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Electrochemical anodizing treatment to enhance localized corrosion resistance of pure titanium

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Abstract:	Titanium has an outstanding corrosion resistance due to the thin oxide protective layer that is formed on its surface. Nevertheless, in harsh and severe environment pure titanium may suffer localized corrosion. Electrochemical anodic oxidation was performed to enhance the corrosion resistance of pure titanium up to the corrosion resistance of titanium alloys based on palladium, molybdenum and nickel. Different anodizing electrolytes, cell voltages and current density were considered. Potentiodynamic tests in chlorides and fluorides containing solutions were carried out to determine the pitting potential for each condition and treatment. All tested anodizing treatments increased corrosion resistance of pure titanium, never reaching the performance of titanium alloys. The best anodization was defined as a compromise among the increase of corrosion resistance and the feasibility of the treatment from an industrial point of view.
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Electrochemical anodizing treatment to enhance localized corrosion resistance of pure titanium

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ABSTRACT

Purpose: Titanium has an outstanding corrosion resistance due to the thin oxide protective layer that is formed on its surface. Nevertheless, in harsh and severe environment pure titanium may suffer localized corrosion. Then costly titanium alloys containing palladium, nickel and molybdenum are used. It is possible to control corrosion at lower cost by electrochemical surface treatment on pure titanium, increasing the thickness of the natural oxide layer.

Methods: Anodic oxidation was performed on titanium by immersion in H₂SO₄ solution and applying a voltages ranging from 10 to 80 V. Different anodic current density were considered. Potentiodynamic tests in chlorides and fluorides containing solutions were carried out on anodized titanium to determine the pitting potential.

Results: All tested anodizing treatments increased corrosion resistance of pure titanium, never reaching the performance of titanium alloys. The best corrosion behavior was obtained on titanium anodized at voltages lower than 40 V at 20 mA/cm².

Conclusions: Titanium samples anodized at low cell voltage were seen to give high corrosion resistance in chloride and fluoride containing solution. Electrolyte bath and anodic current density have a low effect on the corrosion behavior.

Keywords: anodizing, corrosion, electrochemical treatment, pitting, titanium.

INTRODUCTION

Titanium has an outstanding corrosion resistance due to the thin amorphous, non-stoichiometric titanium dioxide protective layer (maximum thickness 10 nm (1)). The film is spontaneously formed on the titanium surface when exposed to aerated environment. This protective layer is very stable and allows using titanium in very severe working condition, such as offshore up to 260°C, acid environment, aerospace (2,3, automotive, high temperature, chemical and food industries (4-6).

Nevertheless commercially pure titanium may suffer different forms of localized corrosion in very harsh environments. Titanium may undergo pitting corrosion in hot salty water above 200°C as well as in hot hydrogen halides, due to the combined effect of the acidic condition, hot temperature and halides presence. Small amount of fluorides may dissolve the passive film due to formation of a titanium soluble salt, TiF_4 (7-8). Titanium may suffer hydrogen embrittlement, occurring on α and α - β titanium alloys due to low hydrogen solubility in α -Ti, and stress corrosion cracking in specific environments, such as anhydrous methanol, nitrogen tetroxide, red-fuming nitric acid or solid cadmium (9).

To face these potential issues, specific alloys containing palladium, nickel and molybdenum were introduced (9-10). These elements promote cathodic reaction, reducing overvoltages, allowing a polarization of the cathodic curve to more noble potentials, forcing the metal to work in the passive region; consequently the corrosion rate is greatly reduced (11). However, titanium alloys based on addition of Pd, Mo and Ni are very expensive.

To overcome this problem, the corrosion resistance of pure titanium may be increased by a variety of surface treatments. Nitration, consisting in the introduction of nitrogen in the

first micrometers of titanium, promotes the formation of TiN and increases corrosion resistance (12,13). The thickness of the natural titanium oxide, and consequently to corrosion resistance, may be increased by using an electrochemical anodizing treatment. An anodic polarization of several volts, up to 100 V, is applied on the titanium surface in a proper electrochemical bath, promoting the increase of the oxide from about 10-20 nm, up to 250-300 nm (14-17). At voltages higher than 100 V, the anodizing treatment causes the instauration of microarcs in the insulating oxide layer; this regime is called “anodic spark deposition (ASD)” or “plasma electrolytic oxidation (PEO)”. The titanium oxide is several micrometers thick, but with a porous structure. This growth mechanism happens on different light metals (18) and is reported to increase titanium corrosion resistance (19); nevertheless, due to higher energy consumption, it is rarely used, mainly to dope the oxide film by very short treatment (20).

Thermal oxidation, typically carried out at temperature higher than 400°C, accelerates the spontaneous formation of titanium film. The obtained oxide is more crystalline, with the formation of anatase phase at low temperature and rutile phase above 600°C (21-22).

Sol-gel treatment of pure titanium showed a moderate increase of corrosion resistance: due to the low stability and reproducibility, this treatment is not considered (23). The same considerations are applicable to other coating techniques, such as vacuum plasma spray coating, plasma spraying and chemical vapor deposition.

Among all the treatments, electrochemical anodizing was preferred, because of low cost and feasibility of the treatment from an industrial point of view.

In this work anodic oxidation have been performed to tune the TiO₂ layer in order to increase its thickness and to obtain a mostly amorphous phase, with the final aim to increase pure titanium corrosion resistance up to the level of more expensive alloys. The anodic oxide film formed on titanium strongly depends on the electrolyte composition, the applied voltage, the current density, the temperature and the surface preparation (24). In

this work, the effects of the first three parameters are investigated, keeping constant temperature and surface preparation. Due to promising preliminary results (25) in increasing corrosion resistance of the anodizing treatment at low voltage, below 100 V, a deeper investigating has been performed and hereafter reported. Moreover, it is possible to combine the increased corrosion resistance with the possibility to use the other well-know properties of low voltages films, such as interference coloration, super hydrophilicity and photocatalyzation.

MATERIALS AND METHODS

Four titanium alloys were tested: two commercially pure titanium with different amount of impurities and two alloys containing palladium, nickel and molybdenum. Table 1 reports the composition of each metal.

Samples were tubular in shape. In order to test external surface, tubes were cut longitudinally. Specimens were then covered with an epoxy-based electrical insulator resin, a part a 2 cm² area used for test and a smaller connection region to ensure electrical contact with testing instruments, as visible in Figure 1.

Figure 1

All samples were polished until grit 600 to ensure the same surface finishing. In order to analyze surface finishing effect, same samples were polished until 2400/4000 grit and then with 6 μm alumina particles until mirror finish.

Titanium samples were anodized through an electrochemical anodization treatment.

Samples were connected to the positive pole of a DC feeder (AimTTi PLH120 DC power supply, able to operate up to 120 V and 0.75 A). The counter-electrode, an activated titanium net, was connected to the negative pole. Anodizing started just after samples immersion. The anodizing bath was a 0.5 M sulfuric acid solution. Treatments were carried

out at 20 mA/cm² constant current density varying the cell voltage in the range 10 V to 80 V. At 20 V feeding voltage, test were performed also at 5 mA/cm² and 50 mA/cm², to study the effect of the current density. At the same voltage, anodizing treatment were performed in Na₂SO₄ 0.5 M, (NH₄)₂SO₄ 0.5 M and in NH₄BF₄ 0.5 M to analyze the effect of the bath composition on the quality of the titanium oxide. Anodization parameters were chosen based on previous knowledge about formed oxide, balancing the need to obtain thick and protective oxide and the necessity not to reach potentials that may lead to oxide crystallization (24, 26-28).

