Material Science Studies

In Situ Interferometric Microscopy of Pd Electrode Surface and Calorimetry during Electrolysis of D₂O Solution Containing Sulfur Ion

In Situ Interferometric Microscopy of Pd Electrode Surface and Calorimetry during Electrolysis of D_2O Solution Containing Sulfur Ion

N. Oyama, M. Ozaki, S. Tsukiyama, O. Hatozaki and K. Kunimatsu*

Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Japan
*IMRA JAPAN CO., LTD., Japan

Abstract

Highly sensitive calorimetry was carried out to assess excess heat production in the presence of sulfur ion (S^{2-}) in electrolyte solutions. Electrolysis of a D_2O solution containing 10mM S^{2-} produced "burst-like" excess heat up to 14% over 12 hours after 6 days' electrolysis. The production of excess heat was absent from a control experiment using $LiOH/H_2O$ in the place of $LiOD/D_2O$. It seemed that the magnitude and reproducibility of the excess heat production were improved by the addition of S^{2-} to the electrolyte solutions. In this study, in situ observations of topographic changes at electrode surfaces during the electrolysis were also conducted using phase measurement interferometric microscopy (PMIM). The absorption of hydrogen into a Pd cathode was clearly seen to bring about surface roughening even at a very low hydrogen content of less than H/Pd=0.005. Original surface topography was readily restored by desorbing hydrogen from the Pd electrode by using it as the anode. The absorption and desorption of deuterium similarly induced the reversible surface topography change. The extent of the surface roughening due to the hydrogen absorption varied with electrode materials and crystal facets of Pd single crystals.

1.Introduction

Excess heat production, which is a major impetus for researches on cold fusion phenomenon, has been reported from electrolysis of D_2O solutions under various experimental conditions. However, low reproducibility makes it difficult to gain a comprehensive understanding of the origin and mechanism of excess heat production. In seeking for an experimental factor which controls the reproducibility, we have conducted calorimetry with changing experimental parameters such as modes of electrolysis, magnitudes of electrolysis current and voltage, electrode pretreatments, etc[1,2]. In this study, calorimetry was carried out in the presence of sulfur ion (S^{2-}) to see if the addition of a substance which accelerated the hydrogen absorption into metals influences the production of excess heat.

We also carried out in situ measurements of topographic changes on cathode surfaces by phase measurement interferometric microscopy (PMIM)[3] during the electrolysis of H_2O and D_2O solutions. Topographic changes induced by the absorption and desorption of hydrogen (and deuterium) were measured at different current densities for Pd and Pd-Ag alloy electrodes. PMIM measurements were also carried out using Pd single crystals with different facets.

Material Science Studies

2. Experimental

2-1. Calorimetry

A detailed description of the system and principle of the calorimetric measurement were presented elsewhere[2]. We used a twin-type microcalorimeter (Model 5111, Tokyo Riko, Japan) and a closed electrolytic cell (25ml) equipped with a Pd black recombination catalyst deposited on a Pt wire. Operating temperature was set at 8°C. The error in the calorimeteric measurement is of the order of a few per cent. Electrolysis of solutions were carried out at a constant current density of 177mAcm^{-2} with a two-electrode system, the cathode being Pd (l=1cm, ϕ=0.1mm) or Pd-Ag alloy (l=1cm, ϕ=0.2mm) wires and the anode Pt gauze surrounding the cathode. The areas of the Pd and Pd-Ag alloy cathodes were 0.28cm^2 and 0.56cm^2, respectively. All the electrode materials were obtained from Tanaka Metals Company (Japan) and used without pretreatment. Electrolyte solutions were prepared from D_2O (Isotech Inc., USA) or H_2O purified through a laboratory water purification system. Li_2S was obtained from Aldrich and used as received. All other chemicals were reagent grade and used without further purification.

We evaluated excess heat in two ways as follows:

$$R_t = (W_{out}-W_{in})/W_{in} \times 100 \qquad (1)$$

$$R_s = (W_{out}*-W_{in}*)/W_{in}* \times 100 \qquad (2)$$

R_t is the excess heat which is estimated based on the total output (W_{out}) and total input energy (W_{in}) integrated from the beginning of the electrolysis. R_s is the excess heat estimated by integrating the output ($W_{out}*$) and input energy ($W_{in}*$) over every one hour, being more sensitive to burst-like heat evolution than R_t.

