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A new approach to the kinetics of $LaNi_5$–H_2(g) systems based on impedance spectroscopy analysis

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Abstract

Impedance spectroscopy analysis (ISA) is extensively employed in electrochemistry as a powerful tool for determining reaction mechanisms. A perturbing electrode potential is applied to the cell and the resulting current is measured. Generally, the perturbation is sinusoidal but this is not a necessary condition, since any non-constant signal (even non-periodic) can be decomposed into a series of sine waves. The transfer function of the system, called its impedance, is measured as a function of the frequency of the perturbation by using a frequency response analyzer. This paper tries to test out the applicability of ISA for studying the reaction of H_2(g) with $LaNi_5$ in the α solid solution. The expression ‘‘transfer function’’ used in the following refers to a parameter analogous to an electrical impedance. Experimental transfer functions are determined for different values of the H to $LaNi_5$ (H/M) ratio. Small amounts of hydrogen are transferred from a reference volume chamber to the reactor where it reacts with activated $LaNi_5$ at constant temperature. The time variation of hydrogen mass flow (excitation of the system) and hydrogen pressure in the reactor (response of the system) are measured during each transfer, and then Fourier-transformed to obtain the transfer functions. A two-step mechanism is employed for analyzing the hydrogen uptake.

Keywords: Kinetics; Impedance spectroscopy; $LaNi_5$

1. Introduction

Over the last years significant progress has been made in characterizing the hydriding of $LaNi_5$. The major problems of obtaining reproducible thermodynamic states have been solved [1] along with the coupling between heat and mass transfer [2–5]. These prerequisites being satisfied, the problem of the determination of the reaction mechanism can now be attempted. While empirical rate laws are available for describing hydriding and de-hydriding kinetics [6,7], they do not provide insight into the mechanisms occurring either in the solid solution or the hydride formation region. In this research the kinetic data will be analyzed in the frequency domain by Fourier transforming the experimental data i.e. the time-dependent H_2 mass flow (excitation of the system) and H_2 pressure in the reactor (response of the system) measured during H_2 absorption. Since the convoluted response of consecutive steps in the time domain is simply the product of their transfer functions in the frequency domain, this technique is very powerful for the analysis of complex reaction mechanisms. It can more sensitively separate the reaction steps than conventional methods based on comparison of the P–t data to proposed reaction sequences.

The technique is analogous to that employed in impedance spectroscopy analysis (ISA), but differs in two important ways, (i) electrical measurement are not made and (ii) a sinusoidal signal is not employed. Keeping in mind that any non-constant signal (even non-periodic) can be decomposed into a series of sine waves [8], it is clear that the use of a sinusoidal perturbation is unnecessary for the determination of transfer functions. The frequency domain in which the transfer function is obtained is therefore limited to the ‘‘frequency content’’ of the non-sinusoidal perturbation.

Results presented are restricted to the α solid solution for which a model based on H diffusion can be easily derived.

2. Experimental procedure and data treatment

The apparatus is shown schematically in Fig. 1.

Thermodynamic, kinetic and calorimetric measurements can be made simultaneously [1,7] and provide data for the determination of the reaction mechanisms. The coupling

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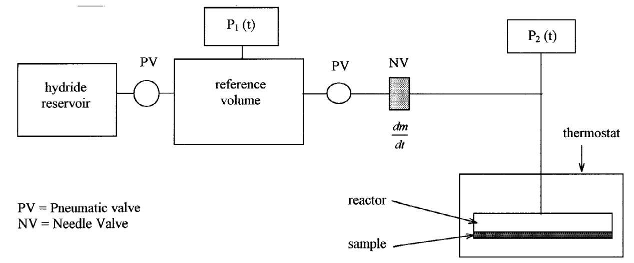

Fig. 1. Schematic diagram of the experimental set-up which is in a temperature-controlled environment.

between kinetics and heat transfer during H_2 absorption is eliminated through the use of a needle valve (NV) to control the hydrogen flux to the reactor. Under such conditions the measured temperature within the sample remains within ±0.15 °C. Prior to each transfer, a pressure difference is set between the reference volume chamber and the reactor. Upon the opening of the pneumatic valve (PV), H_2 is transferred into the reactor and the time variation of the pressure in the reservoir and the reactor are recorded until equilibrium is reached (Fig. 2). The associated change in H/M is of the order of 0.03 in each experiment.

