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# Chronoamperometric study of the passive behaviour of tantalum in hostile media during water addition

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## A B S T R A C T

The ability of tantalum to become passive through water addition in methanol solution during chronoamperometric experiments has been investigated. The achievement of passivity was found to be modulated according to the applied electrical potential and the nature of the aggressive anions. The chronoamperometric curves were interpreted as resulting from the balance between the influence of proton mobility in solution and the building of the passive film.

### Keywords:

Tantalum oxide  
Potentiostatic  
Repassivation

## 1. Introduction

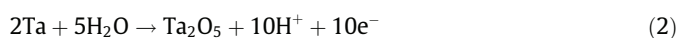
In two previous studies devoted to the electrochemical corrosion of typical valve metals, such as aluminium and titanium, a correlation was shown between the anion aggressiveness towards the passive film and their ability to dehydrate (chaotrope character) [1,2]. These results were found to exhibit the unexpected role played by the water molecules on the interfacial behaviour of the anions during the breakdown of the passive film. The investigated anions were conveniently distinguished according to the sign of the viscosity  $B$  coefficient appearing in the Jones–Dole relationship [3]:

$$\eta = \eta_w(1 + A\sqrt{c} + Bc) \quad (1)$$

where  $\eta$  is the viscosity of aqueous salt solution at molar concentration  $c$  and  $\eta_w$  is the viscosity of pure water. The coefficient  $A$ , which is positive for all salts, is an electrostatic term originating from the interaction between the ions. The coefficient  $B$ , which is either positive or negative, is a direct measure of the strength of the ion–water interactions. With structure-maker ions, say cosmotropes,  $B > 0$ : the hydration shell around the ions is thick and it is held strongly, so that the resistance to flow of these aqueous electrolyte solutions is higher than that of pure water. For structure-breaker ions, say chaotropes,  $B < 0$ : the adjacent water molecules are far away and not oriented. These ions present a relatively weak surface charge density, so possessing a loose hydration shell that can be easily removed.

The resistance of valve metals against corrosion originates from the propensity of the passive film to regenerate sufficiently after an eventual breakdown [4–8]. Therefore, the corrosion process may

be seen as resulting from the competition between the kinetics of metal dissolution and film reparation (self-healing) [9–12]. Among the valve metals, tantalum is known to be the most resistant due to the capacity of the insulating and amorphous  $\text{Ta}_2\text{O}_5$  film to form quickly and cohesively when the metal is oxidized in the presence of water [13–18], according to the reaction:



As a result, tantalum was observed to be unaltered in concentrated and hot aqueous salt or acid solutions, even for long exposure times [19–22]. However when it was placed in anhydrous media, some anions like chloride, bromide or sulfate were found to initiate pitting [23–26]. Nevertheless, when the initial amount of water was increased, the presence of the resulting passive film precluded any corrosion event, so emphasizing the decisive effect of water [27].

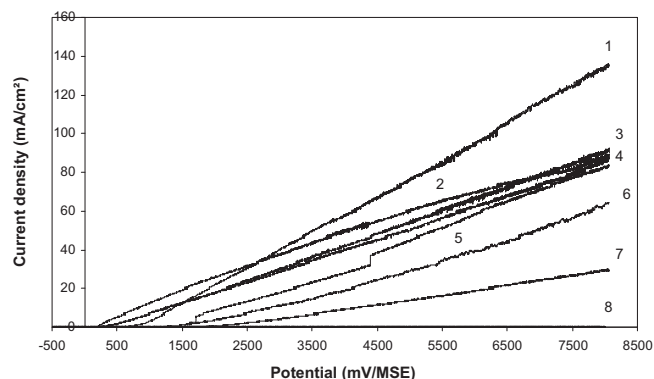
Despite the extensive literature relative to the passive or corrosion behaviour of valve metals [5,9,10,28–32], studies that are concerned with the achievement of passivity in the presence of aggressive species in anhydrous media scarcely exist. As the passive properties of tantalum are intimately related to the presence of water, electrochemical corrosion experiments conducted from anhydrous methanol and where the water content is continuously increased may offer the opportunity to investigate whether there is an influence of the nature of the aggressive anion on the capacity of the passive film to form and/or repair. This question is justified since the added water molecules may be available for the building of the passive film but also concomitantly for the own hydration of the anions present.

In this study, the electrochemical corrosion of tantalum plates in the presence of several acids at 0.1 mol/L concentration in methanol solution has been investigated. Chronoamperometric experiments

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**Table 1**Initial water content, measured conductivity and viscosity  $B$  coefficient value of the corresponding anion of the acidified methanol solution at 0.1 mol/L concentration.

Acid	HClO <sub>4</sub>	HBr	HCl	H <sub>2</sub> SO <sub>4</sub>	CH <sub>3</sub> SO <sub>3</sub> H	HNO <sub>3</sub>	H <sub>2</sub> SiF <sub>6</sub>
wt.% of water	0.61	1.22	0.97	0.14	0.57	0.99	4
$\chi$ (mS/cm)	12.13	9.64	8.69	10.09	8.36	2.77	6.42
$B_{\text{anion}}$ (L/mol)	-0.060	-0.033	-0.007	0.206	0.127	-0.045	0.374



**Fig. 1.** Variation of the current density as a function of the potential (versus MSE) in the presence of the acidified methanol solutions at 0.1 mol/L concentration: HClO<sub>4</sub> (1), H<sub>2</sub>SO<sub>4</sub> (2), HCl (3), HBr (4), CH<sub>3</sub>SO<sub>3</sub>H (5), H<sub>2</sub>SiF<sub>6</sub> (6), HNO<sub>3</sub> (7), and in the presence of HClO<sub>4</sub> aqueous solution at 0.1 mol/L concentration (8).

and conductivity measurements were performed at various electrical potential during water addition to appreciate the achievement of passivity and to gain information about the dominant processes.