2-2. PMIM measurement

PMIM measurements were carried out using a Zygo Maxim·3D Model 5700 laser interferometric microscope (Middlefield, CT) with 40x Mirau objective. The microscope is equipped with a low power He-Ne laser as a light source which emits a coherent and monochromatic (λ=632.8nm) light for optical phase measurement interferometry. PMIM detects the interference intensities on a 256x256 pixel charge injection device array camera over an area of ca.0.06mm^2. From the recorded spatially resolved intensities, the phase, ϕ, of light reflected from the Pd surface is calculated with respect to the light reflected from a reference surface. Differences in phase, $\Delta\phi$, between light reflected from two adjacent points on the surface is converted to an optical height, h.

$$\Delta\phi = 4\pi h/\lambda \qquad (3)$$

Then the optical height can be straightforwardly converted to the physical height, d, yielding an physical image of the surface by

$$h = d \times n \qquad (4)$$

where n is the refractive index of the surrounding medium. More detailed description and measurements theory of the PMIM is given elsewhere[4].

Constant-current electrolysis was carried out using a conventional three-electrode system. Pd, Pd-Ag alloy plates (A=0.9cm^2, thickness: 0.2mm, Tanaka Metals Company) or Pd single crystals disks (A=0.2cm^2, thickness: 2mm, Material-Technologie & Kristalle, Germany) were used as the working electrodes. A Ag/AgCl electrode and Pt spiral wire were used as the reference and counter electrodes, respectively. A potentiostat/galvanostat (Polarization Unit PS-07, Toho Technical Research, Japan) was used in all electrochemical experiments. A relatively small current density (3 to 20 mAcm^{-2}) was employed for the electrolysis to keep the working electrode surfaces free from bubbles which interfered with the in situ PMIM measurements.

PMIM experiments were conducted at an ambient temperature (20±2°C).

Material Science Studies

3. Results and Discussion

3-1. Calorimetry

Using our highly sensitive calorimeter, so far we have occasionally observed the production of excess heat which lasted a relatively short period intermittently after prolonged electrolysis of D_2O solutions: i.e.,"burst-like" excess heat production. In this study, sulfur ion (S^{2-}) was added to electrolyte solutions in order to promote the deuterium absorption into cathodes. Sulfur ion is capable of accelerating the hydrogen absorption into metals by retarding the competitive recombination reaction of the adsorbed hydrogen atoms into molecules and/or by lowering an energy barrier to the hydrogen permeation via strong chemisorption of sulfur ion at cathode surfaces[5].

Figure 1 shows typical calorimetric results obtained during the electrolysis of 0.1M LiOD/D_2O (Figure 1a) and 0.1M LiOH/H_2O (Figure 1b) containing 10mM Li_2S using the Pd cathode. As clearly seen in the R_s plot in Figure 1a, "burst-like" excess heat production up to 14% of the input energy (ca. 0.6W) was recorded several times over 12hr after 130 hours' electrolysis of the D_2O solution. On the contrary, the excess heat production was not observed in a control experiment using H_2O containing the same amount of S^{2-} as shown in Figure 1b. The magnitude of the excess heat generated in the presence of S^{2-} was about five times that recorded for a similar electrolytic system in the absence of S^{2-} ($\sim$5%). Furthermore, it seemed that the addition of S^{2-} to D_2O solutions slightly improved the reproducibility of the excess heat production. These results suggest that the augmentation in the rate of the deuterium entry through the solution/cathode interface is of advantage for the excess heat production.

It is considered that the negative heat balance recorded in the presence of S^{2-} is ascribable to a certain endothermic reaction occurring in the electrolytic cells. When a Pt cathode instead of Pd was used in the presence of S^{2-}, both R_t and R_s were observed to be 0% within experimental error.

