

Formable chromium nitride coatings for Proton Exchange Membrane Fuel Cell stainless steel bipolar plates

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HIGHLIGHTS:

- 50 nm CrN coating on 316L stainless steel promotes corrosion resistance and low ICR
- The etching improves coating adhesion, corrosion resistance and low ICR
- The low ICR and high corrosion resistance is retained after biaxial deformation

KEYWORDS:

PEMFC; chromium nitride coating; ICR; DoE target

ABSTRACT

Among the different coatings developed for proton exchange membrane fuel cell steel bipolar plate, nitride-based coatings present several advantages compared to gold or polymeric coating: high chemical stability, low interfacial contact resistance and reasonable cost. In this work, 50nm thick chromium nitride coatings are deposited by reactive magnetron sputtering on 316L stainless steel foil. They are optimized to fulfill the Department of Energy targets in terms of interfacial contact resistance (ICR) and corrosion resistance, with values of 8.4 mΩ.cm⁻² (at 100 N.cm⁻²) and 0.10 μA.cm⁻² (in 0.6 M H₂SO₄ solution at 0.48 V_{vs. SCE} potential) respectively. Moreover, they retain their excellent properties after high deformation (biaxial deformation of 20% in x-axis and 5% in y-axis), giving the possibility to achieve, in line, the stamping of a bipolar plate from a coated foil. The etching of the substrate, prior to the coating deposition, appears to be determinant to obtain low and stable corrosion current and ICR. The removing of interfacial oxide leads to better coating adhesion and improves the corrosion resistance and electrical conductivity. The enhancement of the properties (low ICR and high corrosion resistance) is durable, with no significant change of the ICR value up to 200 days after deposition.

INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFC) are one of the alternative solutions to the internal combustion engine, especially suitable for transportation applications. Their high power and fast start-up, in addition to their lower environmental impact (if hydrogen is produced from renewable energy) make them a promising technology for the energetic transition. However, the decrease of their weight and cost remains a leitmotiv to improve the competitiveness of fuel cell stacks [1]. In this view, large efforts are currently going on to improve the bipolar plates: thick, heavy and brittle graphite plates formerly used are now replaced by thin and formable metallic ones. Most of all, metallic bipolar plates can be stamped

to form the channels and manufacture the bipolar plates at an industrial scale [2]. The use of metallic plates and more precisely stainless steel (SS) instead of titanium (for its prohibitive cost) is a significant challenge, for the relative good electrical conductivity and corrosion resistance to be fulfilled. Moreover, stainless steel tends to release iron ion into the membrane, leading to its dramatic poisoning. The corrosion resistance of stainless steel arises from its pristine chromium oxide layer at the top surface; unfortunately, this oxide layer induces a too high interfacial contact resistance (ICR) between the bipolar plate and the Gas Diffusion Layer (GDL) and it completely prevents the use of uncoated SS as a bipolar plate. ICR and corrosion resistance are the two characteristics of bipolar plates that researchers try to improve, in line with the US Department of Energy (DoE) target values for 2020: $< 1 \mu\text{A cm}^{-2}$ and $< 10 \text{ m}\Omega \text{ cm}^2$ for corrosion current and ICR respectively, in standard measurements (pH = 3, 0.1ppm HF, 80°C, active peak current $< 1 \times 10^{-6} \text{ A.cm}^{-2}$ with potentiodynamic test at 0.1 mV s^{-1} , -0.4 V to +0.6 V (Ag/AgCl) de-aerated with Ar purge for corrosion resistance and ICR measured on both sides at 200 psi (138 N/cm^2) [3]). The use of surface engineered steel and the deposition of coating is one of the best solutions to achieve a low ICR and good corrosion resistance, and several authors have published studies on metallic coatings with noble or non-noble metal [4–6], carbides [7] and carbon based coatings [8,9], oxide coatings, nitride coatings [10–12], or polymeric ones [13]. Among the different methodologies to deposit a coating, magnetron sputtering has many advantages, as it is a fast, solvent-free and easily scalable process [15,16]. Recent literature gives some surface engineered steels that fulfill the DoE target, but the proposed solutions are not really adapted for mass production.

