A0703

Titanium coatings deposited by thermal spraying for bipolar plates of PEM electrolysers

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Abstract

Proton exchange membrane (PEM) electrolysers are promising systems for generating high purity hydrogen. One of the key components of these devices is the separator or bipolar plate. These plates are normally made of Ti since the passive layer of TiO_{2-x} protects it against corrosion in the aggressive environment of a PEM electrolyser. Unfortunately, this metal is expensive and machining the flow channels is complicated. A more suitable material would be stainless steel (SS). However it corrodes when used for bipolar plates. Additionally, Fe and Cr ions poison the membrane electrode assembly (MEA) of the electrolyser. Therefore, the SS bipolar plates have to be protected with a coating that is corrosion resistant in acid environment and conductive. In this work we produced Ti coatings on SS Crofer® 22 H substrates by vacuum plasma spraying (VPS) technique. Several parameters such as the type of nozzle, the powder feed rate, the plasma gas flow (Ar, N_2 and H_2) were systematically varied. Titanium powder (45 µm) was sprayed in absence of O_2 to prevent the formation of TiO_{2-x}, which would reduce the electronic conductivity of the coating. Dense layers of Ti were produced with high plasma enthalpy. XRD measurements revealed that the resulting coatings were pure α-Ti. The densest coating, deposited with 21.27 MJ kg^{-1}, had a leak rate of 4.3 mbar l cm^{-2}. A coating development on SS bipolar plates resulted in low corrosion currents, demonstrating the promise of a good application for PEM electrolysers with bipolar plates made of stainless steel.

Introduction

Hydrogen will become an important chemical storage medium for renewable energies in the future. At standard temperature and pressure it can be recovered by splitting water molecules using electricity according to:

Anode (oxidation): $2\ H_2O(l) \rightarrow O_2(g) + 4\ H^+(aq) + 4e^-$ $E^0 = 1.23$ V *vs.* SHE, pH = 0 (1)

Cathode (reduction): $2\ H^+(aq) + 2e^- \rightarrow H_2(g)$ $E^0 = 0$ V (2)

When using a proton exchange membrane (PEM) as electrolyte, this electrochemical process is known as PEM electrolysis. PEM electrolysers have great technological potential because of their high power densities, superior gas quality and superior dynamic operation ranges [1]. Key components of this electrochemical reactor that determine stack costs are the interconnects, namely bipolar plates (BP) and gas diffusion layers (GDL). According to reports from Proton Energy Systems, GES and the GenHyPEM European project, the interconnects, i.e. bipolar plates and current collectors, correspond to more than 45 % of the total cost of the PEM electrolyser stack [2-4]. The interconnects of a PEM electrolyser are made of titanium due to its high resistance to corrosion in acid media at high potentials [5]. However the passive layer of titanium dioxide that forms at the interconnects, increases the ohmic resistance, limiting the durability of the electrolyser stack. Furthermore machining the flow channels on the bipolar plate or making porous structures is complicated and costly [6].

A more suitable material for bipolar plates would be stainless steel (SS). However, it corrodes dramatically when used in PEM electrolysers [7]. Additionally, the ions released from the corrosion process poison the membrane electrode assembly (MEA) of the electrolyser. Therefore, the stainless steel has to be protected with a coating that is corrosion resistant in acid environment and conductive, at the same time. A standard approach for developing coatings of BP of proton exchange membrane fuel cell (PEMFC) is by applying a coating with high corrosion resistance and excellent electronic properties [8, 9]. In this sense conductive coatings of TiN [10, 11], TaN [12], SnO_2:F [13], Au [14, 15], etc. have been widely evaluated for corrosion protection of PEMFC bipolar plates. Nevertheless these coatings fail to provide a durable protection of the bipolar plates experiencing pitting corrosion. Therefore it is expected that these coatings will have even less durability when used in PEM electrolyser bipolar plates made of stainless steel.

High-density Ti coatings can be produced using thermal spraying technique [16-19]. Several earlier works attempted producing Ti coatings by thermal spraying; mainly confining to producing porous Ti [20] as dense Ti coatings by these processes was not feasible [21]. Herein we have developed titanium coatings by vacuum plasma spraying (VPS) [22] for stainless bipolar plates of PEM electrolysers. The coatings were evaluated for corrosion protection, in simulated environment (acid medium) of a PEM electrolyser.

