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Design of gel electrolytes for electrochemical studies on metal surfaces with complex geometry

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ABSTRACT

Electrochemical cells commonly employ liquid electrolytes. These cells can present limitations, like studying irregular surfaces or the generation of crevices as a result of delimiting the surface of the working electrode. The current study has developed a gel electrolyte based on agar-glycerol as an alternative to the saline aqueous solutions often used in anodic polarization tests of stainless steels.

Texture analysis and rheological tests were performed to characterize the gel electrolytes and determine the best composition in function of their characteristics of adaptability to provide a suitable contact to complex surfaces. Comparisons between typical aqueous and gel electrolytes in ionic conductivity and electrochemical measurements (anodic polarization curves) were carried out to validate the gel electrolytes for the evaluation of pitting corrosion behavior of metals. Moreover, lack of risk of interference of undesirable crevice corrosion in tests carried out with this type of sensor is also demonstrated.

1. Introduction

The corrosion of metals is of substantial interest in engineering as it can lead to considerable economic loss due to structural failure of critical components in infrastructures. Localized corrosion, such as pitting and crevice corrosion, is one of the most serious problems when passive metals are used in contact with chloride containing or other aggressive solutions [1–3], being often difficult to detect. These corrosion problems can become more severe and challenging in regions of the metal surface with extremely complex geometry. Moreover, specific characteristics of the surface that affect its corrosion behavior (such as phase transformation or microstructural changes [4,5]) are difficult to study in some real components with traditional liquid cell configurations. Phenomena originated during the assembly of metallic components, such as stresses or welds [6], may also affect their corrosion resistance and it is interesting to carry out studies in conditions as realistic as possible.

Electrochemical cells commonly employed with liquid electrolytes present limitations, such as difficulties in the study of irregular surfaces, welded joints and angles. Besides, delimiting the testing area without generating crevices that can interfere in the study is usually a problem that could lead to mistakes when results are interpreted.

Polymer gel electrolytes have been extensively studied due to their potential use in electrochemical devices, such as batteries [7,8], solar cells [9,10], fuel cells [11–13] and electrochromic devices [14,15]. Other authors have proposed a portable corrosion cell based on the use of agar as a gelling agent to perform non-destructive, in-situ electrochemical measurements for application in cultural heritage studies [16,17]. The proposed cell uses a pure agar electrolyte with slightly mineralized water to avoid introducing aggressive ions that could damage the original surface.

Agar is widely used as a gel-forming agent, thickener and stabilizer in processed foods [18–20], pharmaceutical products and cosmetics. It is employed in biotechnology and medicine [21,22], because of its ability to form hard gels at very low concentrations (0.04%) [23], low cost, biodegradability, high degree of biocompatibility and its useful rheological properties [24].

Agar is a complex mixture of polysaccharides found in the cell matrix of red algae as Rhodophyta (Gracilaria, Gelidium and Pterocladia) [11,12], comprising two major components, commonly known as agarose and agaropectin. Agarose is a neutral polysaccharide with a linear structure of repeating units of agarobiose formed by 1,3-linked-D-galactose and 1,4-linked 3,6-anhydro-L-galactose units [13,14]. The type, pattern, and degree of substitution, as well as the molecular weight, determine

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the gelling properties of agar [22]. Agaropectin is an acid polysaccharide containing sulfate groups, pyruvic acid and D-glucoronic acid conjugated to agarobiose [25]. It has been considered industrially less useful than agarose, due to its non-gelling property [26], but its presence justifies the gel conductivity.

The main objective in this work is to develop a polymer gel electrolyte with improved adaptability that can be used as an alternative to traditional liquid electrolytes for electrochemical measurements on complex geometries. Apart from its ability to highly humidify metals with complex geometry surfaces, the conductivity of the gel must be adequate to carry out electrochemical tests. Moreover, the sensor must present a moderate mechanical consistency for a comfortable use and stability during the performance of the experiments.

Good results and reproducibility of tests have been reported for previous experiences in electrochemical measurements carried out using agar as electrolyte [16,17]. However, pure agar gel does not present enough adaptability in difficult angles and irregular surfaces due to an absence of plasticizers. For this purpose, agar, as a gel-forming agent, glycerol as plasticizer (as it has been one of the most used to improve the mechanical properties of agar for other applications [26–30]), and sodium chloride (added to simulate the aggressiveness of one of the classical aqueous electrolytes used in electrochemical measurements) have been mixed to formulate new gel electrolytes with improved adaptability properties.

2. Experimental

2.1. Materials

Technical CULTIMED agar (strength gel 1.5% w/w (Nikan method), 700–1100 g/cm^3), glycerol (99% w/w, $\rho = 1.257–1.261$ g/cm^3) and NaCl (99% w/w) were purchased from Panreac. AISI 304 stainless steel was employed for adaptability images and electrochemical tests. Its composition is shown in Table 1.

Agar (ranging between 2.5 and 0.5% w/w), glycerol (between 0 and 70% w/w) and NaCl (0.5% w/w) were dissolved in distilled water and heated to 90 °C under magnetic stirring. Mixture was stirred continuously for 10 min to ensure homogeneous mixing. The resulting solution was cooled to about 40 °C, and then poured into a mold or an electrochemical cell, depending on the characterization techniques to be applied. Then, the gel was allowed to cure in a controlled environment where the temperature and relative humidity (*RH*) conditions were maintained at 20 °C and 80%, respectively.

2.2. Characterization techniques

2.2.1. Texture analysis

Compression tests were performed on gels after curing times of 1 and 24 h. Measurements were made using a TA.TX.plus Texture Analyser (Stable Micro Systems Ltd., UK) with a 40 mm diameter cylindrical aluminum probe. The height and diameter of the gel cylinders were 10 mm and 22 mm, respectively. The stress-strain curves were obtained at 20 ± 2 °C. A compression rate of 1 mm/min was used for all samples and results are shown as the average of eight replicates. The true stress (σ_T), true strain (ε_T) and the Young's modulus (E) were calculated using the equations described elsewhere [21,31]. E was taken as the calculated slope of the initial gradient of the curve where the strain was below 0.05%.

