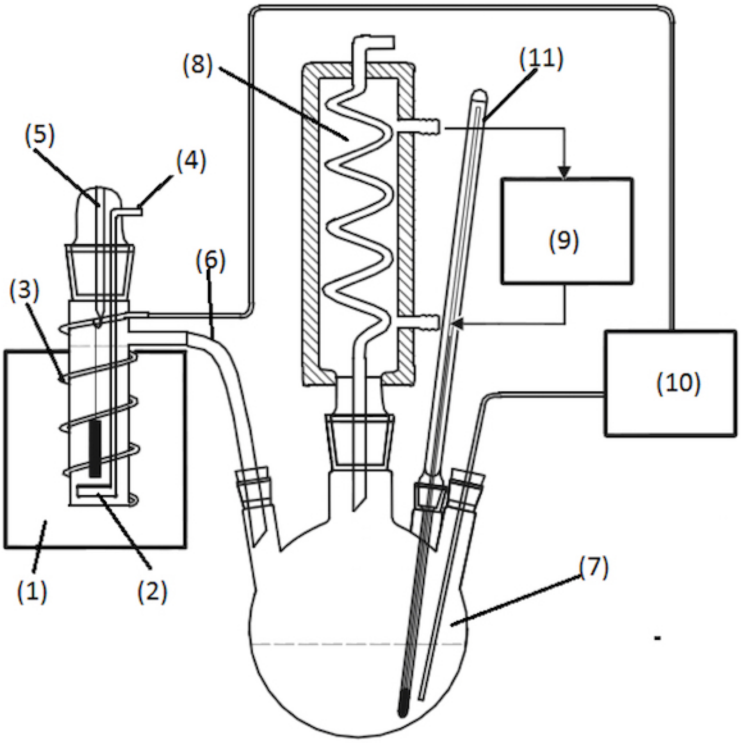

Figure 2: Scheme of laboratory flow apparatus for dynamic testing: (1) tempering silicon bath, frit for air supply, (3) preheating spiral, (4) air inlet, (5) sample hanger, (6) overflow into the storage flask, (7) storage flask, (8) cooler, (9) cryostat, (10) peristaltic pump, (11) thermometer. *Adapted with permission from ref[14]. Copyright 2013. Faculty of Environmental Technology, University of Chemistry and Technology Prague.* Please click here to view a larger version of this figure.

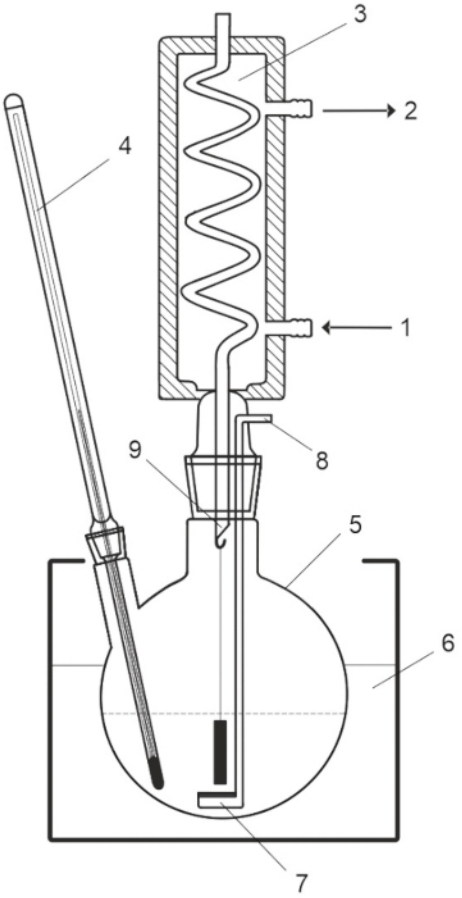

Figure 3: Scheme of apparatus for testing of corrosion effects of oils on construction materials in the presence of oxygen at constant temperature. (1, 2) cooling, (3) reflux, spiral cooler with a ground glass joint and a hook for sample hanging (4) thermometer, (5) flask with a ground glass joint containing sample, (6) thermostat, (7) frit with the tube for gas (air) supply, (8) oxygen supply, (9) sample with a hanger.[15] Please click here to view a larger version of this figure.

