

Sandblasting effect on performance and durability of Ti based $\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode in acidic solutions

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Abstract

The effect of applying sandblasting during pretreatment while preparing titanium based $\text{IrO}_2\text{-Ta}_2\text{O}_5$ anodes by the conventional method was investigated.

It was observed that sandblasting influences the surface morphology both before and after coating as deeper and smaller etching pits are obtained on the substrate before coating process and rougher surface is obtained after coating. As a result larger outer electrochemical active surface area (ECSA) is obtained on the anodes with sandblasting, which was determined based on cyclic voltammetry, whereas the inner ECSA is independent of the pretreatment. The polarization measurements in a quasi-steady state reveal that sandblasting has slight influence on the catalytic activity. Accelerated lifetime tests were carried out in acidic $0.9 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution ($\text{pH} = 2$) at a current density of 5 kA m^{-2} under galvanostatic conditions. It shows that sandblasting would shorten the lifetime of the anode due to oxidation of the titanium substrate. This might be because of the shorter distance between the lowest spot of the outer coating surface and the highest spot of the outer substrate of the anode after applying sandblasting in titanium substrate pretreatment.

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1. Introduction

IrO₂-Ta₂O₅ coated titanium has been developed for the anodes to be used in the electrochemical process where oxygen is evolved, and named dimensional stable anodes (DSAs) [1]. Benefited by its physical properties, this mixed metal oxide coating implies lower oxygen overpotential for the OER than conventional anode such as lead alloys [2, 3, 4]. Besides, this inert anode has good ceramic-electrocatalytic stability against the corrosion and offers long service life than conventional ones in the aqueous sulfate solution and oxidative medium [2, 5]. Therefore it has been diversely employed in industry such as electro-galvanizing of steel, aqueous metal electrowinning, and electroplating industry [6].

There are several methods to produce DSA, such as thermal decomposition, electro-deposition, Sol-Gel, Pechini [7, 8, 9]. The most common way is thermal decomposition technique, where the oxide coating is prepared by decomposition of the respective precursor salts dissolved in an organic or aqueous solution. This technique is widely used in industry due to its low cost and simple operation. However, DSA made by the thermal decomposition still suffers from degradation in industry especially at low pH, at moderate temperature in the electrolyte, and at high current density [10].

Several studies have been done on oxide mixtures since the electrode preparation procedure is significantly affected by the electrode material. A comprehensive study of coating catalysts based on nine different binary oxides was performed by Comminellis and Vercesi [11], where it was reported that the coating with 70 mol% IrO₂ - 30 mol% Ta₂O₅ as catalysts on Ti substrate indicates by far the best electrocatalytic activity towards the OER and long service life in sulfate solution. This conclusion has also been suggested in later works [12, 13, 14, 15]. Besides, ternary and multiple oxides have also been considered as other options in DSA catalyst design for OER [16, 17, 18, 19]. Although

some of those exhibit great performance on OER activity, the application of those DSAs is mostly in laboratory scale due to the uncertain service life and
30 complicated operational environment of DSA in industrial environment.

Except for the choice of the coating catalyst, the microstructure of the coating is also having significant influence on the electrocatalytic properties of the DSAs. In order to achieve better catalytic activity and durability of the titanium based $\text{IrO}_2\text{-Ta}_2\text{O}_5$ DSA under the aggressive operation conditions in
35 real production, many other efforts have been made in past decades through optimizing the preparation procedure of the anode, in terms of calcination temperature, coating procedure, Ir loading amount, adhesion layer, and substrate pretreatment [7, 8, 12, 20, 21, 22, 23, 24].

Yan and co-workers have studied the performance of DSA with different
40 surface treated titanium substrates [21]. Compared to the oxalic acid etching, the anodes with hydrogen treated titanium showed greater improvement on catalytic activity, but not on lifetime and the lifetime were even shorter than the other due to the preferred orientation plane of IrO_2 component. Meanwhile, the anode without its substrate treated presented the worst performance both
45 on catalytic activity and lifetime. Furthermore, it has been reported that etching of titanium in the NH_4HF_2 -based solution can give a long lifetime and a relatively high voltammetric charge, which has been compared with mechanical grinding and etching in a 50 vol.% HCl solution for the coating with an Ir/Ta molar ratio of 7:3 [22]. The author concluded that the lifetime of the anode
50 is strongly affected by the Ti pretreatment, whereas the catalytic activity is mainly depending on the thermal decomposition process. Apparently, substrate pretreatment during anode preparation has important impact on the anodes properties, both when using mechanical or chemical method.

Besides chemical pretreatments mentioned above, sandblasting has been
55 commonly used as the initial step in substrate pretreatment on fresh titanium substrate. For instance, most studies cited above include sandblasting for titanium pretreatment. But none of them has discussed the influence of sandblasting rather than removing the titanium oxide and increasing surface roughness.

Studies regarding the effect of substrate pretreatment such as sandblasting on
60 this type of anode are very limited in the literature. Although in the work of
Huang et al. [22], it is discussed that Al_2O_3 particles were found to be em-
bedded into the Ti substrate after mechanical polishing which resulted in the
coating layer being weakly bonded to the Ti substrate, and this finally leads to
relatively short lifetime. No further work has been done to reveal the intrinsic
65 reason for this phenomenon. Therefore, it is worth to make more contribution
for deeper understanding of the sandblasting effect on the anode.

In this work, titanium substrate was pretreated by sandblasting followed by
etching, and after that the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ coated anode was prepared using con-
ventional thermal decomposition method. Another anode was prepared at the
70 same time with identical coating but on the substrate without sandblasting. The
effect of sandblasting on the anode has been investigated by comparing the per-
formance between the anodes, in terms of surface morphology, microstructure,
electrochemical active surface area (ECSA), and accelerated lifetime. In addi-
tion, the intrinsic impact of sandblasting on this type of anodes was revealed by
75 the study on the deactivation of the anodes, in which a factor as "d-value" was
proposed. We believe that taking the d-value into consideration while preparing
the anode will help to further increase both the catalytic activity and lifetime
of this type of DSA.