2.2.2. Adaptability study on metal surface

The effect of changes to the gel composition on the contact between the gel electrolyte and the metallic surface was evaluated. Gel electrolytes with 1 or 0.5% agar and varying concentrations of glycerol (0 to 70%) were studied after a curing time of 1 h. Images of the gel electrolytes wetting the surface of the stainless steel (ground to 600 #) have been analyzed. The images were taken on surfaces with different angles: 180°, 156° and 107°.

2.2.3. Rheological tests

The modulus and viscosity during the production of gel electrolytes were measured for gels with 0.5% w/w agar and 30, 50 and 70% w/w glycerol. Single frequency oscillatory measurements were performed using a Kinexus Rheometer (Malvern Instruments Ltd., UK) with a serrated parallel plate geometry (60 mm diameter). Gelling profiles were obtained by applying a temperature ramp (using cooling rates of 1, 2 and 3 °C/min) at 1 Hz and 0.5% strain on all gel systems during cooling from 80 to 20 °C. The gelling temperature (T_{gel}) was calculated when a significant change in viscosity is observed [32,33].

2.2.4. Electrical, electrochemical and pH measurements

Ionic conductivity (σ) of gel electrolytes with 0.5% w/w agar as a function of glycerol concentration was studied. The σ was measured with a conductivity meter during the cooling process of the electrolyte, from 80 to 30 °C. After the electrolyte had gelled and cured for 1 h, high frequency electrochemical impedance spectroscopy (*EIS*) measurements were performed to obtain information about the conductivity of the gel.

The corrosion potential (E_{corr}) was monitored during 45 min before EIS measurements. *EIS* spectra were acquired using a perturbation signal of 10 mV$_{\text{rms}}$ of amplitude (at E_{corr}), using a frequency sweep from 10^3 to 10^{-3} Hz and measuring 10 points/decade. After EIS measurements, the σ was then calculated from the electrolyte bulk resistance values employing the formula described elsewhere [10,15] for measurements at room temperature.

The gel electrolyte cells used for electrochemical measurements were based on a traditional cell with 3 electrodes. The reference electrode was a saturated calomel electrode (*SCE*). The counter-electrode was a stainless steel wire, and the surface of the AISI 304 stainless steel (ground to 600#) acted as working electrode with a testing area of 5.3 cm^2.

To study the effectiveness of the gels as an electrolyte in electrochemical tests and how the glycerol concentration influences the results, anodic polarization curves were performed on the AISI 304 surface. The sweeping rate of the potential was 1.2 mV/s. The scan direction was reversed when the current density reached 10^{-4} A/cm^2. Multiple measurements (3–4) of the samples were made to obtain a reliable average of the results and to determine errors.

In order to validate the gel electrolytes, a comparison was made to other cells commonly used in electrochemical measurements with traditional liquid electrolytes. For this purpose, an Avesta cell and a conventional cell with a Teflon ring as a testing area delimiter (designated "flat cell") were used. In both cases, *SCE* was employed

Table 1
Chemical composition (% w/w) of stainless steel AISI 304.

Element	Si	P	Ti	V	Cr	Mn	Co	Ni	Cu	Nb	Mo	C	S	N	Fe
%	0.30	0.025	0.007	0.07	18.66	1.82	0.31	8.06	0.24	0.115	0.19	0.043	0.005	0.048	Bal.

as reference. The exposed area of the working electrode was 0.785 cm^2 in both cases and a liquid electrolyte consisting of a 0.5% (w/w) NaCl solution was used. The morphology of the attack after corrosion tests was studied using optical microscopy.

The pH of the gels was also determined using a pH-electrode.

3. Results and discussion

3.1. Texture analysis

The influence of the agar and glycerol concentrations on the mechanical properties of gels was studied by compression testing. The objective was to obtain a gel that was easily deformable under low stresses to be adaptable to different geometries under the weight of the electrochemical cell. Bearing in mind the results reported by other authors [16,17], a gel of 2.5% agar without plasticizer was used as reference and gels with lower agar concentrations were evaluated.

Fig. 1 shows the σ_T–ε_T curves obtained for gel formulations with decreasing concentration of agar from 2.5 to 0.5% (w/w), and increasing concentration of glycerol from 0 to 20% (w/w). Gels with 0.5% agar and less than 20% glycerol were not characterized because they did not have enough mechanical stability for the study.

The reduction of the agar content from 2.5% to 1% decreases both σ_T at maximum load (σ_u) and true uniform strain (ε_u, the ε_T at maximum load). Moreover, E decreases one order of magnitude (from 0.131 MPa to 0.017 MPa). The gelation process of agar during the cooling as a result of the formation of helices (cross-links between agarose chains) and the subsequent aggregation [34] suggests that the lower amount of agar in the gel, the fewer the number of formed entangled helices, thus reducing the mechanical properties. As the σ_u and E of the gel with 2.5% of agar are relatively high, and it is shown that the use of 1% of agar also decreases the ε_u, the addition of glycerol (as plasticizer) to the 1% formulation was evaluated (Fig. 1).

The addition of glycerol to gels with 1% agar leads to more deformable gels, indicated by a gradual increase in the ε_u. Though an increase in σ_u can also be detected, this increase takes place to a lesser extent than that noticed for ε_u. A remarkable increase in the deformability of the gels is found with an increasing level of glycerol and a decreasing agar content. The gel with 1% agar and 20% glycerol shows similar ε_u values to 2.5% agar, but less than a half of σ_u. Further reductions of agar concentration (0.5%) were formulated in order to determine if gel electrolytes with even lower σ_u could be valid (Fig. 1).

