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Bonastre Cano, JA.; López-Muelas, JL.; Segura Alcaraz, JG.; Gadea Borrell, JM.; Juliá Sanchis, E.; Cases, F. (2019). Cathodic protection of steel guitar strings against the corrosive effect of human sweat. Engineering Failure Analysis. 97:645-652. doi:10.1016/j.engfailanal.2019.01.029



The final publication is available at http://doi.org/10.1016/j.engfailanal.2019.01.029

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Additional Information

Cathodic protection of steel guitar strings against the corrosive effect of human sweat

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Abstract

The steel strings of guitars suffer aggressive corrosion when exposed to human sweat. To mitigate this effect, in this research work guitar strings were subjected to cathodic protection by impressed current. To evaluate the corrosion, electrochemical techniques were used to determine the polarization resistance and the instantaneous corrosion rate, as well as the weight loss by gravimetric measurements. Microphotographs were also carried out to compare the corrosion status of the steel strings by stereoscopic optical and field emission scanning electron microscopy. Impressed current cathodic protection allowed the formation of iron oxides on steel guitar strings to be reduced by around 40%.

Keywords: cathodic protection, corrosion, rope wear, non-destructive testing, polarization curves.

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1. Introduction

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There are few works in the literature that have undertaken chemical studies on the corrosion in strings of musical instruments [1-3]. In these studies, different electric guitar strings (D'Addario E6, A5, D4, g3, b2 and e1 commercial strings) were subjected to corrosive attack by artificial human sweat for 28 days. These studies corroborated that the concentration of nickel ions was below the limit, 0.5 µg cm⁻² week⁻¹ [4], insufficient to produce allergic reactions. However, the prolonged use of oxidized steel strings will inevitably produce dermatological problems. It has long been known that guitarists commonly have dermatitis problems due to the corrosion of the guitar strings subjected to the aggressive action of their sweat. Psoriasis, seborrheic dermatitis and urticaria, among others, are common diseases that musicians may suffer due to the continued use of their guitars over an extended period of time [5-9].

Furthermore, the steel strings of the guitars must finally be replaced by new ones due to the corrosive effect of the sweat from the guitarists' hands. Therefore, in a previous work [10], we studied the morphology and characterized the electrical and acoustic properties of D'Addario D4 strings. D4 Commercial D'Addario electric guitar strings were chosen for our research due to the previous works done with the same type of strings by scientists of Zagreb University [1-3]. The strings of guitars were submerged in artificial sweat. Measurements of electrical resistivity, polarization resistance (R_p), instantaneous corrosion rate (i_{corr}) and electrochemical impedance spectroscopy (EIS) were made. Acoustic measurements were also performed by analysing frequency-amplitude spectrograms. It was established that 2 main mechanisms activated the corrosion process: differential aeration corrosion and galvanic or two-metal corrosion. Good correlation was obtained between the polarization resistance and the amplitude of the fundamental frequency measurements. Both parameters decreased similarly over the 7 days of testing.

The next logical stage in this research was to try to reduce the corrosion rate of the steel guitar strings mentioned above. In the present work, the purpose was to diminish the corrosion rate by applying cathodic protection by impressed-current [11-14]. Rp, Tafel plots, EIS, gravimetric measurements and stereoscopic optical microscopy were performed on the guitar strings with and without cathodic protection.

2. Material and methods

2.1. Materials and chemicals

The specimens under study were commercial electric guitar strings of the type D4 NW026 D'Addario & Company, Inc. The structure of the strings and chemical composition can be found in our previous article [10]. The strings are principally made of steel and have a spiral winding on a hexagonal central wire.

Firstly, the strings were treated with acetone and ultrasonic bath for 5 minutes and dried. For the corrosion tests, the strings were soaked with artificial human sweat. All

results were obtained in duplicate. A piece of cotton was dipped with artificial sweat and the strings were wetted at the beginning of the day. The artificial sweat was synthesized according to the European Standard EN 1811:1998+A1:2008. The reagents needed to synthesize the artificial human sweat were: sodium chloride (99.5%), urea crystal (99-100%) and ammonia (25%) from Panreac, lactic acid (90%) from Fluka.

1g/l hexamethylenetetramine (98% Prolabo) + 1M hydrochloric acid solution (37% Merck p.a. grade) was used to remove oxides from oxidized steel strings.