Although interesting materials are developed at lab scale – with very low ICR and high corrosion resistance – thinking about mass production bring new challenges: by taking into account the manufacturing, the cost and the integration into existing production line, only a limited amount of materials address all the challenges, especially if we consider the forming of the plate from a coated sheet [14,17]. A recent study from Leng *et al.* [14] gives a detailed analysis of the potential candidates for DoE 2020 targets and among the possible materials,

carbon-based and metal nitrides coating are the remaining candidates. Mass 'in line' production of bipolar plates can be achieved *via* the rolling process and stamping of the bipolar plate [18,19]. In this view, the coating is deposited before stamping, but has to retain its properties after deformation. While the use of "thick" coatings (*i.e.* from 0.2 to 2 μm) is beneficial for a stronger barrier against corrosion, it generally improves the level of residual stresses (coming from the film growth) especially at high deposition rate [20]. The generation of residual stresses can dramatically affect the durability of the coating and its performance, and even a small mechanical solicitation of the coating can lead to its break. On the contrary, the use of thin (≈ 50 nm) coating with a full covering of the substrate and good adhesion appears thus to have several advantages: it displays higher toughness and deformability in addition to being more sustainable due to the reduction of deposited matter and the decrease of processing time. However, due to the very low thickness of the deposited film, the top surface of the substrate needs to be carefully controlled prior to deposition, in terms of roughness, contamination and chemical affinity (e.g. presence of undesired oxide layer); the role of the interface between the coating and the substrate becomes critical.

In this view, the present work investigates the deposition of thin chromium nitride coatings on etched and unetched 316L stainless steels. The main novelty of this study lies in the crucial role that the coating/surface plays on the final properties: it is demonstrated that the chromium nitride coating deposited on an etched substrate fulfills the DoE requirements and retains its characteristics after deformation.

MATERIALS AND METHODS

The chromium nitride thin films have been deposited by magnetron sputtering of a chromium target (99.97%, Neyco) on 100 μm thick 316L stainless steel substrate (Aperam coil), in Ar/N₂ atmosphere (Alphagaz 2). The initial pressure before the deposition was 1.4×10^{-6} mbar (1.4×10^{-4} Pa) while the working pressure was set at 3.5×10^{-3} mbar (3.5 Pa). The flow rate of

argon and nitrogen were respectively 200 and 15 sccm, while the target current was set at 1.5 A. These parameters have been adapted from previous experiments to control the nitrogen content, a reasonable deposition rate, and to limit the oxygen content. The thickness of the coating was approximately set around 50 nm, by adjusting the pass rate to 21 cm.min⁻¹, with a single pass. Prior to the introduction in the chamber, the stainless steel is cleaned with ethanol. Two conditions were tested, namely with or without etching, to underline the crucial role of the coating/substrate interface. The etching was done using an Ar⁺ ion beam, working at 3 A (corresponding voltage of 91 V). The working pressure is set at 3 x 10⁻⁴ mbar (3 x 10⁻² Pa) with an Ar flow rate of 10 sccm. The stainless steel sheet passes four time in front of the beam, with a pass rate of 60 cm.min⁻¹.

The roughness of the etched and unetched sample have been investigated using a Bruker Dektak stylus profilometer. The arithmetical mean deviation roughness (Ra), the root mean squared roughness (Rq) and maximum valley depth and peak height (Rv and Rp) are determined from a 3µm long measurement.

