

ELECTROCHEMICAL CHARACTERIZATION OF PASSIVE FILMS ON PURE ALUMINIUM ELECTRODES IN DIFFERENT EXPERIMENTAL CONDITIONS

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The polarization behaviour of pure aluminium was studied by potentiostatic, potentiodynamic and potential decay techniques in KClO₃ aqueous solutions, with and without different aggressive anions. In aqueous solution of KClO₃ without aggressive anions, the potential sweep from the cathodic to the anodic range led to the formation of an insoluble layer of aluminium oxide on the electrode surface, which passivates the working electrode.

The presence of aggressive anions like as Cl⁻, SCN⁻, prevents the formation of the passive film and accelerates the process of anodic dissolution, the more the greater is the concentration of the aggressive anion. Localized pitting is best described by a characteristic parameter called the pitting potential value (E_{π}). E_p is the protection potential and the pitting can be formed only in the E_{π} - E_p polarization range. Electrochemical behaviour of anodised aluminium surface was also studied by (EIS) in KClO₃ solution. Samples were observed by scanning electron microscopy (SEM).

INTRODUCTION

Aluminium, as indicated by its position in the electromotive force series is a thermodynamically reactive metal, among structural metals, only beryllium and magnesium are more reactive. It is a metal with high electronegative standard potential (-1.67 V) and in spite of this, it is highly resistant to most acidic and neutral solutions due to the formation of a protective oxide film on its surface. In oxidizing environments the film formation is very rapid and an attack on the metal is negligible. Hence, aluminium electrodes are easily oxidized to form Al³⁺ species, giving a non-conducting dielectric Al₂O₃ film acts as an excellent barrier inhibiting an electron transfer and hence, the corrosion process. However, the presence of aggressive anions like chloride creates extensive localized attack. Various mechanisms have been proposed to explain the breakdown of the passive film.¹

In the present paper we studied the polarization behaviour of aluminium in different aqueous solutions, particularly regarding either the role played by the oxide layer or pitting corrosion due to the presence of different aggressive anions.

EXPERIMENTAL

The polarization behaviour of pure aluminium was studied by potentiodynamic method using different sweep rates. The working electrode potential was always measured with the reference to the saturated calomel electrode. In order to reduce ohmic resistance, we used a single compartment cell in which the working electrode was situated in the cell center and surrounded by the auxiliary electrode, made of a bright platinum gauze. Prior to each determination, the working electrode was mechanically ground and polished with emery paper of varied granulation up to mirror-luster, degreased in benzene at boiling temperature for 5 min. in order to remove all traces of fat and abrasive power remaining on the surface after polishing.

The determination were repeated with each solution until a good reproducibility of the results was obtained. All experiments were performed at 25°C. The structural analysis has been performed by EIS and by SEM.

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RESULT AND DISCUSSION

For the determination of different characteristic electrochemical parameters, the complete polarization curves were registered. In the case of solid reaction partners taking part in electrochemical reaction reproducible polarization curves cannot be easily taken, due to the formation or dissolution of solid layers on the electrode. In aqueous solutions of 0.3 M KClO_3 typical current-potential curves can be recorded on aluminium (aluminium oxide) working electrode (Fig.1).

After starting the potential sweep from the cathodic range, the formation of an insoluble layer of aluminium oxide (Al_2O_3) on the electrode surface takes place. Analysis of Fig.1 shows that at the E_π potential, the current starts to increase and altering polarization direction, hysteresis can be observed, the current will decrease to zero only at more negative potential (E_p) than E_π . We consider that, E_π is the critical pitting potential and E_p is the protection potential (or repassivation potential). Pitting can be formed only in the $\Delta E_{p-\pi}$ polarization range as it was proved in many experiments. The corrosion behaviour of aluminium can be qualified by these two potential values and by through the ranges of passivation and repassivation.

