



Supplementary transfer function of the transport of hydrogen in self-stressed metals

Piotr Zoltowski*

Institute of Physical Chemistry of Polish Academy of Sciences, Kasprzaka 44/52, 01224 Warsaw, Poland

ARTICLE INFO

Article history:

Received 10 June 2010

Received in revised form

22 September 2010

Accepted 25 September 2010

Available online 31 October 2010

Keywords:

Hydrogen in metals

Transport

Self-stress

Transfer function spectroscopy

EIS

ABSTRACT

It is well established that the transport of hydrogen dissolved in metals is non-Fickian. This results from a non-zero partial volume of such hydrogen. Consequently, any gradient of hydrogen concentration in a metal causes its self-stress. Till now, the proposed transport equations taking stress into account have found analytical solutions only for quasi-equilibrium cases, and the transfer function (TF) spectroscopy is advocated as a unique technique for modelling the transport in question, and, in this way, estimating from experimental data the parameters that determine the kinetics of this process. In this paper, an additional TF – completing the set of previously proposed TFs – is presented and its applicability for estimating the values of the above parameters is numerically analysed with comparison to other analogous TFs. Although this TF is unique – being outwardly applicable also to the cases of foil and thin-layer specimens – it describes properly the transport in question solely in the case of membrane specimen.

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1. Introduction

Many metals and alloys absorb hydrogen [1]. In the simplest case, hydrogen dissolves in the parent matrix of the given metal as an interstitial component, where it is present in atomic form, i.e. H. However, the lattice of the resulting M–H solid, MH_n (where M denotes all metallic components of the solid and n denotes the atomic ratio of H to M), is expanded, or in some cases contracted, nearly proportionally to n , viz. to the concentration of H species in the metal matrix, c (where $c = nc_{\max}$, and c_{\max} is c when H occupies all appropriate interstitial sites). It follows that the absorbed hydrogen has a partial molar volume, V [1–5].

Such M–H systems are the most familiar host–guest systems [5–8]. In particular, the Pd–H system is the most familiar M–H system, and is frequently used as a model for the whole class [1,9].

Pd has fcc structure, and the dissolved H occupies only the octahedral interstitial sites [1,2]. Accordingly, $n \leq 1$. A system, consisting of the bulk Pd specimen in the surrounding gaseous phase containing molecular hydrogen, H_2 , of some partial pressure, p , being apparently at equilibrium at some temperature, T , is characterized by the p – n (e.g. $\frac{1}{2}\log(p)$ vs. $\log(n)$ or $\log[n/(1-n)]$) isotherm [1,2]. Close to the room T , the isotherm has three distinct regions: at $n < 0.015$ and $n > 0.6$ the larger n the larger p is, whilst in between these limits $p = \text{const}$, viz. there is a plateau. For n values below and

above the plateau PdH_n is single-phase, and the respective phases are called α and β , whilst in the plateau region these phases coexist. The plateau is related to the existence of a miscibility gap in the Pd–H solid. As the two phases are isomorphic, in the plateau region PdH_n consists of two types of domains that differ solely by their lattice dimensions, corresponding to the maximal and minimal n characterizing the α - and β -phase, respectively [1,2]. Accordingly, even at apparent equilibrium and when the specimen remains coherent, its lattice is locally strained.

In turn, when the Pd specimen is in the surroundings of a protic solution, the equilibrium in the system is decided by the electrode potential, E , instead of by p [9]. However, at a proper choice of standard p and E values, and the Nernstian proportion of units at the two respective ordinates, the plots of $\frac{1}{2}\log(p)$ vs. $\log(n)$ (or vs. $\log[n/(1-n)]$) and the $-E$ vs. $\log(n)$ (or vs. $\log[n/(1-n)]$) isotherms overlap each other [10,11].

The higher the temperature the narrower the plateau is, till the critical T , T_c , is reached (ca. 295 °C) where the plateau width becomes zero. At $T \geq T_c$ PdH_n is single-phase, for any value of n [1,2]. However, because of the non-zero value of V , even in a single-phase PdH_n solid any gradient of n causes a strain of its lattice and the resulting self-stress [12–17].

The great majority of M–H systems and MH_n solids behave similarly, although there are important quantitative differences in their parameters, e.g. p of the plateau and the respective limiting n values, T_c etc. [1]. To this group also the substitutional alloys of Pd with Ag and Pt belong [1,18,19]. Some Pd–Ag alloys have even found an industrial application in the purifying via filtration of hydrogen. In

* Corresponding author. Tel.: +48 22 343 3282; fax: +48 22 343 3333.

E-mail address: pizolt@ichf.edu.pl

turn, due to the fact that in the case of $(\text{Pd}_{81}\text{Pt}_{19})\text{H}_n$ T_c is $<0^\circ\text{C}$, and at room T and moderate p relatively large n values can be obtained, in studies of the effects of self-stress on the transport of hydrogen in metals the $\text{Pd}_{81}\text{Pt}_{19}$ alloy is most commonly used [11,13–15,20].