Thermal treatment was also considered to oxidize titanium, which is a well-known process to produce a thick and protective oxide (21-22). Calcinations were conducted at 550°C for 1 hour; this temperature was selected to obtain oxide thickness similar to the one obtained with anodization at 20 V, accordingly to the interference color acquired by the sample after treatment (26).

Corrosion resistance of the anodized titanium samples was determined by electrochemical potentiodynamic tests performed with an EG&G Princeton Applied Research potentiostat/galvanostat. Samples were immersed in a 1 L cell, in two electrolytes with increasing halides concentration: NaCl 35 g/L and 100 g/L, NaF 1 g/L, 3.5 g/L, 10 g/L, 20 g/L and 35 g/L. All tests were performed at room temperature. Only in the case of solution NaCl 100 g/L tests were performed also at 95°C.

Potentiodynamic tests were conducted starting -0.1 V with respect the free corrosion potential, measured 30 minutes after sample immersion in the corrosive solution, up to potentials between 1.5 V and 7 V, depending on the corrosive electrolyte. Potential scan was inverted when a 10 A/m² anodic current density was reached. Potential scan rate was 20 mV/min. A silver/silver chloride in a KCl saturated solution was used as reference electrode. Since the duration of a test did not exceed 6 hours, no sealing was necessary and neither chemical ($\Delta\text{pH} \approx 0.05$) nor physical ($\Delta\text{T} \approx 2^\circ\text{C}$) deviations were detected.

To study the effect of the electrochemical anodizing treatment on the cathodic overvoltages, cathodic potentiodynamic tests were conducted in HCl 10% solution, starting at free corrosion potential, decreasing the potential to -1 V Ag/AgCl, with a potential scan rate of 20 mV/min.

All tests were performed in triplicate, with high reproducibility.

RESULTS AND DISCUSSION

Corrosion resistance in chloride containing solution

Figure 2 compares the corrosion behavior of the four tested titanium alloys in NaCl 35 g/L at 25°C. In each graph, for each alloy, the not treated sample, the electrochemical anodized samples at 20 V and 30 V in sulfuric acid and the thermal anodized sample at 550°C for 1 hour are shown.

For both the two commercially pure titanium (UNS R50250, Fig. 2a, and UNS R50400, Fig. 2b), samples anodized at 20 V showed the lowest anodic current density, and consequently the best corrosion resistance, for almost all the potential range. In fact, the corrosion current density is one order of magnitude lower than the one obtained on the commercially pure titanium not treated. The thermal oxidation did not promote any corrosion improvement.

The two titanium alloys (Fig. 2c and Fig. 2d) showed a similar trend. The worst corrosion resistance is shown by the not treated samples. In the case of the thermal oxidized sample, an inversion in the corrosion behavior with respect to the not treated one was observed: calcination gives a worsening of corrosion resistance at potentials below 0.7 V. This is probably due to the less homogeneity of the titanium oxide.

Figure 2

Tests were then performed at high temperature, 80°C and 95°C, to favor localized corrosion. At this stage, roughness effect was also studied by polishing samples until mirror-like finishing. Results of commercially pure titanium UNS R50400 tested at 80°C and 95°C with anodizing or polishing treatments are shown in Figure 3. At 80°C, not treated titanium sample showed a pit initiation at 6.5 V Ag/AgCl, confirmed by the increase of the anodic current density at values higher than 10 A/m². At 95°C, the pitting potential of the commercially pure titanium was reduced to 5.5 V Ag/AgCl. A corrosion resistance enhancement can be noticed both with anodic oxidation treatment at 20 V and with mirror polishing treatment, especially at high potential. Anodization showed better behavior at low potential, which is more interesting for practical application, while polishing increases potential at which anodic current density of 10 A/m² is reached, that is pitting corrosion resistance. It is worth to notice that the anodic curves become very disturbed at potentials close to pitting value due to the formation of meta-pits, in which the material is subject to local failure and successive repassivation.

Figure 3

NaCl concentration was raised up to 100 g/L, in order to promote localized corrosion. Nevertheless, no significant variation in the pitting potential were observed: the potential at which current suddenly increased was in between 5.5 V and 6.0 V Ag/AgCl.

Corrosion resistance in fluoride containing solution

Tests were firstly performed on commercial pure titanium UNS R50400 not treated with increasing NaF concentrations, in order to define the proper fluoride content and avoid

very severe solution. NaF solution from 1 g/L to 35 g/L were tested. Comparisons between non-treated titanium and anodized titanium were conducted at low NaF concentrations.

Results are reported in Figure 4. At NaF content higher than 3.5 g/L, passivity of not treated titanium was completely destroyed: anodic curves showed the typical behavior of an active metal with an increasing current density at increasing potential. At NaF concentration lower than 3.5 g/L, non-treated titanium showed a passive behavior, with a lower passive current density at lower NaF concentration.

Potentiodynamic tests on commercially pure titanium electrochemically anodized at 20 V were performed in solution with NaF content 1 g/L, 3.5 g/L and 10 g/L. It is clearly visible (Figure 4) that the anodizing treatment improved corrosion resistance of commercially pure titanium. The reason is twofold:

- at the same fluoride content, passive current density of anodized titanium is lower than passive current density of non-treated one. Figure 5 shows the anodic current density measured at 1.5 V Ag/AgCl: the current density of the anodized titanium is more than one order of magnitude lower than the value of the not treated titanium
- the critical NaF content to activate passive titanium increased from 3.5 g/L in the case of not treated titanium, to 10 g/L in the case of anodized titanium.

Tests in 3.5 g/L NaF solution were performed to evaluate the effect of the anodizing voltage (voltage ranged from 10 V to 80 V). Each test was repeated three times to guarantee reproducibility. Potentiodynamic curves are visible in Figure 6. A slight correlation between electrochemical behavior and anodizing voltage is visible: titanium samples anodized at voltage lower than 40 V appeared more corrosion resistant than samples anodized at higher voltages. However, the behavior of all the oxidized titanium is

similar and corrosion current density is one order of magnitude lower with respect to the value measured on the not treated titanium.

From these results it appears that titanium oxide thickness, which increases proportionally to the increase of the anodizing voltage (for the treatments carried out is in between 30 nm and 150 nm (24)) is not directly correlated to the corrosion resistance. Conversely, the better corrosion behavior obtained at lower anodizing voltages suggest a possible effect of oxide crystallinity.

Figure 4

Figure 5

Figure 6

Effect of the anodizing current density

Electrochemical anodizing treatments were performed at constant current density, increasing the cell voltage to the desired final value. The parameter “current density” determines the rate of formation of the oxide: the higher the current density, the quicker the oxide formation rate. Figure 7 shows the effect on corrosion resistance of the anodizing current density applied to reach the 20 V voltage. Current densities ranged from 5 mA/cm² to 50 mA/cm². Even if a possible effect on the crystalline structure of the oxide was expected due to the different oxide growth rate, only a marginal effect on electrochemical behavior was observed. Anodization carried out at 5 mA/cm² showed slightly lower anodic current density.

Figure 7

Effect of anodizing electrolyte

To investigate the effect of anodization bath, three solutions were tested apart from sulfuric acid: $(\text{NH}_4)_2\text{SO}_4$ 0.5 M, Na_2SO_4 0.5 M and NH_4BF_4 0.5 M. These solutions were chosen in order to find a treatment suitable for industrial applications; in fact, the use of sulfuric acid solution would have some drawbacks in handling the cell and in the disposal of the used acid. Commercially pure titanium was anodized at 20 mA/cm^2 up to 20 V in every considered bath and then tested in NaF 3.5 g/L solution. Results are reported in Figure 8: the electrolytes did not affect the corrosion behavior.