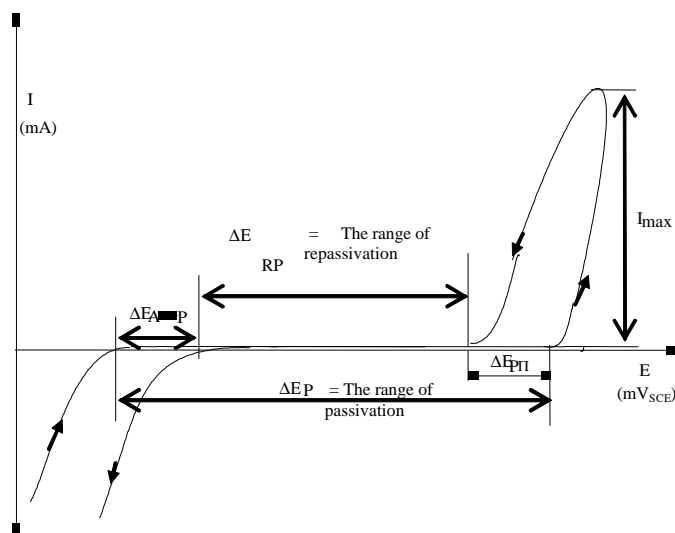
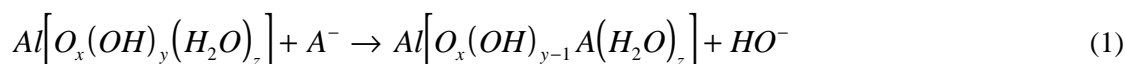


Fig. 1 – The hysteresis curve of pure Al in aqueous solution of KClO_3 0.3 M at 4 mVs^{-1} sweep rate

The increase of the KClO_3 concentration led in all the cases to the increase of the repassivation and passivation ranges, to the decrease of the current peak and to the increase of the $\Delta E_{p-\pi}$ range. We can explain this behaviour taking into account that, the KClO_3 has an oxidant character and hence, the solutions of KClO_3 more concentrated have a stronger oxidant character. This special property determines an increase of the thickness passive film, an increase of the stability and the adherence passive film. The results presented in Table 1 are in concordance with these characteristics.

Further, we studied the influence of the potential sweep rate on the passive characteristics. From Table 1, one can see that at the same concentration of KClO_3 , the increase of the potential sweep rate led in all the cases to the decrease of the passive (ΔE_P), repassive (ΔE_{RP}) and $\Delta E_{p-\pi}$ ranges. In the same time, the increase of the potential sweep rate leads to the increase of the current peak and of the passive current as we can see from Table 1.

In Fig. 2 the hysteresis curves of aluminium in 0.3 M KClO_3 with different aggressive additives are presented. One can see that, the addition of the aggressive anions leads, in all the cases to a decrease of the repassivation and passivation ranges, to an increase of the peak currents and to a decrease of the range $\Delta E_{p-\pi}$ (see Fig. 2 and Tab. 2, 3). The different effects of the addition of the different aggressive anions (see Fig. 2 and Tab. 2, 3) are the consequence of different bonding strength of these anions on different sites of the surface. We suppose that aggressive anions are bonded chemically in the interface as an initial step of the formation of different oxo-, hydroxo- and aniono-complexes to the following:





In the case of Cl^- ion it is possible to obtain the $[AlCl_6]^{3-}$ complex, finally. In presence of different aggressive anions, the quantitative interpretation of this multistep heterogeneous reaction mechanism is complicated. Therefore, a large variety of reactions is possible. We can say, that aluminium pitting corrosion is an electrochemical process, followed by two heterogeneous chemical processes and aggressive anion is a chemical reaction partner.²⁻⁸