The coatings were characterized after deposition (raw coatings), after deformation (deformed coatings), after deformation and corrosion measurements (deformed + corroded coatings). The deformation was achieved by a Marciniak procedure, namely a biaxial deformation of 20% along the x-axis and 5% along the y-axis. Such a deformation represents well the stamping of the channels in stainless steel foil to manufacture the bipolar plate [21]. Indee

The interfacial contact resistance (ICR) was measured by a conventional method reported in the literature [22,23]. The coated sample was pressed between two copper plates, with a gas diffusion layer (GLD) carbon paper that is set between the sample and the copper plate. Before each analysis, a gold coating is tested as reference to confirm the measurement. The resistance was measured as a function of the applied pressure. The value of ICR is given at 100 N.cm⁻², and measured three times.

The corrosion tests were performed in a three-electrode cell in which a platinum sheet acted as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the coated stainless steel sample as the working electrode. The solution was composed of H_2SO_4 0.6 M in ultrapure water (MilliQ, $>18 \text{ M}\Omega$) with a bubbling of oxygen. The temperature was set at 60°C by using a thermostated bath circulating the water in the double jacket of the cell. The potential was set by an Autolab PGSTAT30 potentiostat at $0.48 \text{ V}_{\text{SCE}}$ during 16 h.

The morphology of the coatings was investigated by scanning electron microscopy (SEM) on a JEOL 7500F microscope. In addition to SEM measurements, a raw coating was analyzed by transmission electron microscopy (TEM) on a Tecnai T20 microscope operating at 200 kV. For this analysis, the coating was scratched off the steel with a diamond pin, and a copper grid was rubbed against the scratched surface. This method allows a fast and simple alternative to focus ion beam (FIB) sample preparation and is adapted for coating observation [24]. Diffraction patterns were recorded at different points on the coating layer, and were very similar, confirming the method.

The chemistry of the coatings was investigated by X-ray photoelectron microscopy on a K-Alpha spectrometer (ThermoFischer) using Al $\text{K}\alpha$ source (1486.68 eV) and a spot size of $250 \mu\text{m} \times 250 \mu\text{m}$. The coating was profiled using an Ar^+ beam at 2 keV and 10 μA , using the snapshot mode (pass energy 150 eV, 10 scans) for recording the C 1s, N 1s, Cr 2p, and Fe 2p core levels. The atomic concentrations were determined from the area of each peak, considering a Shirley background. The authors are aware of the possible damage generation using ion beam, and that the concentrations obtained from XPS measurements are subject to modifications [25,26]; however, the comparison between samples remains valid, as the same erosion parameters (ion beam energy and current, spot size) have been used.

RESULTS AND DISCUSSION

Figure 1 presents the TEM analysis of the pristine coating on unetched substrate. The deposited film is composed of fine nanoscale grains (Figure 1a), typical for coatings at such

thickness (50 nm). The diffraction patterns, shown in Figure 1b reveals a crystallized structure. The indexation of the patterns indicates d-spacing of 2.033, 1.437, 1.270, 1.170, 1.075, and 1.013 Å. The experimental d-spacing have been compared with those from CrN and Cr₂N structures, and are in good accordance with a cubic CrN structure (space group 225, Fm-3m) [16,27]. Table 1 presents the indexation of the experimental d-spacings and the deviations with theoretical values.