Figure 8

Effect of electrochemical anodization on cathodic behavior

Cathodic potentiodynamic curves were performed to investigate the effect of the electrochemical anodized titanium on the slope of the hydrogen evolution reaction. It is well-known that the enhanced corrosion resistance of Ti-Pd alloy UNS R52400 is related to the decrease of hydrogen overvoltage given by palladium addition into the alloy (28). Tests were performed in HCl 10%. Results are shown in Figure 9. Cathodic Tafel slopes in the order of 130 mV/decade, 150 mV/decade and 170 mV/decade were measured on UNS R52400, UNS R50400 anodized and UNS R50400, respectively. Anodized UNS R50400 has an effect on the cathodic behavior in between the not anodized titanium and the Ti-Pd alloy; however, the difference in the Tafel slopes is minimum to deduce affordable conclusions.

Figure 9

CONCLUSIONS

Electrochemical anodization treatment can be used to improve the corrosion behavior of commercially pure titanium. Treated titanium has a higher corrosion resistance in both

chloride and fluoride containing solutions. The best improvement was achieved at anodizing voltages lower than 40 V, due to the formation of an almost amorphous compact oxide layer. This enhanced corrosion resistance is independent from the anodizing current density and the anodizing bath. Treatments at low current density are then preferable because of the lower required energy and cost. However, while lower current requires less power, higher current accelerates the process, reducing required time. Since the anodizing bath has a minimum influence on the quality of the film formed, it is suggested to use baths at neutral pH, for example based on sodium sulfate.

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Table 1 - Composition of used metals

Metal	C%	H%	O%	N%	Fe%	other
UNS R50250	< 0,10	< 0,015	< 0,18	< 0,03	< 0,20	
UNS R50400	< 0,10	< 0,015	< 0,25	< 0,03	< 0,30	
UNS R52400	< 0,10	< 0,015	< 0,25	< 0,03	< 0,30	0,12-0,25 Pd
UNS R53400	< 0,10	< 0,015	< 0,25	< 0,03	< 0,30	0,2-0,4 Mo / 0,6-0,9 Ni

FIGURE LEGEND

Figure 1: Specimen covered with a green epoxy-based resin; on the left the 2 cm² area used for test; on the right the bare surface used for electrical connection

Figure 2: Potentiodynamic tests in NaCl 35 g/L at 25°C on not treated titanium, on titanium anodized at 20 V and 30 V, and on titanium thermally treated. a) UNS R50250, b) UNS R50400, c) UNS R52400, d) UNS R53400

Figure 3: Potentiodynamic tests on UNS R50400 at high temperature, with anodization and polishing treatments

Figure 4: Potentiodynamic tests of UNS R50400 in different concentration of NaF with and without 20 V anodization treatment at 25°C.

Figure 5: Anodic current density of not treated titanium and titanium anodized at 20 V in different concentration of NaF at anodic potential 1.5 V vs. Ag/AgCl.

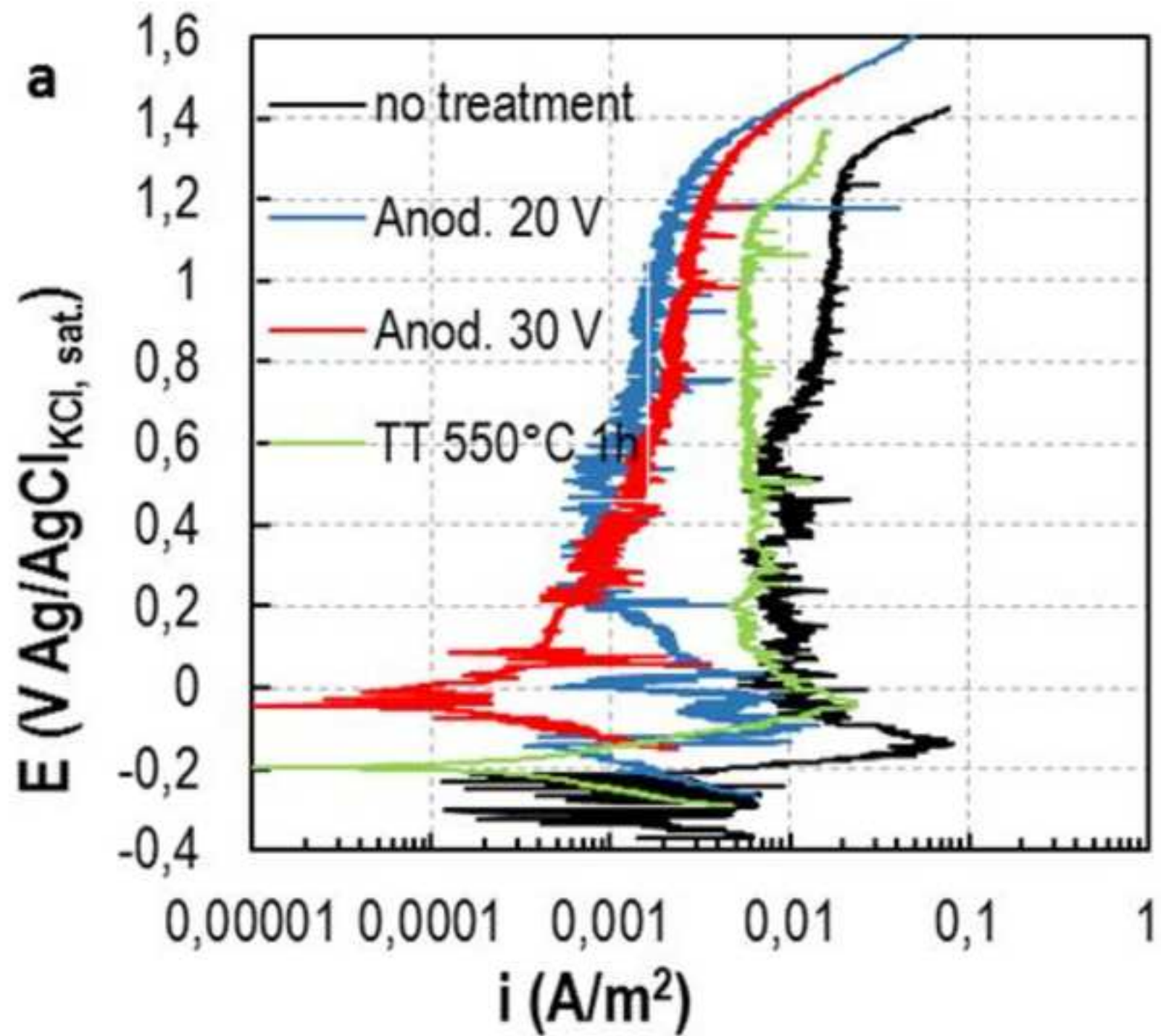
Figure 6: Potentiodynamic tests in NaF 3.5 g/L on UNS R50400 anodized at different voltages at 25°C.

