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There is large agreement that in the rising portion of the bell-shaped curve characteristic of the active/passive transition, the metal is dissolved and simultaneously covered by a blocking species. As its coverage increases, the current reaches a peak and then drops to much lower values, once a monolayer of the blocking species is formed. Further potential increase, beyond the peak, results in a 3-D film growth. Thus the plots of C_{hf}^{-1} -E and R_{hf} -E, where C_{hf} and R_{hf} are the capacitance and resistance of the high-frequency semicircle in the impedance response, are expected to show a discontinuity at the potential at which the 2D layer is completed and 3D growth starts. This is because below that potential, C_{hf} and R_{hf} have the meaning of double layer capacitance and charge transfer resistance, whereas above it they can be interpreted as the 3D film capacitance and the migration resistance of current carriers through the film [1,2]. We have recently observed that some systems (Nb in acid fluoride media or warm aqueous alkali, Mo in concentrated H_3PO_4) together with the usual shape for the steady-state I-E curves, exhibit linear increasing C_{hf}^{-1} -E and R_{hf} -E plots below the peak potential, with no discontinuity at this potential (Fig.1). Simultaneously, a pseudo-inductive loop appears at comparatively high frequencies in the impedance spectra (above 1 Hz, Fig.2). These results suggest that a 3D layer already exists below the peak potential. In the present paper we describe the experimental results for these systems and propose a kinetic model for their interpretation. The model assumes that the metal is covered with a non-stoichiometric oxide containing at least two oxidation states of the cation (Nb(IV) and Nb(V) for Nb, Mo(IV), Mo(V) and Mo(VI) for Mo) already at the free corrosion potential. The processes of oxidative dissolution of the lower valency cations and their transformation to cations of higher valency, leading to passivation, are assumed to explain the shape of the I-E curve. These processes are limited by both charge transfer at the film/solution interface and transport of cation vacancies through the film. Thickening of the oxide film is assumed to proceed simultaneously, and is proposed to be limited by transport of anion vacancies accelerated by interfacial charge[1,2]. The model is able to reproduce both the steady state curve and the impedance response and demonstrates the sensitivity of impedance spectroscopy to the detailed mechanism of the processes during the active-to-passive transition of metals.

1. M. Bojinov, *Electrochim. Acta* **42**,3489(1997)

2. S. Cattarin, M. Musiani and B. Tribollet, *J. Electrochem. Soc.* **149**, B457(2002).

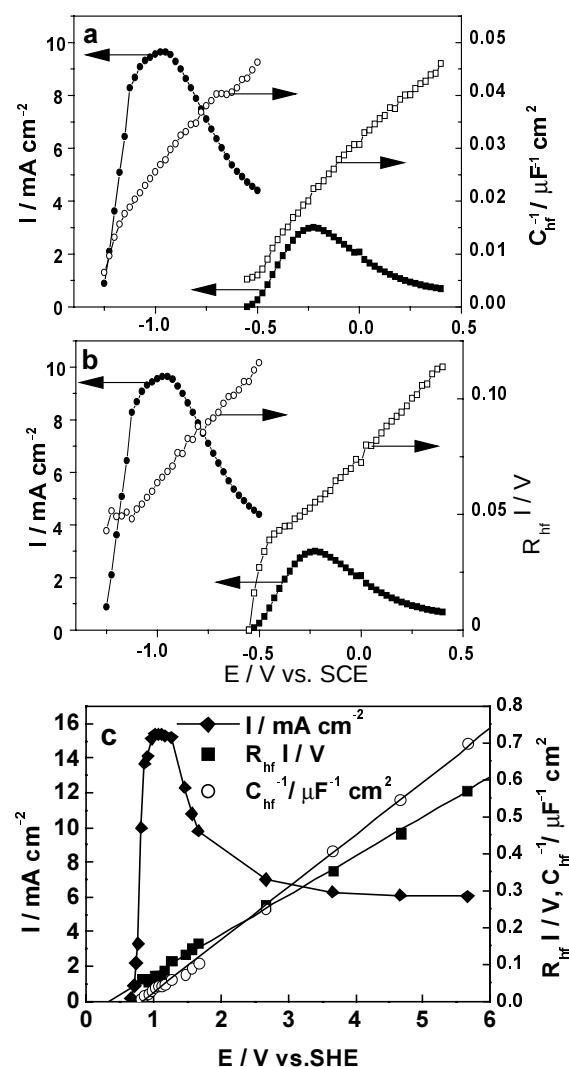


Fig.1. (a) I-E and C_{hf}^{-1} -E plots for Nb in 5 M NaOH at 60 °C (left curves) and 0.4 M fluoride, pH 2 at 25 °C (right curves); (b) I -E and R_{hf} -E plots for the same systems; (c) I-E, C_{hf}^{-1} -E and R_{hf} -E plots for Mo in 14.8 M H_3PO_4 at 25 °C.

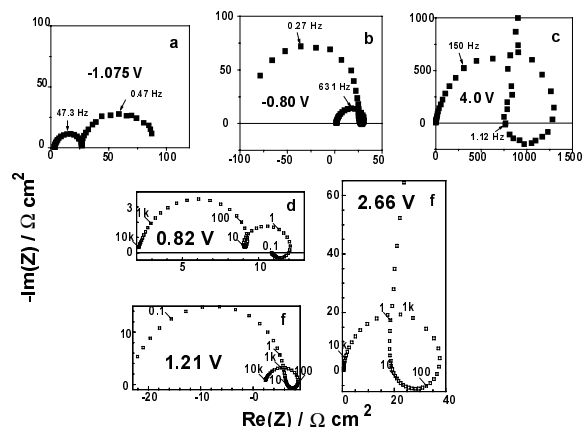


Fig. 2. Impedance spectra for the studied systems in the active-passive transition. (a) to (c) - Nb in 5 M NaOH at 50 °C, (d) to (f) - Mo in 14.8 M H_3PO_4 at 25 °C. Parameter is frequency in Hz.