

Importance of Elasticity in the Transport of Hydrogen in Metals

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Elastic host matrix expands when accepting a guest. Hence, any irregularity in distribution of the guest induces self stress in the system. On the other hand, stress contributes to the chemical potential of components of solids. As stress propagates in the solid with velocity of sound, it may be the cause of nonlocal effects.

The simplest example for studying this phenomenon is the transport of interstitial hydrogen in metals. In 1983 it was noticed the first time for the system consisting of a Pd-alloy membrane (of thickness  $L$ ) separating two chambers, and being primarily at equilibrium at a non-zero pressure of hydrogen. Namely, in response to a sudden change of pressure in one chamber ( $z = 0$ ), in the first period of time the flux of hydrogen in the opposite one ( $z = L$ ) is opposite in sign with respect to the pressure signal. This effect was named *uphill diffusion* (1). The above transport was described by fairly complex equations, which found experimental validation only for early times, when mainly stress decides on the transport (2,3).

This can be overcome by applying the transfer functions (TFs),  $H_s$ , approach. These are the ratio of periodically steady state linear response to a small-amplitude sinusoidal signal, which perturbs equilibrium in the system, to this signal, or *vice versa* (4-6).

In the case under discussion, equilibrium is perturbed by oscillations of hydrogen concentration at one side ( $z = 0$ ) of the membrane specimen. Related oscillations either of the flux of hydrogen at one of the two sides ( $H_{f(z=L)}$ ) (4) or  $H_{f(z=0)}$  (6), or of the concentration of hydrogen at the opposite side, this time being impermeable for hydrogen (5), are considered as alternative responses of the system. In the successive measurements, the frequency,  $f$ , of the signal is changed gradually within a wide range.

Transport equations, taking into account both the Fickian diffusion and the nonlocal effect of stress, were linearized, and solved analytically for the boundary conditions appropriate for  $H_f$  or  $H_c$ , respectively (4-6). They are analyzed for M-H systems of properties similar to those of  $\alpha$ -phase Pd-H and Pd<sub>81</sub>Pt<sub>19</sub>-H ( $D = 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $n$  in  $\text{MH}_n$  from 0.2 to 0.002). In Figures 1, 2 and 3 spectra of  $H_{f(z=L)}$ ,  $H_{f(z=0)}$  and  $H_{c(z=L)}$  computed for  $n = 0.2$  are presented, respectively.

Formally, fitting of all above models to appropriate experimental data allows for determining reliable values of diffusion coefficient of hydrogen and bulk elastic modulus of M-H system, and the dependence of these parameters on hydrogen concentration. However, the three TFs differ in real usability. For instance, in the case of  $H_{f(z=L)}$ , the only important effect of possible nonlinearity is the constant component of the response (7). If a similar effect would appear also in measurements of  $H_c$ , that should rule out this classical method of measuring the diffusion coefficient of hydrogen in metals.

References

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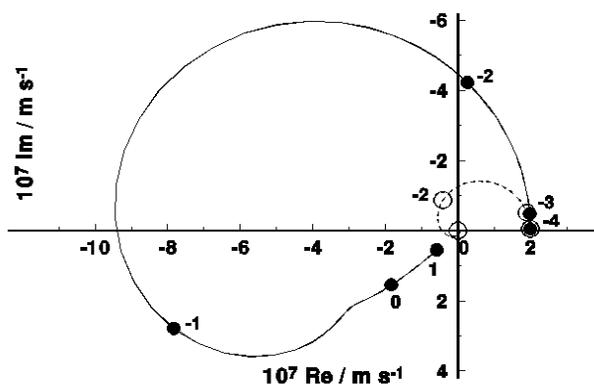


Fig. 1.  $H_{f(z=L)}$ .  $n$  in  $\text{MH}_n$  equal to 0.2. (—●—) and (---○---), the effects of stress present, and absent, respectively. Numbers close to the symbols indicate the decades of  $f$  in Hz.

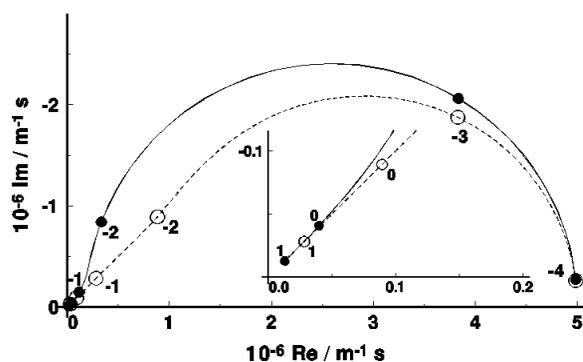


Fig. 2.  $H_{f(z=0)}$ . Legend as for Fig.

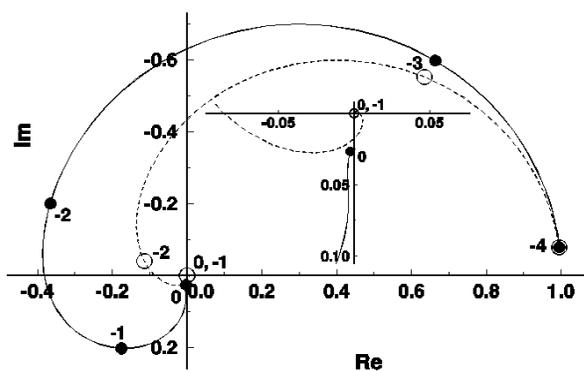


Fig. 3.  $H_{c(z=L)}$ . Legend as for Fig. 1.