Ultrapure water with a resistivity close to 18.2 M Ω cm was obtained from a Millipore-Milli-Q $^{\text{@}}$ Advantage A10 $^{\text{@}}$ System.

For cathodic protection, 0.1 M KNO₃ solution (99% of Panreac Reag. Ph. Eur. grade) was used as electrolyte. 0.5 mm diameter platinum wires (99.99 purity) were used as auxiliary electrodes.

2.2. Electrochemical equipment and experimental procedure

Blausonic (0-30 V, 2.5 A) DC power supplies were used to provide impressed current cathodic protection. The working conditions were 6 V and 20 mA. Proinsa 3511927 and Goldstar DM-311 multimeters were used to carry out potential and intensity measurements.

The experimental assembly for the cathodic protection is shown in Fig. 1. A guitar, multimeters, reference electrode and power supplies can be seen in Fig. 1a. A plastic film was placed between the strings and guitar. In this way, the artificial sweat did not fall on the guitar. Two guitar strings were subjected to cathodic protection at the same time to obtain average values (Fig. 1b). The centre string was not under cathodic protection to compare results. In the centre of Fig. 1c, a clamp holds the steel string subjected to cathodic protection can be seen. The string is immersed in 0.1 M KNO₃ solution. During these tests the guitar strings were subjected to a tensile force of 89 N with a KORG GA-30 device to be tuned to the fundamental frequency of 147 Hz, similar to the state of the string when played by the guitarist.

a)



b)



c)



Fig. 1. Experimental setup for impressed current cathodic protection: a) General view of the cathodic protection system; b) Cathodic protection of the right and left string. Central string without protection; c) End of the protected string immersed in 0.1 M KNO₃.

To perform the measurements of Rp, Tafel plots and EIS, the steel strings were extracted from the guitar. Next, the strings were carefully washed with ultrapure water and dried, and then immersed (length of 3 cm) in an electrochemical cell with 30 ml of artificial sweat. A conventional electrochemical three-electrode cell was used. An Ag/AgCl (3 M KCl) electrode was used as reference electrode. A 0.5 mm diameter platinum wire (99.99 purity) was used as counter electrode. The measurements were carried out after the artificial sweat treatment.

An Ecochemie Autolab PGSTAT302 potentiostat/galvanostat was used. Rp measurements were made at a scan rate of 1 mVs⁻¹. The potential scan was carried out

from -10 mV to +10 mV in relation to open circuit potential (OCP). The Tafel curves were also collected at a scan rate of 1 mVs⁻¹ (\pm 250 mV vs. OCP). EIS measurements were made with an Autolab PGSTAT302 potentiostat/galvanostat with frequency response analyzer. The amplitude of the sinusoidal voltage was \pm 10 mV from OCP. The experimental data were fitted by equivalent circuits using ZView® software (3.1c version) from Scribner Associates Inc.

A Carl Zeiss Stereo Discovery V8 stereoscopic microscope was used to visualize the morphological changes of the samples. An Ohaus Discovery analytical balance was used to perform weight loss measurements. A Zeiss Ultra 55 field emission scanning electron microscope (FESEM) was used to study the morphology of guitar strings using an acceleration voltage of 2 kV.

3. Results and discussion

3.1. Rp and Tafel analysis

As discussed in the *Material and Methods* section, the steel strings with and without impressed current cathodic protection were soaked with artificial sweat daily. The steel strings were extracted from the guitar at 24, 48, 72 and 96 hours and Rp measurements were made in artificial human sweat. Table 1 shows the results of Rp obtained. Rp values for guitar string initially presents very high values. When the strings were immersed 24 hours in artificial sweat, there was a drastic decrease in Rp. However, the string protected by impressed current presented a Rp value 4 times higher than the unprotected one. Although this difference decreased throughout the hours of exposure to artificial sweat, the protected string presented higher Rp values during the entire test period. At the end of the test, the steel string with cathodic protection had approximately double the Rp value compared to the unprotected one.