One should bear in mind that Fick's equations were derived for the diffusion of neutral species in dilute fluid solutions, viz. unstructured. However, in fact, the diffusion flux of the respective component is not proportional to the gradient of its concentration (or activity), as described by the 1st Fick's equation, but to the gradient of its chemical potential, viz. in our case to the gradient of chemical potential of interstitial H in the M matrix, μ [14,15]:

$$J = -\frac{Dc}{RT} \frac{\partial \mu}{\partial z} \quad (1)$$

where J and D respectively denote flux and diffusion coefficient of interstitial hydrogen, and R denotes the gas constant. For simplicity, in this paper the transport is considered to be one-dimensional, along the z coordinate. In turn, as H is in the elastic matrix of M, μ depends not only on c , but also on the mechanical stress, σ , typically caused in MH_n by gradients of c [14]:

$$\mu = \mu(\sigma, c) = \mu(0, c) - V\sigma \quad (2)$$

where $\mu(0, c)$ denotes μ in the stress-free state, whilst σ is the trace of the stress tensor ($\sigma = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$) and is an analogue of pressure. It propagates in the whole specimen volume with the velocity of sound.¹ Hence, in contrast to c , σ is a non-local quantity. On the other hand, the local μ is determined by the local c together with σ . From Eqs. (1) to (2) the main equation of the so-called "Stress Induced Diffusion" results (under assumptions that $V \neq f(c)$ and $D \neq f(c)$) [14,15]:

$$J = -D \left(\frac{\partial c}{\partial z} - \frac{Vc}{RT} \frac{\partial \sigma}{\partial z} \right) \quad (3)$$

In order to solve Eq. (3) the relationship between c and σ has to be defined. Li [12] and Baranowski [14,15] reached this by adaptation of some equations derived by Timoshenko [22] for thermo-stress, which modifies the Fourier equations of thermal conductivity, to the case of the chemo-stress in question. The resulting equations are [14,15]:

$$\sigma_{xx} = \sigma_{yy} = -\frac{V\bar{Y}}{3} \left[c - \frac{1}{L} \int_0^L c dz - \frac{12(z-L/2)}{L^3} \int_0^L \bar{\Delta c} \left(z - \frac{L}{2} \right) dz \right] \quad (4)$$

and $\sigma_{zz} = 0$

where $\bar{Y} = \bar{E}/(1-\nu)$ (\bar{E} and ν are the Young modulus and the Poisson ratio, respectively) denotes the bulk elastic modulus of the solid, and $\bar{\Delta c} = c - c_0$ (c_0 is c in the stress-free state). According to Eqs. (4), c and σ are in a feedback relation. In this way Baranowski got a flux equation [14,15], which can be written as follows (under assumption that $\bar{Y} \neq f(c)$) [8,14,15]:

$$J = -D(1+Ac) \frac{\partial c}{\partial z} + cD \frac{12A}{L^3} \int_0^L \bar{\Delta c} \left(z - \frac{L}{2} \right) dz \quad (5)$$

where

$$A = \frac{2V^2\bar{Y}}{3RT} \quad (6)$$

The first and second terms at the right-hand side of Eq. (5) describe the local and non-local components of J : J_{loc} and J_{nloc} , respectively. $D(1+Ac)$ can be considered as the effective diffusion coefficient of hydrogen, and, consequently, J_{loc} as the Fickian flux;

as always $A > 0$, σ enhances J_{loc} proportionally to c . In contrast, J_{nloc} , resulting solely from σ , is proportional to c .

The calculation of J (Eq. (5)) requires the knowledge of $c=f(z)$. Similarly as in the case of the 2nd Fick's equation, it is defined by a proper balance equation [14,15], which can be written as follows [8,16,17]:

$$\frac{\partial c}{\partial t} = D \left\{ \frac{\partial}{\partial z} \left[(1+Ac) \frac{\partial c}{\partial z} \right] - \left[\frac{12A}{L^3} \int_0^L \bar{\Delta c} \left(z - \frac{L}{2} \right) dz \right] \frac{\partial c}{\partial z} \right\} \quad (7)$$

where t denotes time.

Not only Eq. (7) is complex itself, but also the boundary conditions of transport are t -dependent [14,15]. Namely, when at one side of a membrane specimen ($z=0$) a step change of the primary p is applied and then the new $p_{(z=0)}$ is kept constant, a gradient of c across the specimen is created. Apparently, at both specimen surfaces new local equilibrium c 's, $c_{\text{eq}(0,L)}$, should immediately be established. However, every change of local c is accompanied by a change of σ in the whole specimen; hence, in spite of the pressure being changed only at one surface, both $c_{(z=0)}$ and $c_{(z=L)}$ are t dependent. The two resulting $c_{(0,L)}^\bullet$ are as follows [14,15]:

$$c_{(0,L)}^\bullet = c_{\text{eq}(0,L)} \exp \left\{ -A \left[c_{(0,L)}^\bullet - \bar{c} \pm \frac{6}{L^2} \int_0^L \bar{\Delta c} \left(z - \frac{L}{2} \right) dz \right] \right\} \quad (8)$$

where \bar{c} is the average c at the given t ($\bar{c} = L^{-1} \int_0^L c dz$), and signs "+" and "-" apply to the surfaces at z equal to zero and L , respectively.

In 1983 Lewis et al. found the first experimental proof that the transport of hydrogen in metals is not Fickian [13]. The experimental setup consisted of two chambers, both filled by H_2 -containing gas or acidic aqueous solution, and a thin $\text{Pd}_{81}\text{Pt}_{19}$ membrane separating them. Initially, the above system was at equilibrium at a non-zero activity of the hydrogen species. The experiment was begun by a rapid change of activity of hydrogen species in one chamber (signal, at $z=0$), and the $J(t)$ response in the opposite chamber ($z=L$) was recorded. It was noticed that at the early times, prior to observing a gradual increase of $J(t)$, i.e. in place of the "break-through time" section characteristic for Fickian diffusion ($J(t)$ close to zero [23]), $J(t)$ had the direction opposite to that of the signal. Depending on the sense of the signal, this phenomenon has been called "uphill" or "downhill" diffusion. For instance, in the case of positive signal the section of increasing $J(t)$ was preceded by the "uphill minimum". Since the first observation, this phenomenon has been attributed to the self-stressing of the specimen by gradients of c in the MH_n solid [13]. The same phenomenon was noticed also for specimens of other Pd alloys and Pd itself (e.g. [24]).