Table 1
Kinetic parameters of passivation and repassivation for Al in aqueous solution of 0.3 M $KClO_3$ at 25°C

| Concentration | sweep rate mVs^{-1} | E_{π} mV | E_p mV | $\Delta E_{p-\pi}$ mV | ΔE_p mV | ΔE_{RP} mV | I_{max} mA |
|---------------|--------------------------|-----------------|-------------|--------------------------|--------------------|-----------------------|-----------------|
| 0.1 | 1 | -295 | -545 | 250 | 924 | 659 | 24.9 |
| | 2 | -302 | -547 | 245 | 911 | 653 | 29.39 |
| | 4 | -309 | -549 | 240 | 895 | 649 | 35.78 |
| | 6 | -314 | -552 | 238 | 888 | 634 | 41.3 |
| | 8 | -332 | -566 | 234 | 869 | 632 | 44.62 |
| | 10 | -361 | -588 | 227 | 850 | 616 | 46.15 |
| | 12 | -398 | -595 | 197 | 837 | 605 | 49.66 |
| 0.2 | 1 | -283 | -520 | 237 | 963 | 685 | 15.31 |
| | 2 | -296 | -528 | 232 | 947 | 672 | 24.16 |
| | 4 | -301 | -532 | 231 | 914 | 666 | 28.4 |
| | 6 | -309 | -535 | 226 | 902 | 663 | 32.9 |
| | 8 | -325 | -546 | 221 | 889 | 647 | 37.23 |
| | 10 | -342 | -560 | 218 | 873 | 633 | 39.87 |
| | 12 | -390 | -572 | 182 | 845 | 619 | 43.28 |
| 0.3 | 1 | -265 | -486 | 221 | 992 | 704 | 8.44 |
| | 2 | -274 | -488 | 214 | 990 | 700 | 20.33 |
| | 4 | -283 | -491 | 208 | 974 | 692 | 24.84 |
| | 6 | -304 | -495 | 191 | 957 | 686 | 27.16 |
| | 8 | -318 | -501 | 183 | 944 | 680 | 32.85 |
| | 10 | -324 | -503 | 179 | 925 | 675 | 36.86 |
| | 12 | -387 | -512 | 125 | 909 | 662 | 41.13 |
| 0.4 | 1 | -248 | -452 | 204 | 1089 | 757 | 6.32 |
| | 2 | -265 | -458 | 193 | 1005 | 746 | 11.92 |
| | 4 | -274 | -463 | 189 | 993 | 739 | 18.3 |
| | 6 | -285 | -465 | 180 | 976 | 735 | 22.5 |
| | 8 | -312 | -477 | 165 | 962 | 712 | 25.91 |
| | 10 | -318 | -478 | 160 | 944 | 700 | 28.4 |
| | 12 | -348 | 500 | 152 | 927 | 687 | 33.92 |
| | 1 | -236 | -424 | 188 | 1125 | 803 | 4.16 |
| | 2 | -243 | -427 | 184 | 1063 | 792 | 8.36 |
| | 4 | -250 | -429 | 179 | 1024 | 789 | 14.89 |
| | 6 | -255 | -430 | 175 | 1003 | 784 | 18.13 |
| | 8 | -293 | -453 | 160 | 985 | 769 | 22.4 |
| | 10 | -307 | -460 | 153 | 961 | 745 | 26.3 |
| | 12 | -325 | -473 | 148 | 939 | 723 | 29.65 |

The changing of E_{π} potentials with aggressive ion concentration is due to migration effect, because a competitive adsorption takes place between ClO_3^- , and A^- ions. On an aluminium electrode covered by a passive layer, electrochemical reduction of measurable rate can be detected only quite low overpotentials (Fig. 2 and Tables 2, 3).

Further, we studied the influence of S^{2-} additions on the polarization behaviour of pure aluminium in aqueous solutions of $KClO_3$. In Table 4 and 5 are presented the kinetic corrosion parameters of pure aluminium in 0.3M $KClO_3$ with different amounts of S^{2-} ions.

