DISSOLUTION-PASSIVATION OF TITANIUM IN HIGHLY CHLORINATED AND OXYGENATED AQUEOUS MEDIA. REACTION MECHANISM. APPLICATION TO SUPERCRITICAL WATER OXIDATION CONDITIONS.

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This work evaluates the titanium metal anodic electrochemical behavior in supercritical conditions (up to 400°C and 28MPa) in chlorinated media to estimate the supercritical water oxidation (SCWO) reactors reliability for the treatment of 10% organic wastewaters. Titanium RT dissolution-passivation mechanism in HCl media (pH < 0) is oxygen-independent (Figure 1)[1]. Deduced from “current-potential” and “valence-potential” curves, it is based on four crucial elementary steps with two branches: an *active branch* (trivalent dissolution inversely proportional to the pH), and a *passive branch* (TiO_2 formation (slow tetravalent dissolution)). Depending on potentials, the tri- and tetra-valent species can be found *separately* or *simultaneously.* This leads to a bifurcation model illustrated by the excellent adjustment between experimental and calculated values of the proposed (I, E) laws (6 kinetic parameters,4 limiting steps: 2 electrochemical and 2 chemical ones leading to the solubilization) (figure 2)[2]. The elementary-step activation energies are compatible with respectively those of electrochemical and chemical steps. The evolution of the intermediate adsorbats coverage ratios with the potential illustrates with precision the relative preponderance of each branch and the exact positioning of the passive domain (figure 2).

For pH > 1, in supercritical fluids, the experimental (I,E) curve presents a passivity plateau profile (the dissolution valence is 4) and no activation currents (figure 3). The active branch of the model disappears, the passive one being the only effective issue. The model is based on 3 successive elementary steps (2 electrochemical ones and 1 chemical dissolution step with 5 overall kinetic parameters)[3,4]. The chemical step and the pH are once again the predominant parameters, justifying the ability of titanium to irreversibly form an insoluble passive film even under high pressures and high temperatures (the coverage ratio Θ_4, characteristic of the TiO_2 formation, is 1 (scheme 1b))[2]. It underlines as well, the modifications of the chemical and physical properties of the medium, which becomes apolar beyond the critical point (lower titanium activity in the supercritical domain). The quantification of each elementary step is performed to understand and/or orient the materials behavior according to different factors (pH, chloride ions contents, potentials…).

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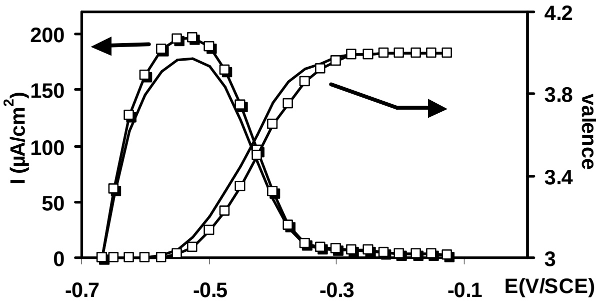


Fig.1 Anodic steady-state (I,E) curves of T60 titanium (Ω = 0 rpm) in HCl 4 mol/l at 21 °C with (—) and without (❑) oxygen and the corresponding valence laws.

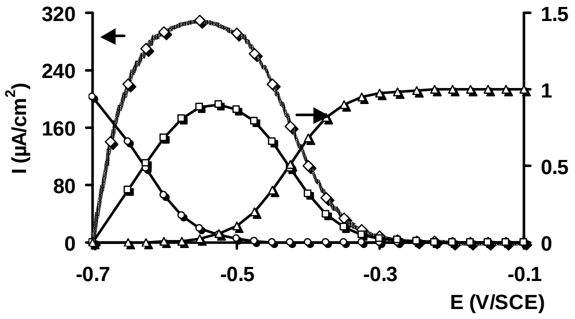


Fig..2: Concordance of experimental points (◊) and simulated anodic curve: . Comparison with the species coverage ratios evolution with the potential, for T60 titanium at 30°C (Ω = 0 rpm) in oxygenated HCl 4 mol/l. ◊: I µA/cm²,❍: 1-Θ_3-Θ_4, ❑: Θ_3, Δ: Θ_4.

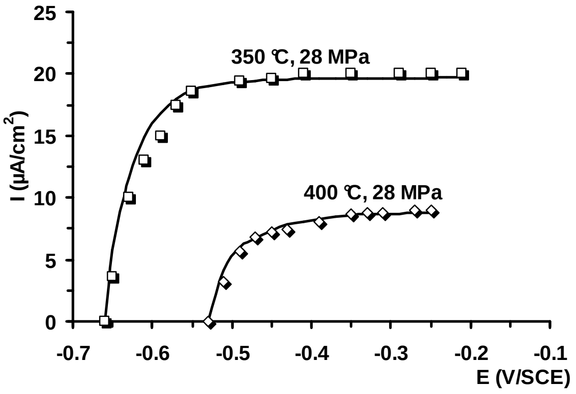
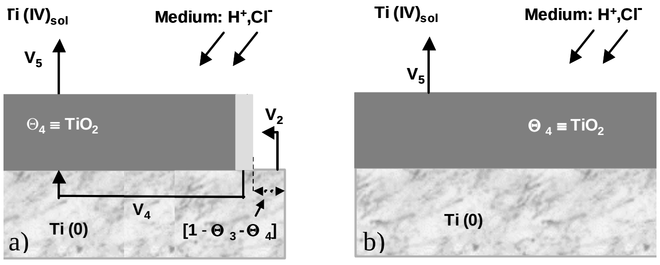


Fig. 3: Experimental (−) and calculated (I,E) curves from the six-parameters model for T60 titanium (Ω = 0 rpm) HCl 310^{-2} mol/l at (❑) 350°C /28MPa,and (◊) 400°C/28 MPa.



Scheme 1: Interface in supercritical conditions: a) at the beginning of the reaction close to the corrosion potential; b) under a passive anodic regime (preponderance of the protecting TiO_2 film).