## 2. Materials and methods

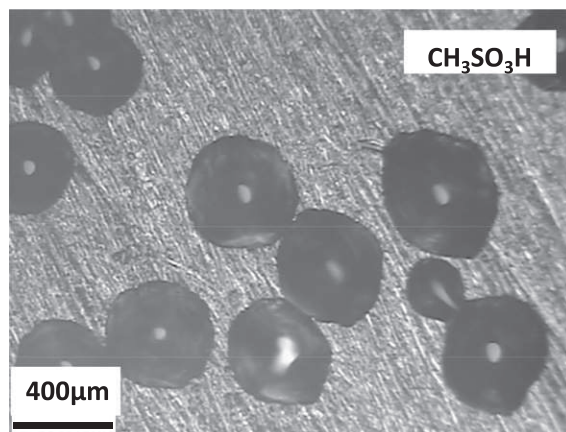
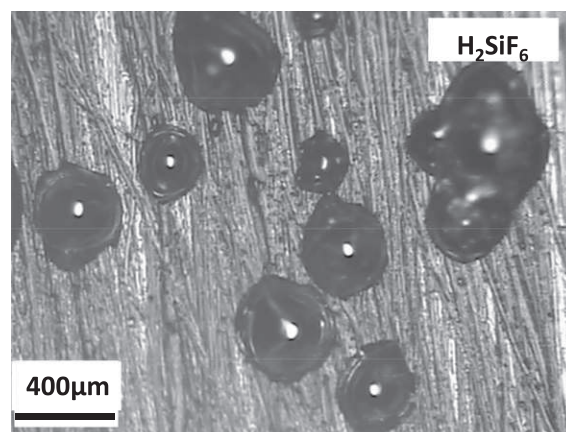
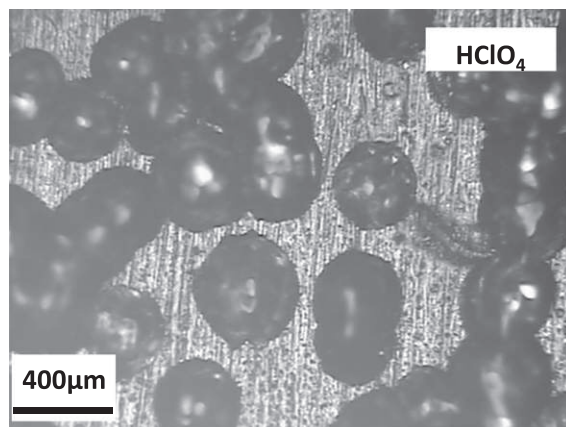
Small tantalum plates were cut from a commercial Ta foil (99.9 wt.%, Goodfellow, UK) with a thickness of 0.03 cm to obtain a rectangular shape (2 cm × 0.6 cm). Just before the experiments, the tantalum plates (both faces) were abraded with emery paper and washed with acetone before etching 1 min into a HF 2 vol.% + HNO<sub>3</sub> 4 vol.%, aqueous solution. Then they were rinsed with methanol and dried in a stream of nitrogen gas.

The following acids: methanesulfonic acid (CH<sub>3</sub>SO<sub>3</sub>H,  $pK_a = -1.9$ ) solution at 70 wt.% (Sigma-Aldrich), hydrochloric acid (HCl,  $pK_a = -7$ ) solution at 37 wt.% (Normapur, Prolabo), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>,  $pK_{a1} = -3$ ) solution at 95 wt.% (Rectapur, Prolabo), nitric acid (HNO<sub>3</sub>,  $pK_a = -1.3$ ) solution at 52.5 wt.% (Rectapur, Prolabo), perchloric acid (HClO<sub>4</sub>,  $pK_a = -10$ ) solution at 70 wt.% (Sigma-Aldrich), hydrobromic acid (HBr,  $pK_a = -9$ ) solution at 47 wt.% (Merck), hexafluorosilicic acid (H<sub>2</sub>SiF<sub>6</sub>,  $pK_a$  unknown) solution at 31 wt.% (Prolabo), formic acid (HCO<sub>2</sub>H,  $pK_a = 3.75$ ) solution at 98.5 wt.% (Prolabo), fluoric acid (HF,  $pK_a = 3.2$ ) solution at 40 wt.% (Prolabo), iodic acid (HIO<sub>3</sub>,  $pK_a = 0.8$ ) solid at 99.5 wt.% (Sigma-Aldrich), were used to prepare 50 mL of solution at 0.1 mol/L concentration in methanol at 99.9 wt.% (Normapur, Prolabo).

The initial water content of the acidified methanol solutions was determined by a Karl-Fischer titration (Mettler Toledo).

The electrochemical experiments were performed with a potentiostat (Radiometer Analytical S.A. Copenhagen, Tacussel DEA 332, potential range 0–8 V) coupled with a digital converter (Radiometer Analytical, IMT 102) and controlled by a PC running the electrochemical software (Radiometer Analytical, VoltaMaster 2). The recorded current was checked with the use of an amperemeter (Metrix MX 55C).

The electrochemical set up was constituted with a tantalum plate as the anode (working electrode) and a flat platinum plate (2 cm × 1 cm) as the auxiliary electrode. The plates were fixed with



**Fig. 2.** Photographs (magnification ×10) of tantalum plates after anodic polarization in the presence of some acids.

crocodile clips; they were immersed at 1.2 cm depth in 50 mL of the studied solution. A mercurous sulfate electrode (MSE), Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> saturated solution, served as a reference electrode. All the potential values given in this work refer to this reference electrode.

Linear voltammograms were performed in the range  $-0.5$  to  $8$  V/MSE with a  $5$  mV/s sweep rate under agitation at  $200$  rpm (magnetic stirrer) of the acidified methanol solution. Some cyclic voltammograms were performed from  $-0.5$  to  $4$  V/MSE and then back to  $-0.5$  V/MSE with a  $10$  mV/s sweep rate without any agitation.