Baranowski demonstrated that J_{nloc} in Eq. (5) properly models the experimental $J(t)$ at early times, until the uphill minimum deepens, viz. the value of $J(t)$ becomes more negative [14,15], and also he predicted that the solution of Eq. (7) at the t -dependent boundary conditions (Eq. (8)) should result at the earliest times in a maximum at the $J(t)$ curve (although in some specific experimental conditions this maximum may disappear) [15]. In fact, in some experiments such a maximum was repeatedly noticed (e.g. [25–27]).

Later on, models that were a little different were proposed [28–30]. However, none of them, including even a non-isothermic one (characterized by a large number of parameters) [31], allowed for a reliable reproduction of the complete experimental $J(t)$ curves, and, consequently, for the estimation of parameters that determine the transport kinetics of H in metal matrices.

Recently, a new chance for modelling of experimental results, and estimating the parameters that determine the rate of H transport in self-stressed metals, was offered by the proposition of studying it by the transfer function spectroscopy (TFS) technique

¹ Mechanical stress can influence in a similar way the transport processes of various species also in quite different systems, as e.g. the transport of ions in insulating solids [21].

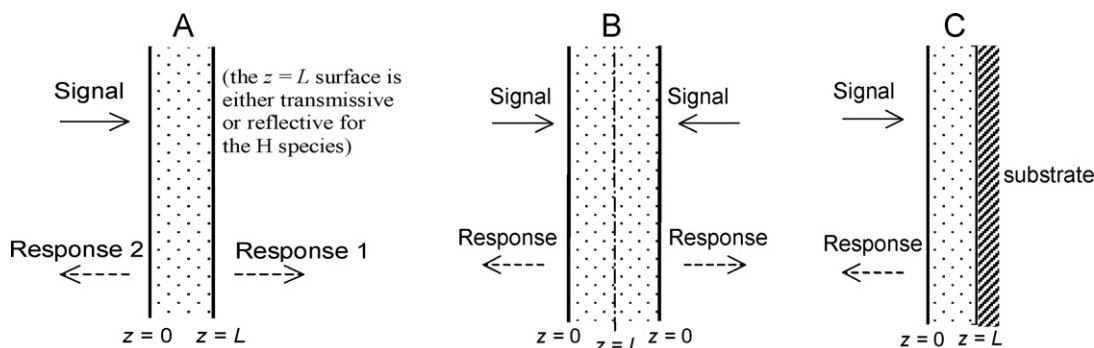


Fig. 1. Alternative specimens used in studies of the transport of hydrogen in metals: (A) membrane, separating two chambers; (B) plate, in a single chamber (the signal is applied symmetrically to both surfaces; consequently, the effective thickness for the transport, L , equals one half of the foil thickness); (C) thin layer on a neutral substrate (as in B, in a single chamber).

[8,17,32–38]. The additional requirement is that the experiments must be performed at quasi-equilibrium of the transport in question [11,16,17]. TFS can be considered as a generalization of electrochemical impedance spectroscopy (EIS) in two aspects: the term ‘impedance’ is confined to the ratio of electrode (more generally, electric) potential, E , and related electric current density, j , in a two-pole system (i.e. in the case of electrode, at the same surface), whereas TFS is free of both those restrictions [16,17,32,39–43]. Hence, TFS allows for determining a particular transfer function (TF) e.g. as the ratio of hydrogen fluxes at two opposite surfaces of a membrane specimen, being responses to a hydrogen concentration signal applied at one of these surfaces. Let’s remind that the main process analysed in the present paper is the transport in the metal’s bulk, and, as a rule, the transport equations are formulated in terms of concentration (c) and flux (J), whereas the quantities used in EIS (E and j) are related only with the electrode’s surface.

Similarly as is typical in EIS [11,43], in the proposed TFS the signal is as follows [16,17,38]:

$$\delta c_{(z=0)} = \Delta c_{(z=0)} \exp(st) \quad (9)$$

where δ and Δ denote small-amplitude and amplitude functions, respectively, and s is the imaginary angular frequency: $s = i\omega$ where $i = \sqrt{-1}$ and $\omega = 2\pi f$ (f is frequency in Hz). Hence, the total $c_{(z=0)}$ is the sum of a constant component, $c_{c(z=0)}$, and $\delta c_{(z=0)}$. At quasi-equilibrium $c_c \neq f(z)$, and it is close to the equilibrium concentration, c_{eq} .

In turn, as far as the following inequality is fulfilled:

$$|\delta c_{(z=0)}| \ll c_{eq} \quad (10)$$

the transport can be considered as linear, i.e. $\delta c_{(z=0)}$ should, formally, result solely in the fundamental harmonics’ responses [8,16,17].

In conditions determined by Eqs. (9) and (10), Eqs. (5) and (7) change as follows [8,16,17,32–34]:

$$\delta J = -D(1 + Ac_{eq}) \frac{d\delta c}{dz} + c_{eq}D \frac{12A}{L^3} \int_0^L \delta c \left(z - \frac{L}{2}\right) dz \quad (11)$$

$$D(1 + Ac_{eq}) \frac{d^2\delta c}{dz^2} - s\delta c = 0 \quad (12)$$

where the first and second terms on the right-hand side of Eq. (11) describe δJ_{loc} and δJ_{nloc} , respectively. Unlike in Eq. (5), the non-local term in Eq. (11) does not depend on z , i.e. $\delta J_{nloc} \neq f(z)$ [16,17,34].