Transfer functions of the system are determined as indicated in Fig. 3. By applying Poiseuille's law to $P_1(t)$ and $P_2(t)$, the time-dependent hydrogen mass flow to the reactor, $\mathrm{d}n_{H2}/\mathrm{d}t$ may be obtained from Eq. (1) (Fig. 3(a)) [7].

$$\frac{\mathrm{d}n_{H_2}}{\mathrm{d}t}=\frac{K_{NV}}{RT}\,[P_1^2(t)-P_2^2(t)], \tag{1}$$

where K_{NV} is a constant determined by the needle valve.

From $P_2(t)$, time-dependent values of the relative chemical potential $\Delta\mu_H(t)$ are obtained from Eq. (2) (Fig. 3(b))

$$\Delta\mu_H(t)=\mu_H(t)-\frac{1}{2}\,\mu^0_{H_2}=\frac{RT}{2}\,\mathrm{Ln}[P_2(t)]. \tag{2}$$

$\mathrm{d}n_{H_2}/\mathrm{d}t$ and $\Delta\mu_H(t)$ are then Fourier-transformed using a FFT algorithm [8]. Transfer functions, $Z_T(\omega)$, are obtained by dividing the Fourier transform of $\Delta\mu_H(t)$ by the Fourier transform of $\mathrm{d}n_{H_2}/\mathrm{d}t$, and plotted in the form of Nyquist diagrams (Fig. 3(c)–(d)). Each datapoint corresponds to a different frequency. Minimum values of the frequency depend on the time required to reach equilibrium. Maximum values are directly related to the sampling frequency. Typically, information is spread out between 10^{-2} and 1 mHz. For comparison, in electrochemical processes the bandwidth ranges from 1 mHz to several hundred kHz.

3. Modelling

For interpreting the experimental transfer functions in the α phase, a diffusion-based model will be employed which assumes the existence of a two-step mechanism for the absorption of hydrogen: (i) chemisorption at the surface of the powdered $LaNi_5$ and (ii) hydrogen diffusion within the bulk material. An analytical expression for the transfer function corresponding to the diffusion process (Z_D) is obtained by solving Fick's law for the appropriate boundary conditions. Details of the calculations cannot be presented within the format of this paper and will be described elsewhere [9]. The calculation assumes a one-dimensional diffusion of H in a sphere of diameter δ.

The surface rate process is taken into account by adding to Z_D a linear flux-force relation (equivalent to a resistor in an electrical circuit), R_{abs}. An equivalent capacitance (C) is also included to account for the "capacitive" properties of the system, i.e. hydrogen adsorption at the $LaNi_5$ surface and/or accumulation of hydrogen in the free volume part of the reactor. A further flux-force relation is added to account for the role of the needle valve (R_{tr}).

The global transfer function $Z_T(\omega)$ is then given by:

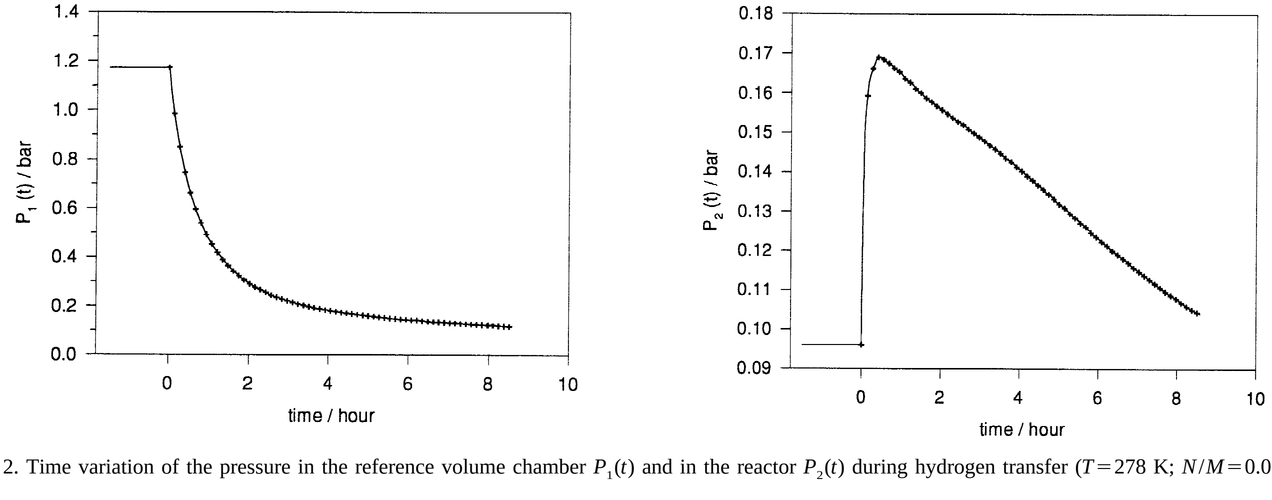

Fig. 2. Time variation of the pressure in the reference volume chamber $P_1(t)$ and in the reactor $P_2(t)$ during hydrogen transfer ($T=278$ K; $N/M=0.096$).