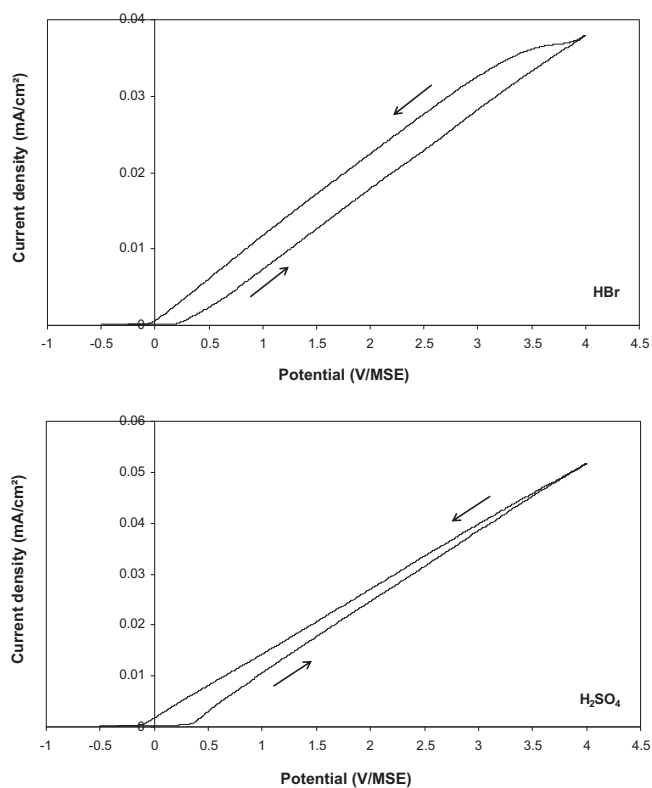
The same device was used for the chronoamperometric studies. The current intensity was recorded as a function of time when a defined electrical potential was applied during the continuous addition of a  $0.5$  mL volume of pure water every  $90$  s into the acidified methanol solutions under agitation at  $200$  rpm (magnetic stirrer).

The conductivity of the acidified methanol solutions was measured with a Tacussel electrode (Tacussel Instrument). The solution conductivity was also measured during the chronoamperometric experiments after each water addition.

The used electrodes were maintained at fixed positions. All the experiments were repeated twice.

An optical microscope (Leica Instrument) equipped with a camera (Kaiser optical system Inc.) was used to observe the qualitative aspect of the corroded tantalum plates (magnification  $\times 10$ ). The images were analyzed with the software Intellicam.

Scanning electron microscope (SEM LEO 435 VP) was used to examine the microstructure of the passive film on tantalum plates.



**Fig. 3.** Cyclic voltammograms of two representative acids (HBr and  $\text{H}_2\text{SO}_4$ ) at  $0.1$  mol/L concentration in methanol solution.

**Table 2**

Applied electrical potential, electrolysis duration, calculated amount of charge, weight loss of tantalum plate and corresponding  $z$  valence of the performed dissolution experiments.

Acid	Potential (V/MSE)	Electrolysis duration (s)	$Q$ (C)	$\Delta m$ (g)	$z$
HBr	7	900	157	0.0548	5.37
$\text{CH}_3\text{SO}_3\text{H}$	7	900	135	0.0503	5.03
$\text{HClO}_4$	5	900	110	0.0432	4.78

### 3. Results and discussion

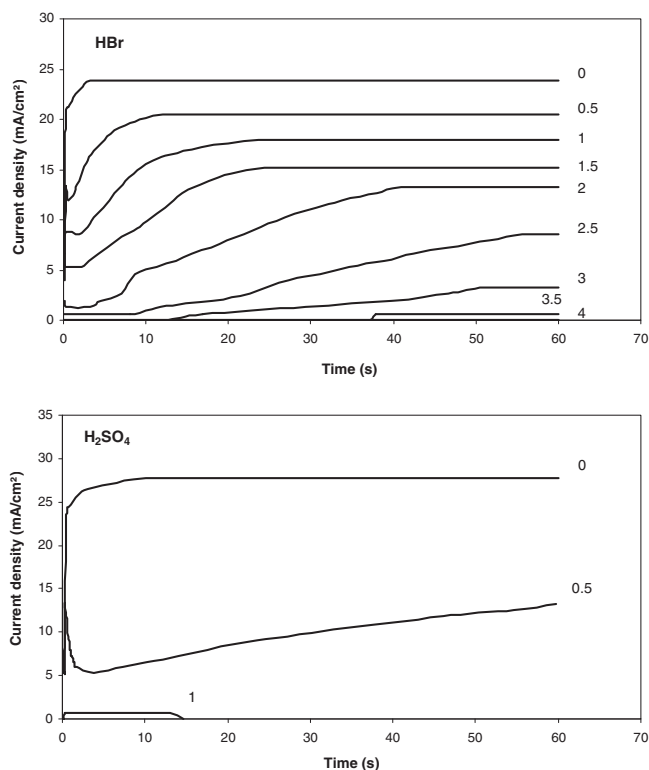
#### 3.1. Choice and categorization of the anions

Owing to the moderate dielectric constant of methanol ( $\epsilon \approx 31$ ), the solubility of many electrolytes is restricted in this solvent when compared to water. Fortunately, the use of the corresponding acids allows preparing much greater concentrations in methanol solutions. Nevertheless, to investigate the influence of the anions, the amount of dissociated ions has to be sufficient enough in such media. This can be assessed through conductivity measurements of the samples. A minimum level of conductivity has to be reached, say at least  $1$  mS/cm, to make reliable electrochemical experiments when the electrodes are further polarized within these conditions. This is the reason why weak acids, those presenting positive  $pK_a$  values in aqueous solution, are not appropriate candidates. Various acids were thus chosen to satisfy these conditions, which allowed also the testing of some anions of interest that were not studied previously [2].

The initial water content (determined by Karl-Fischer titration) and the conductivity of the acidified methanol solutions have been reported in Table 1. The viscosity  $B$  coefficient at  $25$  °C of the corresponding anion is also indicated, so enabling the distinction between the cosmotrope anions, with  $B > 0$ , and the chaotrope anions where  $B < 0$  [3].

#### 3.2. Anodic polarization of tantalum in acidified methanol solutions

The electrochemical corrosion of tantalum plates was appreciated by recording the current density as a function of the increasing electrical potential (versus MSE) in the presence of the various acids at  $0.1$  mol/L concentration in methanol solution, see Fig. 1. Whatever the acid, the curves exhibit the same behaviour where the current density increases from a given potential. The potential



**Fig. 4.** Consecutive chronoamperometric curves at  $2$  V/MSE recorded  $90$  s after a  $0.5$  mL water addition into the acidified (HBr and  $\text{H}_2\text{SO}_4$ ) methanol solution.

values corresponding to the rise of the current density are: 210, 295, 350, 705, 1320, 1550 and 1950 mV/MSE for H<sub>2</sub>SO<sub>4</sub>, HCl, HBr, HClO<sub>4</sub>, H<sub>2</sub>SiF<sub>6</sub>, CH<sub>3</sub>SO<sub>3</sub>H and HNO<sub>3</sub>, respectively. All the tantalum plates showed pitting after anodic polarization. Photographs with some acids are presented in Fig. 2. The aspect is quite similar with pits of about the same size; the number density is however greater in the case of HClO<sub>4</sub>. The presence of a characteristic hysteresis loop appearing in the cyclic voltammogram of two representative acids corroborates the occurrence of pitting corrosion [25], see Fig. 3.