1. Experimental approach

Ti coatings were deposited on sandblasted stainless steel (SS) plates (47 x 47 x 1 mm^3) made of Crofer® 22 H by VPS. The substrate was pre-heated up to 250 °C. Several parameters such as type of plasma torch nozzle, powder feed rate, and flow rates of Ar, N_2 and H_2 were systematically varied. The Ti powder (grain size <45 µm) was sprayed at a chamber pressure of 50 mbar to prevent formation of TiO_{2-x}, which reduces the electrical conductivity of the coating. A number of layers of four led to a coating thickness of 54 µm.

The electrochemical measurements were carried out using an Autolab PGSTAT12 Potentiostat/Galvanostat and a three-electrode cell containing about one liter of diluted H_2SO_4 at 24 ºC. The concentration of the acid for the samples with and without post-treatment was 5 x 10^{-3} M and 0.5 M, respectively. Previously to the electrochemical measurements, the electrolyte was saturated for 20 min, with high purity O_2 (Praxair). A platinum wire and a standard hydrogen electrode (SHE) from HydroFlex® were used as counter (CE) and reference electrode (RE), respectively. Samples of coated SS with an active area of 1 cm^2 were prepared. A sample holder was used as a working electrode (WE).

2. Results

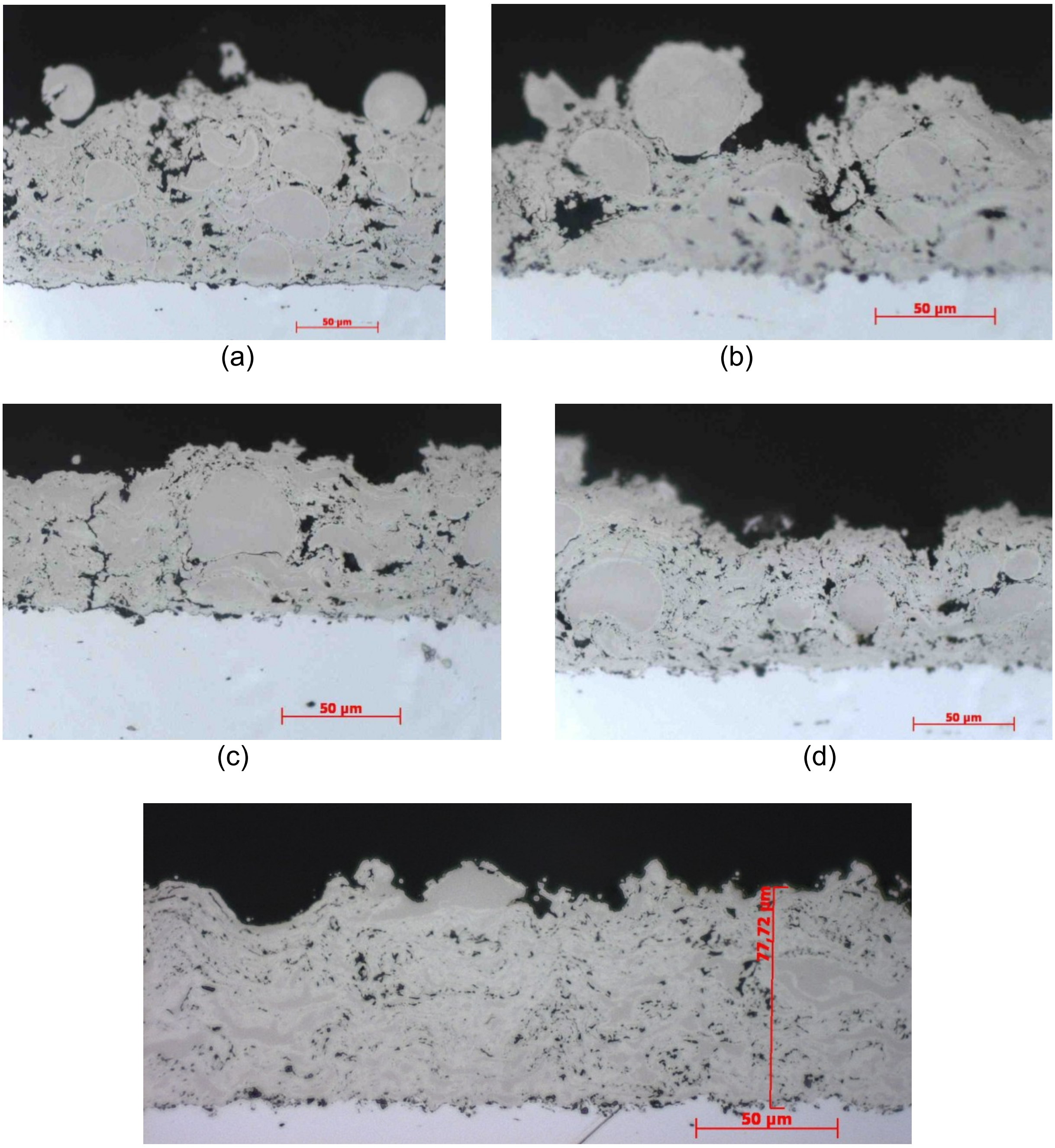
Table 1a groups the parameters that were used to achieve the densest Ti coatings possible. It was established that the leak rate of the coating was inversely proposal to the enthalpy of the plasma jet. Hence for instance, at a constant value of H_2, the coating becomes denser when the current is higher. Dense layers of Ti were produced with high H_2 and low Ar flows. Varying the distance Z between the plasma torch anode and the substrate had only little impact on the porosity of the Ti coatings. The densest coating, deposited with a plasma enthalpy of 21.27 MJ kg^{-1} and had a leak rate of 4.3 mbar l s^{-1}.