We also observed "burst-like" excess heat production using a Pd-Ag alloy cathode the surface of which was modified with Ag_2S in the presence of S^{2-}. The observed maximum excess heat was ca. 6% on almost 0% heat balance.
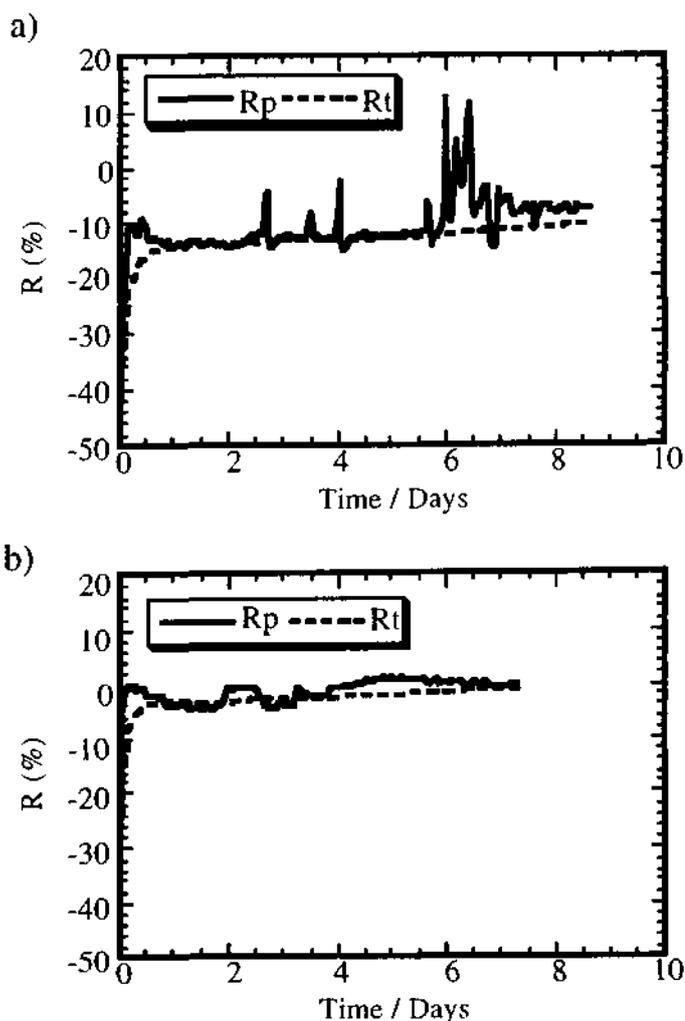
a)

b)

Figure 1. Typical R_t and R_s for the electrolysis of D_2O(a) and H_2O (b) containing 10mM Li_2S using Pd cathode. Constant current density:-177mAcm^{-2}.

Material Science Studies

3-2. PMIM

It is well-known that the absorption of hydrogen into metals causes expansion and distortions of the crystal lattice of the metals, which bring about changes in physical and mechanical properties of the metals. Those property changes are considered to play an important role in cold fusion phenomena. In this study, surface topographic changes accompanying the hydrogen and deuterium absorption and desorption were measured in situ using PMIM.