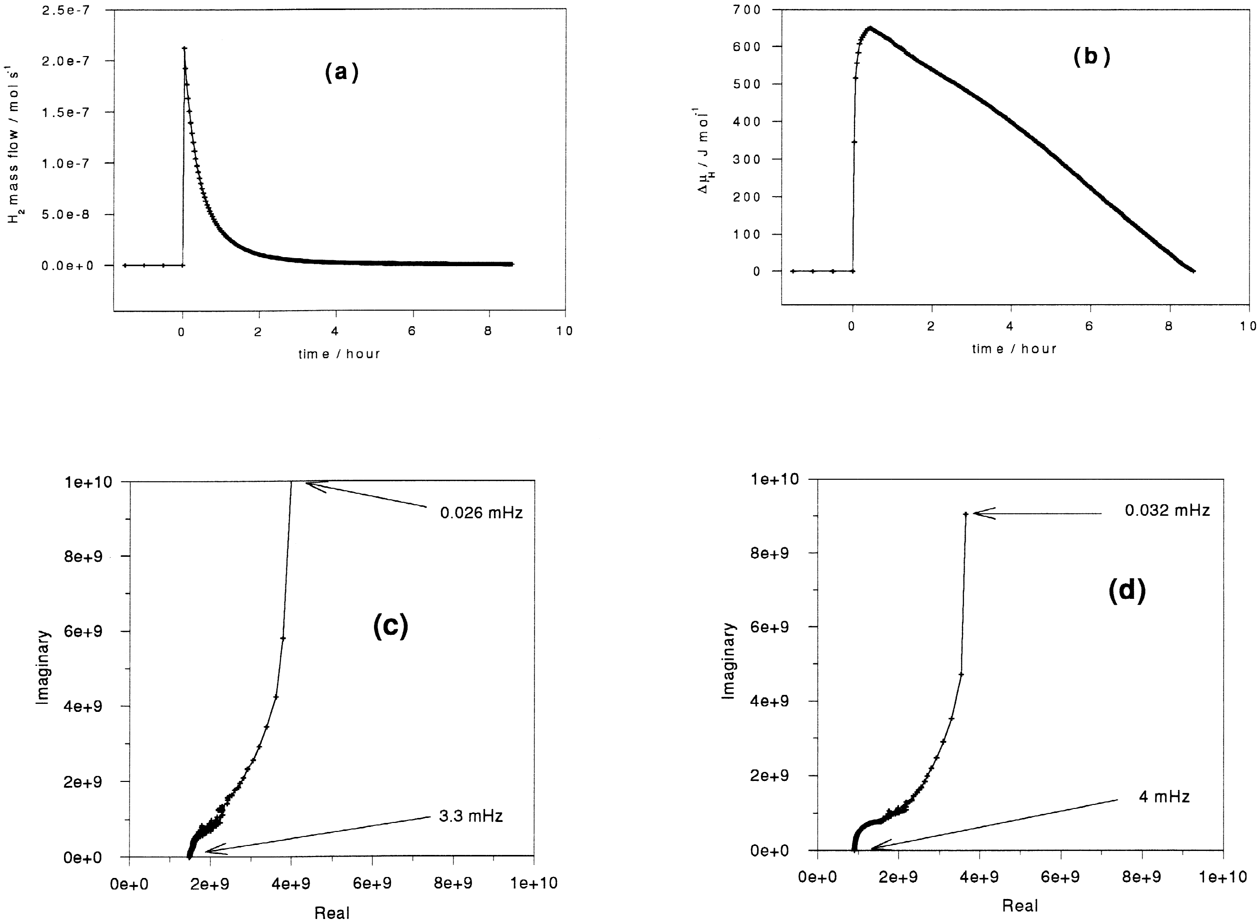

Fig. 3. (a) Hydrogen mass flow vs. time and (b) $\Delta\mu_H(t)$; (c), (d) experimental transfer functions at $H/M=0.035$ and $H/M=0.096$, respectively (278 K).

$$Z_T(\omega) = R_{tr} + \left[\left(\frac{1}{j\omega C + \left(\frac{1}{R_{abs} + Z_D(\omega)}\right)}\right)\right], \tag{3}$$

where $Z_D(\omega)=R_D$ (coth u)/(u), $u=\sqrt{(j\omega)/D_H}\,\delta$, ω is the angular frequency of the perturbation, $Z_D(\omega)$ is the transfer function corresponding to H diffusion, δ is the diameter of the sphere in which the diffusion of H occurs and D_H is the hydrogen diffusion coefficient in the bulk material.

In the low frequency domain, it can be shown that $Z_D(\omega)$ can be expressed as [9]

$$Z_D(\omega) = R_{in} + \frac{1}{j\omega C_{in}}, \tag{4}$$

where R_{in} and C_{in} are, respectively, the resistance and capacitance related to the diffusion of H in $LaNi_5$. The product $R_{in}.C_{in}$, which has units of time, is related to the H diffusion coefficient in the bulk sample [9]

$$R_{in}C_{in} = \frac{\delta^2}{3D_H}. \tag{5}$$

The expression for $Z_T(\omega)$ (Eq. (3)) is similar to that for electric impedance obtained in electrochemical systems under the same assumption of H diffusion in bulk material [10,11].

$Z_T(\omega)$ is plotted in Fig. 4 in arbitrary units for different values of the ratio C/C_{in}. In favorable cases (curve d), the different reaction steps are well separated in the frequency

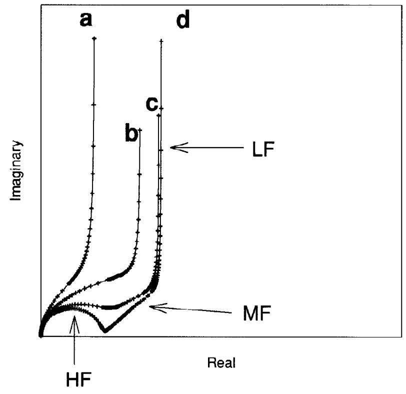

Fig. 4. Plot of the transfer function given by Eq. (1) in arbitrary units for different values of C/C_{in}; (a) $C/C_{in}=0.5$; (b) $C/C_{in}=0.1$; (c) $C/C_{in}=10^{-2}$; (d) $C/C_{in}=10^{-4}$, HF: high frequency domain, MF: medium frequency domain, LF: low frequency domain.

domain, allowing a quantitative determination of the different parameters. In less favorable cases (curve a), the separation becomes difficult. A further complication in analyzing experimental results comes from the dispersion in grain size ($LaNi_5$ particles). This problem must be considered for a precise analysis of experimental data [12].

