Steady-state and Impedance Study of Nb Electrodissolution in Acid Fluoride Medium

Sandro Cattarin[1], Marco Musiani[1], Bernard Tribollet[2]

[1]CNR-IPELP, Corso Stati Uniti 4, 35127 Padova, Italy
[2]CNRS-UPR15, "Physique des Liquides et Electrochimie", Université P. et M. Curie, CP 133, 4 Place Jussieu, 75252 Paris Cedex 05, France

Although the etching of Nb and its alloys in HF solutions is interesting for patterning of magnetic alloys,[1] to the best of our knowledge, no comprehensive study of Nb electrodissolution in acid fluoride media is available.

Figure 1 shows the voltammetric curves of a Nb electrode in a 0.4 M fluoride solution at pH 2. The essential features of these curves and of the steady-state behavior are a first peak, followed by a minimum, a subsequent region of rising current and a pseudo-plateau with negative polarization resistance. j-E curves obtained for different concentrations of fluoride species (c_F) and pH values exhibit similar shapes. Figures 2 and 3 show the dependence of j, measured at a fixed potential of 6 V, on either c_F or pH.

The steady-state results, very similar to those observed for Si in the same medium[2,3], can be explained with similar hypotheses, i.e. the formation of an oxide layer on the first peak and, at higher potentials, a control of the overall kinetics by chemical dissolution of the oxide at the oxide/electrolyte interface by HF and related species[2]. As compared to Si, much lower currents flow for the same c_F and pH in the case of Nb. Consistently, the mass transport effect, significant in the former case, is very minor for Nb. A dissolution valence close to 5 has been measured for the latter over the whole potential range shown in Fig. 1.

Impedance diagrams obtained close to open circuit potential consist of a single capacitive loop. Then, in the active dissolution region, a second lf capacitive loop appears the relative size of which increases with E. By approaching the peak potential, an additional inductive loop becomes visible at intermediate frequencies. In the passivation region, the hf and inductive loops remain similar, but the limiting lf behavior is characterized by a negative resistance. In the second j-rising region, the shape of the diagrams is again similar to that observed just before the first peak. Finally, on the pseudo-plateau, the diagrams consist of a capacitive hf loop, an inductive loop and a lf capacitive vertical line.

The formation ratio of the Nb oxide present on the electrode surface has been estimated as a function of E from the parameters R_{hf}, C_{hf} and C_{lf}, extracted from the impedance diagrams, using a procedure already applied in the case of Si and Ti[3].

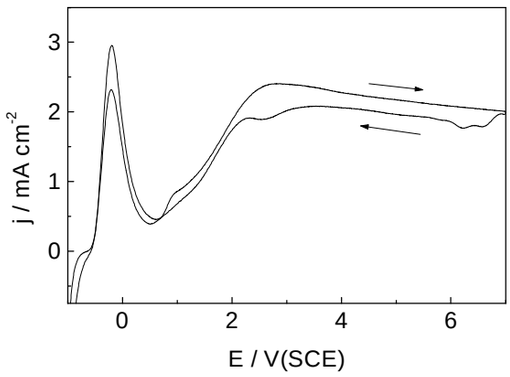

Figure 1. Cyclic voltammetry of Nb in a 0.4 M fluoride solution at pH 2. Scan rate 5 mV s^{-1}.

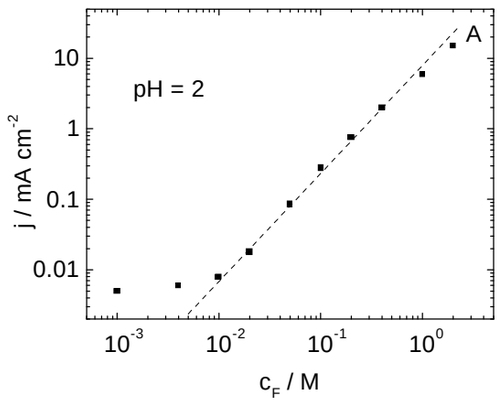

Figure 2. Dependence of the Nb dissolution current, measured at 6 V, on c_F at pH = 2.

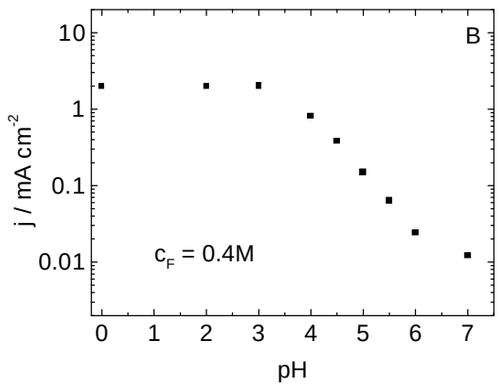

Figure 3. Dependence of the Nb dissolution current, measured at 6 V, on pH at c_F = 0.4 M.

References

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