Comparison of liquid and gel electrolytes for the investigation of pitting corrosion on stainless steels

A Heyn
Otto-von-Guericke-University Magdeburg, Faculty of Mechanical Engineering, Institute of Materials and Joining Technology, Universitätsplatz 2, 39106 Magdeburg, Germany
andreas.heyn@ovgu.de

Abstract. Electrochemical methods have become established for the investigation and testing of stainless steels for their resistance to pitting corrosion. In contrast to liquid electrolytes, which are normally used for this purpose, gel-like electrolytes have clear advantages regarding their usability. However, it must be clarified whether both types of electrolyte lead to the same or different results. In the investigations presented here, various agar-based gel electrolytes were characterized regarding their corrosion-relevant properties, such as chemical composition, rheological properties and the electrolyte film forming on the surface. To compare the two electrolyte types, electrochemical investigations were carried out with graduated agar and NaCl concentrations on the material 1.4301 (AISI 304). Pitting and repassivation potentials were determined by dynamic polarization experiments and the varied factors were statistically evaluated regarding their influence. The results show that liquid and gel electrolytes provide comparable results. However, the pitting corrosion phenomena under external polarization are shallower with gel electrolytes and therefore their repassivation is supported. Also, the use of gel electrolytes with indicators for iron ions, which at the same time act as oxidizing agents and allow polarization into critical areas, gives comparable results. Gel electrolytes are therefore a very good alternative to liquid electrolytes if the detection of corrosion-sensitive surfaces is in focus.

1 Introduction
Stainless steels are among the most commonly used materials when corrosion resistant surfaces and related functionalities are required. However, already during production, but especially during further processing, the materials can be unintentionally modified in such a way that their very good corrosion resistance is no longer guaranteed. A number of testing and examination methods are available to check this. Most of these are, however, laboratory applications, which are costly, time-consuming and destructive. On the part of the processors and users of these steels, however, there is a desire to have a testing method for use on site (point-of-care) to determine the corrosion resistance of a semi-finished or end product quickly and reliably. Electrochemistry is virtually predestined for such questions. However, it is difficult to transfer laboratory methods to practical use because of the necessary equipment and electrodes and, not least, because of the handling with liquid electrolytes. For this reason, research efforts have been made over several years to solve these problems and provide users with a simple and functional testing tool.

The use of gel electrolytes instead of liquid test electrolytes is an important part of a point-of-care strategy in corrosion testing. The liquid electrolyte is immobilized by a network of polymer fibers.
Agar/Agarose is used as a gel-forming polymer because it forms stable gels even in very low concentrations. The gel also has the property of forming a thin electrolyte film on the gel surface by syneresis. This enables electrochemical reactions and measurements on metallic surfaces. However, the question is, are the measurements as well feasible as with liquid electrolytes and are they comparable at all. For this reason, investigations of the pitting corrosion resistance of stainless steel 1.4301 were carried out by means of dynamic polarization and various gel and liquid electrolytes were compared with each other. Furthermore, the “KorroPad” method was tested as possible point of care method and is compared with the polarization results.

2 State of knowledge

Agar offers itself as the basic structure for a gel electrolyte since it leads to stable gels even in very low concentrations in water. Agar is a macromolecular polysaccharide which is obtained from the cell walls of various red algae by extraction with hot water, freeze-thaw processes or spray drying. It consists of about 70 % agarose (gelling) and about 30 % agarpectin (sulphated, non-gelling). A separation to pure agarose is carried out for use in gel electrophoresis. Agar can be mixed with water but is insoluble at room temperature. It melts between 80 and 100 °C and crosslinks physically by cooling. The structure of the solidified macromolecules is described as double helices, which cross-link spatially and, depending on the concentration of the agarose, form cavities in the range of several hundred nanometers, which are filled with the solvent.