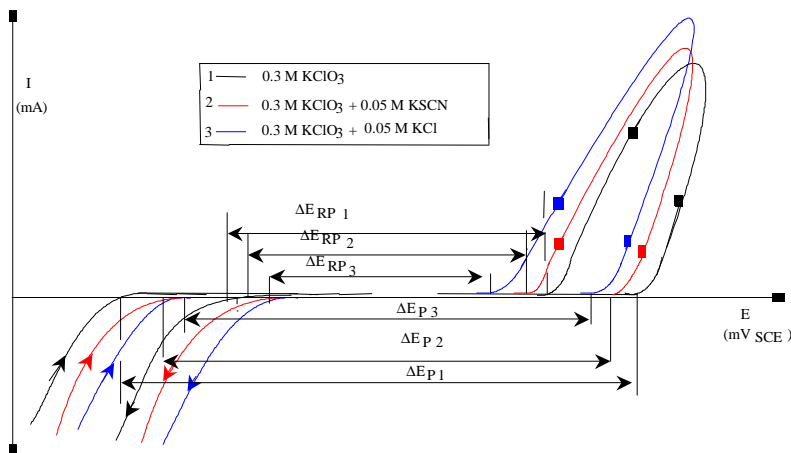


Fig. 2 – The hysteresis curves of pure Al in 0.3 M $KClO_3$ solution with and without different additives at 25°C and the sweep rate of 4 mVs^{-1}

Table 2

Kinetic parameters of passivation and repassivation for Al in aqueous solutions of 0.3 M $KClO_3$ + X M $[A^-]$ at 1 mVs^{-1} sweep rates and 25°C

| Anion | C_{A^-} (M) | E_{π} mV | E_p mV | $\Delta E_{p-\pi}$ mV | ΔE_p mV | ΔE_{RP} mV | I_{max} MA |
|---------|---------------------|-----------------|-------------|--------------------------|--------------------|-----------------------|-----------------|
| Cl^- | 0 | -265 | -486 | 221 | 992 | 704 | 8.44 |
| | $5 \cdot 10^{-3}$ | -273 | -504 | 231 | 934 | 648 | 19.82 |
| | 10^{-2} | -316 | -553 | 237 | 869 | 600 | 25.75 |
| | $2.5 \cdot 10^{-2}$ | -387 | -626 | 239 | 732 | 475 | 51.7 |
| | $5 \cdot 10^{-2}$ | -438 | -681 | 243 | 645 | 396 | 68.31 |
| SCN^- | $7.5 \cdot 10^{-2}$ | -464 | -709 | 245 | 597 | 344 | 83.74 |
| | 0 | -265 | -486 | 221 | 992 | 704 | 8.44 |
| | $5 \cdot 10^{-3}$ | -268 | -493 | 225 | 967 | 678 | 12.3 |
| | 10^{-2} | -295 | -523 | 228 | 911 | 623 | 19.7 |
| | $2.5 \cdot 10^{-2}$ | -322 | -552 | 230 | 885 | 600 | 31.65 |
| SCN^- | $5 \cdot 10^{-2}$ | -364 | -598 | 234 | 772 | 506 | 51.7 |
| | $7.5 \cdot 10^{-2}$ | -398 | -640 | 242 | 683 | 438 | 60.4 |

Table 3

Kinetic parameters of passivation and repassivation for Al in aqueous solutions of 0.3 M $KClO_3$ + X M $[A^-]$ at 6 mVs^{-1} sweep rates and 25°C