At quasi-equilibrium (see Eq. (10)) the Fickian boundary conditions can be applied. These, for the case when the $z=L$ surface is transmissive (t) or reflective (r) for the transport of H species, are

respectively as follows [16,17,32–34,37]:

$$(t) \quad \delta c_{(z=L)} = 0 \quad (\text{at } c_{(z=L)} = c_{c(z=0)} = c_{eq}) \quad (13)$$

$$(r) \quad \delta J_{(z=L)} = 0 \quad (\text{at } c_{(z=L)} = c_{eq} + \delta c_{(z=L)}) \quad (14)$$

In both cases the transport equations in question (Eqs. (11) and (12)) have analytical solutions [16,35,37].

In Fig. 1 three optional forms of the specimen used in the research on the transport of H in metals are presented. The largest choice of experimental conditions is accessible in the case of the membrane specimen, as this can be applied both in gas-phase and in electrochemical experiments, and at transmissive as well as reflective boundary condition at the $z=L$ specimen surface. In contrast, the applicability of both other specimen forms is constrained to electrochemical experiments, and, moreover, solely at the reflective boundary condition.

Up to present, for H transport in self-stressed metals the following TFs were proposed [8,17,32–37]:

$$H_{t(z=L)} = \frac{\delta J_{(z=L)}}{\delta c_{(z=0)}} \quad (15)$$

$$H_{t(z=0)} = \frac{\delta c_{(z=0)}}{\delta J_{t(z=0)}} \quad (16)$$

$$H_{t(L/0)} = \frac{\delta J_{(z=L)}}{\delta J_{t(z=0)}} \quad (\text{viz. } H_{t(L/0)} = H_{t(z=L)} \times H_{t(z=0)}) \quad (17)$$

$$H_{rc} = \frac{\delta c_{(z=L)}}{\delta c_{(z=0)}} \quad (18)$$

$$H_{r(z=0)} = \frac{\delta c_{(z=0)}}{\delta J_{r(z=0)}} \quad (19)$$

Obviously, $\delta J_{(z=L)}$ and $\delta c_{(z=L)}$ apply solely at the transmissive and reflective boundary conditions, respectively, whilst in the case of $\delta J_{(z=0)}$ an additional subscript, indicating the type of boundary condition (either t or r), is necessary [17] (in earlier papers another system of subscripts was used [16,32–37]).

In Eqs. (15) to (19) probably the whole set of possible TFs (except their reciprocals) in terms of δc and δJ is collected. The solution of Eqs. (11) and (12) at the alternative boundary conditions (Eq. (13) or (14)) allows for deriving formulae for these TFs. Hitherto, this was performed for all of them but $H_{r(z=0)}$ (Eq. (19)) [32–34,37]. The respective formulae can be presented as follows [32,34,37]:

$$H_{t(z=L)} = D \left\{ q \frac{(1 + Ac_{eq})}{\sinh(qL)} - c_{eq} \frac{12A}{q^2 L^3} \left[\frac{qL}{2} \coth\left(\frac{qL}{2}\right) - 1 \right] \right\} \quad (20)$$

$$H_{t(z=0)} = \left(D \left\{ (1 + A c_{eq}) q \coth(qL) - c_{eq} \left(\frac{12A}{q^2 L^3} \right) \left[\left(\frac{qL}{2} \right) \coth \left(\frac{qL}{2} \right) - 1 \right] \right\} \right)^{-1} \quad (21)$$

$$H_{t(L/0)} = H_{rc} = \frac{(1 + A c_{eq}) q \sinh^{-1}(qL) - c_{eq} \frac{12A}{q^2 L^3} \left[\frac{qL}{2} \coth \left(\frac{qL}{2} \right) - 1 \right]}{(1 + A c_{eq}) q \coth(qL) - c_{eq} \frac{12A}{q^2 L^3} \left[\frac{qL}{2} \coth \left(\frac{qL}{2} \right) - 1 \right]} \quad (22)$$

where

$$q = \sqrt{\frac{s}{D(1 + A c_{eq})}} \quad (23)$$

It is noteworthy that, in spite of different definitions of $H_{t(L/0)}$ and H_{rc} (Eqs. (17) and (18)) and totally opposite boundary condition at $z=L$ (Eq. (13) or (14)), these two TFs are described by the same formula (Eq. (22)).

The aim of the present paper was to derive the so far lacking formula for $H_{t(z=0)}$, to explore its features and to compare them with those of the other TFs, from the point of view of its probable usefulness in estimating the parameters that determine the rate of H transport in self-stressed metals.

2. Derivation of the formula for $H_{t(z=0)}$

In the case of diffusion of neutral particles in an isotropic matrix the general solution of Eq. (12) is [44]:

$$\delta c = B_1 \sinh(qz) + B_2 \cosh(qz) \quad (24)$$

where B_1 and B_2 are constants, to be properly selected to satisfy the boundary conditions at z equal to zero and L . Taking Eq. (9) into account, $B_2 = \delta c_{(z=0)}$.