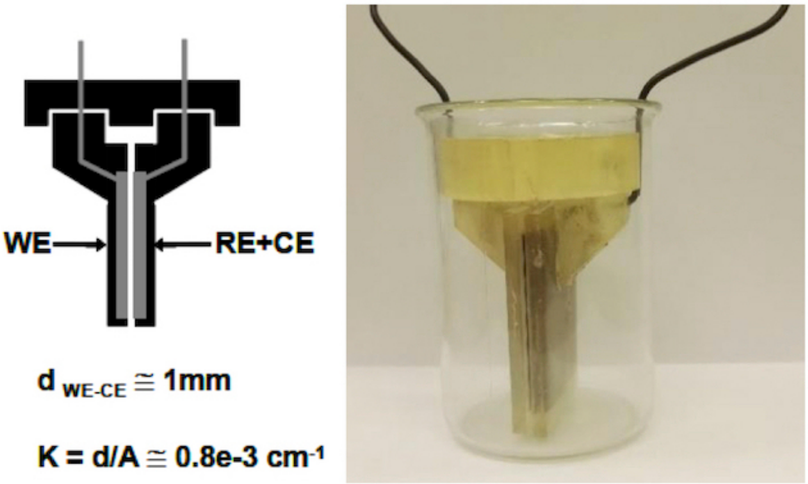

Figure 4: Geometry of a planar two-electrode arrangement with the distance of electrodes of about 1 mm and a cell constant of about 0.810^{-3} cm^{-1}. *Adapted with permission from ref*[10]*. Copyright 2009. Faculty of Environmental Technology, University of Chemistry and Technology Prague.* Please click here to view a larger version of this figure.

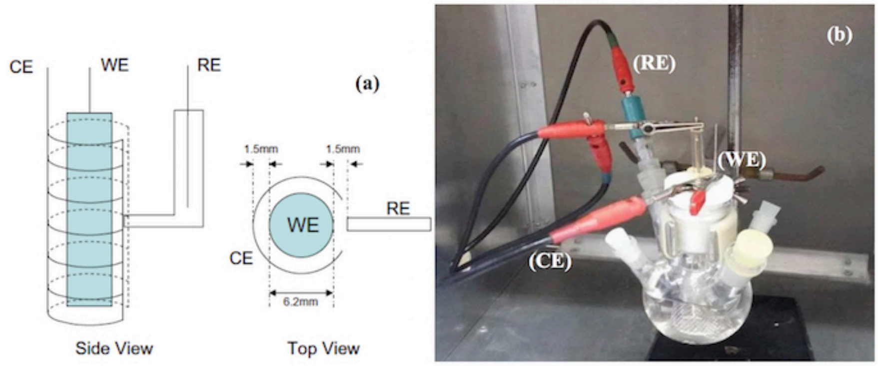

Figure 5: Geometrical arrangement of electrodes in the measuring cell: (a) connection of the measuring cell to potentiostat, (b) working electrode (WE), reference electrode (RE), counter (auxiliary) electrode (CE). Please click here to view a larger version of this figure.

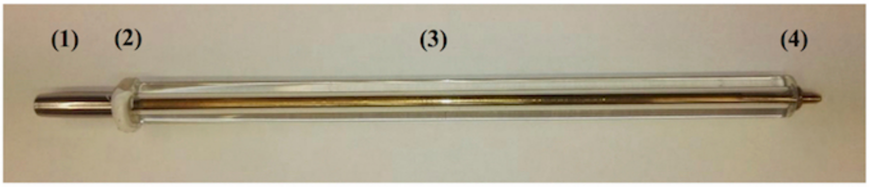

Figure 6: The construction of the working electrode: (1) working (measuring) part, (2) Teflon seal with a Teflon tape, (3) extension for connection of the electrode with a thread isolated on both ends by a glass tube, (4) nut for pulling the electrode and pressing the tube to the working electrode through a seal. Please click here to view a larger version of this figure.