Although the specific research and use of agar gels for corrosion investigations is still comparatively limited, their application for so-called electrographic processes has been known for a long time. As early as 1955, Laque et al. used gel electrolytes mixed with indicators to visualize partial reactions of corrosion processes for teaching material science [1]. In a similar way, many years later Isaacs et al. added chloride and pH indicators to agar gel pads and used them to study aluminum and aluminum alloys [2]. They were able to visualize the location and course of anodic and cathodic partial reactions in localized corrosion on aluminum by means of indicators in the gel. The visualization of corrosion by an indicator for iron ions is also the basic principle of the electrographic Ferroxyl test. This test is still used today to determine the porosity of metallic coatings [3] or to test the porosity of phosphating’s on steel, whereby the use of gelatin instead of filter paper as electrolyte carrier is often recommended. As early as 1959, the Ferroxyl test with gels was used as a test method for implant materials made of stainless steels and other high alloyed materials [4]. A few years ago, the method was further developed for the detection of local corrosion on stainless steels by the Federal Institute for Materials Research and Testing (BAM) [5], patented [6] and can be purchased as "KorroPad" test equipment. It is based on a gel pad with an agar content of 3 % in water and contents of 0.1 mol/L NaCl and 0.001 mol/L potassium ferricyanide. The latter leads to the formation of a stable redox potential which, as a critical test potential if the material is sensitive to corrosion. The chloride ions activate weak points in the passive layer and a local metal dissolution takes place. The iron ions that are dissolved in the solution are complexed by the potassium ferricyanide to form Prussian Blue, a poorly soluble pigment that indicates the local corrosion sites by color and makes them assessable. In recent years, the KorroPad has been increasingly used as a testing agent in different industrial applications. It has been applied to questions regarding the corrosion resistance of stainless steels in industry and research [7], e.g. to optimize their heat treatment [8], to show the influence of surface treatments [9] or for proof of sensitization [10].

An application of gel-like electrolytes to simulate special corrosive conditions has been demonstrated e.g. by Newton and Sykes [11]. They used an agar gel mixed with NaOH and NaCl to examine steel in mortar-like electrolytes and were able to document significant differences to measurements in liquid electrolyte solutions. Spark et al. [12] describe in their studies how corrosion processes in clay soils with the help of agar gels can be simulated under the complex physical-chemical conditions prevailing there. The investigations were carried out on an unalloyed steel and free corrosion potentials and current densities were determined from polarization curves. In further publications the authors describe investigations with agar gels to which peptides have been added [13] in order to simulate microbiologically induced corrosion of pipelines in soils [14]. Vanbrabant et al. also used agar-based gel electrolytes as a
corrosion medium to simulate special media conditions, with simultaneous electrochemical instrumentation to perform electrochemical measurements [15]. They see the advantage of using gels as being closer to media conditions relevant to practice, especially where the transport of corrosion products is limited. Another advantage they see is that the individual stages of corrosion can be visualized in the course of the tests. Applications were presented that better simulate conditions of steel fibers in concrete, galvanized steel (zinc and zinc-aluminum alloys) in agricultural atmospheres and in animal farming.

Agar/agarose gels are also used in corrosion research for tailor-made, often miniaturized reference electrodes in which the bridge electrolytes are immobilized by the gel to minimize the leak rate [16]. In recent years, numerous authors have reported on the use of the gels as electrolyte with electrochemical instrumentation. Monrabal et al., for example, have added agar gels with a high proportion of glycerin (20 to 70 %) in order to realize more flexible top-mounted measuring cells [17] and to better couple them to shaped components. In this way, they are trying to identify weak points in welds of stainless steels [18] and have carried out numerous other electrochemical investigations [19, 20]. However, it is uncertain whether comparable results to liquid, purely water-based electrolytes are possible due to the high glycerin content. Cano et al. also developed a measuring cell based on agar gel as a connecting electrolyte, which makes it possible to carry out electrochemical impedance measurements on monuments and sculptures without causing any significant damage to them [21]. Di Turo et al. pursued the same goal by using gel-based electrolytes for the electrochemical characterization of bronze patina on historical coins [22]. The first own electrochemical investigations with gel electrolytes were started in 2014 and led, among other things, to a methodical approach to determine electrochemical parameters of galvanized steels under atmospheric exposure in order to determine the current state of the protective coatings [23].