| Anion | C_{A^-} (M) | E_{π} mV | E_p mV | $\Delta E_{p-\pi}$ mV | ΔE_p mV | ΔE_{RP} mV | I_{max} MA |
|---------|---------------------|-----------------|-------------|--------------------------|--------------------|-----------------------|-----------------|
| Cl^- | 0 | -304 | -495 | 191 | 957 | 686 | 27.16 |
| | $5 \cdot 10^{-3}$ | -349 | -548 | 199 | 915 | 639 | 32.62 |
| | 10^{-2} | -374 | -577 | 203 | 834 | 585 | 49.53 |
| | $2.5 \cdot 10^{-2}$ | -425 | -631 | 206 | 708 | 461 | 63.9 |
| | $5 \cdot 10^{-2}$ | -483 | -693 | 210 | 622 | 373 | 75.41 |
| SCN^- | $7.5 \cdot 10^{-2}$ | -512 | -725 | 213 | 583 | 334 | 96.2 |
| | 0 | -304 | -495 | 191 | 957 | 686 | 27.16 |
| | $5 \cdot 10^{-3}$ | -318 | -514 | 196 | 932 | 662 | 29.9 |
| | 10^{-2} | -338 | -538 | 200 | 901 | 609 | 35.15 |
| | $2.5 \cdot 10^{-2}$ | -375 | -577 | 202 | 854 | 588 | 41.2 |
| SCN^- | $5 \cdot 10^{-2}$ | -402 | -607 | 205 | 803 | 549 | 55.73 |
| | $7.5 \cdot 10^{-2}$ | -448 | -655 | 207 | 785 | 525 | 68.8 |

Analysis of these tables points out the fact that, once with the addition of the S^{2-} ions the passive process becomes more stronger and now, takes place an increase of the passivation and repassivation ranges, a decrease of the current peak and also, an increase of the $\Delta E_{p-\pi}$ range while the values of the E_{π} and E_p become more electropositive. We can explain this behaviour due to the fact that, the S^{2-} anions interactionate with the Al_2O_3 passive oxide film and form stable complexes on the electrode surface. In this way, the passive film from the electrode surface becomes much more stable, adherent and compact. The increase of the potential sweep rate has the same effect like as the other aggressive anions (see Tables 4 and 5).

Table 4

Kinetic parameters of passivation and repassivation for Al in aqueous solutions of 0.3 M $KClO_3$ + X M S^{2-} at 1 mVs^{-1} sweep rates and 25°C

| Anion | C_{A^-} (M) | E_{π} mV | E_p mV | $\Delta E_{p-\pi}$ mV | ΔE_p mV | ΔE_{RP} mV | I_{max} MA |
|----------|---------------------|-----------------|-------------|--------------------------|--------------------|-----------------------|-----------------|
| S^{2-} | 0 | -265 | -486 | 221 | 992 | 704 | 8.44 |
| | $5 \cdot 10^{-3}$ | -193 | -449 | 256 | 1007 | 1 | 27.41 |
| | 10^{-2} | -122 | -415 | 293 | 1068 | 755 | 22.57 |
| | $2.5 \cdot 10^{-2}$ | -89 | -393 | 304 | 1083 | 776 | 21. |
| | $5 \cdot 10^{-2}$ | -24 | -379 | 365 | 1150 | 780 | 20.41 |
| | $7.5 \cdot 10^{-2}$ | +146 | -304 | 450 | 1258 | 800 | 18.63 |

Table 5

Kinetic parameters of passivation and repassivation for Al in aqueous solutions of 0.3 M $KClO_3$ + X M S^{2-} at 6 mVs^{-1} sweep rates and 25°C

| Anion | C_{A^-} (M) | E_{π} mV | E_p mV | $\Delta E_{p-\pi}$ mV | ΔE_p mV | ΔE_{RP} mV | I_{max} MA |
|----------|---------------------|-----------------|-------------|--------------------------|--------------------|-----------------------|-----------------|
| S^{2-} | 0 | -304 | -495 | 191 | 957 | 686 | 27.16 |
| | $5 \cdot 10^{-3}$ | -245 | -469 | 224 | 982 | 690 | 27.69 |
| | 10^{-2} | -166 | -423 | 257 | 995 | 718 | 28.1 |
| | $2.5 \cdot 10^{-2}$ | -103 | -407 | 304 | 1028 | 720 | 28.32 |
| | $5 \cdot 10^{-2}$ | -45 | -391 | 346 | 1098 | 737 | 28.55 |
| | $7.5 \cdot 10^{-2}$ | +102 | -326 | 428 | 1187 | 748 | 28.74 |

The formation of the aluminium oxide film, in aqueous solutions of $KClO_3$ was pointed out by SEM. The aluminium samples were immersed in 0.5M $KClO_3$ for different immerse times and then were examined by SEM. Analysis of the obtained micrographies after the immersion time of one hour (1h) pointed out that, the aluminium oxide film formed is mainly the adherent structure (see Fig.3) on the aluminium surface.