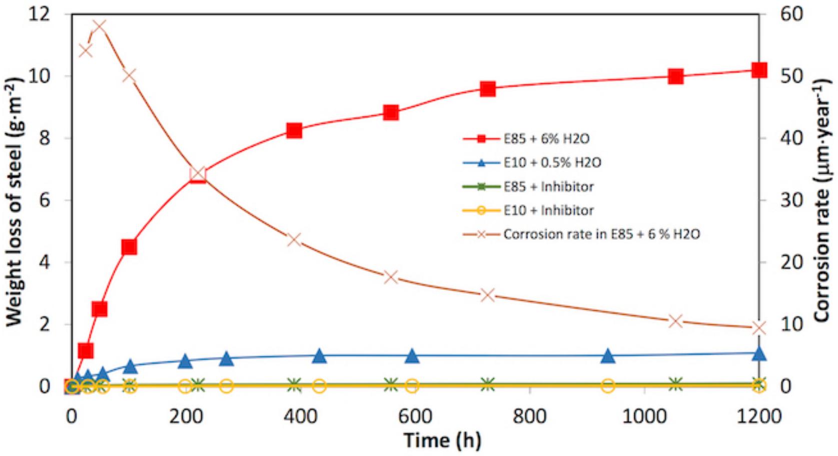

Figure 7: The time evolution of corrosion rate of mild steel in the contaminated E85 fuel and corrosion losses of mild steel in the contaminated E10 and E85 fuels before the addition of a corrosion inhibitor during the static test. Please click here to view a larger version of this figure.

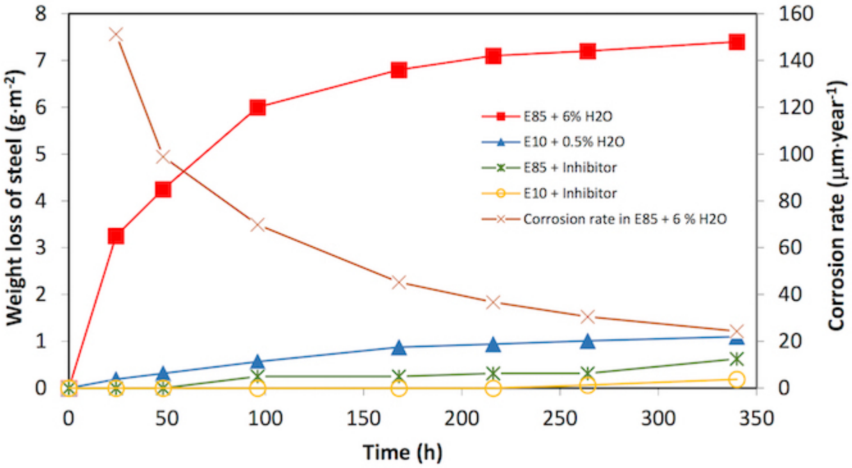

Figure 8: The time evolution of corrosion rate of mild steel in the contaminated E85 fuel and corrosion losses of mild steel in the contaminated E10 and E85 fuels before the addition of a corrosion inhibitor during the dynamic test. Please click here to view a larger version of this figure.

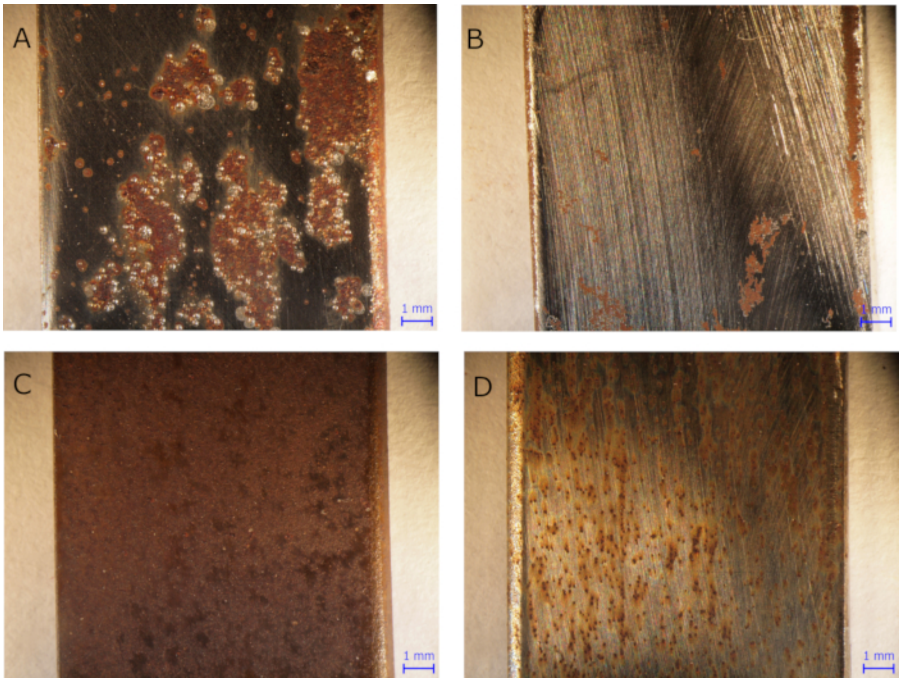

Figure 9: The surface of mild steel tested in the environment of the aggressive E85 fuel without the corrosion inhibitor (A, C) and with the inhibitor (B, D) during the static (A, B) and dynamic test (C, D). Please click here to view a larger version of this figure.