Table 1. Deposition parameters of Ti coatings made by VPS technique.

Input					Output
Sample	Powder feeder rate rpm	Plasma enthalpy (h) MJ kg^{-1}	Z mm	V mm s^{-1}	Leak rate mbar l cm^{-2} s^{-1}
CF-29	1.2	9.09	350	600	53
CF-30	0.7	11.1	350	600	117
CF-31	0.7	12.61	350	600	63
CF-32	0.7	14.62	350	600	48
CF-40	0.7	14.60	320	350	8.4
CF-41	0.7	14.62	320	350	12.6
CF-42	0.7	14.65	320	350	88.8
CF-56	0.7	14.6	320	350	8.4
CF-57	0.7	14.66	320	350	10.5
CF-105	0.7	21.27	320	350	4.3

Vessel Pressure:	50 mbar
Anode type:	M3-6mm
Injector:	Internal
Track separation:	10 mm
Number of layers:	8
Substrate temperature:	250 ºC

Figure 1a shows optical microscope images of the Ti coatings on sandblasted SS, deposited by VPS technique using different plasma enthalpies. As can be observed most of the spherical particles of Ti were melted during the deposition, producing a dense Ti coating. This result was more evident when the deposition of coatings was realized with high plasma enthalpies, as it is shown in Figure 1d and 1e. One advantage of the VPS technique is that large plates of stainless steel, having high aspect ratio, can be coated.



(a) (b)

(c) (d)

(e)

Fig. 1. Optical images of Ti coating deposited on stainless steel with different plasma enthalpies: (a) CF-29, (b) CF-31, (c) CF-32, (d) CF-40 and (e) CF-105.

Figure 2b shows the X-ray diffraction (XRD) pattern of the Ti coating deposited with 5 slm of H_2 and 65 slm of Ar (9.09 MJ Kg^{-1} of plasma enthalpy). In fact, all the coatings had a similar XRD pattern. The coatings were thick enough to produce an intense signal that can be recovered from the diffraction pattern of the SS substrate. Practically all the peaks from the Bragg reflections correspond to the hexagonal Ti or α-family of Ti alloys. It was expected that the Ti surface would be not oxidized during the VPS deposition of coatings, as Ar, He and H_2 were used for the deposition process. Two peaks that correspond to deficient oxygen content $TiO_{0.17}$ can be observed at 38° and 52.5° but it is hardly to conclude that these low-intensity reflections correspond to the oxidized surface of Ti.