The use of gels for corrosion tests can be summarized as follows:

- Triggering and visualization of corrosion processes by indicators in the gel electrolyte
- Electrochemical instrumentation of gel electrolytes to facilitate the characterization of corrosion protection systems and to determine characteristic values
- Simulation of specific corrosion conditions (building materials, soils, food, biological tissue) with solid/liquid phases and reduced mass transfer

3 Corrosion relevant properties of agar gels

For the application of gels as electrolyte for corrosion investigations it is important to determine the corrosion relevant properties of the gels in advance. In the case of the gel former, the chemical composition of the raw products is important, as a certain percentage is added to the aqueous electrolyte and can thus change its corrosivity. The mechanical properties of the gel also play an important role. When used as a test electrolyte, the gel must have a sufficient contact with the surface and the other electrodes but must not change or be damaged in an uncontrolled manner. Another important factor is the electrolyte film that forms on the gel and between the gel and the test surface since this can influence corrosion reactions and electrochemical measurements. It is important to find out how the wetness on the surface is related to the gel former and the electrolyte components. In general, the agar concentration determines the pore sizes and thus most properties, including mass transfer in the gel. This means that the transport of ions and corrosion products within the gel and between the gel and the surface can be influenced in different ways.

To produce an agar gel, a certain amount of agar powder is added to the desired electrolyte, mixed and heated with stirring to a temperature at which the agar dissolves and melts in the aqueous solution. The melting temperature varies according to the type of agar, e.g. 45 °C for low melting agarose, approx. 85 °C for standard agarose or up to 98 °C for agar. After a certain holding time, the melted agar-water mixture is poured off, where the gel-formation starts when the gel transition temperature is reached. The agar gel can be poured into almost any shape and cut into a specific form (e.g. circular pads) after reaching the gel state.
3.1 Properties of agar raw products

The chemical composition of the gel electrolyte consisting of water and agar/agarose is specifically adjusted to the respective metrological requirements. Usually ionic constituents are added in a certain concentration, which have an influence on the physical-chemical properties and thus also on the electrochemical reactions at the phase boundary to the surface. The agar substance, even with only a few percent agar in water, brings its own ions of different types and quantities and adds them to the gel electrolyte. The type and quantity can vary depending on the origin and quality of the agar and must be determined analytically in advance. The corrosion relevant effects can be measured on the finished gel, e.g. as a change in conductivity or in the redox potential. Table 1 shows the contents of corrosion-relevant ions for three commercially available agar substances, the conductivity of a 3% mixture with distilled water and the redox potentials of the mixture and the gels produced from it.

Table 1. Ion contents of agar products and effects on conductivity and redox potentials of agar-water solution and prepared 3% agar gels.

| type of agar               | Cl$^-$ [ppm] | SO$_4^{2-}$ [ppm] | PO$_4^{3-}$ [ppm] | NO$_3^-$ [ppm] | $\gamma$ 3% in H$_2$O [µS/cm] | pH         | $E_{\text{Redox}}$ 3% in H$_2$O [mV, NHE] | $E_{\text{Redox}}$ 3% Gel, fresh [mV, NHE] | $E_{\text{Redox}}$ 3% gel, after 3 h [mV, NHE] |
|----------------------------|--------------|-------------------|-------------------|---------------|-------------------------------|------------|------------------------------------------|---------------------------------------------|---------------------------------------------|
| Agar Extra Pure (Merck, 2015) | 176          | 25.3              | 73.5              | 3.7           | 406                           | 7.7        | 483                                      | 382                                         | 462                                         |
| Agar Gallery Extra Pure (Merck, 2017) | 50.3         | 9.7               | 0.7               | 0.7           | 233                           | 7.6        | 539                                      | 414                                         | 472                                         |
| Agarose Basic (AppliChem, 2017) | 12.3         | 3.3               | 1.0               | 0.7           | 24.5                          | 8.0        | 551                                      | 440                                         | 489                                         |

The difference between the two agar substances, which were purchased as "Extra Pure" from the same manufacturer but at different times, is quite striking. The older batch contains significantly more chlorides as well as sulfates/phosphates, which is also reflected in the conductivity of the solutions produced. The agarose, on the other hand, has a very high purity, which is due to the more complex production (additional separation of the agarosepectin). Regarding pH-value the substances differ only slightly and hardly change the neutral pH-value of the distilled water used. Interesting are also the redox potentials, especially after the single steps of gel production. By heating to 88 or 95 °C oxygen is expelled from the mixture, which leads to approx. 100 mV lower potentials in freshly produced gels. Already after 3 h the redox potentials are more positive again due to the oxygen uptake. A check after 72 h showed no significant increase or decrease. As a conclusion of the investigations on the corrosiveness of the agar base substances it can be stated that they behave relatively neutral. Mixtures with 3% in distilled water, even with 176 ppm chloride in the agar powder, in the end only result in approx. 5.3 ppm chloride in the finished gel, which is at a very low level. For particularly chloride-sensitive applications, however, the introduction via the gel former would have to be considered.