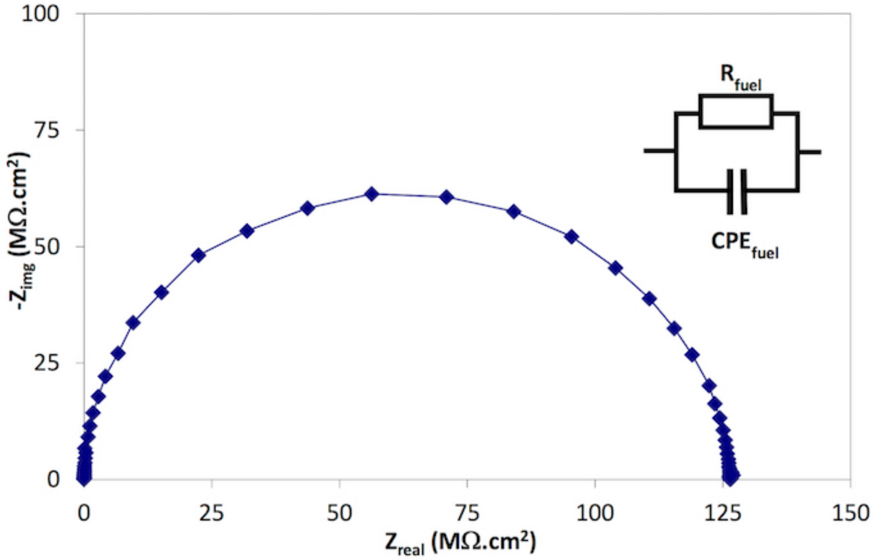

Figure 10: Impedance spectrum measured in the contaminated E10 fuel for mild steel in a planar, two-electrode arrangement after 30 min of exposure and the equivalent circuit used for evaluation (right upper corner). R_{fuel} is the resistance of the environment and CPE_{fuel} is the spatial capacitance of the environment. Please click here to view a larger version of this figure.

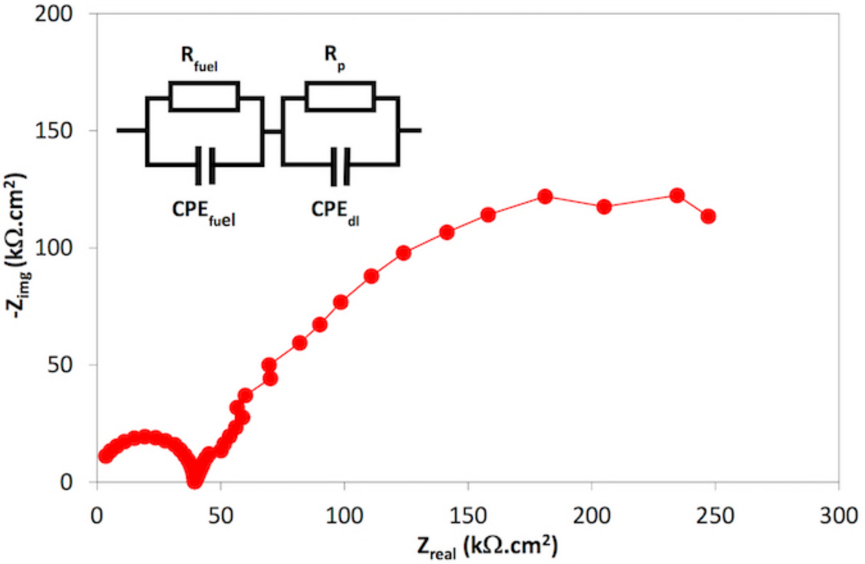

Figure 11: Impedance spectrum measured in the contaminated E85 fuel for mild steel in a planar, two-electrode arrangement after 30 min of exposure and the equivalent circuit used for evaluation (right upper corner). R_{fuel} is the resistance of the environment, CPE_{fuel} is the spatial capacitance of the environment, R_p is the polarization resistance and CPE_{dl} is the capacitance loss of the double layer. Please click here to view a larger version of this figure.