Fig. 2 summarizes the σ_u and ε_u values obtained for gels with 0.5% agar, whose concentrations of glycerol ranged from 20 to 70% (w/w), after curing times of 1 and 24 h. In all the 0.5% agar gels studied, after 1 h of curing, an increased deformability can be detected as the glycerol content increases from 30%, as indicated by ε_u (Fig. 2). σ_u also shows a clear increase from 30% to 50-60% glycerol. The effect of the glycerol additions on the mechanical properties of the gel can be understood assuming a "zipper" model [35]. The H-bonds formed between hydroxyl groups and agarose increase as the number of hydroxyl groups increases, explaining the increase in σ_u. Moreover, H-bonds, when broken, can be easily re-arranged, in contrast to what occurs with covalent bonds. Hence, the breaking of H-bonds does not necessarily imply the breaking of the macrostructural gel piece leading to full cohesive failure.

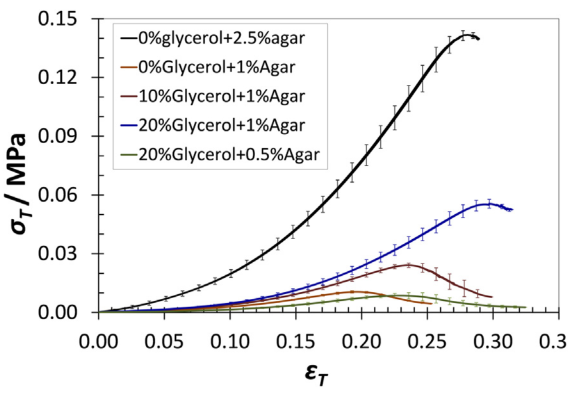

Fig. 1. True stress-true strain (σ_T-ε_T) curves of selected gel electrolytes as a function of agar and glycerol concentration for gels cured for 1 h.

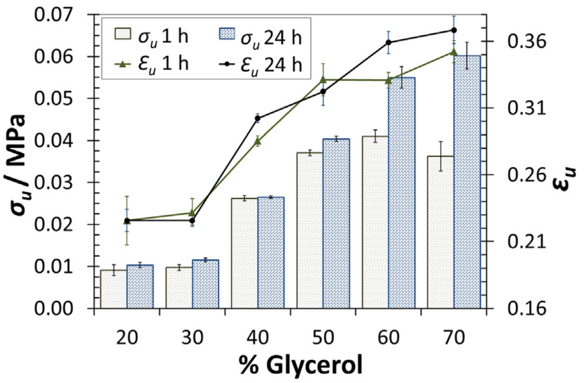

Fig. 2. True stress at maximum load (σ_u) and true uniform strain (ε_u), as a function of glycerol concentration, measured for gel electrolytes with 0.5% agar, for curing times of 1 and 24 h.

Increasing curing time up to 24 h does not cause any change in the mechanical properties of gels with 50% glycerol or less, as the same values are obtained for σ_u and ε_u after 24 h than after 1 h of curing. The result highlights that 1 h curing time is sufficient to cure the gels in the studied conditions, as the water content is sufficient to form H-bonds within the helix structure of agarose [36]. 0.5% agar gels with 60% and 70% glycerol increase their ε_u and σ_u as the curing time extends, indicating that those gel electrolytes need more time to cure, as a result of the low initial water content. If the water content is not high enough to allow the sufficient gelation, water tends to be absorbed from the environment. Gel networks swell by absorbing solvents until thermodynamic equilibrium is reached [37]. During the curing period under high *RH* influence (80%), for example, 0.5% agar + 70% glycerol gel increases its mass 0.7 ± 0.1% after 24 h of exposure in the curing conditions tested, while 0.5% agar + 50% glycerol gel increases 0.4 ± 0.1%. Water absorption from curing environment takes time, explaining the slowness observed in the curing process of high glycerol gels. However, long-term exposures can affect the mechanical properties of the gels. For example, a decrease of 34% was observed in the σ_u of the 50% glycerol gel when the curing at high *RH* was extended from 24 h to 1 week.

Comparing results in Fig. 2 to those in Fig. 1, it can be seen that 0.5% agar gels, with 50% glycerol or more, achieve a ε_u higher than that of a 2.5% agar gel. Moreover, the σ_u necessary to achieve that deformation is clearly lower for low concentrated agar gels with high glycerol content.

3.2. Wettability study

Considering that gel electrolytes with shorter processing times are more applicable from a practical point of view, the following characterization experiments are focused on gels with a curing time of 1 h.

Table 2
Wettability results on irregular surfaces for different gel electrolytes.

Composition of gel electrolytes	180°		156°		107°	
	Wet	Stability	Wet	Stability	Wet	Stability
1% agar + 0% glycerol	✓	✓	✓	X	X	X
0.5% agar + 20% glycerol	✓	✓	✓	✓	✓	X
0.5% agar + 30% glycerol	✓	✓	✓	✓	✓	X
0.5% agar + 40% glycerol	✓	✓	✓	✓	✓	✓
0.5% agar +50% glycerol	✓	✓	✓	✓	✓	✓
0.5% agar +60% glycerol	✓	✓	✓	✓	✓	✓
0.5% agar +70% glycerol	✓	✓	✓	✓	✓	X

Table 2 summarizes the results obtained from the images taken of different gel electrolyte compositions on surfaces with the angles studied. A good shape and wettability is appreciated for all electrolyte gels studied on a flat surface (180°) without visible crevices or burrs.

Difficulties are found in gels with 1% agar or more to wet the irregular surfaces studied (Fig. 3a). Moreover, brittleness problems are also evident. For instance, a small damage can be observed in Fig. 3a (inside the ellipse).