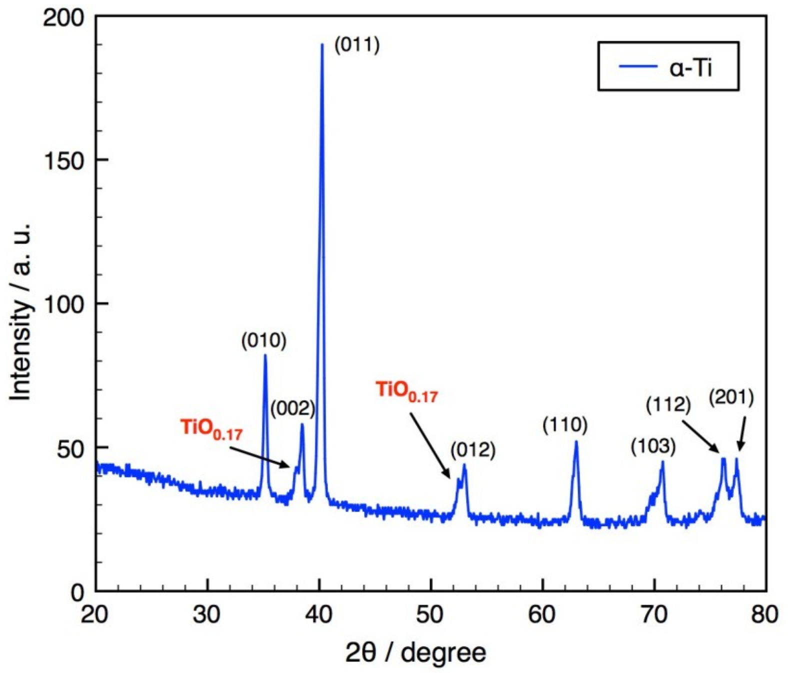
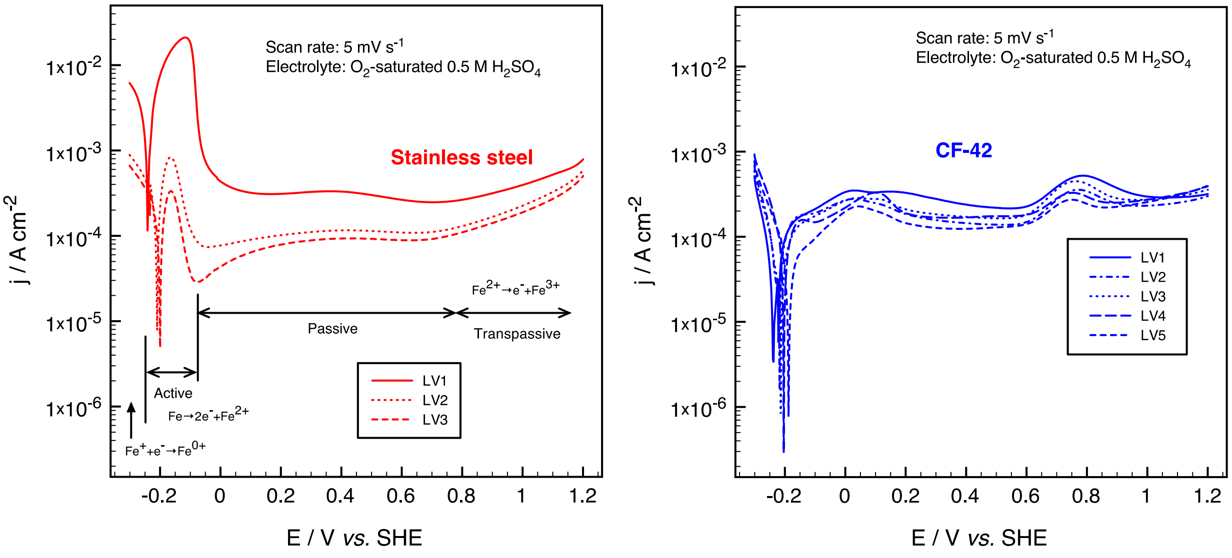


Fig. 2. XRD pattern of the Ti coating deposited using a plasma enthalpy of 9.09 MJ kg^{-1} (sample CF-29).