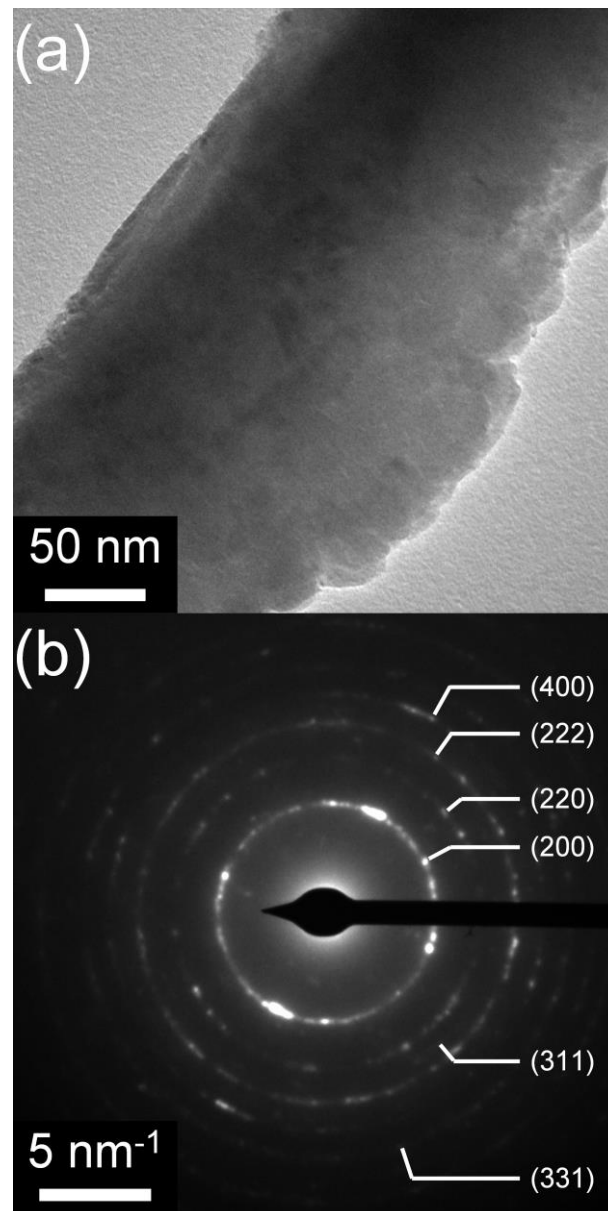


Figure 1. (a) TEM image of a coating fragment, coming from chromium nitride coating deposited on unetched substrate. (b) Selected area diffraction pattern, indexed with the CrN cubic structure.

Table 1. Analysis of diffraction pattern. Comparison between experimental d spacings obtained from the pattern and theoretical d spacings.

d_{exp} (Å)	d_{theo} (Å)	Plane	Relative difference (%)
2.033	2.074	(200)	2.0
1.437	1.467	(220)	2.0
1.270	1.251	(311)	1.5
1.170	1.197	(222)	2.3
1.075	1.037	(400)	3.7
1.013	0.952	(331)	6.5
0.910	0.928	(420)	1.9

Figure 2 and Figure 3 respectively present the SEM observation and the XPS depth profiles of samples, at different levels: pristine (Figure 3a and 3b), after deformation (Figure 2a and 2b, Figure 3c and 3d) and after deformation and corrosion (Figure 2b and 2c, Figure 3e and 3f). The SEM images of pristine sample are not presented, as they do not provide useful information, only showing a good covering of the surface

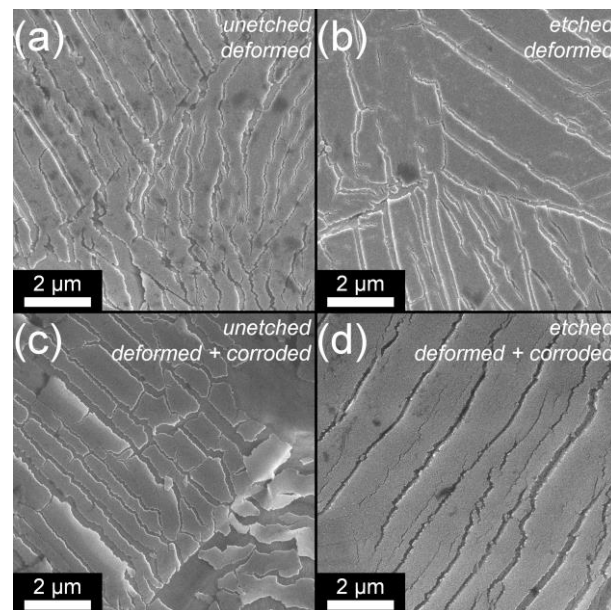


Figure 2. SEM observation of the chromium nitride coating deposited on unetched (a, c) and etched (b, d) 316L substrate, after (a, b) biaxial deformation or (c, d) biaxial deformation and corrosion.