2. Experimental methods

80 2.1. Anode preparation

The DSA samples were prepared by *Permascand AB of Sweden*. Four pure
titanium plates were used as substrates for producing the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode.
The plates were divided into two groups for comparison. One group was firstly
sandblasted with Al_2O_3 powder and then etched with a mixed in-house acid
85 solution in order to get a proper rough surface, whereas the other group was
only etched. It should be mentioned that the etching process was similar for
each sample. A thin interlayer was then formed onto the pretreated substrates to

enhance the adhesion between coating and substrate and improve the resistance to substrate corrosion. The in-house precursor solution with metal weight ratio
90 Ir : Ta of 8 : 2 was then applied onto the coated titanium by using a brush, five and ten times respectively for those plates in each group. After each brushing, 15 minutes followed by drying was done at room temperature. Subsequent calcination was carried out in ambient air at a fixed temperature for 12 minutes. Finally, the plates were cut into circular samples for the following tests.

95 2.2. *Ex-Situ examination*

Zeiss Supra scanning electron microscopy (SEM) and *Agilent 5500* AFM/STM microscope were utilized to observe the surface morphology and surface roughness of the samples. The chemical composition of the prepared anodes were analyzed using energy dispersive spectroscopy (EDS). The phase composition
100 and the crystalline structure of the anodes were studied via x-ray diffraction (XRD) on *Bruker AXS D8 Advance*. The diffraction data were collected by varying the 2θ angle from 10° to 80° with an increment of 0.02° with Cu $K\alpha$ radiation. In addition, grazing incident XRD (GIXRD) was also carried out with grazing incident angle at 3° in order to mitigate the diffraction from the
105 substrate while collecting diffraction data of the coating.

2.3. *Electrochemical characterization*

The OER performance of the prepared anodes was carried out in a typical three electrode cell, where each anode was used as working electrode and a platinum wire was used as counter electrode. A reversible hydrogen electrode
110 (RHE) was used as the reference electrode. In addition, a Teflon sample holder was utilized for the working electrode to expose 1 cm^2 of the anode during the measurements. All tests were performed in $0.9\text{ M H}_2\text{SO}_4$ aqueous solution at 60°C . The electrolyte was de-aerated with purified argon gas purging for 5 - 10 minutes. According to the research from [10] that the active surface area of
115 the anode coating might be changed under the destructive gas evolution due to its porous nature, the valid data should be recorded after initialization of the

anodes during the measurements. Thereby the anodes were scanned at 100 mV s⁻¹ for 100-200 potential cycles.

Cyclic voltammetry (CV) measurements were performed between 0.15 V and 1.4 V *vs.* RHE at different sweep rates (5 - 500 mV s⁻¹) to determine ECDSA. A steady state polarization was conducted at a sweep rate of 5 mV min⁻¹ from 1.4 V for the purpose of revealing the electrocatalytic activity for the anodes. The IR drop was corrected by the electrolyte resistance, which was measured using electrochemical impedance spectroscopy (EIS). Ac amplitude of 10 mV/rms from 0.01 Hz to 100 kHz and with 10 points per decade at 1.5 V were selected as EIS condition.

2.4. Accelerated lifetime studies

The actual service life of this type of anode could be several years, so that the accelerated lifetime tests (ALT) were implemented in this work to investigate the stability of the anodes. The ALT was carried out in Na₂SO₄ solution (pH = 2) at a current density of 5 kA m⁻² under galvanostatic conditions in a two-electrode cell. The temperature for the electrolyte was maintained at 60 °C. The anodes was considered to be deactivated when the cell voltage reached 15 V since the potential of the anodes was monitored during ALT. The accelerated lifetime of the anodes was then recorded at the time when deactivation occurs. X-ray fluorescence (XRF) was utilized to measure the Ir losses of the coatings during ALT.

3. Results and discussion

3.1. Surface morphology and microstructure

Figure 1 displays the surface morphology of the titanium substrate before and after different pretreatment. The primary surface of the titanium shows uneven roughness, as can be seen in Figure 1 (a). The roughness then has been changed after acidic etching, which shows etching pits with comparable uniform distribution on the surface, as shown in Figure 1 (b). Unlike acidic

145 etching, the titanium substrate is quite rough in macro scale after sandblasting. Figure 1 (c) shows that many fragments with irregular shape were induced on the surface. Due to the weak adhesion of the fragments on the surface, some fragments would be washed away in the beginning of subsequent etching. The surface then (Figure 1 (d)) shows etching pits which are similar but smaller as
150 compared with the substrate pretreated only by acidic etching. This is because of the rest of fragments benefit from the continuous etching by the dangling bonds which are produced during sandblasting [25]. AFM observation in Figure 2 reveals that there is a larger variation of height difference on the surface pretreated by acidic etching combined with sandblasting than the one which
155 was only etched. This indicates that the deeper etching pits were obtained on the surface pretreated by acidic etching combined with sandblasting.

The surface morphology of the coating on pretreated titanium substrates was examined. As shown in Figure 3, the coating surfaces all present typical "mud crack" morphology. Cracks are surrounded by relatively flat area with
160 some aggregates. The aggregates are IrO_2 crystalline as we reported in the previous study, as well as the smaller crystals which formed inside cracks [24]. The surface morphology of the coatings with five layers are shown in Figure 3 (a) - (d). Cracks on these coating surface display similar morphology. Besides, it seems that more cracks were induced on the coating surface while applying
165 sandblasting before etching in pretreatment. However, the IrO_2 aggregates on the coating surface present different morphology although the Ir loading is the same. Comparably larger IrO_2 crystals formed insides cracks of the coating surface on the pretreated titanium without sandblasting, and smaller IrO_2 crystals formed in the flat area of the coating surface. While increasing the number of
170 coating layers up to 10, the IrO_2 crystals are all growing larger as can be seen in Figure 3 (e) - (h). This could be attributed to the IrO_2 ripening mechanism during thermal decomposition [12]. As another result, the coating surface of the anodes becomes flatter than the one with five layers. Moreover, the cracks become wider, and the cracks are much longer in the coating with 10 layers than
175 that with five layers on the substrate without sandblasting.