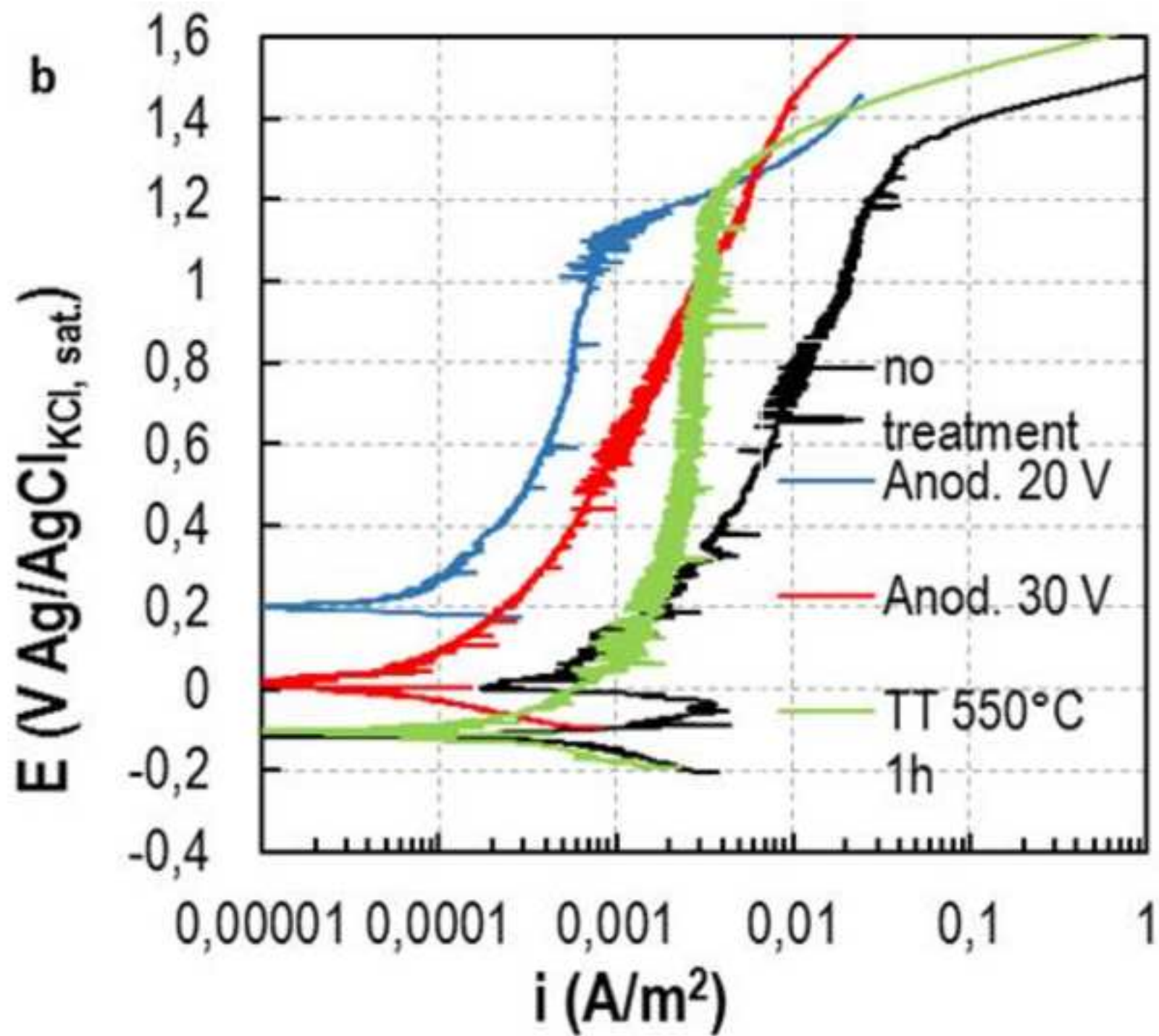
Figure 7: Potentiodynamic tests in NaF 3.5 g/L on UNS R50400 anodized at different current density at 25°C.

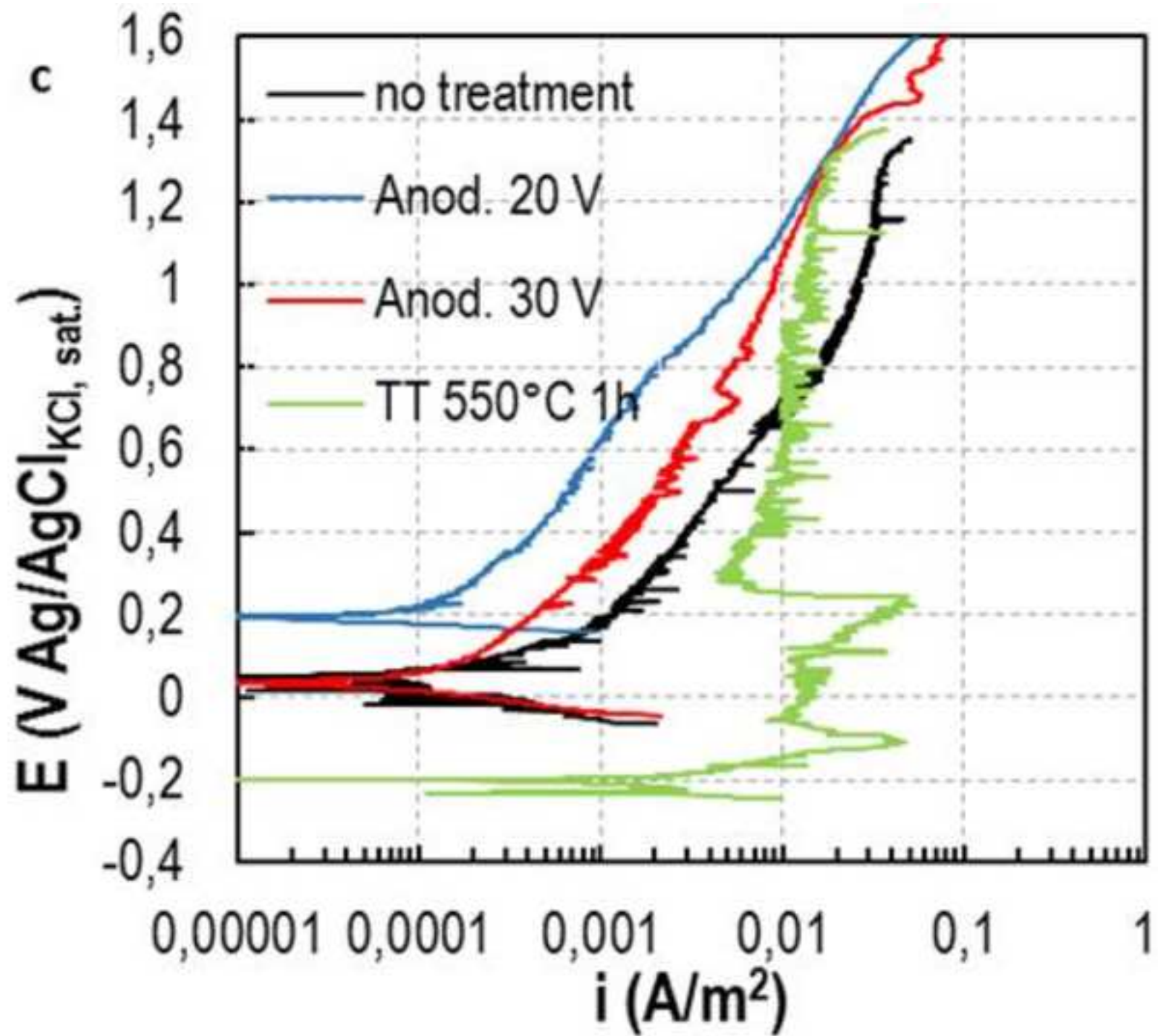
Figure 8: Potentiodynamic tests in NaF 3.5 g/L on UNS R50400 anodized in different electrolytes at 25°C.