The effect of the etching treatment is particularly visible in the XPS depth profile, that shows the removal of the interfacial oxide layer (Figure 3b): no oxygen is reported at the interface of

the layer with the substrate etched prior to the deposition. In the etched and unetched cases, the composition of the coating is similar, with a constant Cr/N ratio of ca. 66/30, deviating from 1:1 (*i.e.* CrN, as obtained from TEM investigation). This deviation is due to the background used for peak area measurement and quantification and/or damage induced by the beam during erosion [25]. A slight oxidation is visible on the extreme surface of both coatings, as often reported for chromium nitride coatings [16,28]; this effect appears more pronounced on the unetched sample (Figure 3a). Looking at the deformed sample, a slight exposition of the substrate occurs, confirmed by the SEM observation (Figure 2a and 2b). This is due to the plastic deformation that the stainless steel substrate can support, but not the coating. Indeed, chromium nitride displays a much lower toughness (4-8 MPa m^{1/2} for CrN while 112-278 MPa m^{1/2} for SS 316L [29,30]) and tensile strength ($\approx$ 355 MPa for CrN [31] while 700 MPa for SS 316L; obtained from tensile test), and breaks at high deformation. The presence of cracks and the exposition of the substrate is responsible for the detection of iron in the coating (and to a lower extent of the oxygen), as the XPS beam reaches the surface of the substrate through the cracks while simultaneously analysing the thin coating. The iron content determined by XPS is thus a good indicator of the degree of coating fracturation and extent of exposed surface area of the substrate. After deformation, the iron content is similar in both samples (Figure 3c and 3d), in accordance with the corresponding SEM micrographs (Figure 2a and 2b). The SEM images were processed to estimate the fraction of the delaminated area. Percentages of delamination (*i.e.* non-covered to total area ratio) were calculated equal to 10.7% and 10.9% for the unetched and etched samples, respectively.