To get information about the corrosion reaction, dissolution experiments were performed in the presence of some acids to determine the involved valence  $z$ , according to the Faraday's law:

$$z = \frac{QM_{Ta}}{F\Delta m} \quad (3)$$

where  $Q$  is the amount of charge passed during a defined electrolysis duration at a given electrical potential ( $Q = \int i \cdot dt$  corresponds to the chronoamperometric curve area; it is calculated by the VoltMaster 2 software),  $M_{Ta}$  is the molecular weight of tantalum (181 g/mol),  $F$  is the Faraday constant (96,500 C/mol),  $\Delta m$  is the weight loss of a tantalum plate. The experimental conditions together with the results relative to a 1.512 cm<sup>2</sup> immersed surface area of the working electrode are reported in Table 2. The obtained  $z$  values ( $z = 5.06$  in average) advocate for a pitting process releasing tantalum V species [23], in accordance with the oxidation reaction:



These results indicate that tantalum is irreversibly corroded in methanol through a pitting process whatever the nature of the acid. The natural passive film of a few nanometers on the tantalum surface is not able to resist to the attack of the anions in such conditions, most importantly it can not regenerate. Indeed, the situation is radically different in aqueous solution where no corrosion event is detected. As a representative example, the anodic polarization of HClO<sub>4</sub> aqueous solution at 0.1 mol/L concentration is also displayed in Fig. 1, see curve 8. The electrical response remains equal to zero, so confirming the high protective role played by water in the building of a renewable and cohesive Ta<sub>2</sub>O<sub>5</sub> passive film. In the presence of anions, the passive film may be attacked through a direct penetration and/or an erosion process, together with flaws and cracks that may appear in its structure, but the kinetics of reaction (2) is so high within these conditions (excess of water) that it regenerates rapidly, thus preventing any metal dissolution [23,27,31].

### 3.3. First trends about the passive behaviour of tantalum

To inspect the influence of water on passivity, preliminary chronoamperometric tests were devoted to determine which water amount had to be added to observe significant effects when an electrical potential was further applied. It was decided to pour a 0.5 mL water volume into the acidified methanol solution under agitation at 200 rpm and to wait for 90 s before the electrical current was recorded. This procedure was repeated until no current was detected. The consecutive curves for HBr and H<sub>2</sub>SO<sub>4</sub> are presented in Fig. 4 in the case of an applied potential of 2 V/MSE. Passivity is found to be achieved for a cumulative water volume of 4 mL in the case of HBr whereas 1 mL is sufficient with H<sub>2</sub>SO<sub>4</sub>. As the formation of the passive film, according to reaction (2), should be independent of the acid solution before application of the electrical potential, this suggests there is probably an influence of the anion nature on the aggressiveness towards the incipient passive film when the electrical potential is applied.

### 3.4. Chronoamperometric experiments during water addition

To evaluate the capacity of the passive film to form and repair on tantalum in hostile conditions, chronoamperometric experiments were performed at some defined electrical potentials during a continuous addition of 0.5 mL of pure water every 90 s in the acidified methanol solution. The curves are presented in Figs. 5–7.

In all the cases, when the magnitude of the electrical potential is equal to 1 or 2.5 V/MSE, the current density is observed to fall finally to zero, so reflecting that passivity has been achieved. As evidence, hydrogen gas evolution was no more observed at the platinum cathode at the end of the experiment. The aggressiveness of the anions towards the tantalum anode, leading to oxidation reaction (4), can not thwart film formation on its surface when water is added because the kinetics of reaction (2) is dominant. Nevertheless, the time required to reach passivity is longer at 2.5 than at 1 V/MSE. The anions are more attracted at a greater potential and they are thus rendered more aggressive for the incipient film, so that greater water amounts have to be supplied to obtain a sufficiently resistant film. The SEM pictures in Fig. 8 show the presence of a passive film with a relatively smooth deposit on the tantalum surface for two representative anions (Br<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>).

When the applied potential is higher, say cases at 5 and 7.5 V/MSE, a clear distinction is observed according to the nature of