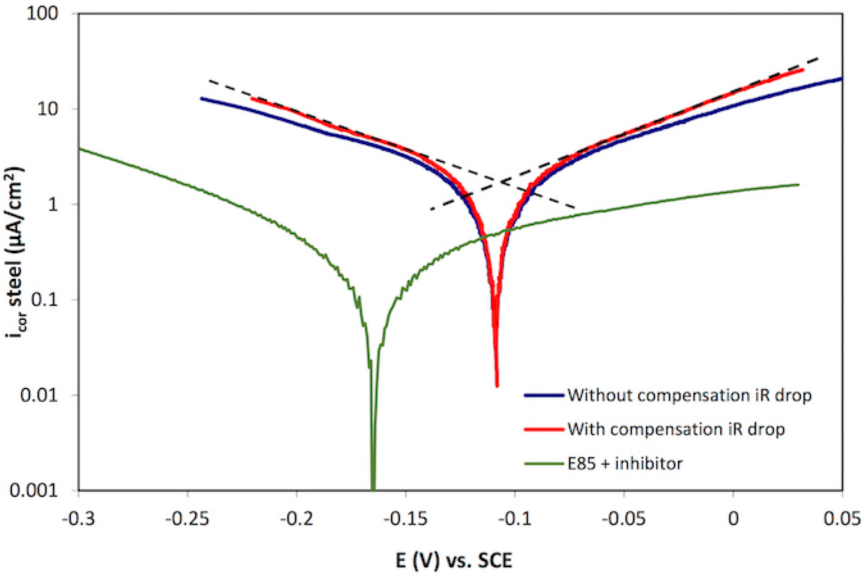

Figure 12: Polarization curves of mild steel in the environment of the contaminated E85 fuel measured in a three-electrode arrangement. Please click here to view a larger version of this figure.

Method	Parameter	E10 + 0.5 % of H_2O	E10 + 0,5 % of H_2O + inhibitor	E85 + 6 % of H_2O	E85 + 6 % of H_2O + inhibitor
Static test	Corrosion rate before pickling (mm×year^{-1})	0.1	0,03	9.5	1.2
	Corrosion rate after pickling (mm×year^{-1})	5.5	1,3	17.9	3.4
	Inhibitor efficiency (%)	76.3		80.7	
Dynamic test	Corrosion rate before pickling (mm×year^{-1})	1	0,6	24.3	0.1
	Corrosion rate after pickling (mm×year^{-1})	13.5	4,9	56.5	17.9
	Inhibitor efficiency (%)	63.4		68.4	
Electrochemistry in a planar, two-electrode arrangement	Resistivity (kW×m)	6440	6180	2.83	2.79
	Permittivity	2.9	3,0	21.8	21.5
	Polarization resistance (kW ×cm^2)	-	-	287.5	851.3
	Capacity of electrical double-layer (mF×cm^{-2})	-	-	20.4	8.1
	Inhibitor efficiency (%)	-		66.3	
Electrochemistry in a three-electrode arrangement	Polarization resistance (kW×cm^2)	-	-	20.4	49.6
	Tafel b_k (mV)	-	-	132.5	105
	Tafel b_a (mV)	-	-	325.1	213.6
	Corrosion potential (mV)	-	-	-109.5	-165.1
	Current density (mA×cm^{-2})	-	-	2	0.6
	Instantaneous corrosion rate (mm×year^{-1})	-	-	15.5	4.8
	Inhibitor efficiency (%)	-		69.2	

Table 1: Corrosion data of mild steel and efficiency of an inhibitor determined by five different methods.

Material	Initial weight (g)	Weight after pickling (g)	Sample area (m^2)	Corrosion rate (µm×year^{-1})
Steel	7.8025	7.8012	0.001	2.5
Brass 1	11.8687	11.8619	0.0012	9.9
Brass 2	10.5686	10.5645	0.002	3.6

Table 2: Corrosion rates (after pickling) of brass and steel samples exposed in the environment of the engine oil contaminated with an aggressive E100 fuel (15 vol. %) within 14 days of the static test under a reflux cooler.