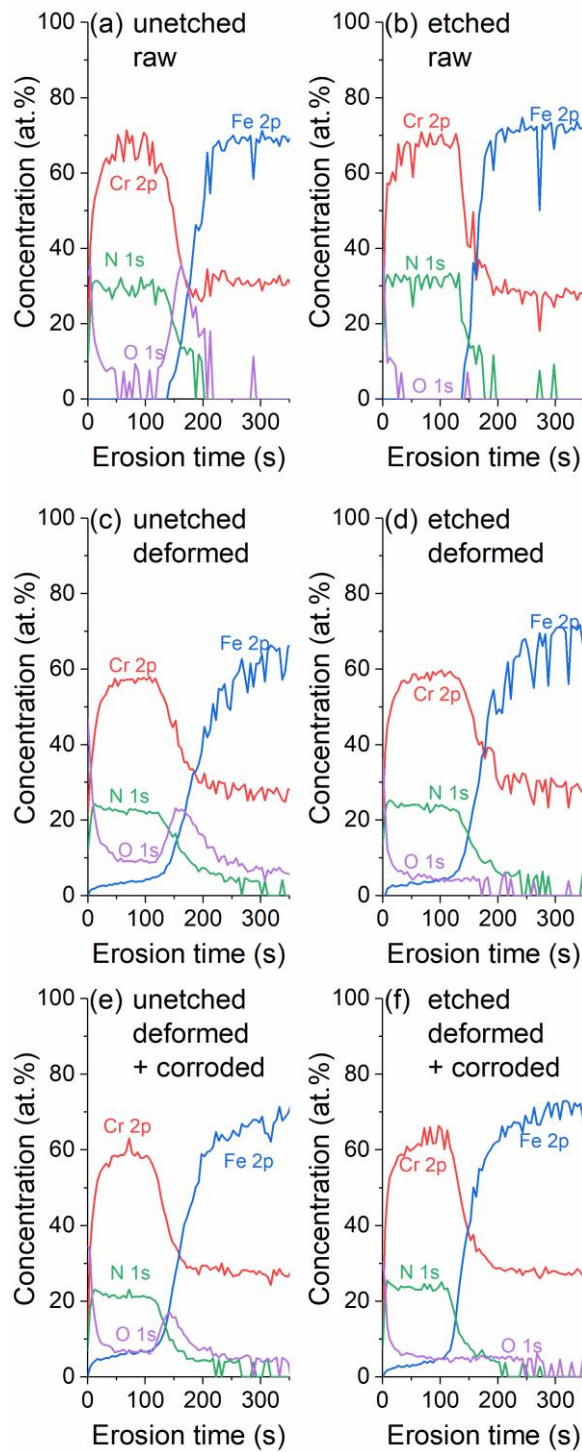


Figure 3. XPS depth profiles of the etched and unetched samples, after deposition (a and b), after deformation (c and d), and after deformation and corrosion (e and f).

Looking at the deformed and corroded samples (Figure 2e and 2f, Figure 3e & f), two different behaviors are noted: the iron content is much higher for the unetched sample (around 6.5 at.%; Figure 3e, while it is of 3.5 at.% for etched deformed and corroded sample; Figure 3f),

and present a much higher delamination (Figure 2c). The fraction of delaminated area is estimated around 33%, while it is only 12% for the etched sample. Thus, the etching of the substrate prior to deposition drastically improves the adhesion of the coating and its deformability. This improvement is attributed to the removal of interfacial oxide.

These results are in accordance with the study of Barshilia et al.[32], demonstrating the superior adhesion of PVD coating, when interfacial oxide is removed. They demonstrated that the better adhesion also originates, in a lower extent, from the increase of the surface roughness. The roughness modification has been investigated by profilometry, with the determination of Ra, Rq, Rp and Rv parameters on unetched and etched substrate after coating deposition (**Figure 4**). A slight increase of the roughness is reported, with Ra value increasing from 135 ± 6 to 155 ± 7 nm, giving a possible better interlocking the substrate/coating interface [32]. However, this “mechanical” effect has certainly a very low significance compare to the “chemical” effect, namely the suppression of the interfacial oxygen.

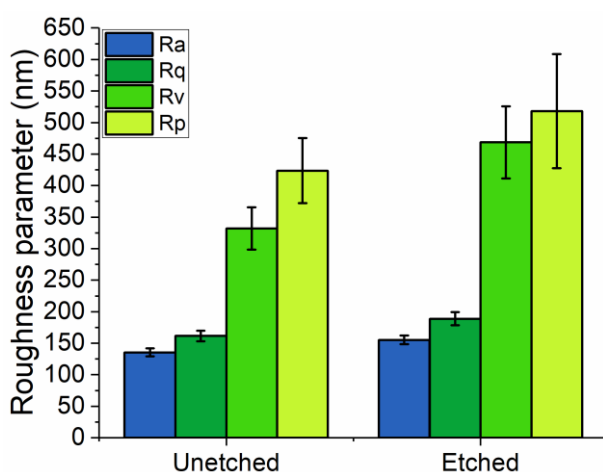


Figure 4. Determination of roughness parameters before and after etching

The electrochemical properties of the films have been investigated. The corrosion current is determined by potentiostatic experiments on the deformed samples, for a more realistic comparison of a stamped coated bipolar plate. In these measurements, for each sample, a chronoamperometry at 0.48 V_{vs. SCE} (equivalent to ~0.7 V_{vs. NHE}) was applied during 16 h and

the corrosion current was measured at the end of the chronoamperometry. The interfacial contact resistance was also measured, on undeformed samples only.

The values obtained with the 50 nm chromium nitride coating is given in Table 2 and were compared to those measured on similar coatings in published works. When the stainless steel substrate is etched, the coating fulfills the DoE target value in terms of ICR and corrosion current and has superior properties to other CrN coatings, deposited either by cathodic arc or magnetron sputtering. After biaxial deformation, the coating deposited on the etched substrate retains its low corrosion current, with a low level of cracks and delamination. This improvement is attributed to the removal of interfacial oxide, as confirmed by the XPS depth profile.