Table 1. Rp values as a function of the exposure time for D4 NW026 guitar strings immersed in artificial sweat solution.

t / hours	$Rp(\Omega \cdot cm^2)$	$Rp(\Omega \cdot cm^2)$	
	Unprotected string	Protected string	
0	115574	118528	
24	876	3613	
48	1102	1903	
72	1237	1587	
96	788	1387	

Next, Tafel plots [15, 16] were also collected to compare the results of protection against corrosion in protected and unprotected strings at the end of the period of exposure to artificial sweat. Table 2 shows the results obtained. As with the Rp analysis, the values obtained for a new string presented very high values of Rp and very low values of i_{corr} . The values of B constant were appropriated in relation to data described in the literature for steels [15]. The i_{corr} values increased considerably at the end of corrosion test in artificial human sweat. Nevertheless, it should be noted that the value of i_{corr} is reduced by half in samples protected by impressed current compared with unprotected ones. Obviously, Rp values were double in the protected samples with respect to the unprotected ones.

Table 2. Results of the Tafel analysis for protected and unprotected D4 NW026 guitar strings immersed in artificial sweat solution.

Tafel Analysis					
New string	:				
i _{corr}	0.2 μAcm ⁻²				
В	0.03 V				
Rp	182744 Ω·cm ²				
Strings after 96 hours in artificial sweat					
	Unprotected string	Protected string			
i _{corr}	64.4 μAcm ⁻²	32.4 μAcm ⁻²			
В	0.04 V	0.04 V			
Rp	621 Ω·cm ²	1235 Ω·cm ²			

3.2. EIS analysis

In order to corroborate the data obtained previously, EIS analyses were performed. Fig.2 shows the Nyquist plots [17] for protected and unprotected guitar strings. The plots show the impedance values for the strings after being impregnated with artificial human sweat for 24 hours. Qualitatively it can be seen that the resistive-capacitive (RC) loop is larger for the string protected with impressed current in relation to the unprotected one. The values of resistance (Z') and capacitive reactance (Z'') are significantly higher in the string protected by impressed current.

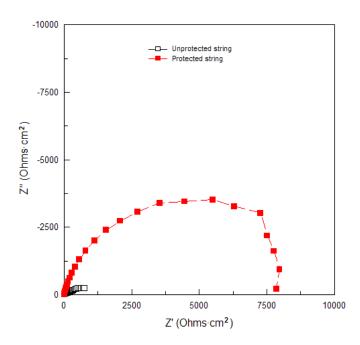


Fig. 2. Nyquist plots for protected and unprotected D4 NW026 guitar strings immersed in artificial sweat solution for 24 hours. Frequency range from 10⁵ to 10⁻² Hz.

In order to quantify the obtained impedance spectra, the data were fitted by the equivalent circuit of Fig. 3. As the experimental data of Fig. 2 showed a single RC loop, the electrical response could be modelled to a typical RC circuit [15, 18-25]. The electrical elements that make up the circuit were: the electrolyte resistance (Re), the Rp and double layer capacitance (Cdl) due to electrode interface. Table 3 shows the values obtained for steel strings impregnated with artificial sweat for 24, 48, 72 and 96 hours with and without impressed current cathodic protection. After 24 hours of corrosive attack, the Rp of the protected string by impressed current showed a difference of more than an order of magnitude in relation to the unprotected one. Data for 48 hours showed similar values. However, for 72 and 96 hours, the values of Rp were again significantly higher for the steel strings protected by impressed current. The results obtained by means of the EIS AC technique were coherent with those obtained by DC techniques such as Tafel analysis and Polarization Resistance, as discussed above. In summary, the steel guitar strings subjected to cathodic protection by impressed current had a significantly lower corrosion rate compared to unprotected ones.

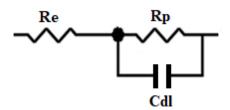


Fig. 3. Equivalent circuit for fitting experimental impedance data of guitar strings immersed in artificial sweat solution. Re: electrolyte resistance, Rp: polarization resistance and Cdl: double layer capacitance.

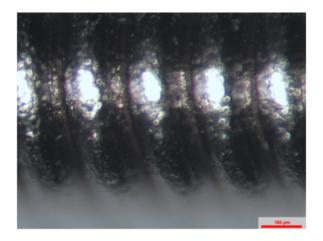
Table 3. Re, Rp and Cdl values as a function of the exposure time for D4 NW026 guitar strings immersed in artificial sweat solution. EIS fitting data according to the circuit of Fig. 3.