3.2 Mechanical properties

Agar gels are regarded as viscos-elastic, i.e. they combine the properties of solids and liquids. The proportion and type of polymer as well as the electrolytic components can influence these properties. Rheological measurements were carried out to investigate the viscos-elastic properties. A rheometer type MCR301 from Anton Paar was used in plate-plate mode. Using oscillation rheometry, so-called amplitude sweep curves were recorded at a displacement frequency of 10 rad/s (corresponds to 1.6 Hz) and a steady increase in deformation. The parameters of the investigated agar gels were varied according to
polymer type, concentration and electrolyte composition, which are of interest for corrosion investigations. The gel samples had a diameter of 20 mm and a thickness of 4 mm. Figure 1 shows as an example the course of storage and loss modulus versus deformation for a neutral 2 % and 4 % agarose gel with addition of 0.1 mol/L NaCl.

![Figure 1](image1.png)

**Figure 1.** Loss ($G''$) and storage modulus ($G'$) curves in an amplitude sweep test for agar gels containing 2 % or 4 % agar and 0.1 mol/L NaCl.

It can be clearly seen that the height of the modules correlates with the agar concentration, as does the position of the intersection of the storage and loss module, which corresponds to the so-called crossover point or yield stress at which the gel structure is destroyed. Figure 2 shows the effect of various parameters on the yield stress. The orthogonal experimental designs were evaluated using the ordinary least squares method.

![Figure 2](image2.png)

**Figure 2.** Influences of agar type, agar concentration and electrolytic additives on the flow voltage ($G'=G''$, least squares mean - LSM) at which gel destruction begins.
A dominant dependence of the yield stress on the agar concentration is shown. Compared to the standard agar, agarose forms stiffer gels. Neutral salts such as NaCl have no significant influence in the mechanical properties up to 1 mol/L. On the other hand, acidic and alkaline solutions have been shown to weaken the gel network, which can be seen in the decrease in yield stress. The highest concentration of H$_2$SO$_4$ in the gel, which still allowed stable gels, was 0.1 mol/L.

3.3 Syneresis-based electrolyte film

In order to determine the supply of electrolytes at the surface of the gels, a methodology for extracting the electrolyte film from the surface was developed, which is relatively simple and functional. For this purpose, circular gels with a diameter of 15 mm were extracted from a gel plate. These are placed in a suitable plastic container and weighed with a precision balance. The container with the gel is then placed in a device in which a Whatman Grade 1 filter paper (11 µm pore size) is pressed down with 45 cN for 3 seconds (corresponds to a contact pressure of approx. 0.25 N/cm$^2$ in relation to the surface). This contact pressure is below the yield stress of the gels determined by rheological measurements and is sufficient to absorb the electrolyte film on the surface of the filter paper without damaging the gel. The gel in the container is then weighed again. The difference in mass is proportional to the volume of the removed electrolyte film and can be converted to an equivalent of the electrolyte film thickness, considering the geometry and electrolyte density.

In this way, a large number of different gels with variations in agar concentration and electrolyte components were investigated. In addition, the top and bottom sides of the gels were also examined separately. On the bottom side the gels solidify on a solid (polished acrylic glass) and on the top side in air. The factors with the greatest influence were the gel concentration and the solidification side or the surface that is formed. Based on the dependence of the electrolyte film thickness on the concentration of the gel former, a strong correlation with the gel network and the pore size is also likely. Figure 3 shows the equivalents for the electrolyte film thickness as a function of the agar concentration and the side on which it was measured in a diagram.

![Figure 3](image_url)

Figure 3. Determined equivalents for electrolyte film thicknesses of agar gels as a function of agar concentration and side of the gels.

A possible explanation why the top and bottom sides are so different from each other can first be deduced from the roughness of the surfaces. The gels were poured onto polished acrylic glass in a liquid state and solidified there. They thus adopt the smooth surface profile on the underside. On the upper side, on the other hand, they can dry out and shrink slightly during solidification, as there is virtually no
air resistance to these processes. This makes the surface somewhat rougher and wavier, which means that a smaller proportion of the electrolyte film may be extracted.