On the other hand, an increase in the glycerol content improves the wettability for gel electrolytes with 0.5% agar (Fig. 3b). The result is in accordance with the mechanical properties (Figs. 1 and 2), considering that gels with a high agar content and a low glycerol concentration are hard and not very deformable, while gels with high glycerol content are less brittle and more deformable, after a curing time of 1 h.

Good stability (absence of cracking) is not maintained for gels with 0.5% agar and 20, 30 or 70% glycerol meaning they were not suitable to be used on irregular surfaces. Those gels exhibit slight breakages after a few minutes (an example of which is shown in Fig. 3c). For gels with a low glycerol content, this failure can be related to their low mechanical strength, which is unable to stand the force applied to reach adequate deformability that allows a good wettability on irregular surfaces. For gels with high glycerol content, the failure can be related to an insufficient curing after 1 h, and these gels cannot be used when angular surfaces are taken into account. The best adaptability and stability for the study on irregular surfaces was shown by gels with 40% and 50% glycerol (Table 2). These tests clearly show that different gels can be formulated depending on the complexity of the surface.

Agar based gels can be subject to a spontaneous losses of water on standing. This phenomenon, known as syneresis [30,32], can contribute to assure the good contact between metal and electrolyte in electrochemical measurements. This fact indicates the suitability of the gels for performing measurements on rough and porous surfaces as a result of gap filling.

3.3. Rheological tests

The viscoelastic properties of gels depend on their microstructure as well as the interaction between the agarose helices. These factors can be modified by processing parameters such as the cooling rate [38]. Viscosity measurements were carried out on gels with 30, 50 and 70% glycerol, as a function of temperature. In addition, a range of cooling rates was also investigated (1, 2 and 3 °C/min) to determine if aggregation rate modifies the material rheological properties of gels. No significant differences were found for the cooling rates studied.

Fig. 4 shows the change in viscosity as a function of temperature for gel electrolytes cooled at 2 °C/min. Two distinct regions can be identified for gels with 30 and 50% glycerol. Region A, in which the slope is almost flat, corresponds to the solution stage before the onset of the ordering of agarose. Region B, in which a marked increase in viscosity is observed, can be identified with the stage of ordering and aggregation of helices [39]. Viscosity increases in this region as a result of the formation of a small gel nucleus and of the constant increase in both the number and volume fraction of the formed particles [40]. The solubility of agar is higher in water than in a water-polyol mixture [35]. The reduced degree of solvation of agar in a water-glycerol solvent is shown to change the ordering transition, possibly leading to faster rates of polymer aggregation [21]. Gels with 30% glycerol saturate the measurements before reaching 20 °C, confirming the faster gelation process in low

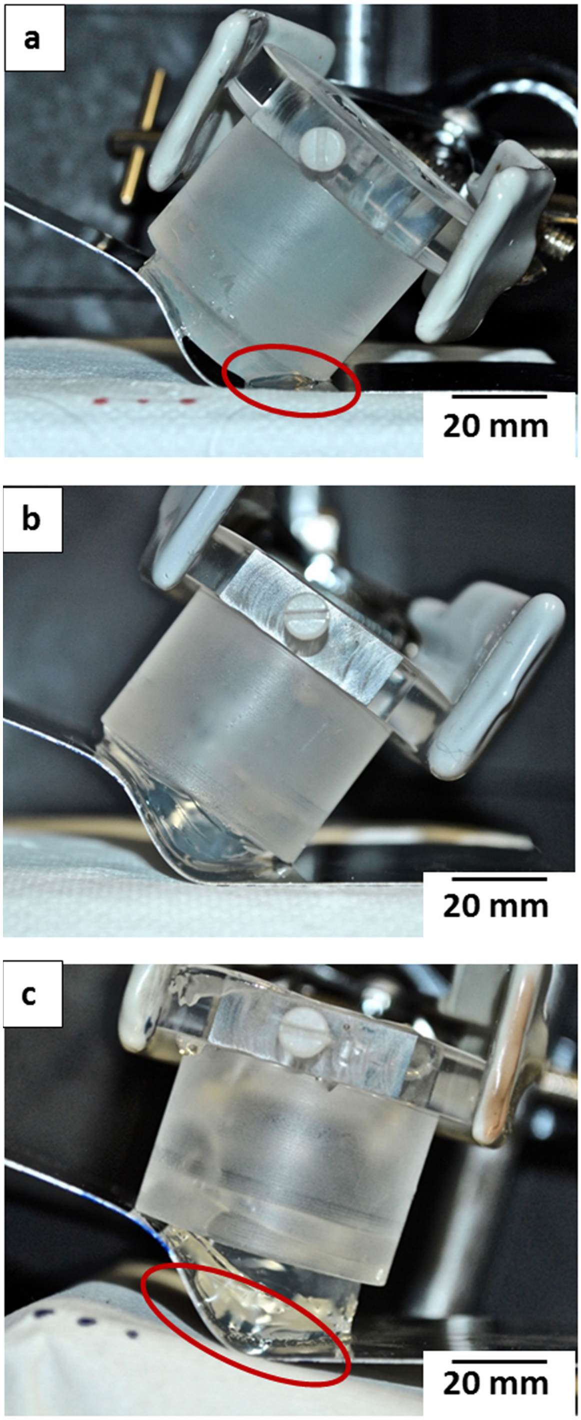

Fig. 3. Wettability images of different gel electrolyte on metallic surface with an angle of 107° at 1 h (a) 1% agar + 0% glycerol, (b) 0.5% agar + 50% glycerol and (c) 0.5% agar + 70% glycerol.