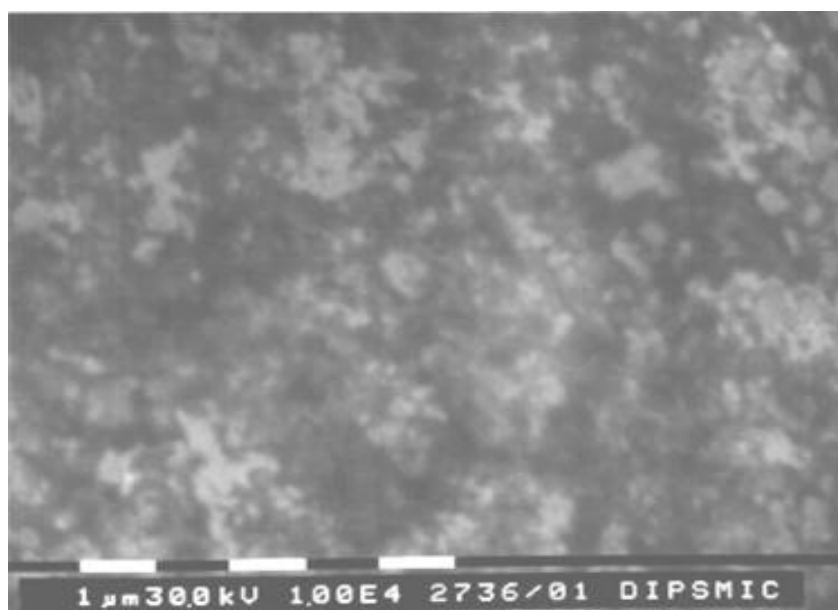


Fig. 3 – SEM for aluminium in 0.5 M $KClO_3$ solutions after immersion time of 1 h

After the immersion time of 4 h (four hours) the structural analysis has been shown that, the oxide layer is formed very well (see Fig.4). At the inner side the oxide layer is dense, compact and adherent while at the outer side the oxide layer is much more porous and it is formed from particles much more large and much more soluble. The inner side of the oxide layer is formed from α Al_2O_3 , while the outer side is formed from β Al_2O_3 .

The Nyquist diagrams obtained for the system: Al/0.5M KClO_3 confirms the obtained data by SEM measurements. Once with the increase of the immersion time takes place an increase of the polarization resistance and hence, leads to the decrease of the corrosion rate of the aluminium electrode. This decrease of the corrosion rate is due to the formation of an oxide film with an increasing thickness which protects aluminium electrode.