Shown in Figure 2 are typical in situ PMIM optical images representing topographic changes at a Pd electrode surface observed during the electrolysis of 0.1M LiOH/H_2O solution at 10mAcm^{-2}. Figure 3 shows time-course change in PV (Peak-to-Valley) which is a measure of surface roughness: the distance between the highest and the lowest points in a certain surface profile plot. In the course of the electrolysis, the absorption of hydrogen into the Pd cathode caused significant surface roughening (Figure 2a-c). While there was retention time for the surface roughening, it began at a very low hydrogen content such as H/Pd=0.005. The retention period was dependent on the current density and almost independent on the charge passed (ca. 5mCcm^{-2}), indicating a certain amount of hydrogen is required to be absorbed to cause the surface roughening. In the course of the electrolysis the Pd cathode surface became too rough for PMIM (the plateau region in Figure 3) and thus the optical image failed to represent the physical surface correctly (Figure 2c). Original surface topography was readily restored by desorbing hydrogen from the Pd electrode using it as the anode (Figure 2d) or, more slowly, leaving it in air for 24 hours. No qualitative differences were observed in topographic changes due to the absorption of hydrogen and deuterium.
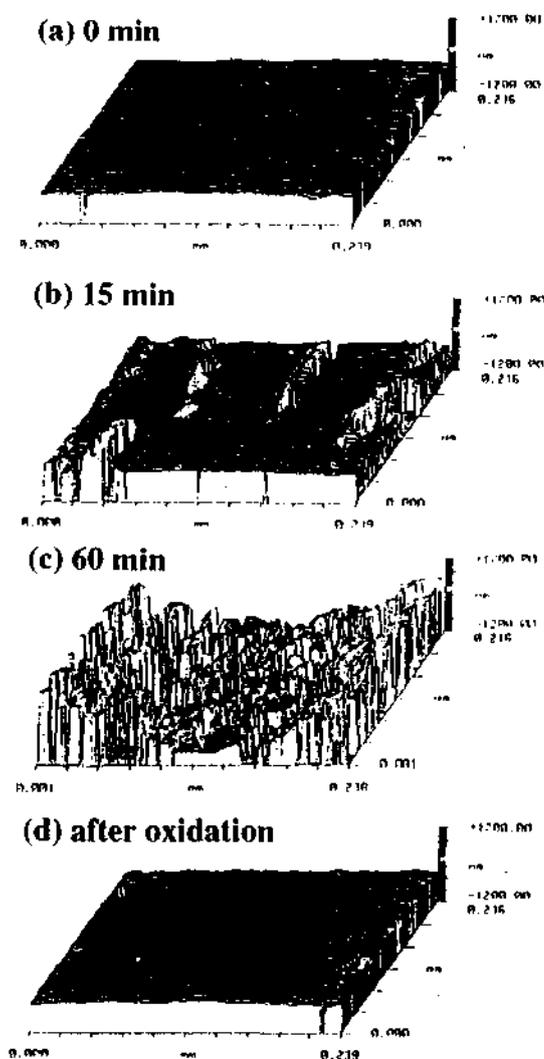
(a) 0 min

(b) 15 min

(c) 60 min

(d) after oxidation

Figure 2. PMIM optical images and of Pd electrode profiles of surfaces obtained during the electrolysisof 0.1M LiOH/H_2O. Current density:10mAcm^{-2}.
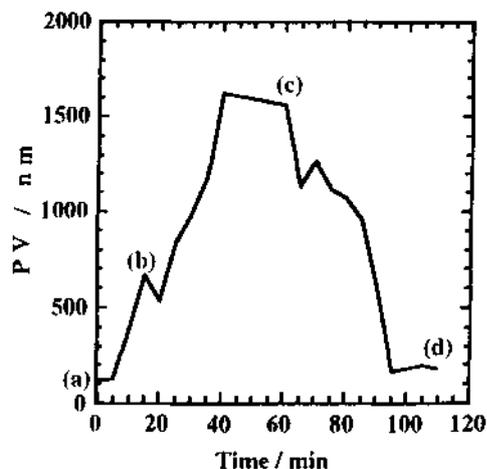
Figure 3. Peak-to-valley (PV) vs. time curves for Pd electrode surface during the electrolysis of 0.1M LiOH/H_2O. A$_{Pd}$=0.12cm^2. Currentdensity:10mAcm^{-2}. (a), (b), (c) and (d) correspond to the points where the images shown in Figure 2 were obtained.

237

Material Science Studies

The electrolysis was carried out using cathodes of Pd single crystals and topographic changes were measured. As shown in Figure 4, Pd (111) underwent significant topographic change as observed for the polycrystalline Pd, while surface topography of Pd (100) remained unchanged during the electrolysis. These results indicate that in Pd single crystals the distortions of the crystal lattice due to the hydrogen absorption occurs preferentially in a certain direction. When hydrogen atoms occupy the octahedral sites in Pd crystal, hydrogen atoms intercalates between Pd (111) planes, which could expand the distance between the (111) planes.

Topographic changes were measured also for Pd-Ag alloy electrode surfaces. Compared to the Pd, Pd-Ag alloys were found to be highly resistant to the topographic change as shown in Figure 5.