In turn, from Eqs. (11) and (14) it follows that:

$$\left. \frac{d\delta c}{dz} \right|_{z=L} = \frac{12A c_{eq}}{(1 + A c_{eq}) L^3} \int_0^L \delta c \left(z - \frac{L}{2} \right) dz \quad (25)$$

In order to solve the above definite integral, the indefinite integrals of $z \sinh(qz)$ and $z \cosh(qz)$ functions are needed. They can be derived using the well-known indefinite integral of $z \exp(qz)$ function (e.g. [45]). Consequently:

$$\int z \sinh(qz) dz = \frac{z}{q} \cosh(qz) - \frac{1}{q^2} \sinh(qz) + C_1 \quad (26)$$

$$\int z \cosh(qz) dz = \frac{z}{q} \sinh(qz) - \frac{1}{q^2} \cosh(qz) + C_2 \quad (27)$$

Accordingly, at the reflective $z=L$ surface [33]:

$$\int_0^L \delta c \left(z - \frac{L}{2} \right) dz = \frac{B_1 \{ (qL/2) [\cosh(qL) + 1] - \sinh(qL) \} + B_2 \{ (qL/2) \sinh(qL) - \cosh(qL) + 1 \}}{q^2} \quad (28)$$

Now, from Eqs. (24), (25) and (28) it follows that:

$$B_1 = \delta c_{(z=0)} \frac{\frac{12A c_{eq}}{(1 + A c_{eq})/(qL)^3} \left[\frac{qL}{2} \sinh(qL) - \cosh(qL) + 1 \right] - \sinh(qL)}{\cosh(qL) - \frac{12A c_{eq}}{(1 + A c_{eq})/(qL)^3} \left[\frac{qL}{2} [\cosh(qL) + 1] - \sinh(qL) \right]} \quad (29)$$

In turn, from Eq. (11) it follows that:

$$\delta J_{t(z=0)} = -D(1 + A c_{eq}) \left. \frac{d\delta c}{dz} \right|_{z=0} + c_{eq} D \frac{12A}{L^3} \int_0^L \delta c \left(z - \frac{L}{2} \right) dz \quad (30)$$

Hence, taking Eqs. (24), (28) and (29) into account, one obtains:

$$\delta J_{t(z=0)} = \delta c_{(z=0)} D \frac{(1 + A c_{eq}) q - \frac{24A c_{eq}}{q^2 L^3} \left[\frac{qL}{2} - \tanh \left(\frac{qL}{2} \right) \right]}{\coth(qL) - \frac{12A c_{eq}}{(1 + A c_{eq})/(qL)^3} \left[\frac{qL}{2} \coth \left(\frac{qL}{2} \right) - 1 \right]} \quad (31)$$

Finally,

$$H_{t(z=0)} = \frac{\delta c_{(z=0)}}{\delta J_{t(z=0)}} = D^{-1} \frac{\coth(qL) - \frac{12A c_{eq}}{(1 + A c_{eq})/(qL)^3} \left[\frac{qL}{2} \coth \left(\frac{qL}{2} \right) - 1 \right]}{(1 + A c_{eq}) q - \frac{24A c_{eq}}{q^2 L^3} \left[\frac{qL}{2} - \tanh \left(\frac{qL}{2} \right) \right]} \quad (32)$$

Under assumption that there is no self-stress (i.e. V or \bar{Y} equal to zero), viz. the transport is Fickian, Eq. (32) simplifies to:

$$H_{t(z=0)} = (\sqrt{Ds})^{-1} \coth(qL) \quad (33)$$

In this case $H_{t(z=0)}$ is directly proportional to the impedance of the so-called “restricted” or “reflective” diffusion, well known in EIS ([11,17,40–43]), in full analogy to the case of $H_{t(L/0)}$ (see Eq. (21)) and the impedance of the so-called “bounded” or “transmissive” diffusion ([32,34,36,40–43]).

3. Analysis of the derived $H_{t(z=0)}$

In Fig. 2 plots of several exemplary spectra of $H_{t(z=0)}$ in the coordinates most widely used in TFS (analogous as in EIS) are presented. Just as for the earlier derived similar TFs [35,37], these spectra were computed at $10 \text{ Hz} \leq f \leq 0.1 \text{ MHz}$, for a MH_n 50 μm thick membrane specimen ($L = 5 \times 10^{-5} \text{ m}$) of properties similar to those of $\alpha\text{-PdH}_n$ and $(\text{Pd}_{81}\text{Pt}_{19})\text{H}_n$ [32–37]: $D = 1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (close to this in $(\text{Pd}_{81}\text{Pt}_{19})\text{H}_n$ and about three times smaller than in $\alpha\text{-PdH}_n$), $\bar{Y} = 1.844 \times 10^{11} \text{ Pa}$, $V = 1.77 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and $T = 298.2 \text{ K}$, whilst for c_{eq} three values were used, alternatively: 2.5×10^4 , 2.5×10^3 and $2.5 \times 10^2 \text{ mol m}^{-3}$ (n equal to ca. 0.2, 0.02 and 0.002, respectively); the first value is close to the largest c observed experimentally in $(\text{Pd}_{81}\text{Pt}_{19})\text{H}_n$, and the last one is about ten times smaller than the upper limit of c in $\alpha\text{-PdH}_n$.

Similarly as in the case of $H_{t(L/0)}$ ([32,34–37]), the plot of $H_{t(z=0)}$ in its conventional complex plane (Fig. 2A) is located solely in the 1st quadrant. In the case of Fickian transport, the curve of $H_{t(z=0)}$ can be considered as composed of two nearly straight-line sections, in the low- and high-frequency regions (lf and hf), characterized by the limiting values of phase angle, φ , equal to -90° (nearly vertical line, of constant real component) and -45° , respectively (see Fig. 2C, as well) [11,43].

The effect of stress in these two frequency regions is different. In the complex plane plot, the lf region is only moved to smaller values of the real component, whilst in the case of the hf region the curve's shape is quite changed: its primary straight-line

shape diminishes towards the highest frequencies and, at lower frequencies, the curve becomes convex, with a curvature that is greater the larger c_{eq} is (see, especially, the insertion in Fig. 2A). The above change of shape of the primary hf section by the stress is to some extent similar as in the case of for $H_{t(L/0)}$ [35–37].