If one excludes an influence of the surface, there is another, equally plausible and possible reason for the observed behavior, which can be found in the inner gel structure just below the surface. Drying during solidification can cause the polymer fibers to concentrate and lead to a zone with a denser gel network. This was already observed in 2007 by Labille et al. [24]. Diffusion experiments have shown that a zone approx. 120 µm thick exists at the edge of the gel, which has a significantly denser network. According to the authors, an agarose gel with a nominal 1.5 % polymer content at the edge has a diffusion behavior that corresponds to a gel with 5 % agarose and thus a denser network. This finding can be transferred to the context in Figure 3 (dotted arrow). If, for example, one assumes that a gel with 2 % agar on the top side actually corresponds to a gel with approx. 4.5 % agar, the determined courses fit together very well. It can be seen that with increasing agarose concentration, the equivalent for the electrolyte film thickness decreases more and more, i.e. the amount of liquid at the surface decreases. It should therefore be noted that the side solidified in air has a zone with a denser gel network and is therefore somewhat drier.

The influence of different ions on the electrolyte film thickness is, on the other hand, significantly less and in some cases not statistically relevant, e.g. for NaCl contents between 0.1 and 1 mol/L NaCl. Compared to distilled water as electrolyte base, acidic and alkaline electrolytes have slightly higher equivalents for the electrolyte film thickness. As in the rheological investigations, the relationship to the gel network or pore size is shown here. If the gel network is slightly weakened by certain ions in the electrolyte, the syneresis-induced leakage of electrolytes from the gel increases.

4 Application of Agar-based Gels for corrosion experiments on stainless steels
Corrosion tests on stainless steels are often carried out with the aim of determining the resistance to a particular type of corrosion. In most cases this is pitting corrosion. Resistance to pitting corrosion depends largely on the stability of the passive layer against the adjacent electrolyte and its ability to reform after mechanical or chemical degradation. This, in turn, depends on a number of alloy and material-related, surface-related and media conditions. The complex interaction of these factors in a corrosion system makes corrosion testing of stainless steels a recurring task. In industrial practice, the aim is to be able to carry out these corrosion tests on semi-finished and end products for quality assurance, as quickly, easily and virtually non-destructively as possible. The use of gel electrolytes instead of liquid electrolytes is one way to achieve this. Whether the use of liquid and gel electrolytes leads to the same or different results is shown by the following investigations.

4.1 Materials and experimental procedures
The stainless steel type X5CrNi18-10 (1.4301 or AISI 304) was used for the comparative investigations on the pitting corrosion resistance. The chemical composition of the steel was determined by spark spectrometry and is listed in Table 2. The element concentrations are within the range of the standard. It is noticeable that the sulfur content is at the upper permissible limit.

| Table 2. Chemical composition of the investigated material X5CrNi18-10 (1.4301). |
|---|
| Fe | C | Cr | Ni | Mo | N | P | S | Mn | Si | Cu | V |
| bal. | 0.04 | 18.0 | 9.51 | 0.47 | 0.03 | 0.02 | 0.01 | 1.49 | 0.35 | 0.13 | 0.05 |

Samples measuring 65x24 mm were cut from 2 mm thick metal sheets and prepared for the tests. The surface was wet ground with 180 grit sandpaper and finally with 500 grit. Before the tests, the samples were stored for 24 h in an air atmosphere with more than 95 % relative humidity at 22 °C.

NaCl concentrations of 1, 0.316 and 0.1 mol/L were selected as the electrolyte component of the liquid and gel electrolytes that causes pitting corrosion. The electrolytes were prepared with distilled
water and pure NaCl (99.95 purity). For the gel electrolytes an agar concentration of 2, 3 and 4 % was chosen. Agar of the brand ExtraPure Empore (Merck, see table 1, product of 2017) was used for this purpose, which was weighed and then mixed with the NaCl solution. The mixture was then heated to 95 °C with stirring until the agar was melted and a transparent solution was obtained. The mixture was poured into acrylic glass bowls, resulting in a gel thickness of about 6 mm. Circular gels with a diameter of 14 mm were pierced out of the gel plates for the experiments. The bottom side of the gels was always coupled to the sample surface.