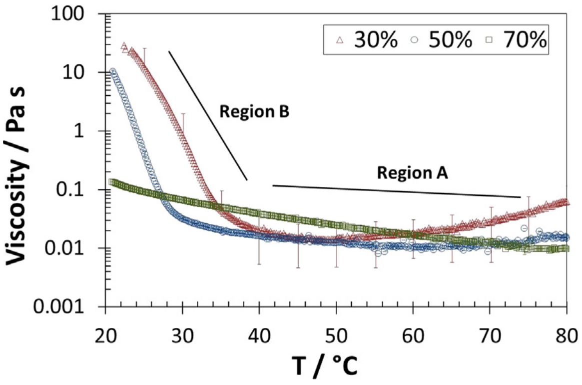

Fig. 4. Viscosity as a function of temperature during gel production process, at a cooling rate of 2 °C/min, for samples with 0.5% agar and 30, 50 and 70% glycerol.

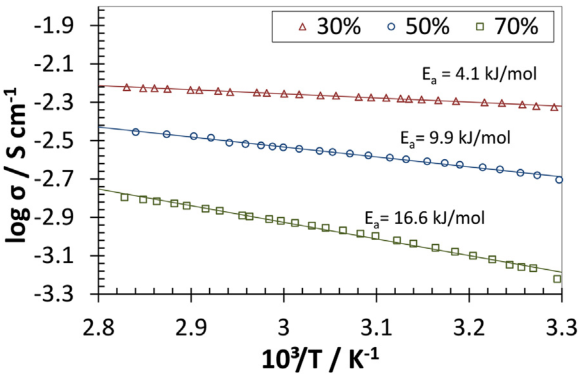

Fig. 5. Effect of the temperature and glycerol concentration (w/w) on the conductivity (σ) of the electrolyte with 0.5% agar, during cooling process.

glycerol gels (Fig. 4). T_{gel} values can be obtained from G' and G'' measurements during cooling for gels with 30 and 50% glycerol. These values match the viscosity changes in Fig. 4, being 39 ± 6 °C for 30% glycerol and 27 ± 1 °C for 50% glycerol.

Nevertheless, only one region (Region A) can be identified for gels with 70% glycerol. This behavior, being a response to a phase separation that occurs when the concentration of glycerol is so vastly in excess, can also be related to the curing problems observed for this gel in mechanical tests (Fig. 2). The proximity of junction zones between the molecules of agarose is insufficient to result in a rise in viscosity. The greater solubility of agar in water than in glycerol hinders the movement of the helices and limits subsequent joining. The resultant viscosities of the gels with 70% of glycerol tend towards values between glycerol and water viscosities, suggesting it was a measurement of the synergized liquid above the gel which would have a much lower viscosity.

The viscosities of the 0.5% agar electrolytes when they are poured in the mold of the cell (40 °C) are similar and adequate to assure a good filling, independently of the glycerol content.

Overall, it was shown that the final temperature is more important than the cooling rate during the production of the gels. Studied gels with glycerol content up to 50% have a stable structure against temperature changes close to room temperature. However, these gels with high adaptability become mechanically unstable when temperatures increase, indicating that they could not be useful for corrosion tests that are subject to increasing temperatures as the determination of critical pitting or crevice temperatures.

3.4. Electrical and electrochemical measurements

3.4.1. Effect of glycerol and temperature on the conductivity of the electrolyte

The σ of gels depends on several factors, such as the concentration, cationic or anionic types of charge carriers, the mobility of charge carriers and the temperature [15]. To verify the σ model that governs the σ properties of these systems, σ versus temperature dependence for a selection of gels was measured during cooling in the temperature range of 80–30 °C. The results are shown in Fig. 5.

It can be noted that the decrease in temperature leads to a decrease in the σ of all gels. Fig. 5 shows the linear adjustment according to an Arrhenius model. The quality of the fitting suggests the major contribution to the conductivity is ion hopping between coordination sites [41]. Ions (mainly from added salt, although a certain contribution of agar cannot be discarded due to its agaropectin) are mainly transferred through H-bonds in gels. Those gels are water-rich, Changes in conductivity can also be affected to a lesser extent by segmental motion of polymer chains as Vogel-Tammann-Fulcher (VTF) model suggests [42]. VTF model describes the curvature of conductivity-temperature plot, as 70% glycerol curve suggests. The contribution to the conductivity of both models has often been reported [14,15,43].

From the linear fitting of the experimental data, the activation energy (E_a) values were obtained. Fig. 5 shows the tendency of the E_a to increase as the glycerol content increases. This increase in the activation energy for the hopping process could be related to a lower mobility of charge carriers, as there is an increase in the number of junction zones in the gel electrolyte with the increasing glycerol concentration (also shown in mechanical properties and adaptability, Figs. 2 and 3). Hence, though glycerol has proven to be an interesting additive for achieving a good deformability of the gel electrolyte (Fig. 2), glycerol has a detrimental influence on the σ. The presence of glycerol reduces the motion because of the zipped structure that it contributes to create in the gel.

The results in Fig. 6 show the influence of the glycerol concentration in the σ of already solidified gel electrolytes at room temperature. The value corresponding to a 0.5% NaCl aqueous solution is included as reference. 0.5% agar gels with glycerol have lower σ than that of the aqueous solution, but the change is not dramatic. The less glycerol concentrated gel (20%) shows a σ of 6.6 mS·cm^{-1} and the saline solution has a σ of 9.5 mS cm^{-1}. Plasticizers are used to increase the conductivity of solid polymer electrolytes [15,29] but this research deals with gel electrolyte with a high content of water, where the mobility of charge carriers is easier than in glycerol.