4. Discussion

The similarities between the measured (Fig. 3(c) and Fig. 3(d)) and calculated (Fig. 4) behavior of $Z_T(\omega)$ clearly supports the validity of the modelling. In certain cases, e.g., $C/C_{in} < 10^{-4}$, three distinct regions appear in the frequency domain (Fig. 4(d)):

- The high frequency (HF) semi-circle is related to the chemisorption step of the mechanism, in combination with a capacitive effect (surface or volume); the HF limit of the transfer function on the real axis is related to the rate transfer characteristics of the needle valve.
- The medium (MF) 45° linear segment is related to H diffusion in $LaNi_5$.
- The low frequency (LF) vertical line results from the insertion resistance R_{in} in series with the insertion capacitance C_{in} as shown in Eq. (4).

In view of the behavior of the model, quantitative information may be extracted from each region of the experimental transfer functions.

4.1. HF domain

The semi-circle along the real axis in the HF domain corresponds to the surface step of the reaction sequence. From the figures, it is possible to determine (i) the value of R_{tr}, related to the needle valve, (ii) the value of R_{abs}, related to the interfacial kinetics of chemisorption and (iii) the capacitance C related to the capacitive characteristics of the system. Due to the present space limitations, a comprehensive determination of these parameters at different operating temperature and as a function of the number of cycles of hydriding will be presented elsewhere [9].

4.2. MF and LF domain

Analysis of $Z_T(\omega)$ in the LF region can give the value of the hydrogen diffusion coefficient (Eq. (5)). It has been shown elsewhere [3] that under our experimental conditions, the grain size distribution is centered around ca. 100 μm. By taking this value for δ, it is possible to estimate an average H diffusion coefficient of 10^{-8} cm^2 s^{-1} (278 K) which is consistent with other data in the literature. Tanaka et al. found a value of $3 \cdot 10^{-7}$ at 423 K in unactivated $LaNi_5$ in the low concentration region [13]. More recently, Schönfeld et al. found the same value from quasi-elastic neutron scattering measurements at 423 K [14].

4.3. Effect of H/M

The diffusion model based on hydrogen absorption in the α solid solution successfully describes the experimental results. The reaction mechanism is expected to change upon increasing H/M as shown in Fig. 5. Around the dilute phase solubility limit ($H/M \approx 0.5$) where the hydride phase begin to precipitate, the low frequency asymptotic behavior begin to disappear and a second circle appears (Fig. 5(d)). This second circle might be related to the phase transformation process since a semi-circle in the Nyquist diagram indicates a surface-controlled reaction step. This statement is consistent with the observations made by Gray on the absorption plateau for $LaNi_5$–H_2 [15].

5. Conclusions and perspectives

This work deals with the determination of the mechanism of the reaction between H_2(g) and $LaNi_5$ in the α solid solution. Fourier transformation of transient signals obtained in the time domain during hydrogen absorption is used to produce transfer functions of the system at different stationary points of the isotherm.

A model assuming a two-step mechanism is proposed: (i) chemisorption of hydrogen at the surface of $LaNi_5$, and (ii) diffusion of H into the bulk material. The corresponding transfer function is derived, which includes the role of the needle valve and a capacitive effect.

Comparison of the measured and calculated transfer functions leads to the following conclusions:

- Under our experimental conditions, at low hydrogen contents (i.e. $H/M < 0.5$), the experimental transfer function is similar to the one obtained from the model. It can be concluded that the model is suitable for describing hydrogen absorption in this domain.
- From the experimental transfer functions, the H diffusion coefficient is found to be of the order of 10^{-8} cm^2 s^{-1} at 278 K.
- For H/M values above 0.5, where the hydride phase begins to precipitate, the Nyquist diagrams of the transfer function differ from those for $H/M < 0.5$ because a second circle appears in the low frequency domain suggesting the onset of a new mechanism.