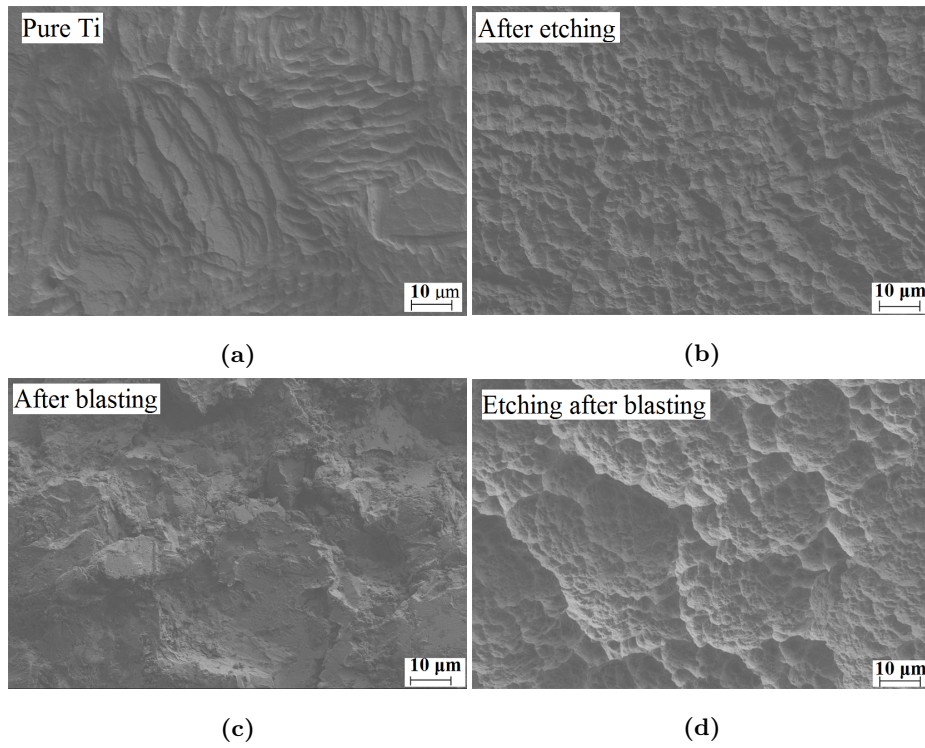


Figure 1: SEM images of titanium substrate before and after different pretreatments (a) pure Ti substrate (b) etched Ti substrate (c) sandblasted Ti substrate (d) sandblasted then etched Ti substrate

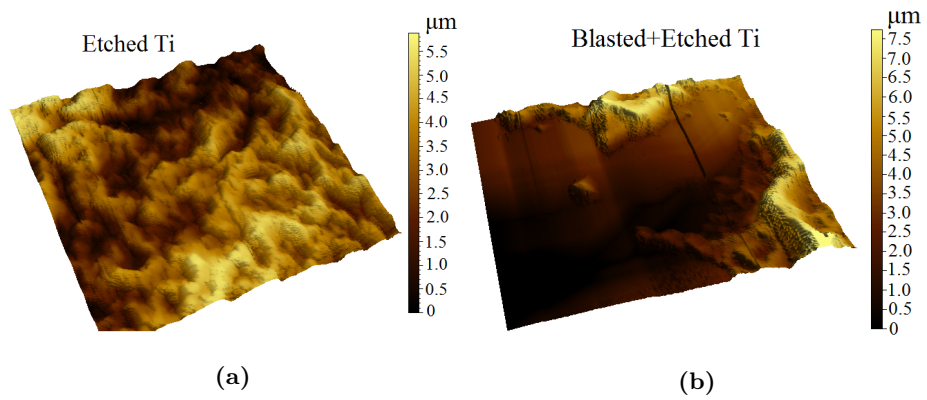


Figure 2: AFM images of titanium substrates with different pretreatments (a) etched Ti substrate (b) sandblasting combined etched Ti substrate

