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The decomposition of electrochemically loaded palladium hydride: a thermal analysis study.

L.E.A. Berlouis*, P.J. Hall, A.J. MacKinnon, A.W. Wark, D. Manuelli, V. Gervais, J.E. Robertson

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK

Abstract

Palladium samples electrochemically loaded with hydrogen have been examined in terms of their desorption characteristics using the thermal analysis methods of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The temperature of maximum desorption is shown to depend on the H:Pd ratio n when loading was carried out at current densities $i_D \leq 2$ mA cm^{-2}. The molar desorption enthalpy ΔH_M, derived from the DSC and TGA data as a function of n (0.48–0.9), was found to be in good agreement with literature values at lower n but deviated at higher n.

Keywords: Palladium; Electrochemical loading; Thermal desorption

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1. Introduction

The interaction of hydrogen with palladium is one of the most extensively characterised metal–gas systems [1]. The hydrogen molecule is known to undergo dissociative chemisorption on the Pd surface with minimum activation energy. Whilst this phenomena is common to several other transition metal surfaces and demonstrates the importance of such heterogeneous catalyst in hydrogenation reactions, it is the unique high solubility of the hydrogen atom into the bulk palladium lattice which sets this metal apart from all others. The ca. 1:1 H:Pd ratio that can be achieved would make this a prime candidate for hydrogen storage, were it not for the cost of the metal. Nevertheless, detailed characterisation of this system could well yield valuable insights into the hydrogen absorption characteristics of more viable hydrogen storage materials such as $LaNi_5$, FeTi and Mg_2Ni. The purpose of the present work was to investigate, using the thermal analytical techniques of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), the hydrogen desorption process from the Pd lattice after various degrees of hydrogen absorption following electrochemical loading from aqueous LiOH solutions.

2. Experimental

The palladium foil used in these experiments (0.1 mm×100 mm×100 mm) originated from the Aithaca Chemical Corporation (USA) and was of 99.95% purity. Samples of this foil (ca. 3 mm×3 mm) were employed as the cathode in an electrochemical cell with constant current densities in the range of 1–100 mA cm^{-2}. Before each loading, the Pd coupons were cleaned in propan-2-ol in an ultrasonic bath and dried in a stream of nitrogen gas. The coupons were then etched in aqua regia for 10 s, washed copiously with distilled water and then placed in the electrode holder and into the electrochemical cell. The electrolyte employed was reagent grade LiOH (BDH) in singly distilled water. After each loading experiment, the sample was removed from the electrochemical cell, rinsed in distilled water and then dried in a nitrogen stream. The coupons were then placed in either the DSC or TGA apparatus for thermal analysis with N_2 or Ar gas as sample purge at a flow-rate of 40 ml min^{-1}. The DSC used in the study was a Mettler-Toledo DSC 30 with a TC11 TA Processor interface unit. In this instrument, the total heat flux was directly measured. The TGA employed was the Perkin-Elmer TGA 7 with a TAC 7/DX controller with a balance sensitivity of 0.1 μg. In both thermal techniques, a sample heating rate of either 5 K min^{-1} or 10 K min^{-1} was employed.

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*Corresponding author.

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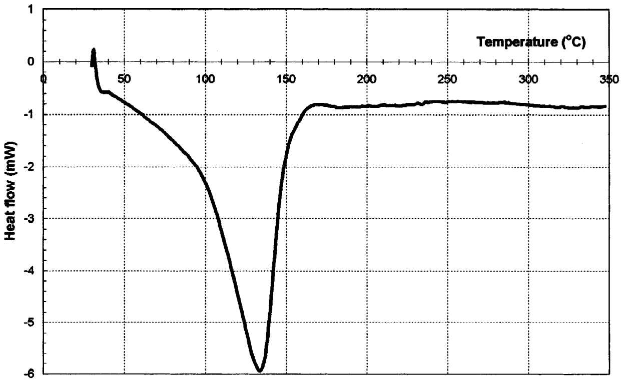

Fig. 1. Differential scanning calorimetry curve for the desorption of hydrogen from a palladium sample (11.9 mg) loaded for 5 h at a current density of 2 mA cm^{-2} in 0.1 M LiOH solution.

3. Results and discussion

A typical DSC curve is shown in Fig. 1, obtained in this instance for the hydrogen desorption reaction from a Pd sample of weight 11.9 mg after loading for 5 h at a current density i_D of 2 mA cm^{-2} in 0.1 M LiOH. The desorption here was characterised by a single endotherm, signifying that the electrochemically loaded hydrogen was to be found in nominally one site, namely the octahedral site of the face centred cubic lattice of palladium. Fig. 2 plots the temperature of maximum desorption T_{max} from the DSC and the variation of H:Pd ratio, n estimated assuming a constant enthalpy of desorption of 19.26 kJ mol^{-1} of H, after Wicke and Nernst [2], against loading time. Although the curves in the figure have no intrinsic meaning and are present to indicate the trend in the data, the figure clearly indicates a variation in both T_{max} and n with loading and a “peak” is seemingly achieved after 6 h loading. This variation in T_{max} is unexpected since all the loadings were carried out at one i_D (2 mA cm^{-2}) and hence, at a single overpotential [3–7] in 0.1 M LiOH. The explanation for this may lie in a “subsurface” hydrogen layer, as reported by several authors [8–12] from thermal desorption experiments and by Conway and Jerkiewicz [13] from their evaluation of the thermodynamic and electrokinetic properties of hydrogen absorption into metals. In the work by Behm et al. [9], Pd single crystals were employed under low coverage by hydrogen gas where only the very top surface layer would have been affected. In the present work however, the current densities employed and the duration of the electrochemical loading would result in substantial loading and expansion of the polycrystalline Pd material. Thus, the nature of such a subsurface region, which would control both absorption and desorption of hydrogen, could alter as the structure expands with increased loading. According to Behm et al. [9], hydrogen atoms desorbing from the surface are immediately replaced by atoms from just below that surface. Thus, if the activation energy for the latter process is altered with the amount of structural change and self-induced lattice strain [14] caused by the loading, then this may well explain why there is a marked shift in T_{max} with increasing H:Pd ratio. This dependence is however by no means a straightforward first order process.