For the investigations with liquid electrolytes, a perforated foil was first glued to the prepared surface to limit the working electrode area (1.54 cm²), which proved to be insensitive to crevice corrosion. A measuring cell for an electrolyte volume of 4 mL was clamped onto the foil. The counter and reference electrode were immersed into the cell from above and positioned approx. 5 mm from the surface. A platinum sheet was used as counter electrode and a saturated Ag/AgCl electrode (reference potential +197 mV vs. NHE) as reference electrode. For the investigations with the gel electrolytes, the sample surface was also covered with a perforated foil. The gel electrolyte was positioned on the separated working electrode surface (1.54 cm²). A counter electrode made of a titanium mixed oxide grid was applied to the top of the gel and the Ag/AgCl reference electrode was coupled to its ceramic diaphragm. A constant contact pressure of approx. 0.25 N/cm² was set using a balance located under the sample. Figure 4 shows the two measurement setups.

Cyclic polarization experiments were carried out to determine the pitting corrosion and repassivation potentials. First the free corrosion potential was measured for 5 min and then the specimen was polarized from -150 mVAg/AgCl vs. OCP with 1 mV/s in anodic direction. If a current density of 100 µA/cm² was exceeded, polarization was performed back in the cathodic direction at the same speed. The critical potential was determined when exceeding 10 µA/cm². The repassivation potential was determined when the current density dropped below 10 µA/cm² after reversing the polarization direction.

Furthermore, experiments were carried out with gel electrolytes of the same NaCl content, to which potassium ferricyanide (K₃[Fe(CN)₆]) was additionally added (Korropad method). The addition causes on the one hand an increase of the free corrosion potential and on the other hand released iron ions are complexed to Prussian Blue, which leads to circular blue indications at the site of pitting corrosion. The gradations here were 1 mmol/L, 3.16 mmol/L and 10 mmol/L. The variant with 1 mmol/L K₃[Fe(CN)₆] and 0.1 mol/L NaCl corresponds to the contents of the "normal" Korropad [5], all other variations have a higher corrosiveness. Gels with 3 % agar and a thickness of about 2 mm were prepared from the brand ExtraPure (Merck, see table 1, product of 2017). The maximum achieved corrosion potential was measured on the applied gel pads in order to identify the level of polarization. After the 20-minute run, the gel pads were scanned and subjected to a semi-automatic image analysis to determine the percentage of
indications from the total area. For this purpose, a self-developed software was used, which is based on color space separation and automatic recognition of circular structures.

After the experiments, the surfaces of the investigated samples were examined by scanning electron microscopy in order to compare the morphology of the pitting corrosion defects that occurred. The investigations were performed with the scanning electron microscope Evo 15 (Zeiss).

### 4.2 Determination of the pitting corrosion behaviour of stainless steel 1.4301

To investigate the pitting corrosion behavior of a stainless steel, the determination of critical potentials and repassivation potentials by means of dynamic polarization is an established procedure. The results are subject to a certain range of fluctuation depending on the material and test. In order to find out whether there is a statistically significant difference between gel and liquid electrolytes and whether the gel concentration has an influence, a full-factorial experimental design was set up and carried out three times randomly. The evaluation was carried out by analysis of variance based on the method of least squares. Figure 5 shows an example of the cyclic polarization curves for liquid and 3 % agar electrolyte with the graded NaCl contents.

![Figure 5. Cyclic polarization curves on the material 1.4301 when using gel and liquid electrolytes with different NaCl concentrations.](image)

As expected, the NaCl content has the greatest influence, but regardless of whether a gel or liquid electrolyte is used. It can also be seen that the current densities in the passive area tend to be lower when using the gel electrolyte. Whether the critical potentials differ significantly depending on the type of electrolyte can only be shown by statistical evaluation of all the experiments, even if in Figure 5 it initially appears as if the current density increase in the case of the gel electrolytes occurs at slightly lower potentials. In the case of the repassivation potentials, likewise only the strong dependence on the NaCl content can be seen from individual test data.