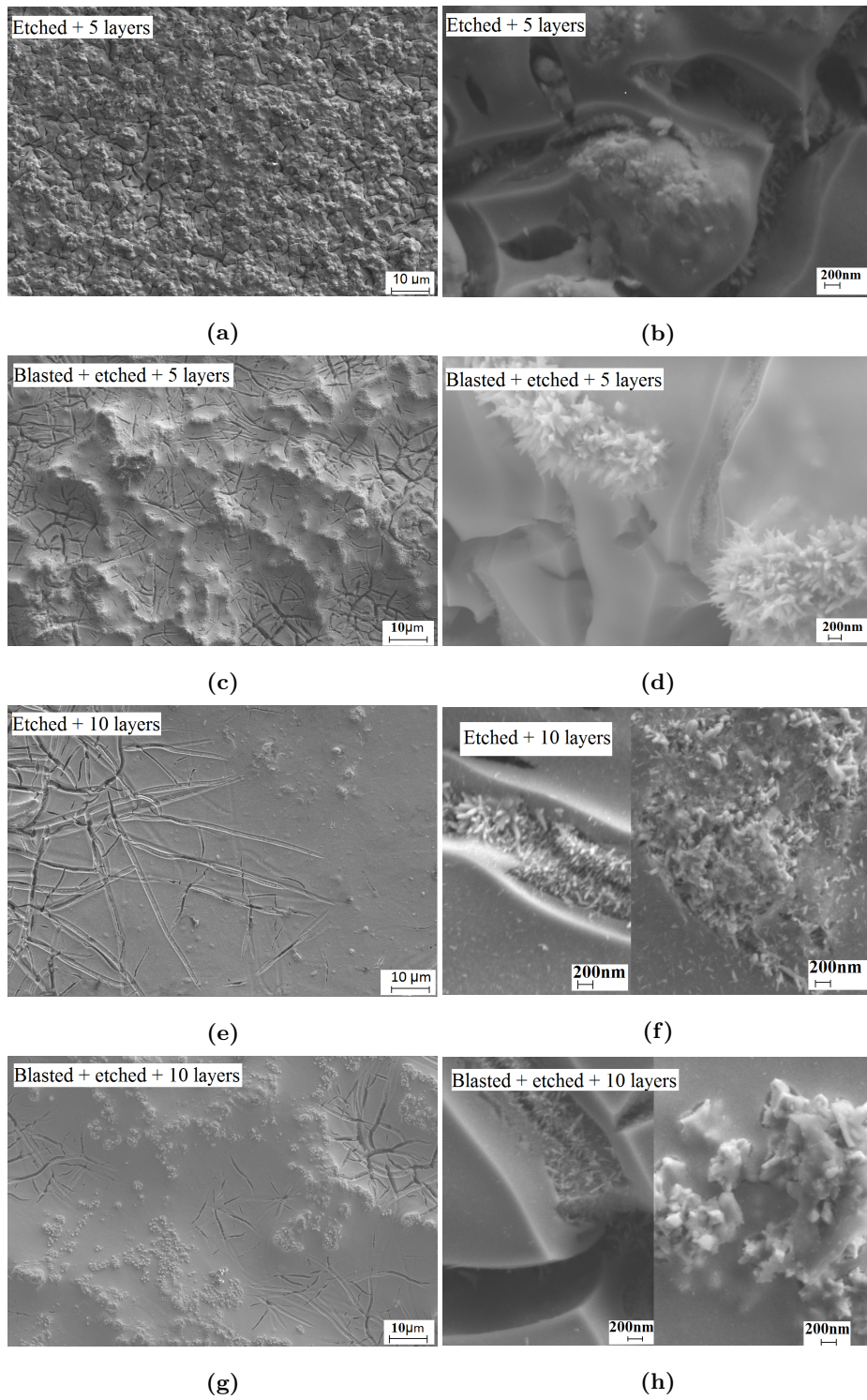


Figure 3: Surface morphology of all anodes (a) & (b) etched titanium substrate with 5 coating layers, (c) & (d) sandblasted and etched titanium substrate with 5 coating layers, (e) & (f) etched titanium substrate with 10 coating layers, (g) & (h) sandblasted and etched titanium substrate with 10 coating layers

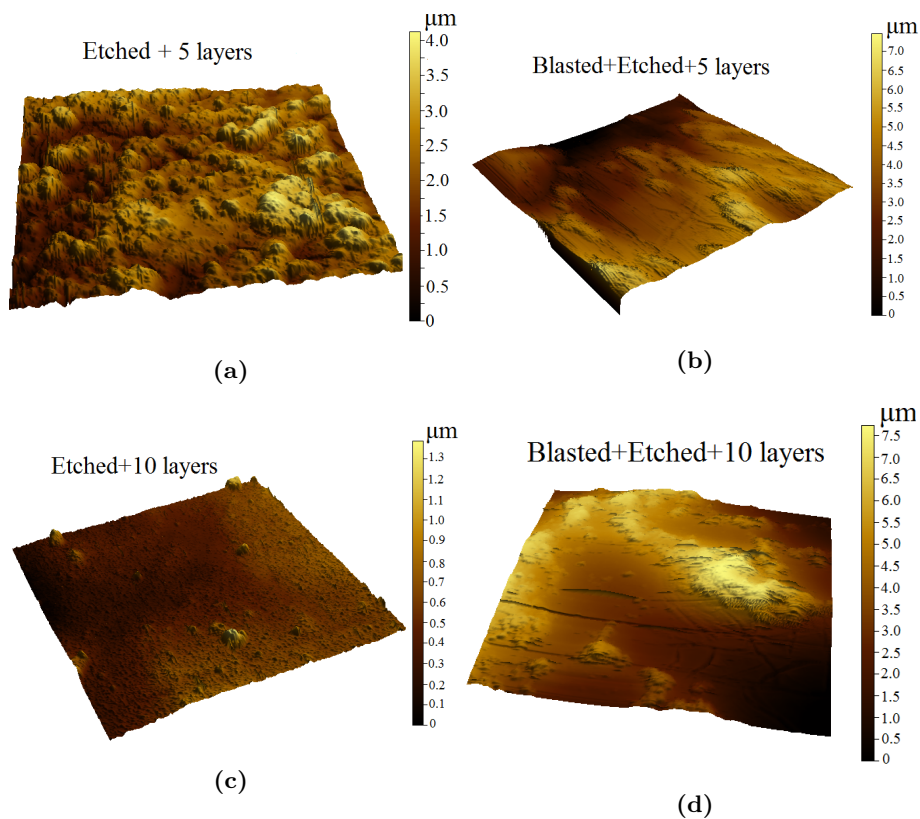


Figure 4: AFM graphs of anodes coated with different amount of layers on different pretreated titanium substrate (the area of all graphs are $50 \mu m \times 50 \mu m$)

The morphology of the coating surface was also observed by AFM, as shown in Figure 4. It demonstrates the variation of surface height for all four samples. For the coating on the etched substrate, the surface roughness becomes much smaller after increasing the coating layers from five to ten. For the coating on the substrate pretreated by etching combined with sandblasting, it is hard to reveal the roughness difference by AFM. Nevertheless, coating on the substrate with sandblasting has higher roughness than the one without sandblasting. Apparently sandblasting has a significant influence on the morphology of coating surface since it changed the morphology of the substrate initially.

The X-ray diffraction patterns of all samples are shown in Figure 5. The

intensity difference of Ti characteristic peaks after pretreating indicates the composition change of the titanium phase on the surface. This is attributed to the in-house made etchant which selectively corrodes the microstructural features of the titanium surface even though the primary titanium crystal of the substrate
190 has a preferred crystal orientation. Besides, sandblasting would also change the surface composition as it generates granulation on the surface. It should be mentioned here that some Al_2O_3 crystals were residual after sandblasting which then would be removed during subsequent etching, as can be seen in the related XRD characteristic peaks of Al_2O_3 phase in Figure 5. Regarding the
195 full width at half maximum (FWHM) of Ti patterns of the pretreated samples, the average titanium grain size on the surface area of the one with sandblasting is smaller than the one without. This is consistent with the results from SEM observation.