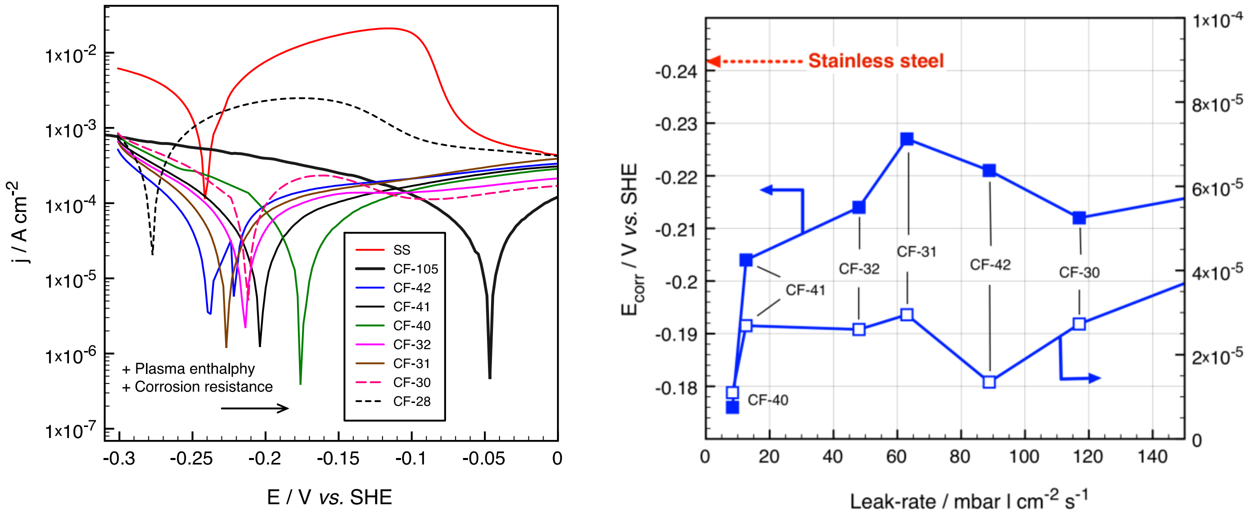
The potentiodynamic polarization curves of the sandblasted SS substrate and the Ti coating deposited with a plasma enthalpy of 14.65 MJ kg^{-1} are shown in Figure 3a and 3b, respectively. Three characteristic regions can be observed on the linear voltammogram of SS, namely the active, passive and trans-passive. This later corresponds to oxidation of Fe^{2+} to Fe^{+3} [23].



(a) (b)

Fig. 3. Potentiodynamic polarization curves of (a) stainless steel and (b) sample CF-42 deposited with a plasma enthalpy of 14.65 MJ kg^{-1}. Measurements were carried out at a scan rate of 5 mV s^{-1} in O_2-saturated 0.5 H_2SO_4, at 24 ºC.

The anodic peak of Fe oxidation and the current density centered at -0.11 V vs. SHE, gradually decreases with the successive scans, namely LV1, LV2, and LV3. This effect is due to the electro-polishing of the SS sample and the constant release of Fe^{2+} and Cr^{3+} into the acid solution. On the contrary, we can observe in Figure 3b that the active zone of oxidation of Fe^0 to Fe^{2+} is inhibited in the coated sample, which is a consequence of the corrosion protection by the Ti coating and decrease of the active surface of the SS substrate.



(a) (b)

Fig. 4. Potentiodynamic polarization curves of Ti coatings produced with different enthalpies. (b) Dependence of the corrosion potential (E_{corr}) and current (I_{corr}) with the leak-rate of the Ti coating. Measurements were carried out at a scan rate of 5 mV s^{-1} in O_2-saturated 0.5 M H_2SO_4, at 24 ºC.

Table 2. Electrochemical parameters of some of the Ti coatings deposited on stainless steel (SS)

Sample	OCV V	E_{corr} (obs) V	E_{corr} (calc) V	i_{corr} A	β_a V dec^{-1}	β_c V dec^{-1}	R_p Ω
SS	-0.05	-0.241	-0.241	6.77E-04	0.034	0.033	0.73
CF-30	0.12	-0.212	-0.214	2.73E-05	0.016	0.03	7.66
CF-31	NA	-0.227	-0.228	2.95E-05	0.049	0.081	58.70
CF-32	0.18	-0.214	-0.212	2.60E-05	0.055	0.061	56.00
CF-40	0.04	-0.176	-0.178	1.10E-05	0.043	0.023	39.40
CF-41	0.01	-0.204	-0.203	2.69E-05	0.064	0.095	97.50
CF-42	0.22	-0.221	-0.233	1.35E-05	0.035	0.039	43.70

E_{corr} (obs):	Measured corrosion potential
E_{corr} (calc):	Calculated corrosion potential
j_{corr}:	Corrosion current density
β_a:	Anodic Tafel slope
β_c:	Cathodic Tafel slope
R_p:	Polarization resistance

Samples of coated SS using different plasma enthalpies were evaluated for corrosion protection in acid medium. Figure 4a shows a zoom-in of the measured polarization curves in the active zone of corrosion. Relevant electrochemical parameters such as the Tafel slopes and polarization resistance were determined and grouped in Table 2. The polarization resistance (R_p) was calculated using the following equation [24]:

$$R_p = \frac{\beta_a \beta_c}{2.3 j_{corr} (\beta_a + \beta_c)} \qquad (1)$$

where $ß_a$, $ß_c$, j_{corr}, and R_p are the Tafel slopes of the anodic and cathodic reactions, the corrosion current density and polarization resistance, respectively. As the active area (geometric) of the samples is 1 cm^2, then $j_{corr} = i_{corr}$.