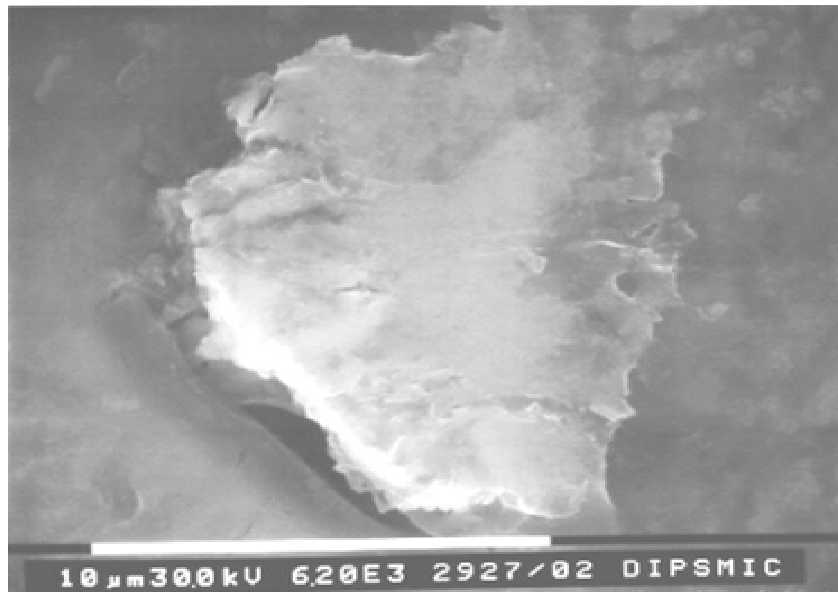


Fig. 4 – SEM for aluminium in 0.5 M KClO_3 solutions, after immersion time of 4 h

Bode diagrams from Fig. 6 also confirms the obtained data by SEM measurements. The appearance of two time constants points out the formation of two interfaces, in our case an interface between surface aluminium and the α form of Al_2O_3 ($\text{Al} / \alpha \text{Al}_2\text{O}_3$) and the second interface between the β Al_2O_3 and electrolyte solution ($\beta \text{Al}_2\text{O}_3 / 0.5\text{M} \text{KClO}_3$).

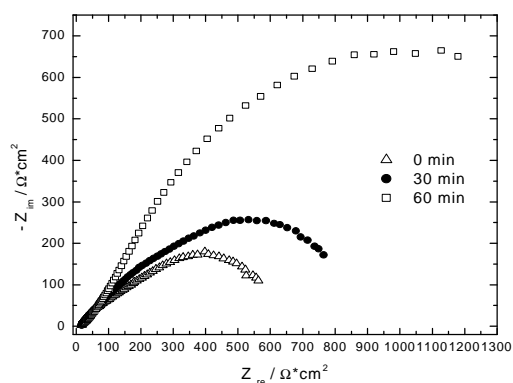


Fig. 5 – Nyquist diagrams for aluminium in 0.5 M KClO_3 solutions at different immersion times

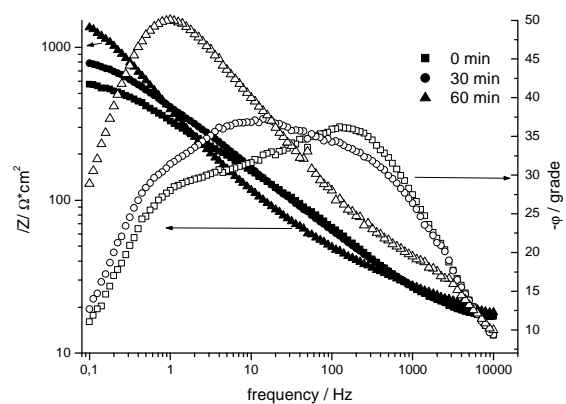


Fig. 6 – Bode diagrams for aluminium / 0.5 M KClO_3 system, at different immersion times

CONCLUSIONS

The breakdown of the passive film takes place by migration of the chloride ions through the oxide film up to the metal-film interface;

The increase of the KClO_3 concentration led in all the cases to the increase of the ΔE_p , ΔE_{RP} and $\Delta E_{p-\pi}$ and to movement of the E_π and E_p towards more electropositive values;

The addition of the aggressive anions leads in all the cases to accelerate of the corrosion process;

After a certain immersion time in 0.5M KClO_3 two species of aluminium oxide ($\alpha \text{Al}_2\text{O}_3$ and $\beta \text{Al}_2\text{O}_3$) are formed;

Occurred measurement by EIS and SEM pointed out the formation of the α and β forms of Al_2O_3 ;

Aluminium pitting corrosion is an electrochemical process, followed by to heterogeneous chemical processes and aggressive is a chemical reaction partner.

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