The IrO_2 phase is observed with (110), (101), (200) and (211) planes in the
200 anodes. There is no Ta_2O_5 related diffraction peaks being captured since the Ta_2O_5 phase is amorphous in this case [26]. However, $\text{Ir}(\text{Ta})\text{O}_2$ solid solution could be formed in the binary compound which will induce lattice strain into the coating layer [24]. As a result the observed background is quite broad and therefore it is difficult to determine the crystallinity of IrO_2 based on XRD patterns.
205 Nevertheless, it can be predicted that the average grain size of IrO_2 crystals is larger in 10 layers coating than in five layers coatings regarding the FWHM of related IrO_2 peaks. This was stated before in surface morphology discussion so that the crystallinity should be higher in the coating with 10 layers regarding the crystallization process [12]. Furthermore, one characteristic peak of titanium located at 35.1° is detected only in the sample with sandblasting after coating.
210 This is due to the composition change in the surface of titanium substrate after pretreatment, as a result, less (100) titanium planes were obtained by using only etching. This would affect the crystallization of IrO_2 crystal during thermal decomposition, and then the coating surface presents different surface morphology
215 even with the same coating, so that the composition of the multicrystalline IrO_2 phase in the coating could be different.

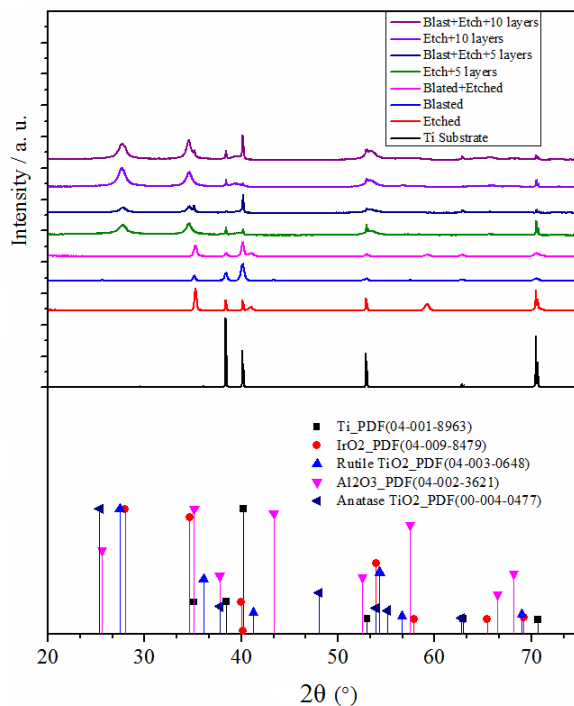


Figure 5: XRD patterns of titanium substrate before and after pretreatments, and after coated with different amount of coating layers

3.2. Electrochemical properties analysis

Cyclic voltammograms were obtained on the prepared anodes to evaluate the behavior in supporting electrolyte, as shown in Figure 6 (a). The anodic and cathodic progress presented as reversibility on the curves because of the pseudo-capacitor properties of this type of electrode. The broad redox peaks correspond to the $\text{Ir}^{3+}/\text{Ir}^{4+}$ surface transition as reported in the work of Moradi and Dehghanian [27]. The increase in anodic charge at the same potential value among the samples is due to the enhancement of the surface roughness by using sandblasting in pretreatment and/or the increase of the amount of coating layers. Figure 6 (b) shows the estimated values of the ECSA (or the number of active sites) of the anodes based on extrapolation of the voltammetric charge in the potential range between the hydrogen evolution reaction and the OER

as suggested in the work of Burke and Murphy [28]. More detailed information
230 regarding the voltammetric charge calculation could be found in our previous
study [24] and Comninellis's work [11]. It is found that the charge value is
proportional to the amount of coating layers. This indicates that sandblasting
favors the increase of ECSA, as well as the increase of coating thickness. Ap-
parently the increased loading of the coating will offer more active sites on the
235 surface, and so does combining sandblasting to etching in pretreatment. This
is in agreement with Krýsa's work [12].

It was found that sandblasting only affects the value of outer charge and
the inner charge is only dependent on the loading of the coating in this case.
Regarding the basis of electrochemical "true" surfaces represented by anodic
240 charge [11, 28], the number of active sites is strongly dependent on the coating
composition and surface morphology. Thereby the ECSA is mainly confined
by the surface morphology in the current work for identical composition for all
coatings. As mentioned above larger IrO₂ crystals formed in the flat area on
the coating surface when applying sandblasting in pretreatment. Apparently
245 those needle-like IrO₂ crystals will expose more Ir centers to the electrolyte
for oxidation during the anodic process. Hereby sandblasting is beneficial for
obtaining larger ECSA as more active sites have been offered, but this only
favors the outer part of the ECSA.

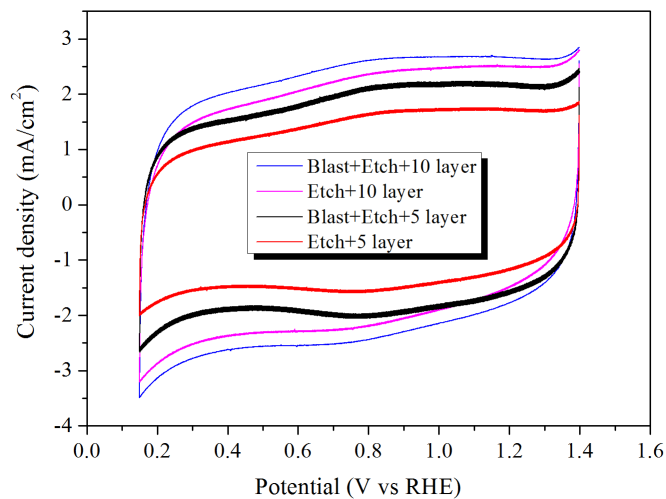
Compared to the outer surface, the inner surface is less accessible for proton
250 exchange, and here the inner surface is referred to as the part of the surface
such as narrow pores, deep inside cracks, crystal defects, and grain boundaries
[24]. The morphology factor (φ) was calculated as can be seen in the insert
table in Figure 6 (b), which describes the fraction of the region that is more
difficult to access on the electrode surface [29]. Although the integrated charge
255 value as inner shows that more active sites were offered on the inner surface of
10 layers coating, a less accessible region exists in the coating surface with 10
layers. This could be attributed to a much flatter area formed on the surface
with increase of Ir loading amount, so that less deep inside cracks are formed
in the coating with 10 layers. It might also be influenced by crystal defects and

260 crystallinity of IrO₂, but in this case it is not possible to conclude. However, it can be manifested that only Ir loading will affect the inner part of ECSA.