As for all other TFs proposed for modelling the transport of hydrogen in self-stressed metals (Eqs. (20)–(22)), $H_{t(z=0)}$ depends on c_{eq} , V , L , T , D and \bar{Y} (see Eqs. (6), (23) and (32)). The first four parameters can be determined from independent experiments, and then considered as constants. In turn, as it follows from the indicated equations, D and \bar{Y} are in no direct relationship. Hence, the

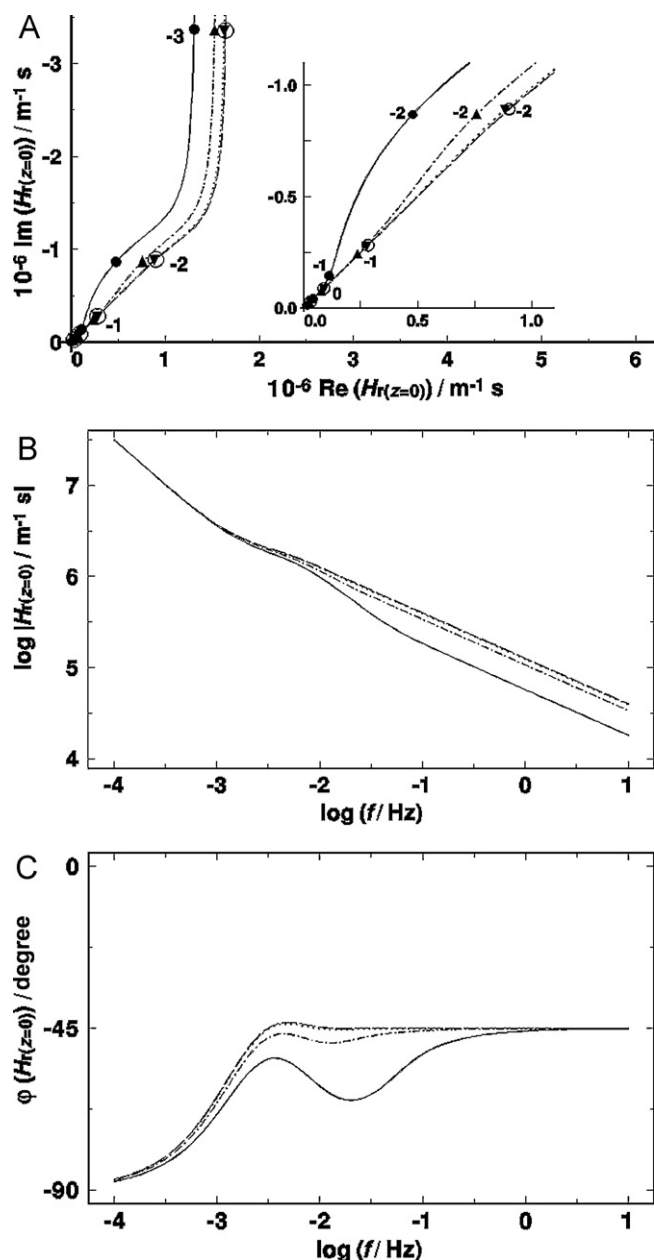


Fig. 2. Plots of the spectra of $H_{r(z=0)}$ in the complex plane (A), log of their modulus vs. $\log f$ (B) and their phase angle, ϕ , vs. $\log f$, at various values of c_{eq} : $2.5 \times 10^4 \text{ mol m}^{-3}$ (—), $2.5 \times 10^3 \text{ mol m}^{-3}$ (---) and $2.5 \times 10^2 \text{ mol m}^{-3}$ (···), and at the largest c_{eq} ($2.5 \times 10^4 \text{ mol m}^{-3}$) under the assumption that the effects of stress are neglected, viz. the transport is Fickian (—). In (A): (i) numbers close to the symbols (\bullet , \blacktriangle , \blacksquare and \circ at particular curves) indicate the respective $\log f$, and (ii) insertion, zoom of the area close to the origin of coordinates.

experimental spectra of $H_{r(z=0)}$ should allow for a simultaneous estimation of these two parameters. Moreover, a set of spectra recorded at various values of c_{eq} should allow for estimating $D = D(c)$ and $\bar{Y} = \bar{Y}(c)$ [32–35]. However, in this respect the properties of particular TFs are differentiated [35,37].

The usefulness of $H_{r(z=0)}$ for estimating D and \bar{Y} was analysed applying the same flowchart as earlier for other TFs [35,37]. Because actual experimental spectra still do not exist, they were generated at the nominal values of c_{eq} , V , L , T , D and \bar{Y} , viz. the same as used in computing the spectra presented in Fig. 2. However, because, on one hand, in experiments $f < 1 \text{ mHz}$ are only seldom used, and, on the other, at $f > 1 \text{ Hz}$ the actual spectra may be easily influenced by effects of hindrances of surface processes [11,43], the computation

was performed at a narrower range of f than for preparing Fig. 2. Namely, spectra for $1 \text{ Hz} \geq f \geq 1 \text{ mHz}$ were computed, for ten logarithmically distributed values per decade. Next, in order to simulate experimental random errors, both components of these spectra were truncated to three- and two-digit values, resulting in relative errors of magnitude up to 0.5 and 5%, respectively.

To these pseudo-experimental spectra the model defined by Eq. (32) was fitted. In this procedure only D and \bar{Y} were free parameters, whilst c_{eq} , V , L and T were fixed either at their nominal values or, but for T , individually altered by $\pm 2\%$, in order to simulate the uncertainty of these quantities that would arise when they were determined from independent experiments [46].