From the experimental data the values for \( E_{\text{crit}} \) and \( E_{\text{rep}} \) were determined and subjected to statistical analysis. Figure 6 first shows the dependencies of the pitting corrosion potential on the NaCl content and the medium used, calculated as least squares mean values with corresponding error differences. As expected, a large influence and a high significance for the NaCl content can be seen. The distance between the individual NaCl variations is approx. 38 mV, between 0.1 and 1 M NaCl it is 77 mV. With regard to the type of medium or the content of agar, however, only a minor influence can be observed. The liquid electrolyte does not differ significantly from the agar variants with 3 and 4 %. In contrast,
the agar gel with 2 % differs slightly, but statistically significant, from all other variants. The explanation for this was found when carrying out the experiment. In the gel variant with 2 % agar, a small amount of electrolyte escaped between the edge of the gel and the sample surface when pressed against the surface. It is likely that some of the water evaporated during the experiment, causing the NaCl concentration at the edge to rise slightly. As a result, pitting corrosion will occur at these points even at slightly more negative potentials. The effect was stronger at low NaCl contents and, averaged over all variants, leads to approx. 10 mV lower pitting corrosion potentials.

Figure 6. Least squares mean values for $E_{\text{crit}}$ as a function of NaCl concentration and medium (agar gel of different concentration and liquid electrolyte).

Figure 7 shows the dependence of the repassivation potential on the NaCl content and the medium used, calculated as least-squares mean values with corresponding error differences. As expected, a large influence and a high significance for the NaCl content can also be seen here. The distance between the individual NaCl variations is approx. 54 mV, between 0.1 and 1 M NaCl it is 108 mV. With regard to the type of medium or the content of agar, however, only a minor influence can be observed. The repassivation potential for the liquid electrolyte is 20 to 24 mV lower compared to agar gels of different concentrations. The reason for this lies in a different morphology of the resulting holes, see chapter 4.4.

Figure 7. least squares mean values for $E_{\text{rep}}$ as a function of NaCl concentration and medium (agar gel of different concentration and liquid electrolyte).
4.3 Use of indicators for the detection and localization of corrosion

To investigate the pitting corrosion resistance of stainless steels, gel-based electrolytes can also be used without external polarization. In contrast to external polarization, an appropriately concentrated oxidizing agent is required to set critical pitting potentials. The indication of pitting corrosion, characterized by a current increase under external polarization, is done here by an indicator for iron ions. This makes point-of-care application much easier, as no further measurement technology is required. Polarization effect and indication of iron ions is realized by K$_3$[Fe(CN)$_6$]. Starting from the standard concentration of the so-called Korropad [5] with 0.1 mol/L NaCl and 1 mmol/L K$_3$[Fe(CN)$_6$], a test matrix with graded higher contents of NaCl and K$_3$[Fe(CN)$_6$] was investigated on the material 1.4301.

Since this is a test method without external polarization, it is important to know the location of the open corrosion potential (OCP) that is established on the samples. The potential position determines whether the respective critical potential is reached or whether the sample is in the passive state or in the area of metastable pitting corrosion. For this reason, the maximum OCP values achieved by all gel variants were measured as well as the redox potentials on platinum. Figure 8 shows a summary of the results.

![Figure 8. Maximum OCP values measured immediately after applying the gel pads to the passive surface of the samples of material 1.4301 and on platinum.](image)

It can be seen that the content of K$_3$[Fe(CN)$_6$] significantly and NaCl slightly influences the location of the OCP on stainless steel as well as on a platinum electrode. At high contents of NaCl and K$_3$[Fe(CN)$_6$] the values scatter considerably more on stainless steel and do not reach the expected high potential values. This is due to the fact that stable pitting corrosion already occurs there. As a result, the OCP is shifted in a negative direction, since a high proportion of active corrosion sites leads to a strong electron surplus in the metal.

The gel pads were scanned after the experiments and evaluated by means of image analysis. Figure 9 shows exemplary images of the corrosion indications for all investigated gel variants with the mean area fraction and compares the critical pitting potentials from the potentiodynamically determined values. Stable pitting corrosion is indicated on some gel pads, recognizable by isolated large displays and a comparatively high area fraction. However, only those variants with simultaneously high NaCl and high K$_3$[Fe(CN)$_6$] concentrations are affected. At 10 mmol/L K$_3$[Fe(CN)$_6$] and 0.1 mol/L NaCl, for example,
only metastable pitting corrosion occurs, since the $E_{\text{crit}}$ of approx. 360 mV, determined from the potentiodynamic tests, is not reached. With 1 M NaCl and 1 mmol/L $K_3[Fe(CN)_6]$ a transition from metastable to stable pitting corrosion seems to have been detected, since the OCP and $E_{\text{crit}}$ are close together. Some larger indications are already visible, but also many smaller ones, whose area is small.