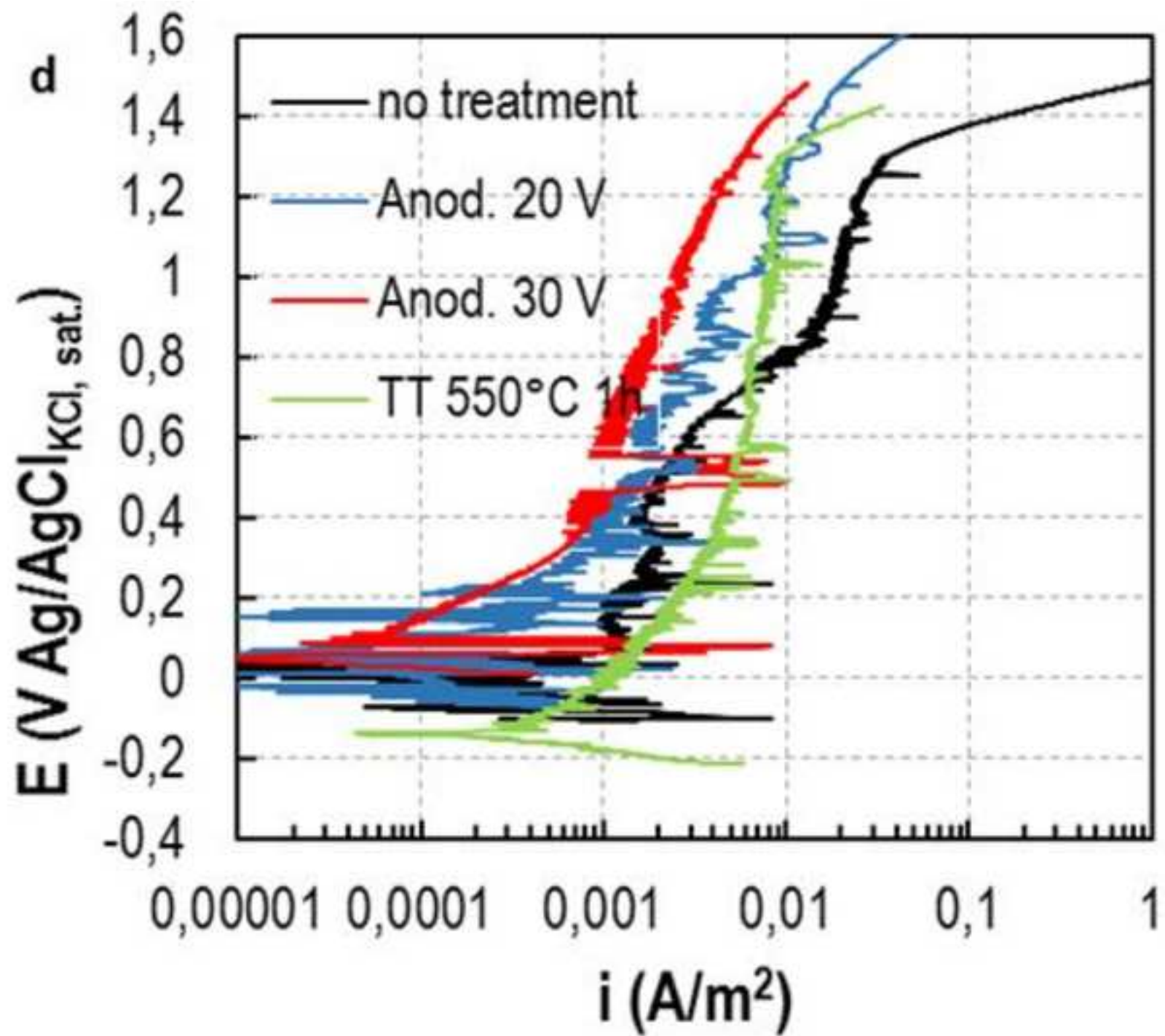
Figure 9: Cathodic curves in HCl 10% at 25°C.