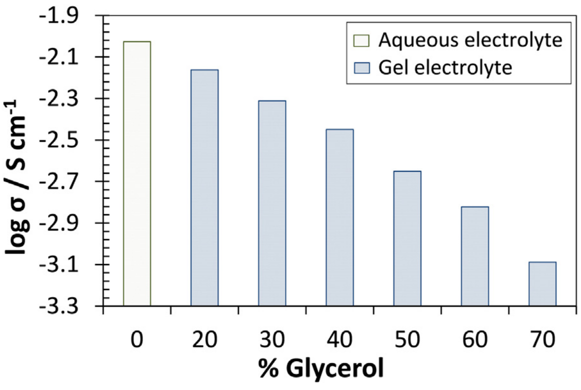

Fig. 6. Effect of glycerol concentration (w/w) on the conductivity (σ) of the electrolyte with 0.5% agar, measured at room temperature through EIS measurements.

3.4.2. Effect of glycerol in anodic polarization curves. Comparison among cells with gel electrolytes and traditional cells with aqueous electrolytes

The gel electrolytes have neutral pH, close to that of 0.5% NaCl aqueous solutions (Table 3). A very slight acidification is detected due to glycerol additions, but its influence on the pitting resistance of stainless steels can be guessed to be negligible.

Some experiments were carried out with the aim of verifying if changes detected in the σ of the electrolyte can affect the electrochemical measurements. E_{corr} of the stainless steel was monitored during the first 45 min of exposure to the electrolytes. Fig. 7 shows examples of E_{corr} stabilization for common cells employed with aqueous electrolytes and the designed cell with gel electrolytes, using different contents of glycerol. A slight increase in E_{corr} values is appreciated with the increase in glycerol content, being around −150 mV *vs. SCE* for gel electrolytes for 20% glycerol and −50 mV *vs. SCE* for gels with 70% glycerol.

An interference of reduced O_2 access to the surface could have been feared in gel electrolytes, especially when they are glycerol-rich. Considering the E_{corr} values of the stainless steel-gels system and those of the stainless steel-NaCl solution (Fig. 7), it can be assumed that the O_2 dissolved in the gel is enough to avoid meaningful changes in the development of pitting corrosion of stainless steels. A meaningful decrease on the oxygen is expected to shift the E_{corr} of the system towards more cathodic values, and this phenomenon is not observed.

Cells with gel electrolytes present a suitable stabilization of E_{corr}, fast and reliable for subsequent electrochemical studies, and its results are comparable to commercial device results. E_{corr} is an equilibrium potential between the anodic and the cathodic processes whose stabilization reflects changes in the passive layer or the surface of the metal needed to achieve the equilibrium when the material under study is exposed to the testing electrolyte. The fast stabilization of E_{corr} in a value close to that initially recorded suggests that the contact of the gel with the metal induces minor changes on the surface of the metal studied. However, the changes observed for E_{corr} during the stabilization for systems with liquid electrolytes are more significant, suggesting that a more meaningful transformation of the passive layer on stainless steel can take place. Besides, the Avesta cell presents the greatest difficulty in stabilizing because of its design [44].

Fig. 8 presents polarization curve examples on the stainless steel employing gel electrolytes with 20, 40, 50 and 70% glycerol at 1 h curing time. These are typical curves corresponding to a passive system and show a re-passivation ability, as the studied stainless steel has in a 0.5% NaCl solution when it is polarized in the conditions of this study. The addition of glycerol causes a shift of the cathodic branch of the curve towards higher potentials while the anodic branch is also shifted to lower intensities. Both phenomena reflect that glycerol addition hinders the anodic reaction but not the cathodic one. No effect related to oxygen diffusion through the gel due to glycerol additions can be guessed in the curves, confirming that mentioned in the discussion of Fig. 7. As the tested stainless steels are passive and the control of the process is clearly anodic, the addition of glycerol causes a decrease on the corrosion intensity (i_{corr}). This would be explained because the σ and the mobility of ions are worse in gel electrolytes with high concentrations of glycerol. The higher ohmic drops between anodes and cathodes in the corrosion cells formed on the surface of the metal can cause this reduction of i_{corr}.

Table 3
pH of gel electrolytes with 0.5% of agar and different concentrations of glycerol.

% of glycerol	0	20	30	40	50	70
pH	7.1	6.9	6.8	6.6	6.5	6.2

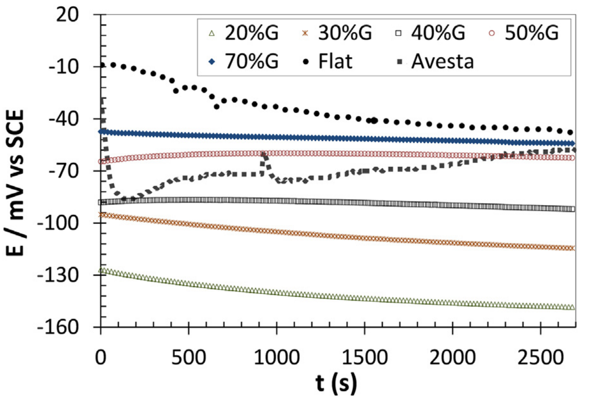

Fig. 7. Stabilization of corrosion potential (E_{corr}) for different gel electrolytes with different glycerol contents (%G) and aqueous electrolytes (flat and Avesta cell), on 304 stainless steel.

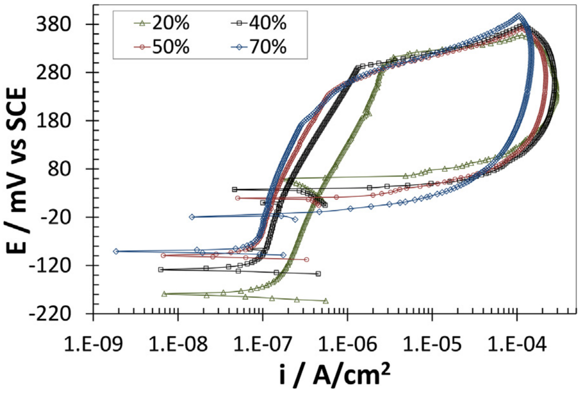

Fig. 8. Examples of polarization curves with gel electrolytes with different glycerol (%G) content on 304 stainless steel.