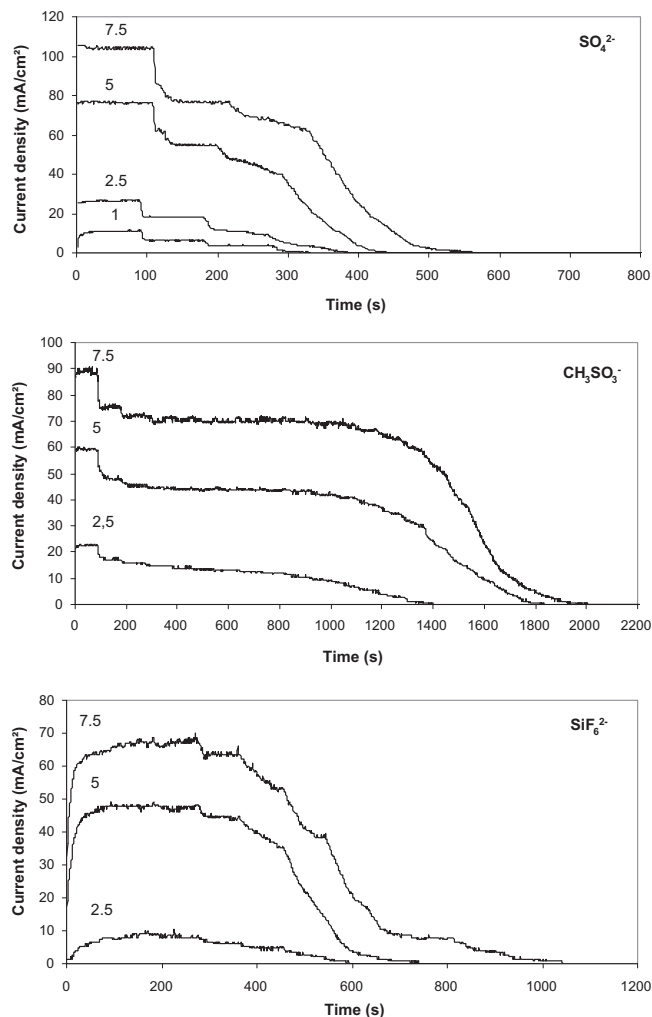
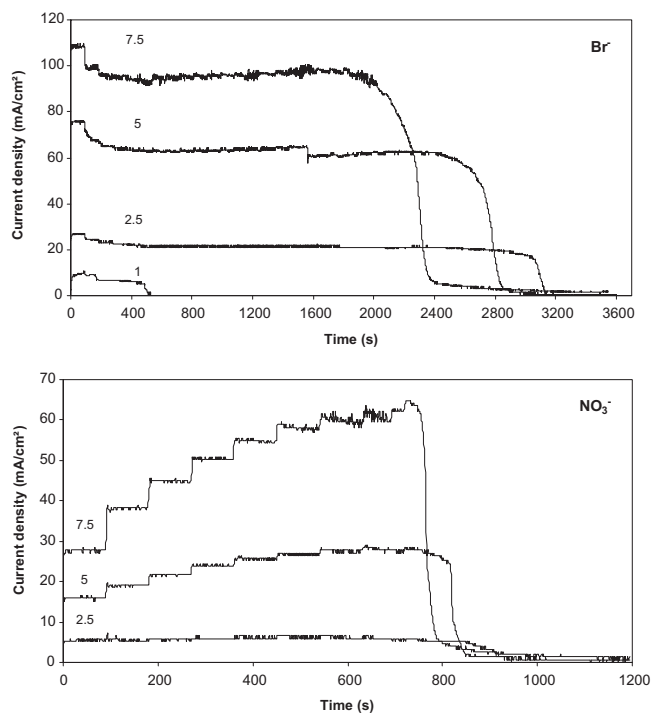
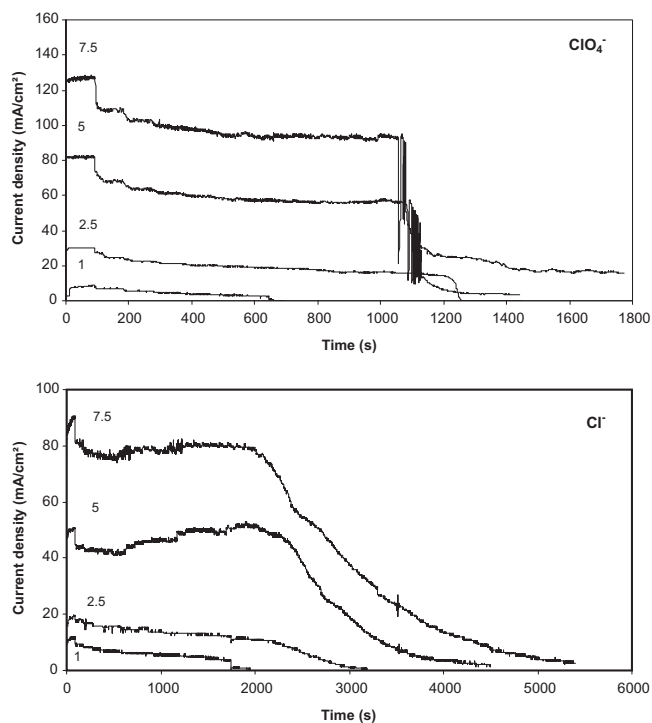


Fig. 5. Chronoamperometric curves during water addition at different potentials (versus MSE) in the presence of cosmotrope anions: SO<sub>4</sub><sup>2-</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>, SiF<sub>6</sub><sup>2-</sup>.

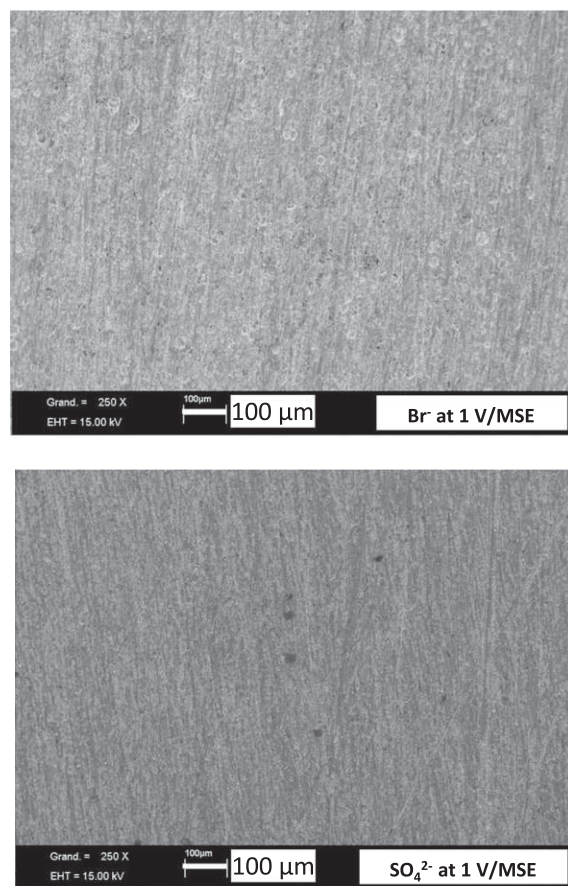


**Fig. 6.** Chronoamperometric curves during water addition at different potentials (versus MSE) in the presence of chaotrope anions:  $\text{Br}^-$ ,  $\text{NO}_3^-$ .



**Fig. 7.** Chronoamperometric curves during water addition at different potentials (versus MSE) in the presence of chaotrope anions:  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ .

the anions. Whereas passivity is effectively obtained (say the current density becomes nil) with the cosmotope anions:  $\text{SO}_4^{2-}$ ,  $\text{CH}_3\text{SO}_3^-$ ,  $\text{SiF}_6^{2-}$ , see Fig. 5, the current density decreases for a long time and it approaches more or less asymptotically the time axis but without reaching zero with the chaotrope anions:  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,