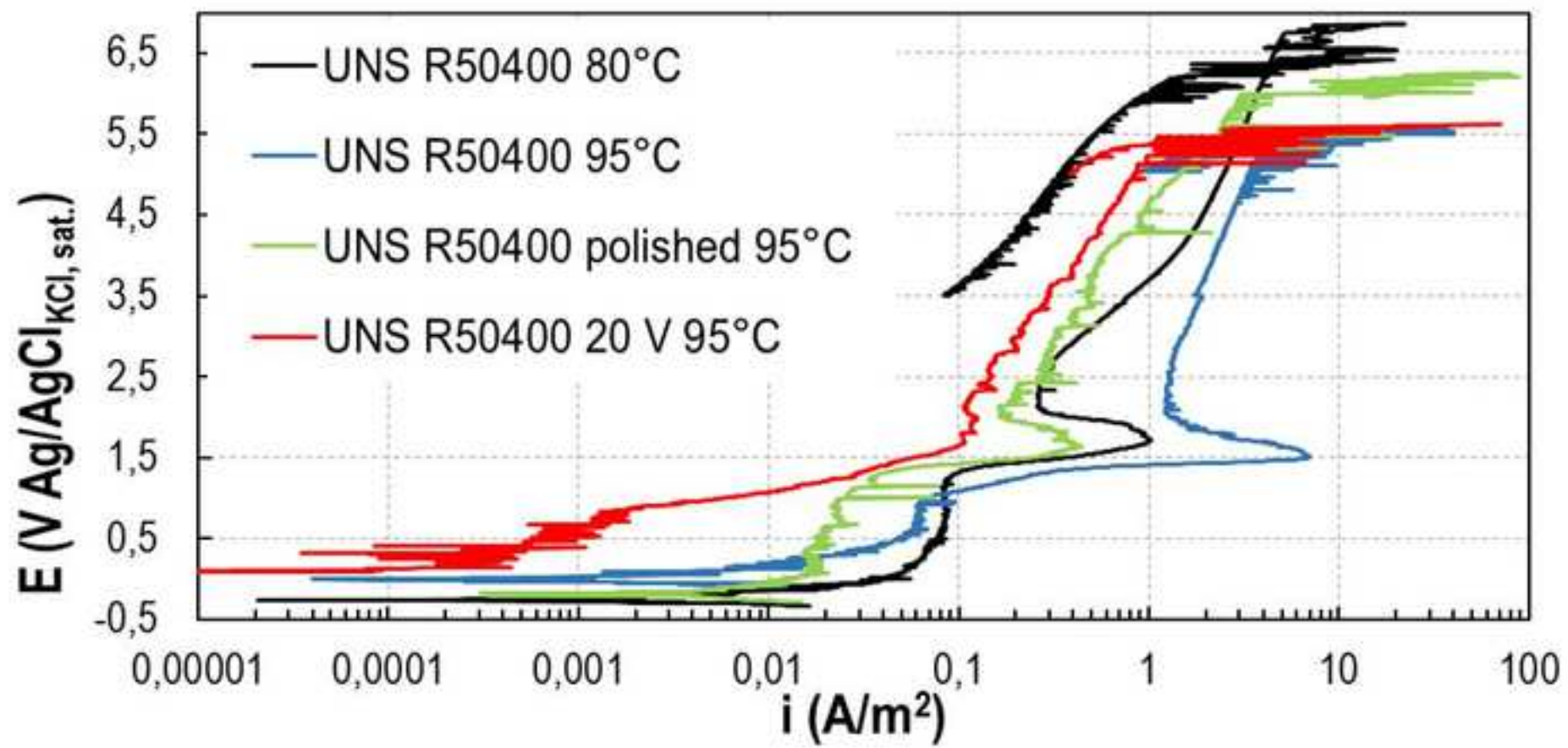


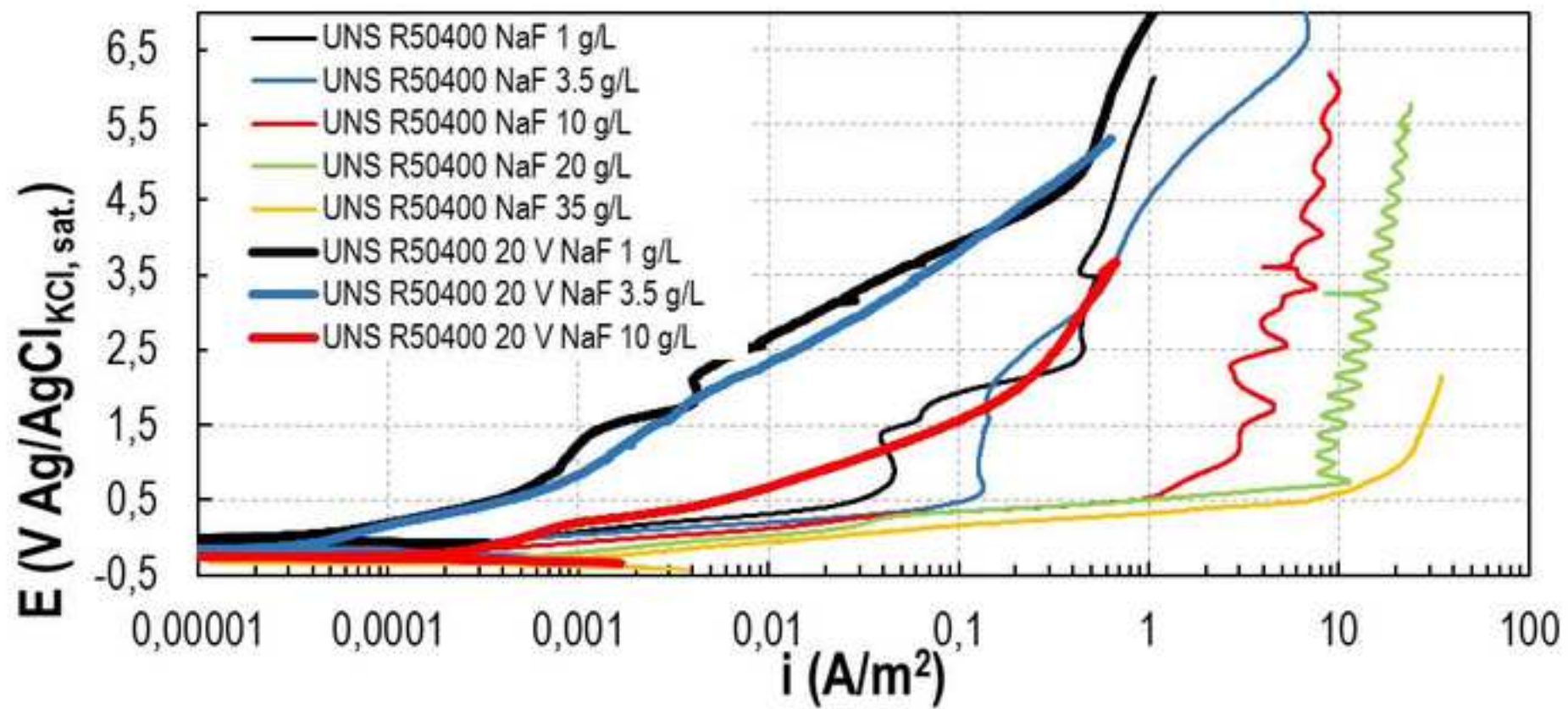


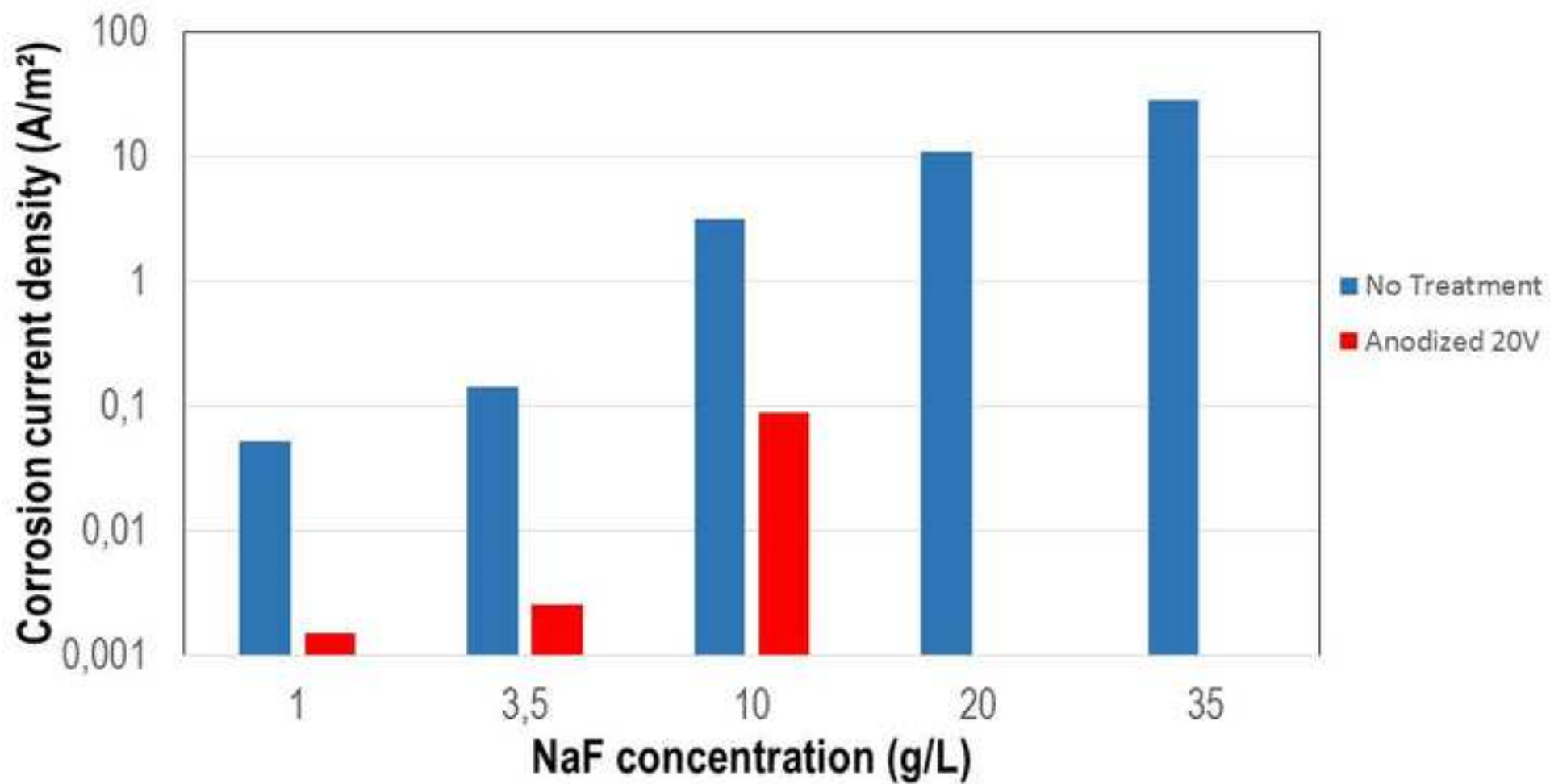