The main differences in polarization test results due to glycerol concentrations are summarized in Figs. 9 and 10. Results of similar parameters obtained in liquid electrolytes are included in the figures for comparison. Fig. 9 plots i_{corr} and the maximum intensity during backward swept (i_{max}). As stated, a slight decrease in i_{corr} value with an increase in the concentration of glycerol is distinguished.

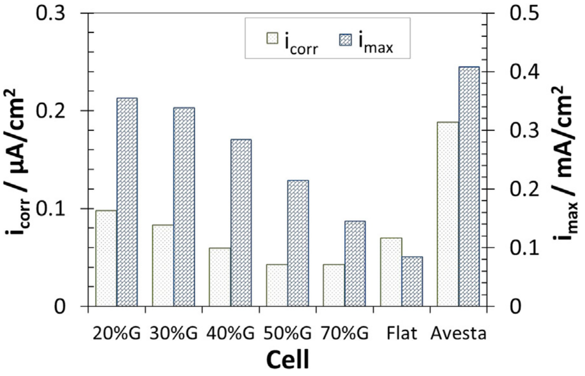

Fig. 9. Corrosion intensity (i_{corr}) and maximum intensity (i_{max}) obtained from anodic polarization curves on 304 stainless steel.

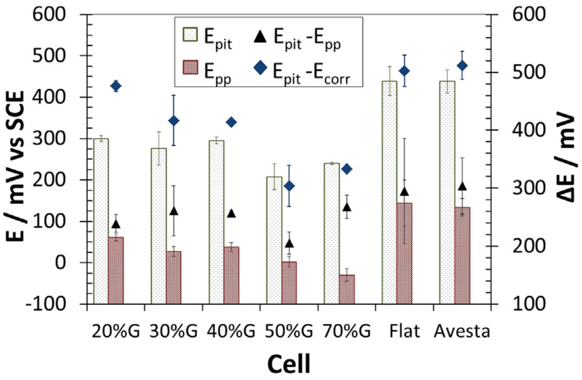

Fig. 10. Pitting potential (E_{pit}), pitting protection potential (E_{pp}), pitting susceptibility ($E_{pit}-E_{corr}$) and repassivation ability ($E_{pit}-E_{pp}$) obtained from anodic polarization curves on 304 stainless steel.

In all cases, i_{corr} values for gel electrolytes are comparable with i_{corr} values obtained in the aqueous electrolyte of the flat cell. In gels with 0.5% agar + 40% glycerol, which has previously demonstrated optimum adaptability (Table 2) and good mechanical properties (Fig. 2), the i_{corr} can be considered identical to that obtained in the flat cell (Fig. 9). i_{corr} values for Avesta cells draw attention as being the highest, probably because the distilled water flow incorporated into the system during the measurement and the design of the cell affects the passivation of the stainless steel.

The i_{max} has been previously related to the dangerousness of the morphology of the pits caused by the anodic polarization [45]. The results in Fig. 9 show that i_{max} increases as the glycerol content of the gel decreases. The findings suggest that pits generated in low glycerol gels have a more aggressive shape than those generated in high glycerol gels. The values obtained for this parameter for gel electrolytes are always intermediate between those obtained from curves obtained in "flat" and Avesta cells.

Fig. 10 shows the pitting potential (E_{pit}) and pitting protection potential (E_{pp}) obtained from the polarization curves. E_{pit} in gel electrolytes is relatively similar for gels with different glycerol concentrations. A slightly minor E_{pit} value has been measured in glycerol-rich gels (50–70%). The distance $E_{pit}-E_{corr}$ has always been considered as a measurement of pitting susceptibility. As the length of the passive region decreases in gel electrolytes as the glycerol content increases, it can be assumed that stainless steels show lower pitting resistance in high glycerol cells. The higher resistance of this electrolyte (Fig. 6) can favor the microcorrosion cells and the onset of the pits. The measurements carried out in