4. Conclusion

In this study we carried out calorimetry in the presence of sulfur ion (S^{2-}) and in situ measurements of topographic changes at electrode surfaces using PMIM. Results from the calorimetric experiments implies that the acceleration of the deuterium absorption into the cathode due to the addition of S^{2-} improves "burst-like" excess heat production. PMIM clearly showed that the hydrogen absorption-desorption caused the reversible topographical change. The extent of the surface roughening due to the hydrogen absorption was strongly dependent on not only the electrode materials but also crystal facets of the electrode surfaces.

References

1) N.Oyama et al., *Bull.Chem.Soc.Jpn*, 63, 2659 (1990).
2) N.Oyama et al., *Frontiers of Cold Fusion, Proceedings of the Third International Conference on Cold Fusion*, Ikegami H., Ed.; Universal Academy Press, Inc., pp67-70 (1993).
3) K.Takada, T.Haseba, T.Tatsuma, N.Oyama, Q.Li, H.S.White, *Anal.Chem.* 67, 4446(1995).
4) C.P.Smith, D.C.Fritz, M.Tirrell, H.S.White,*Thin Solid Films*, 198,369(1991).
5) *Corrosion of Metals and Hydrogen-Related Phenomena*; Flis, J., Ed.; Elsevier: Amsterdam, pp 254-263(1991)
6) Piesl, H. *Topics in Applied Physics Hydrogen in Metals I*; Alefeld G.; Volkl, J., Ed.; Springer-Verlag: Berlin, pp53-74(1978).

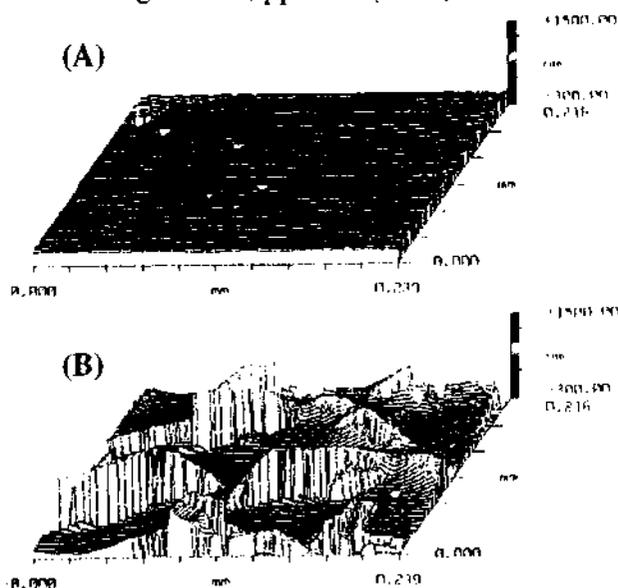Figure 5. PV vs. time curves for Pd-Ag alloy surfaces during the electroreduction of 0.1M LiOH/H$_2$O. Current density:10mAcm^{-2}.

Figure 4. PMIM optical images for Pd single crystal cathodes during the electroreduction of 0.1M LiOH/H$_2$O. (A) (100) and (B) (111). El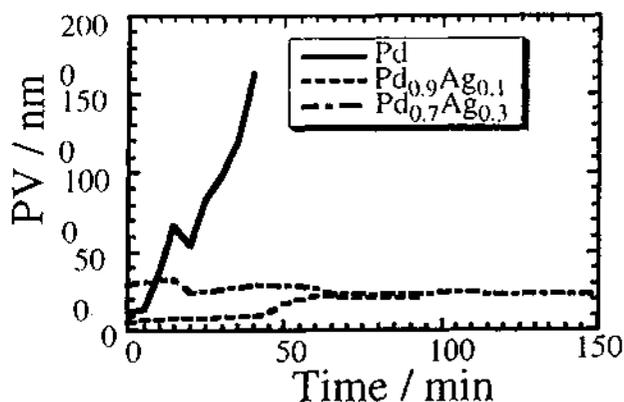ectrolysis time (A) 20min and (B) 50min.