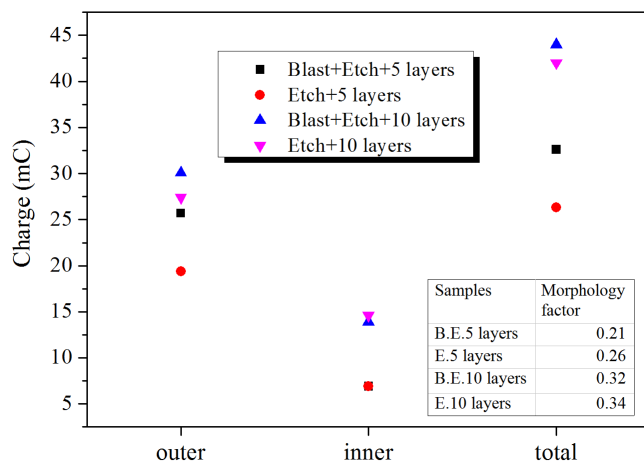
The steady-state polarization curves of all anodes are presented in Figure 7. As can be seen, the curves are quite close to each other. This indicates the catalytic activity of all anodes is comparable to each other. It is observed that 265 employing sandblasting in titanium pretreatments can improve the catalytic activity but in a very limited range. Additionally, this improvement would be weakened while increasing the coating loading from 5 to 10 layers. Regarding the surface morphology of the anodes, which are different to each other, and which determines the ECSA, so that eliminating the influence of ECSA on catalytic 270 activity is necessary for further investigation. Thereby, the polarization curves are normalized with respect to outer charge, as shown in Figure 7 (b).

Interestingly, the anodes present similar catalytic activity on per unit ECSA. This implies that the catalytic activity of the catalyst itself is independent of pretreatment and coating loading. The slight difference can be ascribed to the 275 difference of IrO₂ crystallinity and its phase composition among the samples, as we reported in previous work [24]. Therefore, applying sandblasting in substrate pretreatment will not benefit to the catalytic activity of the catalyst itself in this case.

Moreover, two Tafel slopes have been found on all anodes, and they are approximately 50 mV dec⁻¹ at low current densities and 120 mV dec⁻¹ at high 280 current densities. This is a general phenomenon for OER on this type of electrode and in agreement with another work [30]. Experimentally, increase in Tafel slope with applied potential could be a result of a reduction in the effective electrode surface area with increasing gas evolution at the higher applied 285 potentials [10]. The similar value of Tafel slope for all anodes reveals that neither sandblasting nor coating loading will affect the kinetics of OER on this specific type of anode in this case.

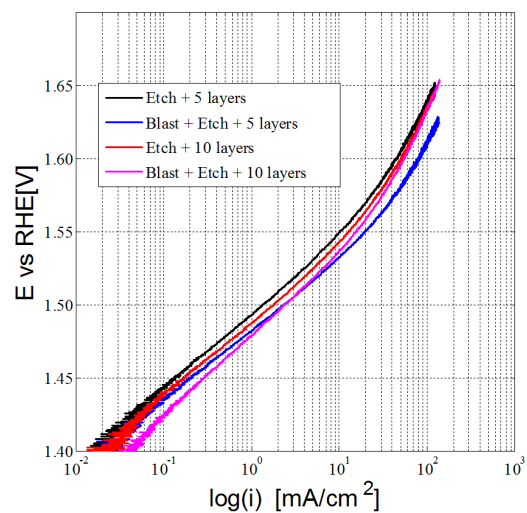


(a)

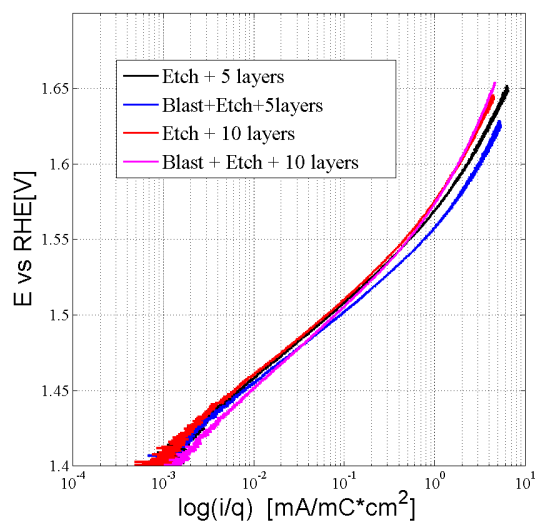


(b)

Figure 6: (a) Stabilized cyclic voltammograms of different samples, the scan rate is 50 mV s^{-1} and (b) voltammetric charge calculated by integration and extrapolating of CV curves



(a)



(b)

Figure 7: (a) IR compensated polarization curves of different anodes, at scan rate of 5 mV min^{-1} and (b) Normalized polarization curves on different anodes with respect to outer charge, which gives a measure of the electrocatalytic activity per unit active surface area

3.3. Accelerated lifetime test

In order to determine the effect of sandblasting on the stability of the anode, accelerated lifetime tests have been carried out. The Ir content of the anode has been measured over time during the test. Figure 8 shows the results of the tests and the measurements. The lifetime value of the anode without sandblasting is approximately 2550 hours, whereas the lifetime value of the anode with sandblasting only lasts approximately 1600 hours. This indicates that applying sandblasting in substrate pretreatments will shorten the lifetime even though it favors the increase of ECSA and catalytic activity per unit catalyst. It has also been found that the anode with sandblasting still has about 94 wt% iridium left in the coating when the anode ends up at 15 V as a raised anode potential, whereas the anode without sandblasting only have 18 wt% iridium in the coating. The values of Ir content change over time indicate that the Ir loss rate for these two anodes are more or less the same until one ends up firstly and which is approximately 9.6×10^{-4} wt% per day. This is because their catalytic activity is similar at high current densities as seen in Figure 7(a). According to the proposed deactivation mechanism of this type anode in acidic solution, the deactivation happened by passing three stages: "active", "stable", and "de-active", in which (a) part of coating such as superficial agglomerates is lost by erosion under the attack of intense oxygen evolution in the initial stage of electrolysis, (b) then the coating suffers under a steady state corrosion for a long period, and as a result the Ir content decreases slowly, (c) the remaining part of the coating begins to lose metallic conductivity and shows very poor electro-catalytic activity with obvious increase of anode potential, and as a result the Ir content decreases rapidly [31, 32]. It has also been concluded in those studies that Ir dissolution dominates the loss of iridium in "active" and "stable" stages, and peeling off would take place in "de-active" stage as a result of the oxidation of Ti substrate.