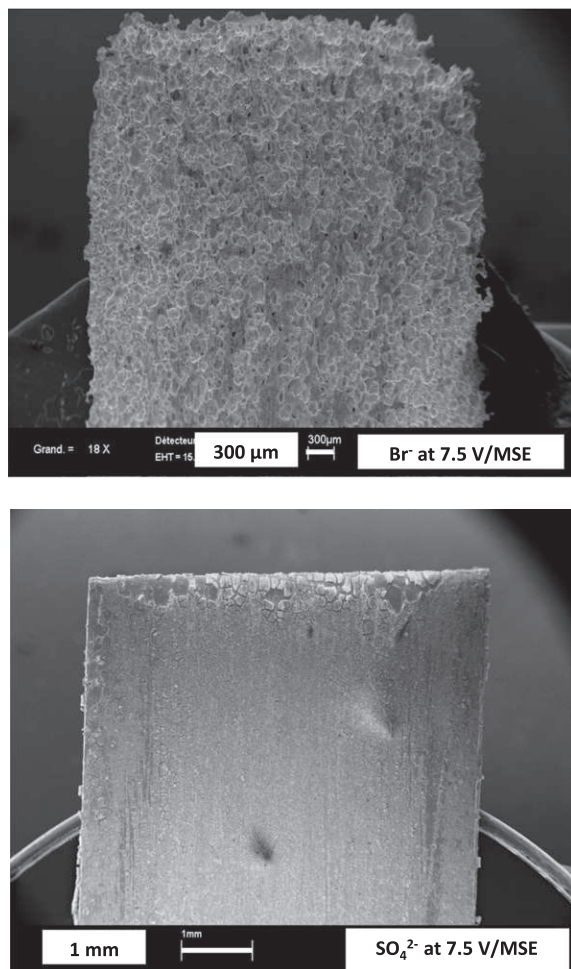
**Fig. 8.** SEM pictures of tantalum plates after chronoamperometric experiment at 1 V/MSE with two representative anions.

see Fig. 6, and  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ , see Fig. 7. This discrepancy may be ascribed to the ability for the cosmotope anions to catch water molecules to form a tightly attached hydration shell around them. Passivity can then be achieved since these anions tend to preserve their own hydration instead of altering continuously the passive film, as the chaotrope anions do [1,2]. These specific hydration effects are also expected to occur at low electrical potentials but these are not so much discriminatory since anion aggressiveness can not challenge efficiently film formation.

The propensity to significantly hamper the formation of a protective passive film is much more pronounced in the case of the chaotrope anions at high potentials. The aspect of the tantalum plates in Fig. 9 confirms that the passive film is severely damaged in the case of the chaotrope anion  $\text{Br}^-$ , when compared to the situation with the cosmotope anion  $\text{SO}_4^{2-}$ .

The influence of the anion nature can be evidenced through the comparative behaviour of the chronoamperometric experiments and conductivity measurements that were recorded simultaneously during water addition. Representative examples are shown for two chaotrope anions:  $\text{Cl}^-$ , see Fig. 10, and  $\text{NO}_3^-$ , see Fig. 11, and two cosmotope anions:  $\text{SO}_4^{2-}$ , see Fig. 12, and  $\text{CH}_3\text{SO}_3^-$ , see Fig. 13. The curves have been superimposed with a different ordinate axis. For the chaotrope anions at high potential, the shapes are very similar from the beginning. At low potential, the electric response is readily influenced by the formation of the passive film; it is particularly the case for  $\text{NO}_3^-$ . For the cosmotope anions ( $\text{SO}_4^{2-}$  and  $\text{CH}_3\text{SO}_3^-$ ), the difference between the curves at low and high potential is not so distinct.

These observations indicate that the added water molecules have an influence both on the mobility of the ions in solution

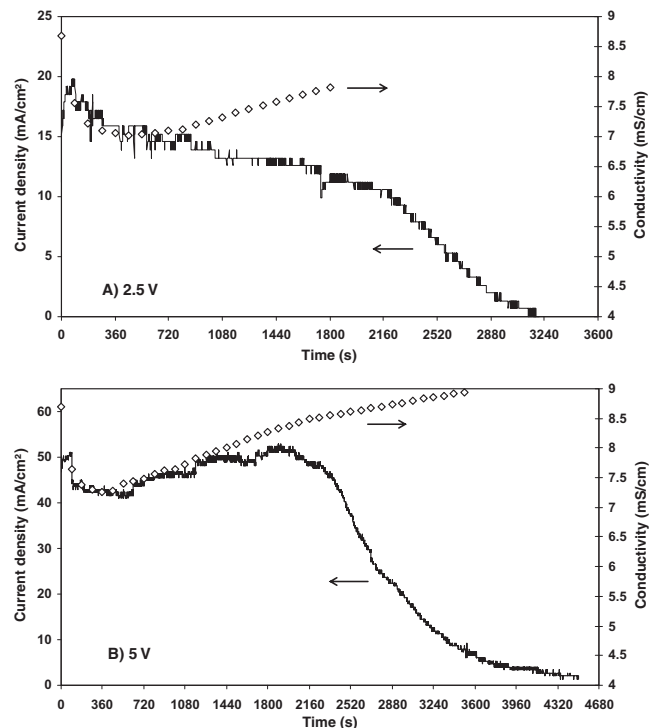


**Fig. 9.** SEM pictures of tantalum plates after chronoamperometric experiment at 7.5 V/MSE with two representative anions.

and on the building of the passive film at the tantalum anode. In fact, the variation of the solution conductivity is qualitatively well described by that of the conductivity of the acidified methanol solutions when the same amount of pure water (0.5 mL) is added stepwise (every 90 s) without any applied electrical potential. The corresponding conductivity curves for HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>SO<sub>3</sub>H, are reported in Fig. 14.

The first decrease and the following increase of the conductivity of many acidified alcoholic solutions during water addition have been already reported in the literature and interpreted by invoking a Grotthuss-type hopping mechanism due to preferential protonation of water than alcohol molecules [33–36]. As the protons are held more strongly to water molecules the conductivity decreases. It starts to increase once a continuous network of water molecules has been constituted. However this is not a general tendency since with HNO<sub>3</sub> the conductivity increases monotonously. Some acids like iodic acid (HIO<sub>3</sub>) or formic acid (HCO<sub>2</sub>H) are also found to exhibit the same behaviour as HNO<sub>3</sub>, whereas others like fluoric acid (HF) present the previous results, see Fig. 15.

Anyway, the influence of water on proton mobility has an important implication at the electrochemical level. In the prime instants after water has been added, the current density and thus the corrosion rate, is proportional to the extent of the proton reduction reaction occurring at the cathode which is effectively dependent on proton mobility [34,35]. This justifies the parallel variation that it is observed between the current density and the solution conductivity. The whole electric response is thus expected to result from



**Fig. 10.** Simultaneous chronoamperometric and conductivity measurements during water addition in the presence of HCl at (A) 2.5 V/MSE and (B) 5 V/MSE.

the balance between the influence of proton mobility and the formation of the passive film which is however perturbed by the concomitant attack of the anions.