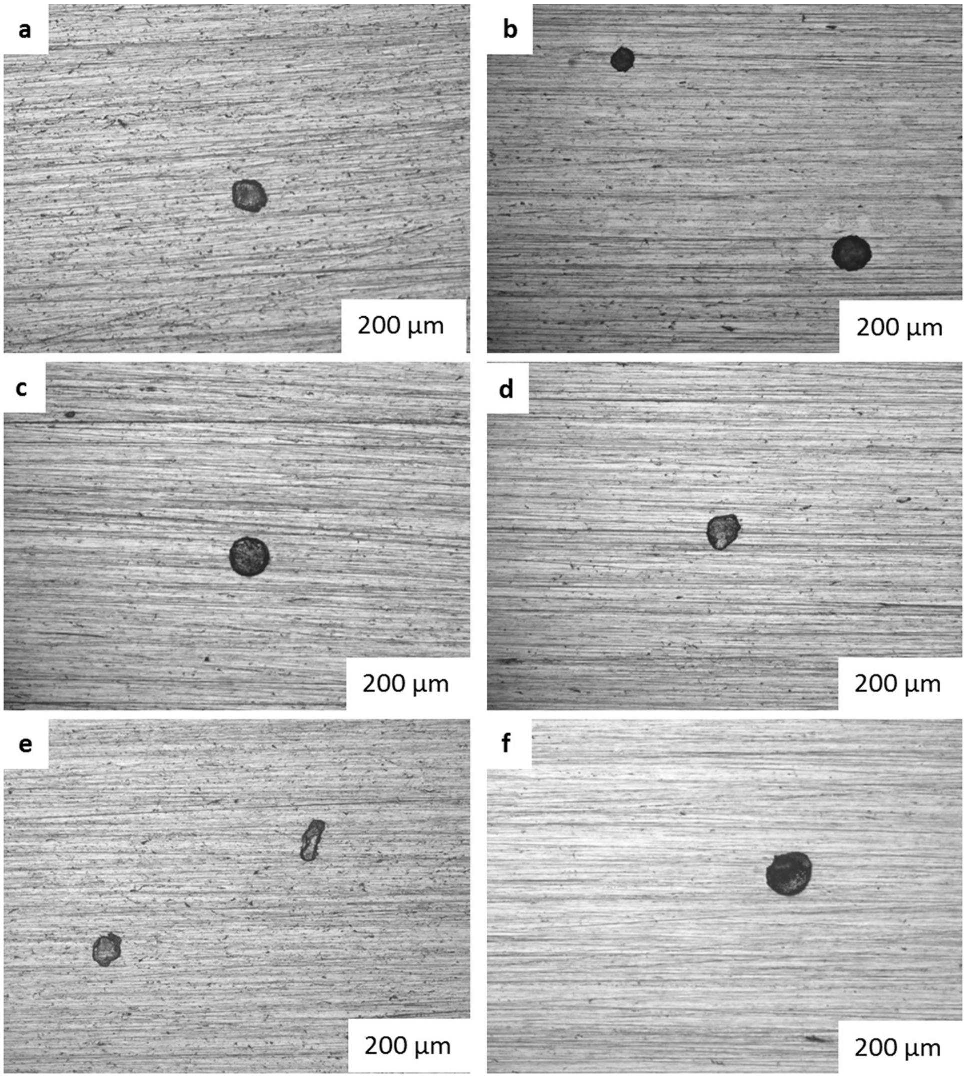

Fig. 11. Morphology of the attack after the polarization curves with gel electrolytes with (a) 20, (b) 30, (c) 40, (d) 50 and (e) 70% of glycerol, and (f) with aqueous electrolyte in flat cell.

cells with gel electrolyte exhibit E_{pit}-E_{corr} lower than those carried out in cells with aqueous electrolytes, indicating that gel electrolytes mean slightly more aggressive environments for localized attacks of passive metals. In Avesta cell, the marked E_{pit} increase can be justified by the dilution of the medium due to the flow of distilled water used to avoid the corrosion crevice, which causes a lower chloride concentration.

An increase in the content of glycerol produces a slight decrease in E_{pp}, but the re-passivation ability ($E_{pit}-E_{pp}$) remains constant in all cases except in Avesta cells, in which it seems to be lower.

The morphology of pits after anodic polarization curves was studied. A greater number of pits can be appreciated when gel electrolytes are employed and when the content of glycerol increases. At the same time, some differences in morphology were found among the attacks generated in the different concentrations of glycerol studied. Fig. 11 presents images of the pits after the polarization curve tests. The shape of the pits seems to be more irregular as the concentration of glycerol increases. Pits formed in gels with 20, 30 and 40% glycerol are circular (Fig. 11a–c), like those generated by polarization in aqueous 0.5% NaCl (Fig. 11f). However, the pits in 50% glycerol gels and, especially in 70% glycerol gels, are more irregular, suggesting a change in their growth mechanism. This would be associated to the lower σ of the electrolyte (Fig. 6) that causes the breakdown of the passive layer and the irregular growth of the pitting.

Contrary to what sometimes occurs with other types of electrochemical cells, crevice corrosion has not been found in any of the cases where gel electrolytes were employed. Interference of crevice corrosion in pitting susceptibility measurements is unfortunately quite common. This interference could be explained because it is not always easy to avoid the crevices when delimiting the studying area on the working electrode when using liquid electrolytes. Corrosion can occur as a consequence of the formation of crevices during the assembly because crevices are oxygen-poor. The generation of differential aeration micro-cells makes the metal inside the crevice act as anode. Moreover, other types of cells can appear inside the crevice after differential aeration cell (pH cells, ion-concentration cells), fostering the attack. However, when gel electrolytes are employed, if any difference in the aeration of the electrolyte appears over the surface of the tested metal, it is just the opposite: the regions more prone to be air-rich are those close to the electrolyte boundary. So, in this case, the region would tend to act as a small cathode and no interference in the pitting susceptibility measurement would occur.

The results obtained in this work show that electrolyte gels designed are suitable to carry out tests of pitting susceptibility by anodic polarization on complex stainless steel surfaces. This gel can possible be used for other electrochemical corrosion tests at temperatures close to room temperature, but further research need to be carried out about the viability of gel electrolytes to simulate any corrosive environment. Although some environments can be easily simulated, others could require much more complex optimization work.

4. Conclusions

Gel electrolytes were successfully obtained to be employed in electrochemical cells to perform polarization curves of stainless steels in chloride contaminated media. Different compositions with low agar content and a different plasticizer concentration were characterized for their use as electrolytes in electrochemical cells. These gel electrolytes allow replacing a conventional aqueous electrolyte in corrosion studies on metal surfaces and offer the following important advantages:

- Excellent adaptability to complex geometry.
- Fast stabilization of $E_{corr.}$
- No risk of crevice corrosion interferences.

The most satisfactory results for this application were shown by gel electrolytes with 0.5% agar and glycerol concentrations of about 40%. Gels with higher agar content can have adaptability problems to complex geometry because they need higher stress to be deformed. Moreover, gels with 30% or less glycerol concentrations crack easily. Gels with 50% or more glycerol concentration have electrical resistivity meaningfully higher than those usual in liquid electrolytes that can affect the development of the corrosion process, as the changes seen in the pits shapes proves. The curing times also become longer and for high glycerol gels and they are more prone to viscosity changes at temperatures slightly higher than room temperature.

The polarization curves of the stainless steels in gel electrolytes are comparable to that obtained in aqueous NaCl electrolytes. The passive region in the gel electrolytes studied is somewhat minor to that in aqueous electrolytes and tends to decrease with the glycerol content in the gel.

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