**Figure 9.** Comparison of results on the critical potentials of the material 1.4301 determined by potentiodynamic tests (left) and results from Korropad tests with graded NaCl and $K_3[Fe(CN)_6]$ contents.

### 4.4 Comparison of pitting corrosion appearance in gel and liquid electrolytes

The results of the polarization experiments with gel and liquid electrolytes proved to be comparable, with only slight difference in the repassivation. Even in the gel pads used without external polarization, the $K_3[Fe(CN)_6]$ was able to achieve approximately the same critical potentials and thus pitting corrosion occurs. To clarify whether the pitting corrosion appearance differ when gel and liquid electrolytes are used, the samples were microscopically examined after the experiments, see Figure 10.

**Figure 10.** Pitting corrosion appearance after the tests on 1.4301, a) gel electrolyte under external polarization, b) liquid electrolyte under external polarization, c) gel electrolyte without external polarization (NaCl + $K_3[Fe(CN)_6]$).
If one compares the appearance of the resulting pits, it is noticeable that in gel electrolytes under external polarization (Figure 10 a) the metal dissolution sites tend to be more shallow, open and extended. This makes it more likely that the electrolyte is less concentrated with chlorides and that a pH drop through hydrolysis is less pronounced. The repassivation can proceed faster, which is expressed by more positive repassivation potentials, see figure 7.

In contrast, liquid electrolytes and external polarization (Figure 10 b) tend to produce hemispherical and thus deeper holes, in which remnants of a perforated hole cover can still be seen at the edge, indicating initially hidden pitting corrosion. This allows the occluded electrolyte to decouple from the bulk and mix less well. In addition, a voltage drop due to geometrical reasons delays the repassivation at the bottom of the hole.

However, such flat corrosion appearance has only occurred with the gel electrolytes in the case of external polarization. If pitting corrosion is initiated under free conditions, e.g. by the presence of a sufficient amount of K₃[Fe(CN)₆] and NaCl in the electrolyte, then the corrosion appearance in the gel electrolytes are comparable to those in the liquid electrolytes (Figure 10 c). At an earlier stage, the pits still have a perforated cover, which dissolves or detaches as pitting corrosion progresses.

5 Conclusions
Agar-based gel electrolytes are a viable electrolyte alternative for the investigation and testing of stainless steels with regard to pitting corrosion. They have the advantage that the liquid electrolyte is immobilized in the gel and a thin electrolyte film is formed on the surface, which enables electrochemical measurements. NaCl contents of different concentrations in the gel can be used without significantly changing the gel matrix.

Potentiodynamic experiments to determine pitting and repassivation potentials on gel and liquid electrolytes show a very good agreement between the electrolyte types. At low contents of 2 % agar in the gel, however, there is a risk that electrolyte will leak out at the edge, evaporate and thus cause pitting corrosion too early. When using gels under external polarization conditions, stable pitting corrosion leads to shallower pits, which in turn leads to more positive repassivation potentials, as repassivation takes place more easily. In contrast, these shallow pitting corrosion appearances do not occur in gel electrolytes without external polarization. Here the pit morphology is comparable to that of liquid electrolytes.

Agar gels can be used very well as test electrolyte for testing the pitting corrosion resistance of stainless steels even without external polarization. By adding K₃[Fe(CN)₆] to the chloride-containing solution in the gel, specific potential ranges can be set which are in the passive range (with metastable events) or already in the stable pitting corrosion range depending on the material and surface condition. Using the example of the used material 1.4301 with graded K₃[Fe(CN)₆]-NaCl contents, the position of the potentiodynamically determined critical potential ranges could be confirmed. It should be noted that the material used here has a relatively poor pitting corrosion resistance compared to other batches of the same type, which is due to the slightly increased sulfur content.

Acknowledgement
The author would like to thank Mrs. M.Sc. Christine Becker (OvGU Magdeburg) for performing the electrochemical measurements and electrolyte film thickness, Mr. M.Sc. Ludwig Gropler (OvGU Magdeburg) for manufacturing of setups for measuring electrolyte film thickness, iLF Magdeburg GmbH for performing the rheological measurements and BAM Berlin (FB 7.6) for the chemical analysis of the agar raw materials. Special thanks also go to Mr. M.Sc. Sebastian Hütter (OvGU) for programming the image analysis.

Funding
Funded by the German Research Foundation (DFG) - Project number 330472124
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