### 3.5. Interpretation of the chronoamperometric curves

A simple model may be proposed that has the sole objective to describe the observed qualitative variation of the current density as a function of time during water addition. Conventionally, the electrical potential difference between the polarized electrodes in the system is expressed according to the following equation:

$$\Delta E = (E_{i=0,a} - E_{i=0,c}) + (\eta_a - \eta_c) + R_T i \quad (5)$$

where  $E_{i=0,a}$  and  $E_{i=0,c}$  are the anodic and cathodic Nernst potentials respectively;  $\eta_a$  and  $\eta_c$  are the anodic and cathodic overvoltages respectively;  $R_T$  is the total resistance and the term  $R_T i = U$  is the ohmic drop.

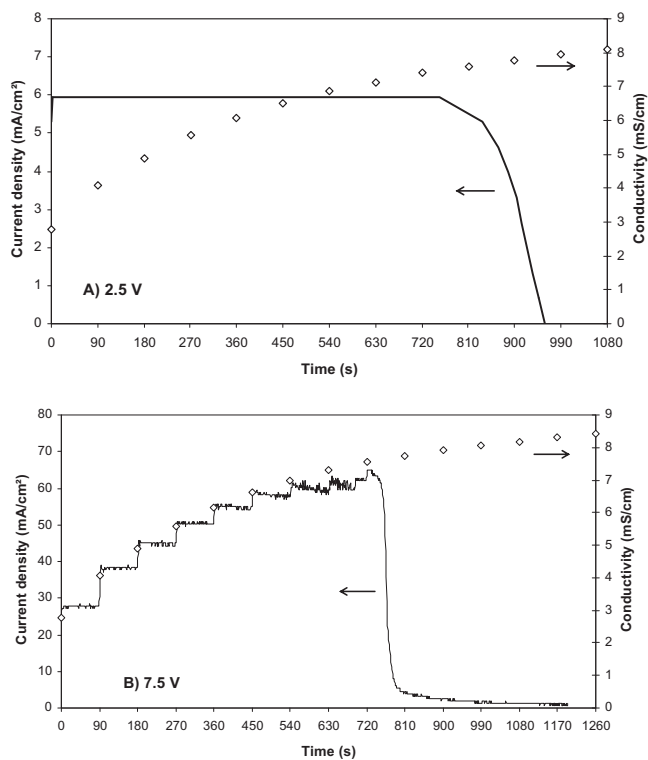
Thus, the ohmic drop can be expressed as:

$$U = \Delta E - (E_{i=0,a} - E_{i=0,c}) - (\eta_a - \eta_c) = R_T i \quad (6)$$

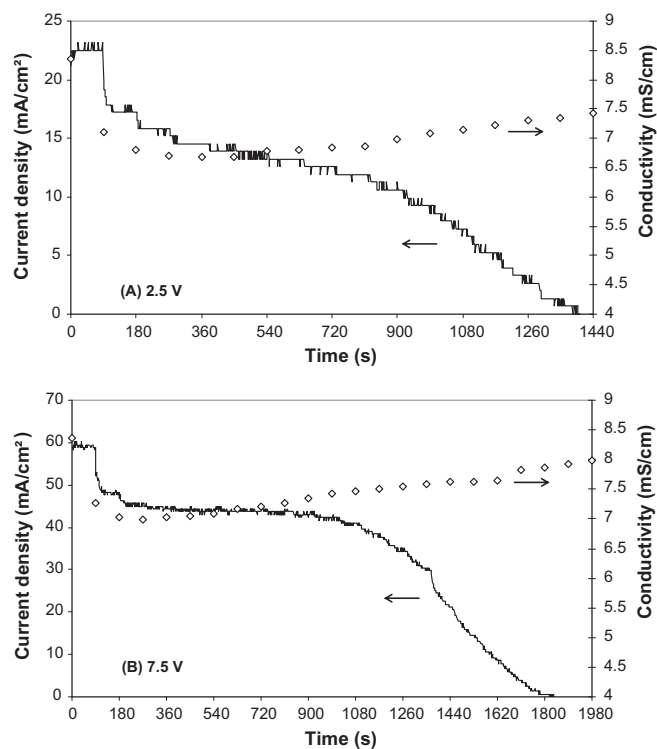
The measured electrical current is assumed to correspond to the following relation where  $U$  is expected to remain broadly constant:

$$i = \frac{U}{R_T} = \frac{U}{(R_s + R_f)} = \frac{U}{\left(\frac{K}{\chi_s} + R_f\right)} \quad (7)$$

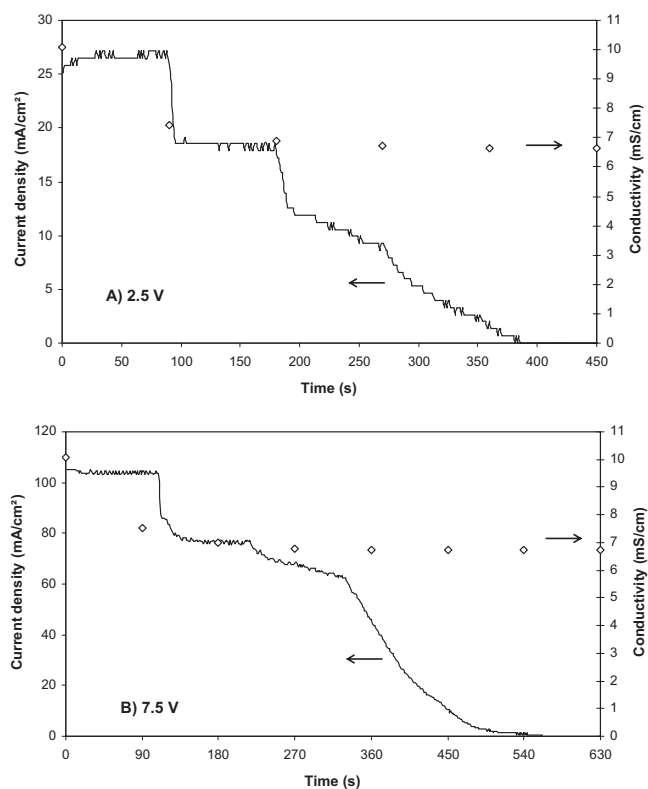
The total resistance  $R_T$  between the electrodes results from the sum of two contributions. The term  $R_s$  is the solution resistance which is inversely proportional to the solution conductivity  $\chi_s$  owing to the charge and the mobility of the ionic species. It is essentially represented by that of the protons (the conductivity of the anions being much lower).  $K$  is the ratio of the distance between the electrodes and their active surface. The term  $R_f$  represents the film resistance originating from the building of the passive film at the