+ / h	Re (Ω·cm²)		Rp (Ω·cm²)		Cdl (μF/cm ²)	
t / h	Unprotected	Protected	Unprotected	Protected	Unprotected	Protected
24	11	9	357	6629	7	1
48	6	6	1229	1287	2	2
72	7	5	804	1187	3	2
96	7	6	668	2402	19	2

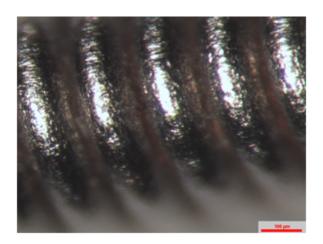
3.3. Stereoscopic optical microscopy and gravimetric weight loss measurements

The results obtained by electrochemical measurements have shown that the cathodic protection by impressed current considerably improves the protection of guitar strings in artificial sweat. It is interesting to show the morphology of the guitar strings subjected to the corrosion tests. The steel strings were impregnated, in the same way as in the electrochemical tests, with artificial sweat for 96 hours. Fig. 4 shows optical microphotographs of D4 NW026 guitar strings. Fig. 4a corresponds to a new guitar string before being immersed in artificial sweat. These images demonstrate how the steel string have a grey colour, both in the winding and in the central core of the string. Fig. 4b shows the morphology of the unprotected string after corrosive attack in artificial sweat for 96 hours. In this case a reddish-brown coloration appears in the central core of the guitar string. A significant amount of iron oxides have been formed in the central core of the steel guitar string. Fig. 4c corresponds to the microphotograph of the guitar string protected with impressed current. In this case, the coloration is a little less reddish-brown compared to Fig. 4b.

a)



b)



c)

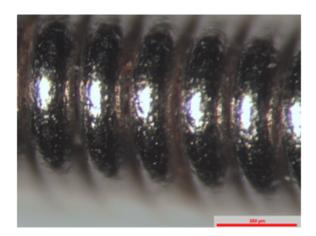
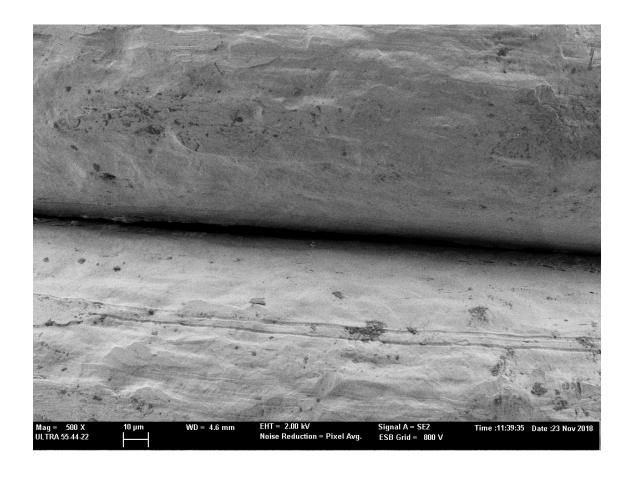


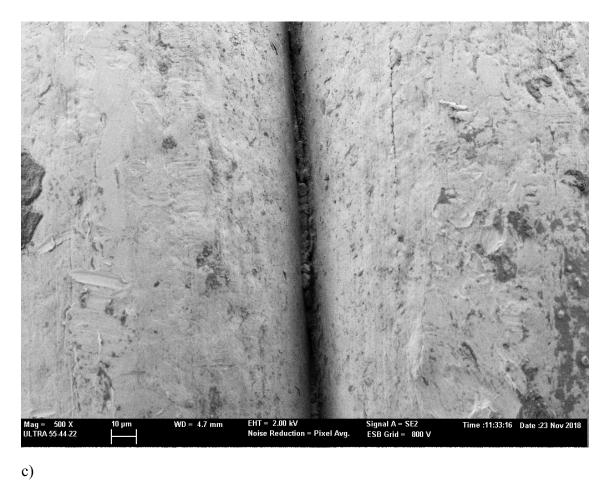
Fig. 4. Stereoscopic microphotograps of D4 NW026 guitar strings: a) New guitar string; b) Unprotected string immersed 96 hours in artificial sweat; c) Protected string immersed 96 hours in artificial sweat.