Figure 4b presents the corrosion potential (E_{corr}) and current (i_{corr}) dependence with the leak rate of the Ti coating. E_{corr} and i_{corr} were determined from the linear voltammograms performed at 24 ºC, in O_2-saturated 0.5 H_2SO_4 with a sweep rate of 5 mV s^{-1}. Coatings with leak-rates of less than 120 mbar showed lower corrosion currents (i_{corr}) and more positive corrosion potentials (E_{corr}) than the SS substrate. As we can observe in Figure 2b the E_{corr} and i_{corr} decrease, as the leak rate is lower, which is directly correlated to the density of the coating. As expected the highest protection for corrosion was provided by the densest coating, which was deposited with 21.27 MJ kg^{-1} of plasma enthalpy. The coatings protect the SS substrate from corrosion and the results obtained from the electrochemical half-cell measurements are in good agreement with the improvement through the variation of VPS parameters.

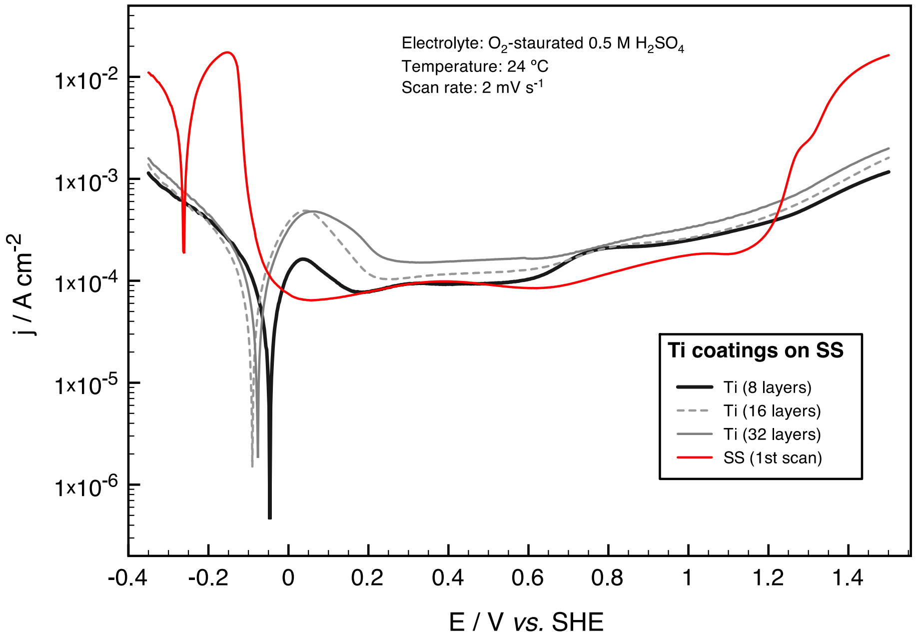


Fig. 3. Potentiodynamic polarization curves of the densest coating (CF-105) deposing 8, 16 and 32 layers of Ti. Measurements were carried out at a scan rate of 2 mV s^{-1} in O_2-saturated 0.5 H_2SO_4, at 24 ºC.

To try increasing the corrosion protection, more than 8 layers of the Ti where deposited on the sandblasted SS substrate. The potentiodynamic polarization curves of 8, 16 and 32 layers of Ti deposited with 21.27 MJ kg^{-1} of plasma enthalpy are shown in Figure 3. We observed that increasing the number of layer of Ti does not provide more protection against corrosion, but totally the contrary. Further electrochemical characterization has to be carried out to explain this negative effect. However, it is an advantage that a Ti coating of 77.8 µm thick, see Figure 1e, already provides a reasonable protection against corrosion in acid medium. In this sense, the Ti coatings deposited by VPS technique are promising for developing SS bipolar plates of PEM electrolysers.

3. Conclusions

We have developed conductive and corrosion resistant coatings made of Ti for PEM electrolyser bipolar plates. Vacuum plasma spraying technique was used and the densest Ti coating was deposited on stainless steel, using 21.27 MJ of plasma enthalpy. The coatings protect the stainless steel substrate from corrosion and allow reducing the production costs of PEM electrolyser bipolar plates that are currently being used. Moreover, the deposition technique used for producing the coating can be easily set up for industrial production of bipolar plates with large surface.

Acknowledgments

A.S. Gago thanks the Deutscher Akademischer Austauschdienst (DAAD) for financial support, scholarship A/12/91767.

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