The perspectives offered by this work are as follows:

- Numerical identification of the experimental transfer functions at different operating temperatures can provide quantitative information on the two-step mechanism controlling H_2 solution into the α phase. The roles

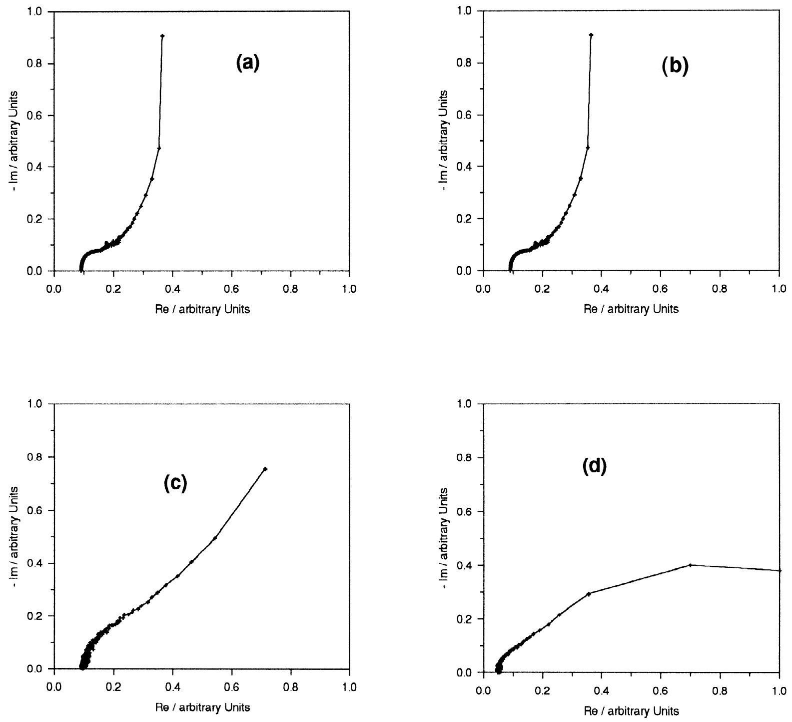

Fig. 5. transfer functions obtained for $LaNi_5–H_2$ at 5 °C. (a) $H/M=0.1$; (b) $H/M=0.3$; (c) $H/M=0.6$; (d) $H/M=0.7$.

of pressure activation and multicycling may also be described quantitatively.

- The exact nature of the capacitance C is not yet established. Experiments at constant reactor volume but with different amounts of $LaNi_5$ (and therefore at different values of the reaction surface) should allow us to ascertain whether this capacitive effect is related to the powder surface or to the reactor volume.
- Concerning the two-phase domain, the same technique can be applied. New insight on the kinetics and thermodynamics of $LaNi_5–H_2$ in the presence of hysteresis may be expected.
- This work can be extended to other intermetallic–H_2(g) systems.

References

[1] P. Dantzer, M. Pons and A. Guillot, *Z. Phys. Chem., 183* (1994) 205.

[2] P. Dantzer and E. Orgaz, *J. Less-Common Met., 147* (1989) 27.

[3] M. Pons and P. Dantzer, *Z. Phys. Chem., 183* (1994) 213.

[4] M. Pons and P. Dantzer, *Z. Phys. Chem., 183* (1994) 225.

[5] E.H. Kisi and E. Mac A. Gray, *J. Alloys Comp., 215* (1994) 201.

[6] P.D. Goodell and P.S. Rudman, *J. Less-Common Met., 89* (1983) 117.

[7] H.Y. Caï, P. Millet and P. Dantzer, *J. Alloys Comp., 231* (1995) 427.

[8] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.H. Vetterling, *Numerical Recipes: The Art of Scientific Computing*, Cambridge University Press, 1986.

[9] P. Millet and P. Dantzer, *J. Alloys Comp.*, to be submitted.

[10] J.S. Chen, J.-P. Diard, R. Durand and C. Montella, *J. Electroanal. Chem., 406* (1996) 1.

[11] G. Barral, J.-P. Diard and C. Montella, *Electrochim. Acta, 29* (1984) 239.

[12] M.H. Mintz and Y. Zeiri, *J. Alloys Comp., 216* (1994) 159.

[13] S. Tanaka, J.D. Clewley and T. Flanagan, *J. Phys. Chem., 81* (1977) 1684.

[14] C. Schönfeld, R. Hempelmann, D. Richter, T. Springer, A.J. Dianoux, J.J. Rush, T.J. Udovic and S.M. Bennington, *Phys. Rev. B, 50* (1994) 853.

[15] E. Mac A. Gray, *J. Alloys Comp., 408* (1992) 49.