In order to better distinguish the morphological characteristics of the strings with or without protection, FESEM microscopy was performed. Fig. 5a shows the morphology of a new guitar string. It is interesting to note how the interstitial zone between the winding presents black color. There is no formation of oxides from the core of the string. Fig. 5b shows the unprotected guitar string immersed for 96 hours in artificial human sweat. It is clearly seen how corrosion products have been formed in the interstitial zone. Different zones of the strings were also analyzed by FESEM and the morphological characteristics were the same. Fig. 5c shows the FESEM microphotograph of a cathodic protected string immersed for 96 hours in artificial sweat. Corrosion products can be seen in the interstitial area of the string, but in less quantity than in the unprotected string (Fig. 5b). In the protected string, there is a higher number of black areas where corrosion products were not formed. In relation to the winding of the strings (white areas), the guitar string unprotected has a higher number of gray areas (damage due to corrosion) compared to cathodic protected string.

a)



b)



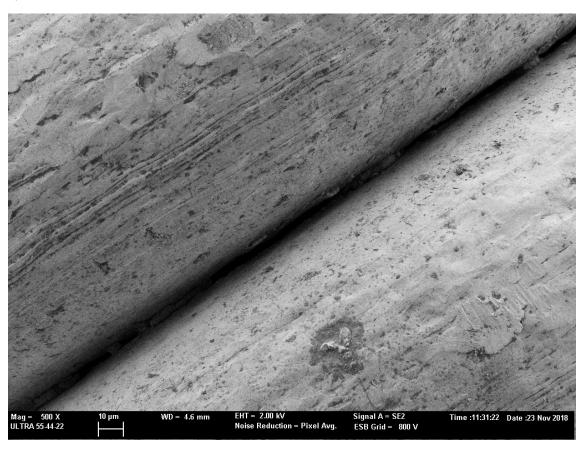


Fig. 5. FESEM microphotograps of D4 NW026 guitar strings: a) New guitar string; b) Unprotected string immersed 96 hours in artificial sweat; c) Protected string immersed 96 hours in artificial sweat.

It is also usually interesting to corroborate the electrochemical results by measurements of weight loss in the samples due to the corrosive process.

The steel strings were also impregnated with artificial sweat for 96 hours. Guitar strings with and without protection by impressed current were analyzed. At the end of the 96 hours of corrosive attack, the guitar strings were extracted, cleaned with ultrapure water and treated with hexamethylenetetraamine and hydrochloric acid, as indicated in 2.1. *Materials and chemicals* section. In this way, the iron oxides formed in the steel strings during the corrosive attack in artificial sweat were eliminated.

The values of gravimetric weight loss obtained are shown in table 4. The gravimetric weight loss decreased considerably for the guitar string with cathodic protection. The protected string presented around 40% less weight loss compared to the unprotected one. A lower formation of iron oxides was confirmed for the cathodic protected string due to a less severe corrosive attack.

Table 4. Gravimetric loss of D4 NW026 guitar strings after 96 hours of immersion in artificial sweat solution.

	Unprotected string	Protected string
Initial weight	2.4750 g	2.4470 g
Final weight (oxide removed)	2.4505 g	2.4317 g
Weight loss	0.0245 g	0.0153 g
Weight loss %	1.0 %	0.6 %

4. Conclusions

The results obtained in this research allow the following conclusions to be reached:

- Electrochemical measurement evidence that steel guitar strings immersed for 96 hours in artificial human sweat are effectively protected by impressed current cathodic protection. These results justify the viability of constructing an integrated system of corrosion protection in the instrument.
- The results obtained by microscopy and weight loss analysis were consistent with the electrochemical measurements performed.
- The weight loss due to the formation of iron oxides is around 40% lower for the steel strings protected by impressed current compared to the unprotected ones.
- Rp is a simple, quick technique which can be used to evaluate at any time the corrosion rate of the steel guitar strings in artificial human sweat. In addition, the test is non-destructive.

Acknowledgement

Authors wish to thank to Spanish Agencia Estatal de Investigación de Economía (AEI) and European Union (FEDER funds) for the financial support (contract MAT2016-77742-C2-1-P).

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FIGURE CAPTIONS

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