Table 2. Comparison between chromium nitride coated stainless steel for PEMFC bipolar plate from this work to reported works.

Interfacial contact resistance		Corrosion resistance		Materials	Reference
ICR ($\text{m}\Omega \text{ cm}^2$)	Pressure (N cm^{-2})	Corrosion current ($\mu\text{A cm}^{-2}$)	Electrolyte		
8.4	150 N cm^{-2}	0.10	0.6 M H_2SO_4 , 60°C, 0.7 $\text{V}_{\text{vs. NHE}}$	CrN on etched SS 316L	This work
46.7	150 N cm^{-2}	0.22	0.6 M H_2SO_4 , 60°C, 0.7 $\text{V}_{\text{vs. NHE}}$	CrN on unetched SS 316L	This work
23	150 N cm^{-2}	0.3	0.5 M H_2SO_4 , 2 ppm HF, 80°C	CrN by arc ion plating	[22]
520	50 N cm^{-2}	0.015	10^{-3} M H_2SO_4 , pH = 3, 2 ppm HF, 80°C	CrN by PVD	[33]
<10	138 N cm^{-2}	<1	pH = 3, 0.1 ppm HF, 80°C, potentiodynamic test at 0.1 mV s^{-1} , -0.4 V to +0.6 $\text{V}_{\text{vs. Ag/AgCl}}$, Ar purge	2020 DoE target	[34]

In addition, the effect of the coating aging on the ICR performance has been investigated, by measuring the evolution of the ICR as a function of the time (Figure 4), the sample being exposed to air more than 180 days. The ICR value slightly increases in the first 100 days, and

stabilize around $10\text{m}\Omega.\text{cm}^2$, demonstrating the great stability of the coating and the coating-substrate interface.

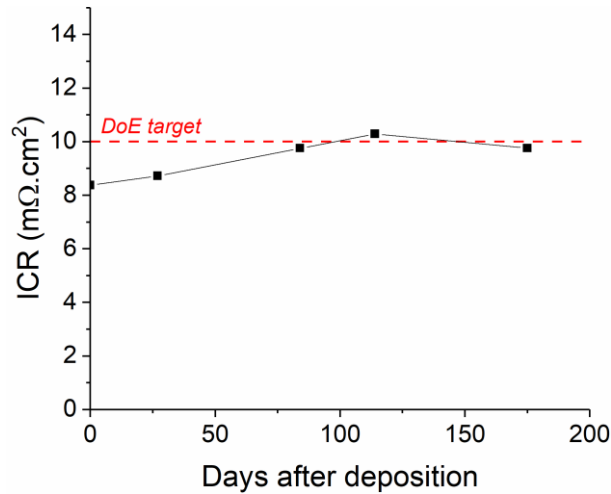


Figure 5. Aging of the coating: evolution of the ICR value of the chromium nitride coating deposited on etched SS 316L substrate (undeformed), as a function of time.

CONCLUSION

The present study investigates the use of chromium nitride thin film as a protective coating for Proton Exchange Membrane Fuel Cell stainless steel bipolar plates. A 50 nm chromium nitride thin film was deposited on etched and unetched 316L stainless steel substrates. The coating deposited on etched substrate fulfills the DoE requirements in terms of corrosion current and interfacial contact resistance. Most of all, a bi-axial deformation (from 5% to 20%) was applied on the coated steel sheet in order to simulate a continuous process including PVD deposition and stamping of bipolar plate. After deformation, the sample obtained by CrN deposition after etching of the stainless steel substrate still fulfills the DoE requirements and presents a low degree of coating breakage. The etching prior to coating deposition allows the removing of interfacial oxide, beneficial for coating adhesion, resistance to corrosion, and electrical properties in terms of interfacial contact resistance.

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