According to the curves of the decrease of Ir content over time in Figure 8, it is difficult to determine the "active" stage as there is no observed Ir content drop in the beginning. This "active" stage might exist in a very short period or

possibly does not exist at all in this case. But the curves meet a "stable" stage
 320 as it can be seen that the referred Ir loss of both anodes in 1500 hours is less
 than 10 wt%. Moreover, there is no obvious "de-active" stage for the anode with
 sandblasting as the anode ended after 1500 hours. This implies the anode with
 sandblasting might be actually deactivated in "stable" stage. Alternatively, the
 "de-active" stage is not always accompanied with a rapid Ir loss. Apparently,
 325 not all anodes will finally deactivate by passing these three stages.

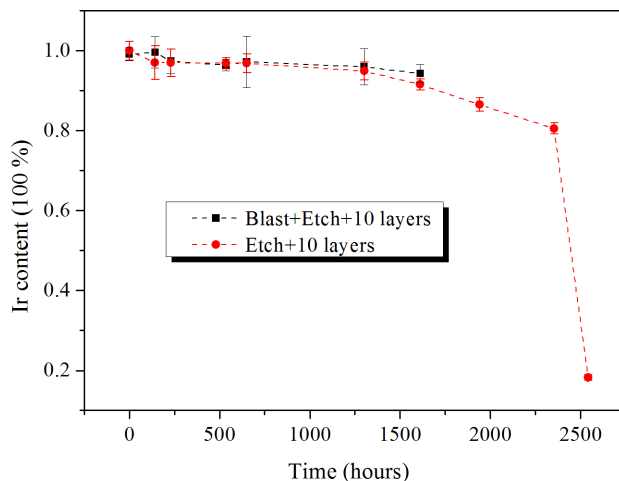


Figure 8: Iridium content versus time during accelerated lifetime test of the 10 layers coating pretreated by different procedures

3.4. Deactivation analysis

In order to find out what causes the deactivation of the anodes, the anode surface after ALT have been investigated by using SEM combined with EDS. As can be seen in Figure 9, parts of the coating have peeled off after ALT on both
 330 anodes. More coating peeled off on the anode without sandblasting, which is consistent with Ir loss results. The morphology of residual coating on the anode shows almost the same morphology as for a prepared fresh anode, especially the one with sandblasting. Besides, it is easy to see the coating as layers over layers

Table 1: Surface composition by EDS analysis in wt%

Area	O	Ta	Ir	Ti
A1	24.5	-	-	75.3
A2	17.7	20 30	50 60	1.8
A3	18.8	20 30	50 60	1.5
A4	34.6	-	-	63.8

in the edge of adjacent area between the residual coating and the rest. And it
335 shows with more sharpness in the edge of the anode with sandblasting than the
other, which can be attributed to the Ir dissolution. As mentioned above, the
Ir dissolution happened continuously during the whole ALT, the morphology of
the adjacent area with less sharpness indicates more Ir dissolution.

The related surface composition has been analyzed based on EDS analysis
340 in four different regions, which are A1 - A4 in Figure 9, as presented in Table 1.
Because of the composition is referring to commercial anodes, it is not possible
to give the specific values for iridium and tantalum, so that the amount of
those two elements are given within a range. It can be seen that no iridium
and tantalum are detected in A1 and A4, which indicates that the coating
345 was detached from the substrate as small whole parts instead of layer by layer
during ALT. The substrate would be directly exposed to electrolyte while the
detachment happens. Meanwhile, an increase on the amount of oxygen element
has been observed. As a result, oxidation of Ti substrate could happen.

In Figure 10, the anatase TiO_2 phase has been found on both deactivated
350 anodes based on XRD investigation. It confirms the oxidation of the substrate
during ALT as we predicted. Once this oxidation happens, the contact resistance
would be built up on the interface between the coating and the substrate, which
causes a massive potential loss and finally increased the anode potential. This is
different compared to Huang et al. [22], Al_2O_3 has no influence on accelerated
355 lifetime in our case. Although it has been detected right after sandblasting, no

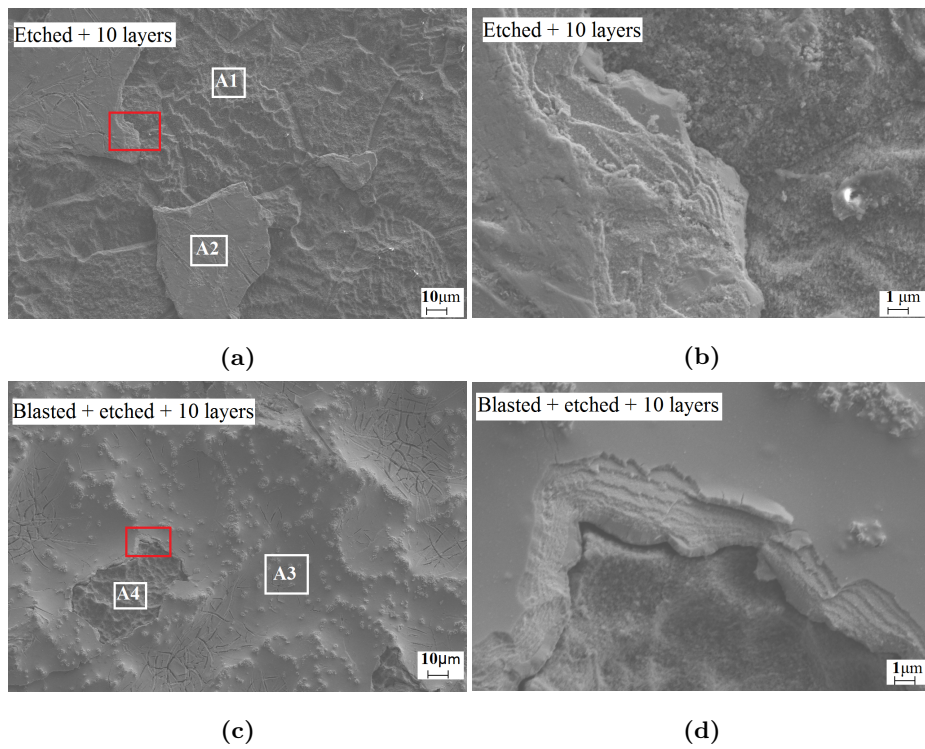


Figure 9: SEM images of deactivated anodes (a) etched titanium substrate with 10 coating layers, (b) megascopic area in the red square of (a), (c) sandblasted then etched titanium substrate with 10 coating layers, and (d) megascopic area in the red square of (c)

Al_2O_3 phase was detected in the coatings on sandblasted substrate.

