

Long Term In-situ Impedance Spectroscopy in High Temperature (360°C) Water on Pt and on Corrosion Layers on Zr and Zr Alloys

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Corrosion in high temperature water is often studied via ex-situ methods, such as with weight gain or spectroscopies like scanning electron microscopy, done after interruption or shut down of the corrosion experiment. As reported previously /1/, we use an experimental set up in a static autoclave which allows in-situ electrochemical analysis, in particular via impedance spectroscopy (IS). The use of ceramic seals and cooled Teflon feed-throughs coupled to batched IS analysis provides quasi-continuous long term data, unlike in work reported so far. Continuous IS analysis accounts for cyclic corrosion-layer growth where relatively fast layer breakdowns are more or less buried in long periods of moderate changes in layer response. Such behavior is, e.g., observed at Zr (alloys). Closely spaced counter electrodes for acceptable R_s , symmetrical cells, and floating operation yield frequency ranges and data qualities known from ambient temperature IS. Moreover, different corroding (Zr, Zr alloys) and not corroding (Pt) samples are monitored in parallel in recent work. This procedure takes into account long experiment times, allows direct comparisons, and facilitates separation of processes superimposed in the IS signals. At present, there is some lack of quantitative data on the electrochemical processes in the solid (oxide) as well as at the solid/liquid interface. In addition to potential contributions of surface roughness, IS includes contributions of the interfacial reaction, the solid (volume) dielectric, and, moreover, the layered structure of that dielectric. This complicates isolated application of models existing in the corresponding scientific fields.

This contribution will focus on two subjects. First the electrochemistry at the not corroding (Pt) electrodes is treated. As seen in the Figure 1 a classical impedance according to the Randles model is often obtained, which allows determination of parameters of the interfacial process (charge-transfer rate, C_{HH} , diffusion-layer term, species' concentrations), as well as their evolution with time. Apart from an intrinsic scientific interest, these parameters provide an in-situ reference on the long term stability of the electrochemical environment (pollution, H₂ pressure...).

As second subject, results on corroding Zr (alloys) are treated over exposure times of up to about 400 days. Ionic (O²⁻) conduction of the corrosion oxide is known to cause an initial layer growth according to parabolic to cubic growth laws. Above a critical thickness in the μm range which depends on the purity or alloy composition and pre-treatment, stress induced layer rupture occurs, as confirmed for different Zr (alloy)

materials. Subsequent layer re-growth at the metal/oxide interface then leads to structured ("dense" vs. "porous") oxides. IS provides the time evolution of oxide conductivity and total oxide thickness from HF capacitance and dielectric function (cf. /1/). In addition, the time evolution of several subsequent rupture processes is traced (at Zr-Sn). Different dielectric losses in the sub-layers cause an impedance response characteristic for a bi-layer dielectric. The example in Figure 2 compares impedance in the initial cubic growth range (single phase peak) with the one after 3 rupture/re-passivation cycles which leads to a double phase peak. High dielectric losses are characteristic for both layers.

Results of presently running experiments aiming at a comparison corrosion of pure Zr with different Zr alloys (Zr-Sn, Zr-Nb) will be presented. These materials show differences in (electronic) conductivity and cycle behaviour.

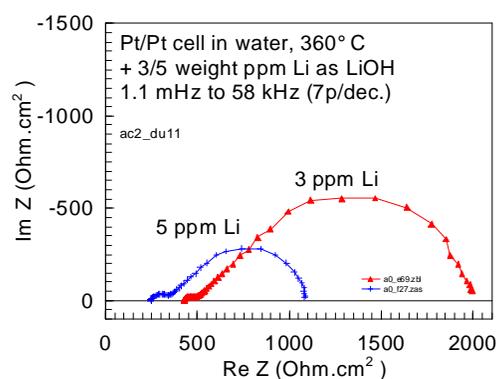


Figure 1. Impedance of a Pt/Pt cell at the open-circuit potential in 360°C electrolyte.

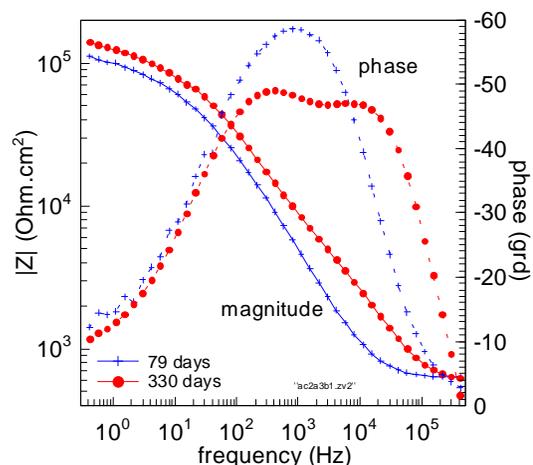


Figure 2. Impedance of a Zr-Sn alloy (1.2 % Sn) at the open-circuit potential at 360°C at different oxidation times (electrolyte as in Fig. 1; 3 ppm Li).

References

- /1/ J. Schefold, D. Lincot, A. Ambard, E. Moleiro, O. Kerrec, (a) *Proceedings 7th Internat. Symposium on Electrochemical Methods in Corrosion Research EMCR 2000, Budapest (2000) No. 58.* (b) *Proceedings 13^{ème} Forum d'Impédances, Paris (2000).*
- /2/ *Dechema Corrosion Handbook*, D. Behrens (Ed.), VCH, Weinheim, Vol. 1 (1987) p. 244, and Vol. 4 (1989) p. 185.