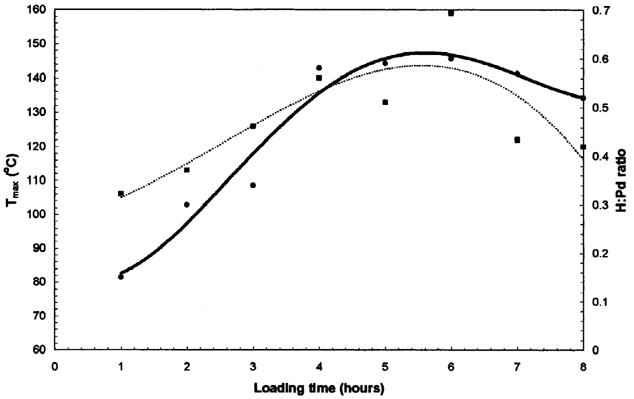

Fig. 2. Variation in the temperature of maximum desorption T_{max} (■) and the H:Pd ratio (●) with loading time at a current density of 2 mA cm^{-2} in 0.1 M LiOH solution.

In contrast to these findings carried out at 2 mA cm^{-2}, Table 1 shows that at the higher loading current density of 30 mA cm^{-2}, no clear trend in T_{max} was observed even though the duration of loading for these samples ranged between 1 and 70 h. This must simply be reflecting the fact that at the lower current density, hydrogen absorption is a less efficient process due to the competition from the Tafel reaction (2Pd-H$_{ads}$→2Pd+H$_2$) which removes the ad-

Table 1
Molar enthalpy of desorption from simultaneous measurement of the enthalpy of desorption and weight loss for Pd sample electrochemically loaded with a current density of 30 mA cm^{-2} in 0.1 M LiOH

DSC sample weight (mg)	Enthalpy of desorption (mJ)	T_{max} (°C)	TGA weight loss (%)	H:Pd ratio (n)	Molar enthalpy of desorption (kJ mol^{-1})
7.509	900	158	0.452	0.48	28.207
3.968	483	155	0.570	0.61	21.355
3.134	429	148	0.611	0.65	22.403
2.912	369	158	0.643	0.69	19.707
5.900	796	166	0.697	0.75	19.356
5.715	751	174	0.739	0.79	17.782
2.800	326	157	0.842	0.90	13.826
3.350	414	145	0.837	0.90	14.765

sorbed hydrogen. The high hydrogen chemical potential at the surface necessary for driving hydrogen into the Pd bulk does not then materialise. On the other hand, at higher current densities, a high surface concentration of hydrogen will be rapidly formed. The associated change in the nature and structure of the subsurface layer with lattice expansion will likewise be rapidly established and this layer will then determine the activation for the desorption process.

The variation of the molar enthalpy of desorption (ΔH_M) with n in Table 1 was evaluated from the simultaneous measurements of the enthalpy of desorption and of the weight loss from a single loading experiment. This data is compared to that given by Wicke and Nernst [2] in Fig. 3. A much greater variation in molar enthalpy was found by these authors from the slope $\frac{\Delta H_M}{n} \approx -44.9$ kJ mol^{-1} as compared to -30.8 kJ mol^{-1} from our experiments. This discrepancy could be due to the different methods and the experimental conditions by which the relationships were arrived at. The work by Wicke and Nernst [2] was carried out on a single Pd sample foil where changes in pressure upon hydrogen absorption were recorded. In our case, the nature of the dual DSC and TGA measurements necessitated the re-use of some of the Pd coupons, with the sample cleaning and preparation steps repeated after each experiment. Surface treatment will undoubtedly play a major role in the electrochemical loading of hydrogen into the palladium. Furthermore, it is likely that some memory effect, e.g., a residual lattice expansion, will remain in the sample after each loading. This structure modification could have perhaps contributed to the higher enthalpy of desorption recorded in our experiments for the higher H:Pd ratios.

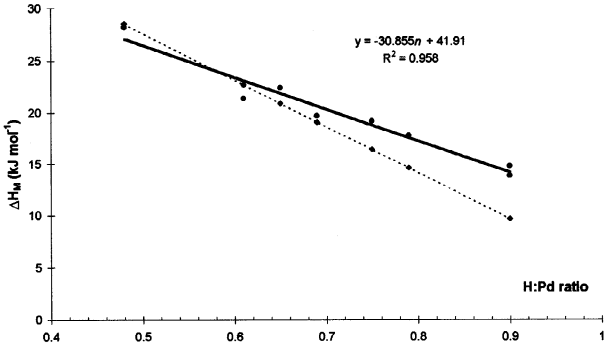

Fig. 3. Variation in the molar enthalpy of desorption ΔH, as a function of n, the H:Pd ratio obtained from simultaneous DSC and TGA experiments (·). Molar enthalpy data derived from Wicke and Nernst (♦) [2].

4. Conclusions

From measurements of the enthalpy and weight loss during desorption, it is clear that the activation process for the process depends markedly on the electrochemical conditions employed during loading. The temperature of maximum desorption has been found to vary with the H:Pd ratio at $i_D \sim 2$ mA cm^{-2} and this has been attributed to the gradual change in the structure and nature of a subsurface layer which controls the desorption rate. Surface pretreatment and structural changes in the Pd samples on loading are also thought to contribute to the lower ΔH_M dependence on n.

Acknowledgments

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