On the left-hand side of Table 1 the results characterizing the quality of the above fittings are collected. They consist of standard deviation of particular fits, σ_{fit} , relative changes of the best-fit estimates of \bar{Y} and D with respect to their nominal values at the indicated alteration of c_{eq} , V or L , and correlation coefficients of \bar{Y} and D estimates, ρ [35,37,42,43,46,47]. For comparison, on the right-hand side of this table analogous data collected recently for $H_{t(z=0)}$ [37] are given.

These data indicate that the features of $H_{r(z=0)}$ are, in general, very similar to those of $H_{t(z=0)}$, although for instance the two TFs are characterized by a nearly opposite sensitivity of the \bar{Y} estimate to the alteration of L . Hence, the analysis of $H_{r(z=0)}$ allows for maintaining the earlier opinion [37] that, when in experiments a membrane specimen is used, $H_{t(L/0)}$ (see Eqs. (17) and (22)) is the most promising TF for determining estimates of \bar{Y} and D .

However, some specific issues related to $H_{r(z=0)}$ have to be mentioned, especially as it is the sole TF that, formally, can be measured for specimens of any other form (see Fig. 1). On one hand, measurements of $H_{r(z=0)}$ impose the smallest requirements with respect to the equipment, because only one surface of the specimen (at $z=0$) is under control and monitoring. On the other hand, one should take into account that even in the case when the opposite specimen surface (at $z=L$) is under control (viz. in the case of all “t” TFs, $J_{(z=L)} \neq 0$), and when $|\delta c_{(z=0)}|$ is as small as 0.1% of c_{eq} (see Eq. (10)), $\delta J_{(z=L)}$ is not confined to the fundamental harmonic, and, in particular, it has a zero-harmonic component [8]; in other words, even when the $z=L$ surface is transmissive, $\delta J_{(z=L)}$ has a constant component. Hence, one should suppose all the more, irrespective of specimen form, that is also the case when the $z=L$ surface is not under control (Eq. (14)), as in the case of both H_{rc} and $H_{r(z=0)}$ (Eqs. (18) and (19), respectively).

Nevertheless, for plate and thin-layer specimens (Fig. 1B and C) certain individual specific features of $H_{r(z=0)}$ should be indicated.

In the case of the plate specimen (Fig. 1B), $\delta c_{(z=0)}$ is applied symmetrically at its two opposite surfaces. Consequently, inside the specimen $c_{(0 < z \leq L)}$ changes according to the mirror symmetry with respect to the plane at one half of the plate’s thickness (in this case, being equal to $2L$). The two related σ change alike, but, as they are of non-local character and have opposite directions, they compensate one another. Therefore, in the plate specimen the transport of H should be considered as Fickian [37].²

In turn, in the case of the thin-layer specimen the layer of M is on a rigid neutral substrate of dissimilar properties, and due to the adhesion it is clamped to this substrate. Therefore, even at apparent equilibrium, viz. in the absence of a gradient of $c_{(0 \leq z \leq L)}$ forced from outside, the adherence blocks off the adjustment of lattice dimensions of M to c in the plane normal to the z coordinate. Hence, as recently suggested, the M layer is permanently under stress, and the dependence of c on p or E can obey neither Sieverts’ nor the Nernst equations [17]. Lately, this has been experimentally proved

² Accordingly, in [11] the correction of D for self-stress was a misunderstanding.

Table 1
Results of fitting of $H_{f(z=0)}$ and $H_{t(z=0)}$ to three- and two-digit spectra (resulting in errors up to $\pm 0.5\%$ and $\pm 5\%$, respectively).