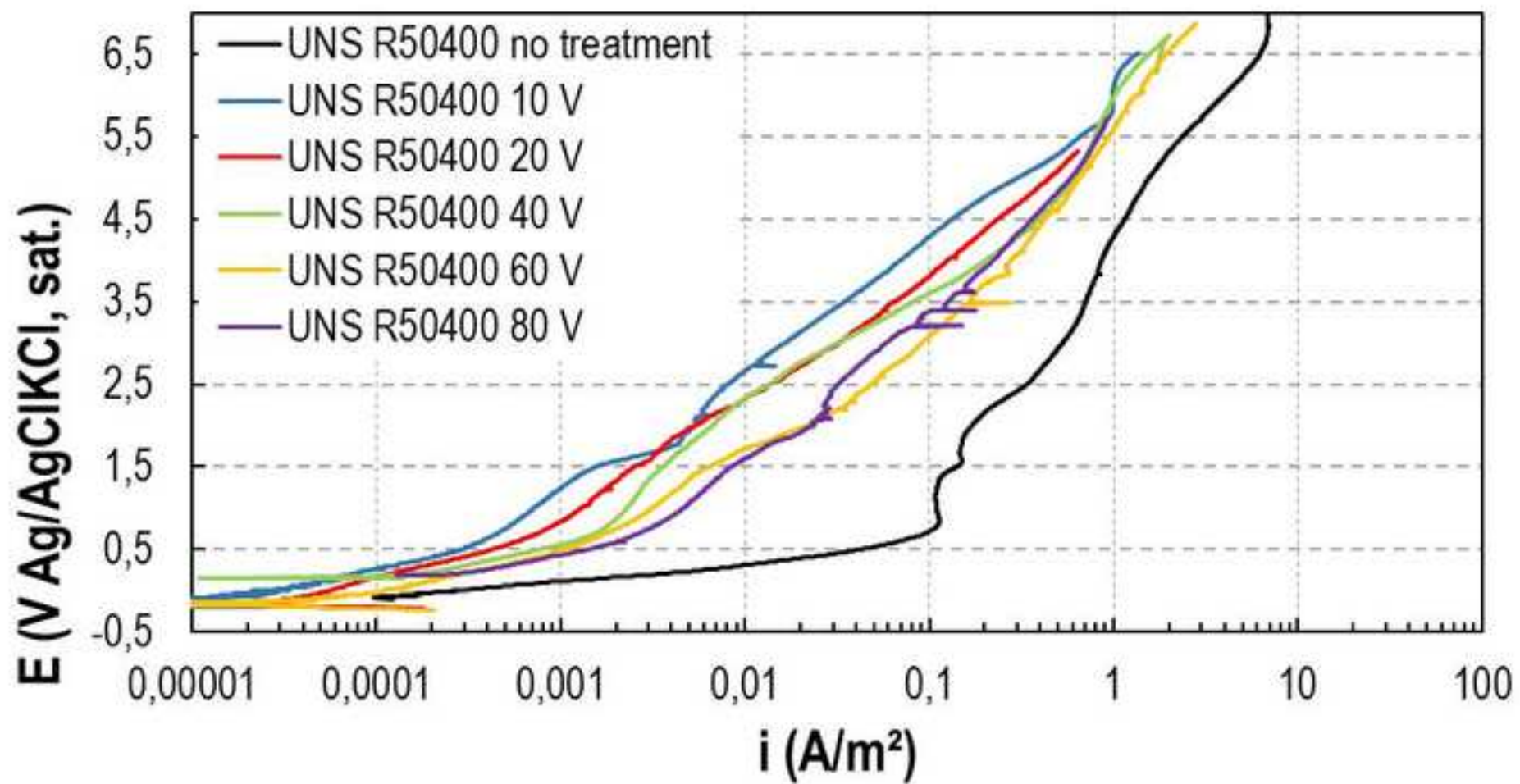


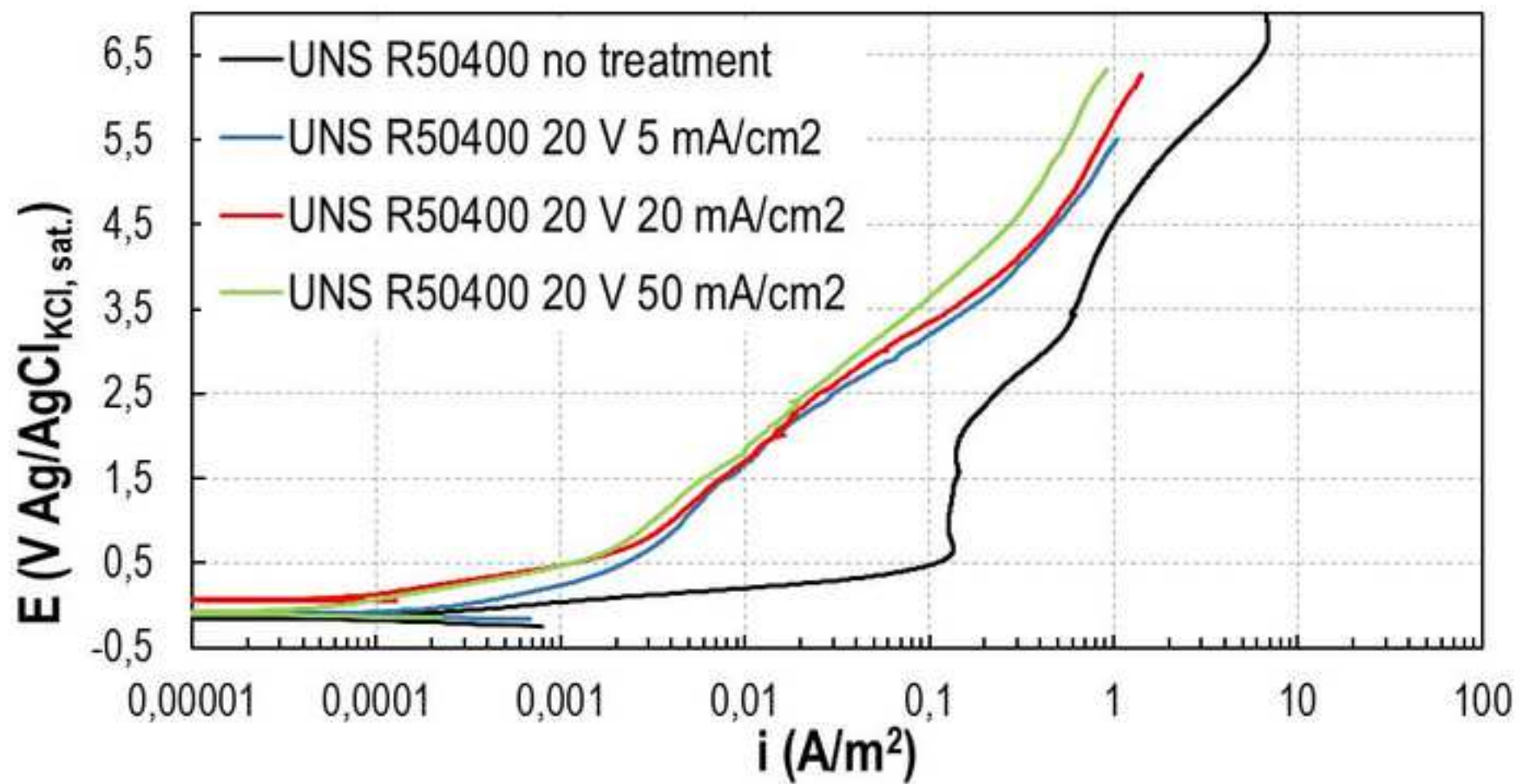


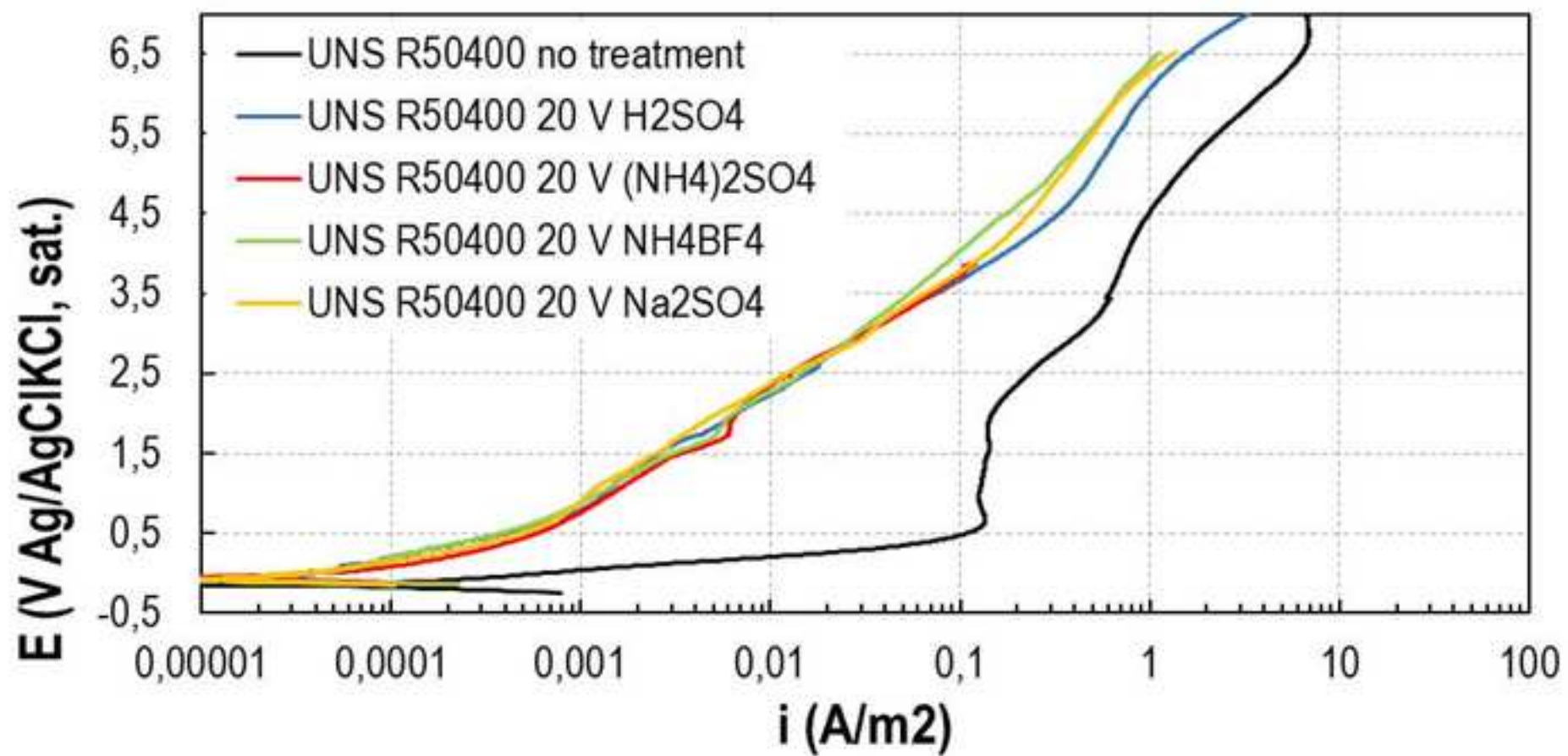