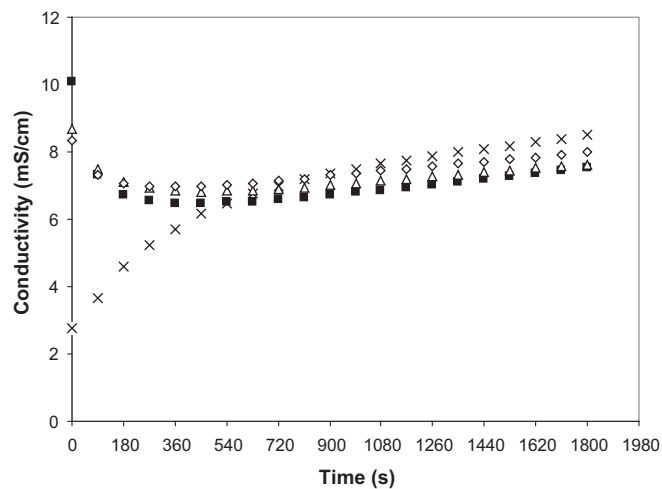
**Fig. 11.** Simultaneous chronoamperometric and conductivity measurements during water addition in the presence of  $\text{HNO}_3$  at (A) 2.5 V/MSE and (B) 7.5 V/MSE.



**Fig. 13.** Simultaneous chronoamperometric and conductivity measurements during water addition in the presence of  $\text{CH}_3\text{SO}_3\text{H}$  at (A) 2.5 V/MSE and (B) 7.5 V/MSE.



**Fig. 12.** Simultaneous chronoamperometric and conductivity measurements during water addition in the presence of  $\text{H}_2\text{SO}_4$  at (A) 2.5 V/MSE and (B) 7.5 V/MSE.



**Fig. 14.** Variation of the conductivity of acidified methanol solutions at 0.1 mol/L concentration as a function of time during water addition:  $\text{H}_2\text{SO}_4$  (■),  $\text{HCl}$  (Δ),  $\text{CH}_3\text{SO}_3\text{H}$  (°),  $\text{HNO}_3$  (×).

tantalum surface during water addition. It is expected to increase monotonously with the water content but it is variably affected by the anion aggressiveness according to the applied potential.

At low potential, when the anion aggressiveness is not too important, the influence of the film resistance ( $R_f$  term) is detected to be dominant over the effect of the solution conductivity (say proton mobility principally) when the curve of the current density does not follow anymore the shape of the conductivity curve, see cases A in Figs. 10, 12 and 13. In the case of  $\text{NO}_3^-$ , see case A in Fig. 11, the current density remains practically constant from the beginning, so indicating that the resistance due to the incipient film matches quantitatively the increase of the solution conductivity.

Within these conditions, the formation of a cohesive passive film over the anode surface is promoted when the water content increases. As a consequence  $R_f$  is expected to become infinite so that the current density then reaches zero, as it is effectively observed.



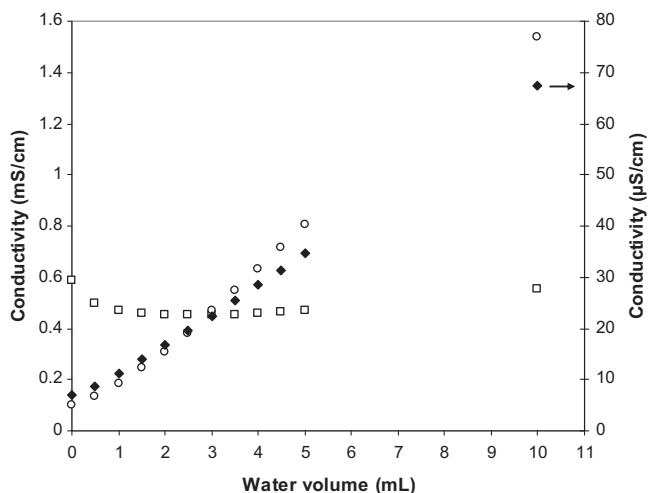


Fig. 15. Variation of the conductivity of acidified methanol solutions at 0.1 mol/L concentration as a function of the water volume: HCO<sub>2</sub>H (◆), HIO<sub>3</sub> (○), HF (□).

When the potential is higher, although the kinetics of reaction (2) may be expected to be faster, the influence of the  $R_f$  term is much more delayed for the chaotrope anions since the anion aggressiveness is enhanced, see cases B in Figs. 10 and 11. As a result, the variation of the current density follows faithfully the shape of the conductivity curve for a long period: the influence of the proton mobility is dominant. After significant water addition, the building of the passive film ( $R_f$  term) becomes no longer negligible and the curves cease to be parallel. The current density decreases abruptly but the anion aggressiveness is such that a uniform and fully insulating passive film can not be obtained: a leakage current is recorded indefinitely. However, it was checked and confirmed that when the experiments were stopped during 90 s and then restarted, no electrical current was detected. This indicates that passivity can be achieved successfully once the continuous flow of the aggressive anions has been interrupted, thus allowing a sufficient repairing of the film.

In the case of the cosmotope anions, the chronoamperometric and conductivity curves move away earlier from one another, see cases B in Figs. 12 and 13. This reflects that the building of the passive film is favoured, whatever the potential ( $R_f$  increases up to infinite), since the anion aggressiveness against the passive film is significantly reduced once a hydration shell has been constituted around these anions.

#### 4. Conclusions

The achievement of passivity of tantalum through water addition in hostile media during chronoamperometric experiments was found to depend on the applied potential and the nature of the aggressive anions. The comparison between the simultaneous chronoamperometric and conductivity measurements is original and useful to appreciate the dominant process: the building of a protective passive film over the influence of proton mobility in solution. The results inferred from this study, with such a valve metal as tantalum, corroborate the crucial influence exerted by anion-specific hydration effects, so contributing to get a better understanding of the whole corrosion/passive behaviour of valve metals.

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