Altered parameter		$H_{t(z=0)}$								$H_{t(z=0)}$ [37]							
		Three-Digit spectra				Two-Digit spectra				Three-Digit spectra				Two-Digit spectra			
		σ_{fit} (%)	Change (%) of		ρ	σ_{fit} (%)	Change (%) of		ρ	σ_{fit} (%)	Change (%) of		ρ	σ_{fit} (%)	Change (%) of		ρ
			\bar{Y}	D			\bar{Y}	D			\bar{Y}	D			\bar{Y}	D	
At $c_{\text{eq}} = 2.5 \times 10^4 \text{ mol m}^{-3}$ ($n \approx 0.2$)																	
None		0.09	−0.05	+0.07	−0.73	0.92	+0.14	+0.05	−0.78	0.09	−0.03	+0.09	−0.73	1.0	+0.1	−0.84	−0.75
c_{eq}	+2%	0.09	−2.0	+0.07	−0.73	0.92	−1.8	+0.05	−0.78	0.09	−2.0	+0.09	−0.73	1.0	−1.9	−0.84	−0.75
	−2%	0.09	+2.0	+0.07	−0.73	0.92	+2.2	+0.05	−0.78	0.09	+2.0	+0.09	−0.73	1.0	+2.1	−0.84	−0.75
V	+2%	0.09	−3.9	+0.07	−0.73	0.92	−3.8	+0.05	−0.78	0.09	−3.9	+0.09	−0.73	1.0	−3.8	−0.84	−0.75
	−2%	0.09	+4.1	+0.07	−0.73	0.92	+4.3	+0.05	−0.78	0.09	+4.1	+0.09	−0.73	1.0	+4.2	−0.84	−0.75
L	+2%	0.62	−1.1	+1.1	−0.80	1.2	+1.9	+0.79	−0.79	0.78	−1.9	+1.6	−0.75	1.2	−1.8	+0.67	−0.75
	−2%	0.63	+1.4	−1.2	−0.80	0.94	+0.59	−0.31	−0.76	0.81	+1.9	−1.3	−0.74	1.4	+2.0	−2.3	−0.75
At $c_{\text{eq}} = 2.5 \times 10^3 \text{ mol m}^{-3}$ ($n \approx 0.02$)																	
None		0.11	+0.74	−0.17	−0.84	1.0	+0.53	−0.27	−0.84	0.10	+0.19	−0.03	−0.71	0.87	−3.2	+0.21	−0.79
c_{eq}	+2%	0.11	−1.2	−0.17	−0.84	1.0	−1.4	−0.27	−0.84	0.10	−1.8	−0.03	−0.71	0.87	−5.1	+0.21	−0.79
	−2%	0.11	+2.8	−0.17	−0.84	1.0	+2.6	−0.27	−0.84	0.10	+2.2	−0.03	−0.71	0.87	−1.2	+0.21	−0.79
V	+2%	0.11	−3.2	−0.17	−0.84	1.0	−3.4	−0.27	−0.84	0.10	−3.7	−0.03	−0.71	0.87	−7.0	+0.21	−0.79
	−2%	0.11	+4.9	−0.17	−0.84	1.0	+4.7	−0.27	−0.84	0.10	+4.3	−0.03	−0.71	0.87	+0.80	+0.21	−0.79
L	+2%	0.37	−6.0	+1.8	−0.89	1.1	−1.7	+0.40	−0.85	0.47	−3.6	+0.90	−0.76	1.0	−6.7	+1.1	−0.80
	−2%	0.38	+6.6	−1.9	−0.88	1.0	+2.5	−0.82	−0.84	0.46	+3.9	−0.95	−0.76	0.90	+0.65	−0.73	−0.77
At $c_{\text{eq}} = 2.5 \times 10^2 \text{ mol m}^{-3}$ ($n \approx 0.002$)																	
None		0.10	−2.4	+0.05	−0.86	1.1	+21	−0.72	−0.86	0.10	−1.4	−0.02	−0.76	1.1	−18	+0.58	−0.78
c_{eq}	+2%	0.10	−4.3	+0.05	−0.86	1.1	+19	−0.72	−0.86	0.10	−3.4	−0.02	−0.76	1.1	−19	+0.58	−0.78
	−2%	0.10	−0.44	+0.05	−0.86	1.1	+23	−0.72	−0.86	0.10	+0.6	−0.02	−0.76	1.1	−16	+0.58	−0.78
V	+2%	0.10	−6.2	+0.05	−0.86	1.1	+16	−0.72	−0.86	0.10	−5.3	−0.02	−0.76	1.1	−20	+0.58	−0.78
	−2%	0.10	+1.6	+0.05	−0.86	1.0	+26	−0.72	−0.86	0.10	+2.6	−0.02	−0.76	1.1	−14	+0.58	−0.78
L	+2%	0.31	−55	+2.2	−0.91	1.2	+3.8	+0.01	−0.87	0.37	−28	+0.89	−0.76	1.1	−43	+1.5	−0.78
	−2%	0.38	+54	−2.2	−0.90	1.1	+35	−1.4	−0.86	0.38	+25	−0.90	−0.77	1.2	+8.1	−0.21	−0.77

[48–50]. Hence, the application of thin-layer specimens should be limited to cases where other specimen forms are not allowed, as for instance in quartz-crystal microbalance experiments [51–55], and the results obtained using specimens of this form should be treated with distrust, for the M–H isotherm as well as for H transport.

Therefore, only membrane specimens allow for a proper determination by TFS at quasi-equilibrium of the bulk elastic modulus of the M–H solid under study.

4. Conclusions

- For a new transfer function (TF) for the transport of hydrogen dissolved in a self-stressed metal close to equilibrium, $H_{T(z=0)}$, being the ratio of a small-amplitude sinusoidal signal of hydrogen concentration to the flux harmonic response at the same surface ($z=0$) of a thin specimen ($0 \leq z \leq L$), when its opposite surface ($z=L$) is reflective (r), the formula was derived and the main features of this TF were analysed.
- As in the case when the transport of hydrogen is Fickian, the plots of $H_{T(z=0)}$ spectra are in the 1st quadrant of the conventional complex plane, but they differ in shape. Mainly, the presence of stress results in the formation on the respective curve of an additional convex region that exists in between the nearly straight-line high- and low-frequency regions of limiting phase angles of -45° and -90° , respectively. The presence of stress results also in a decrease of the nearly constant real component of the low-frequency section.
- The usefulness of $H_{T(z=0)}$ for acquiring reliable estimates of the diffusion coefficient of hydrogen and the bulk elastic modulus of the specimen (i.e. the parameters that decide the kinetics of the transport in question) was analysed numerically using the example of a metal with properties similar to those of α -phase Pd–H and Pd₈₁Pt₁₉–H solids. The results suggest that in this respect $H_{T(z=0)}$ is similar to an analogous TF defined earlier for the case of a transmissive (t) opposite surface ($z=L$), $H_{T(z=L)}$.
- Outwardly, $H_{T(z=0)}$ is the sole TF applicable in the cases of all the three possible forms of specimen: membrane, plate and thin-layer. Moreover, it is the sole TF applicable, formally, in the cases of foil and thin-layer specimens. However, in a plate specimen, for reasons of symmetry the transport is simply Fickian, whilst in the case of a thin-layer specimen the layer under study is always stressed due to its adherence to the rigid substrate of dissimilar properties. Consequently, $H_{T(z=0)}$ properly describes the transport of hydrogen only in the case of a membrane specimen.

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