Regarding the oxidation mechanism of titanium substrate in the report of Hu et al. [31], the electrolyte penetrated the coating all the way down to the substrate during ALT, and then oxidation of substrate happened due to the OER. Combined with the simultaneous Ir dissolution, the oxidation extended to the adjacent substrate and a thin oxide film formed. Normally this process happens fast and the anode potential will be raised rapidly. As a result the formed oxide layer becomes thicker, and under the intensive gas evolution the spalling of the coating takes place then result in a large amount decrease of Ir content in a short time, as shown in Figure 8. Apparently the penetration ability of the electrolyte down to the substrate is easier through the coating on the sandblasted substrate. Besides, the approached electrolyte into the area between coating and substrate is also faster on the anode with sandblasting. Hereby, the substrate oxidation is easier and faster on the anode with sandblasting. This is why the edge of the coating in the adjacent area of deactivated anode presented different sharpness regarding the longer the surface is suffering in the electrolyte under ALT the more Ir dissolves.

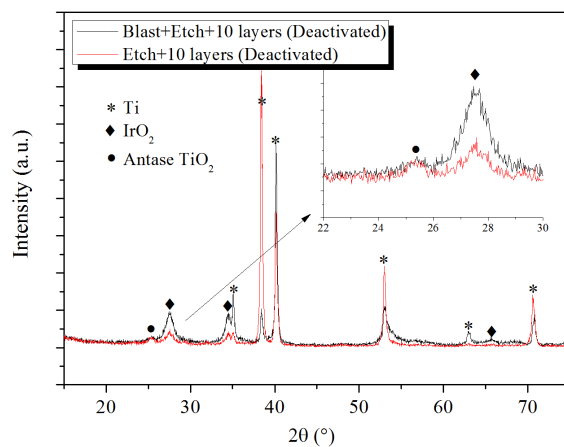


Figure 10: XRD patterns of deactivated anodes pretreated with different method

A schematic diagram has been proposed to illustrate the influence of applying sandblasting on the durability of the anode, as shown in Figure 11. Initially sandblasting induces more roughness on the surface of titanium substrate after pretreatment, which gives height difference (as $h1 < h2$) to the top level of the titanium substrate compared to the one without applying sandblasting. As a result different top levels were obtained after loading the same amount of identical coating (as $h3 < h4$). This is why it shows difference on the surface morphology, and is essentially attributed to the influence of sandblasting on the crystallization process of IrO_2 phase during thermal decomposition. Note that these two top surfaces are not parallel to each other regarding the coating formation process. Besides, regarding that the inner charge is the same while the Ir loading is the same, the porosity of the coating should be same since it is independent of the pretreatment. Therefore, the area between the "top level" on these two samples should be same, which indicates the variation of the distance (*d-value*) between the lowest spot of the outer coating surface and the highest spot of the outer substrate (as $d1 > d2$).

Due to the porous structure of the coating in micro scale, adsorption of OH intermediates will also take place in inside of the coating by water molecules diffusion through those micro pores, although most of the adsorption of intermediates takes place on the outer surface of the coating [10]. Once OER started on the interface between the substrate and the coating, the coating would start to lose mechanical stability rapidly because of oxidation of the titanium substrate [32]. Therefore, $d1 > d2$ implies that the travel distance of OH intermediates down to substrate surface is comparably shorter in the coating on sandblasted substrate, and thus the deactivation of the anode with sandblasting in this case happens earlier than the other. Accordingly, we believe that it is possible to make improvement on both the catalytic activity and the stability of the anodes in industrial application by obtaining a proper *d-value* while applying sandblasting into pretreatment of Ti substrate.

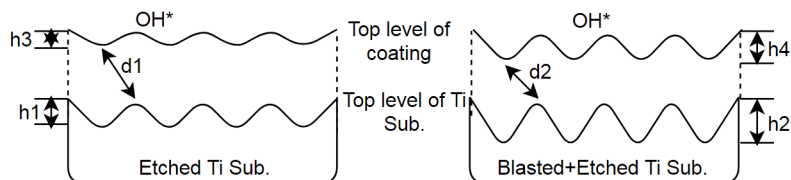


Figure 11: The schematic diagram of the path for OH^* in the coatings on different substrates

4. Conclusion

The influence of applying sandblasting in pretreatment of titanium substrate on the electrochemical properties of the $\text{IrO}_2\text{-Ta}_2\text{O}_5$ anode was investigated. The results indicate that firstly sandblasting increased the surface roughness and secondly deeper and smaller etching pits were formed on the substrate. This is beneficial to increase the catalytic activity as it increase the outer ECSA by affecting the surface morphology after coating but in a limited range. In addition, the catalytic activity of the catalyst itself is independent of the pretreatment. However, applying sandblasting in pretreatment in this case does not favor the durability of the anode as the accelerated lifetime of the anode with sandblasting is 1000 hours shorter than the one without sandblasting. The deactivated anode with sandblasting still has approximately 95% coating left in the coating, whereas the anode without sandblasting only has approximately 18% coating left after deactivation. This can be attributed to the shorter distance (*d-value*) between the lowest spot of the outer coating surface and the highest spot of the outer substrate in the anode with sandblasting than that in the other. To obtain an appropriate *d-value* thus becomes more significant while applying sandblasting in pretreatment for preparation of this type of anode.

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