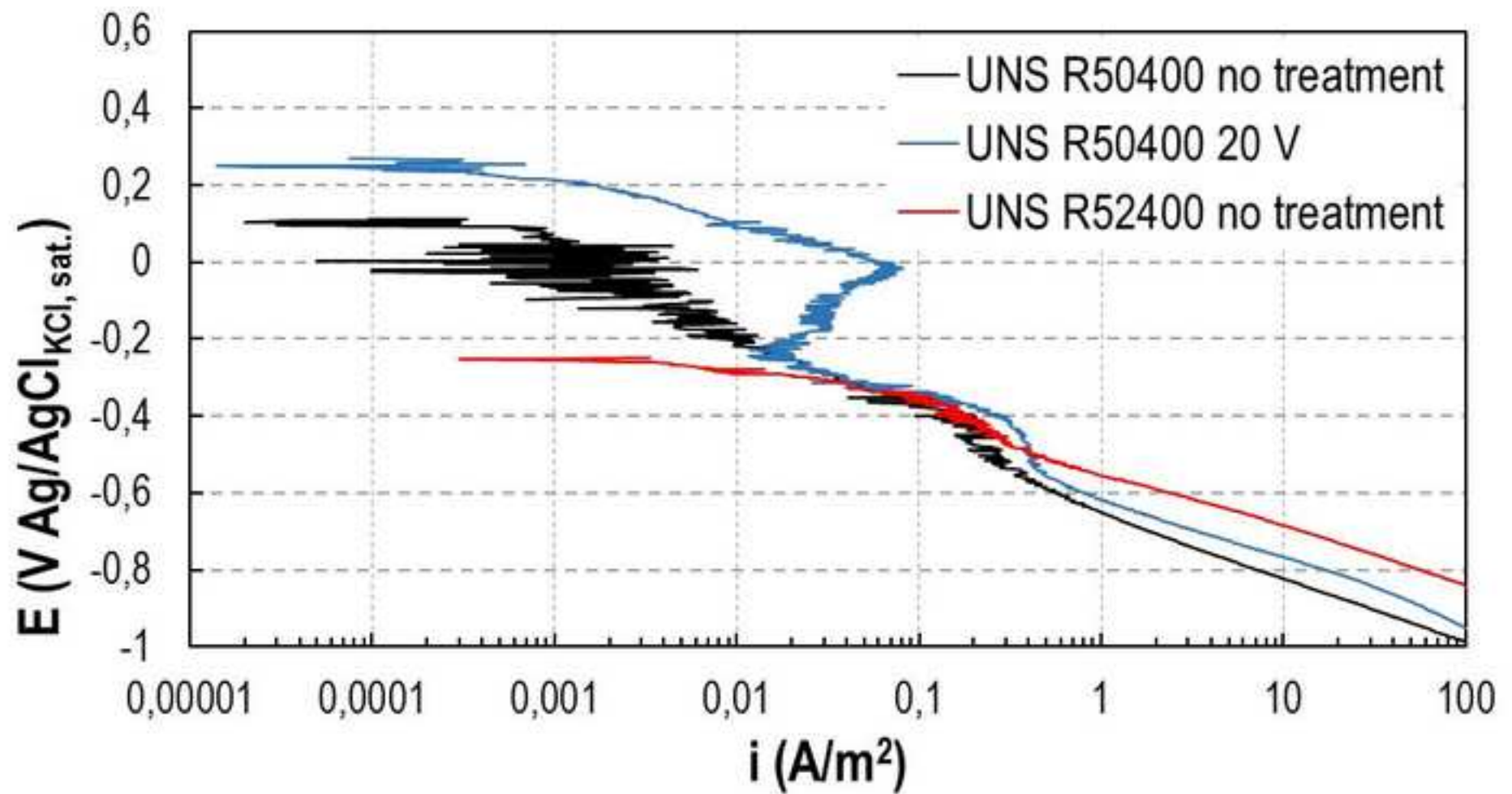












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