Discussion

The basic principle of the dynamic test and both static tests is the evaluation of weight losses of metallic samples in metal-corrosion environment (fuel) systems depending on time until steady state is achieved (*i.e.*, no further weight loss occurs). The corrosion rate of the metal in the corrosion environment is calculated from the weight loss and time. The advantage of the long-term static corrosion test (**Step 1**) is the reliability of the obtained results, the simplicity and low requirements on material and instrumental equipment. On the other hand, it is a time-consuming method, as much time is needed to achieve steady state of the metal-fuel system to evaluate the corrosion rates.

The main advantage of the presented dynamic test in comparison with the static test is a significant shortening of the measurement times to achieve steady state in the metal-fuel system. The apparatus is designed so that it is simple to operate and handle with the tested materials. The testing can be performed in an oxidative (air) or an inert (nitrogen) atmosphere. Another advantage is the possibility to test metal-fuel systems at different test conditions (temperature, flowrate of corrosion environments and gaseous media). Also, the apparatus allows for the prediction of fuel aging, the testing of fuel quality or the testing of fuel influence on metallic and non-metallic materials. Metals and environments are tested at substantially more severe conditions than in comparison with the static test. The main disadvantage of the methods are higher demands on material and instrumental equipment and energy consumption.

The static test under a reflux cooler (**Step 3**) allows for the testing of materials in an environment of viscous liquids (*e.g.*, an engine oil after the expiry of its shelf life or contaminated with biofuels) at elevated temperatures and in the presence of an oxidative or an inert atmosphere. The disadvantages are similar as those for the dynamic test.

The presented electrochemical methods can inform one about the time course of the corrosion potentials, the instantaneous corrosion rates, the processes occurring at the metal-environment interfaces and also about the transmission properties of the corrosion environments, such as permittivity and environmental resistance (conductivity). These methods are relatively simple, fast and give reliable and reproducible results. On the other hand, they have higher demands on instrumental equipment (potentiostat, galvanostat) that allows for measurement in non-aqueous environments.

The presented two-electrode electrochemical system (**Step 6**) is very simple and easily demountable, which allows for the easy control of the electrode surface and its treatment by grinding and polishing before measurements. Other advantages are the large surface of both electrodes, which allows for an even spread of the corrosion density, and also the small distance between both electrodes, which makes it possible to perform measurements even in less conductive environments, such as gasolines without base electrolytes. The system design allows for the measurement of electrode properties for the evaluation of instantaneous corrosion rates of metallic materials even for contaminated or oxidized E10 fuels after longer exposure times[22,23]. It was found that the main limiting factors for the corrosion data measurements using EIS in a two-electrode arrangement are resistivity of 4.7 MΩ·m and relative permittivity of fuel of 2.69[22,23].

The presented three-electrode electrochemical system (**Step 7**) makes it possible to measure the polarization characteristics that cannot be measured in the two-electrode system. Due to the suitable cell geometry, it is possible to measure the polarization characteristics in less conductive, non-aqueous environments such as uncontaminated EGBs containing 40 vol. % of ethanol[22,23].

In order to compare data obtained from the presented methods to each other, it is necessary to keep the ratio of the liquid (fuel) vs. metal surface area the same for each method. If not, only the trends of the results obtained by individual methods can be compared to each other as presented in our previous publications[22,23], where different trends in the results of electrochemical methods and static tests (different ratios of metal sample area and corrosive environment) are compared depending on the ethanol content of the fuel, the contamination and the degree of oxidation (water content, acidic substances, peroxides, *etc.*).

For all presented methods, it is necessary to pay attention to the treatment of the metallic samples. The sample treatment must always be performed in the same manner, otherwise measurements can be loaded by an error. It is crucial to always use sandpaper with the same grain size and the used sandpapers must be disposable, *i.e.*, one piece of sandpaper for each sample and measurement. The surface must be adjusted evenly, it cannot contain any surface defect such as scratches, pits, *etc.*

For electrochemical methods, it is important to pay attention to the electrodes against overflow, especially for the working electrode in a three-electrode arrangement. For the working electrode, it is also important to pay attention to the contact between the working part of the electrode and the attachment for attaching of potentiostat. Electrodes should not touch each other. It is desirable that the bridge of the reference electrode is as close as possible to the working electrode. It is desirable to evenly arrange the auxiliary electrode around the working electrode so that the current density between them is evenly distributed.

Disclosures

The authors have nothing to disclose.

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