Harnessing Hydrogen

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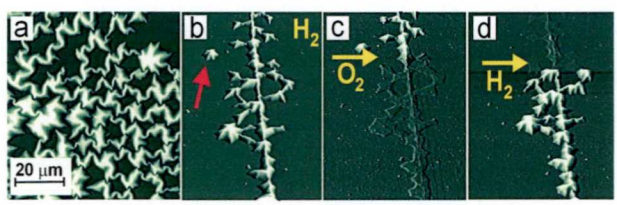
A common question currently linking specialists in various disciplines concerns new sources and carriers of energy that can be used globally in an ecological way in the future

This subject is related to the ever greater energy demand now being observed in the world, and consequently to increased atmospheric pollution, mainly caused by the extensive burning of traditional fuels. Most of the energy demand increase will be caused by the requirements of transport and generating power. If the current pace of energy consumption continues, we are in danger of seeing a strong, 70% increase in worldwide CO_2 emissions by the year 2030, reaching 38 billion tons (International Energy Agency, 2002). Other scenarios prepared by the Intergovernmental Panel on Climate Change (IPCC) indicate that in order to stabilize atmospheric CO_2 concentrations at safe levels, global emissions will need to be cut by 50%-60% against 1990 levels by the year 2050. A solution to this problem can be found in the global development of new sources and carriers of energy.

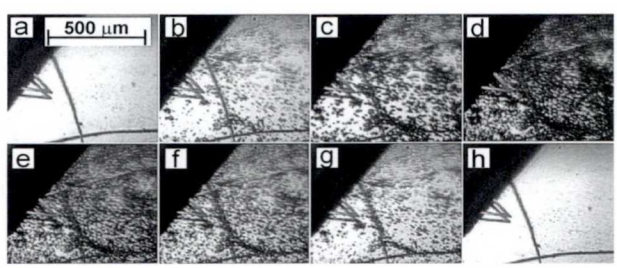
Hydrogen is a clear option to replace oil as an automotive fuel, and to compete with other energy carriers (like electricity) in various mobile and stationary applications. An important advantage of hydrogen as a fuel lies in the fact that engines using it give off a waste product that is ecological: it is simply pure water. An important question in this field concerns technical methods for the effective storage of hydrogen - the development of new hydrogen batteries. The goal is to develop a method whereby hydrogen can be stored at the highest possible concentration in a safe and economical way. A new, alternative idea uses a chemical method whereby hydrogen is stored inside metals in the form of metal hydrides. While it may seem incredible, the concentration of hydrogen in the form of hydrides seen in some metal systems can even be higher than in liquid hydrogen itself. The process of hydride formation starts on the metal surface - or more precisely, not on the whole surface area but rather at small nanometric locations selected by nature, which we call "active sites." From these sites the atoms of hydrogen start to penetrate the bulk of the metal. Understanding these active sites' properties is one of the fundamental concerns for optimizing hydrogen-metal systems in such applications. This is also the goal of our research.

We have applied microscopic methods to monitor the structure of a thin palladium (Pd) film surface *in situ* in the course of palladium hydride formation, and its decomposition due to the change of gas phase composition. The conditions were close to those expected in real hydrogen batteries - observations were performed under a flow of gases at atmospheric pressure. The study used a combination of techniques: a short response time method allowing observation in real time (a video technique) and atomic force microscopy (AFM), which offers high-resolution recording of the surface nanostructure at a chosen step of the reaction.

Figure 1 shows frames extracted from a video recording of the same area of Pd film surface during the successive introduction of hydrogen (a-d) and oxygen (e-h). The area is easily recognized by two perpendicularly oriented



Atomic force microscopy (AFM) imaging of surface structure under a hydrogen atmosphere (a), and in situ observation of structure formation and decomposition during changes of gas atmosphere (b-d, red arrow marks single star structure)



Video-camera observation of a palladium film under an atmosphere of hydrogen (a-d) and oxygen (e-h). The palladium film around the cracks is bright as a consequence of light reflected by the smooth metal surface. Evident changes on the film surface are observed when a hydrogen atmosphere is introduced -randomly distributed black spots are formed within several seconds

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The growing energy demand now being observed in the world is encouraging motor companies to seek new solutions. One of the examples of a new technology is the Citaro city bus, powered by fuel-cell engines. Thirty such busses will appear on European streets in the coming year

cracks visible on the images as thin black lines, which were made with a needle prior to the experiment. The palladium film around the cracks is bright as a consequence of light reflected by the smooth metal surface. Evident changes on the film surface are observed when a hydrogen atmosphere is introduced: randomly distributed black spots are formed within several seconds. This phenomenon is a consequence of hydride formation and the local transition of the film surface from smooth to rough. Light is dispersed but not specularly reflected by such surfaces. Consequently, the density of light reflected from these areas decreases and we perceive rough parts of the surface as black spots. However, when the gas phase composition is changed to oxygen the black spots disappear, leading to the reconstruction of a smooth surface. This is a consequence of palladium hydride's decomposition in an oxygen atmosphere. These changes are therefore reversible: the introduction of hydrogen produces black spots, while oxygen restores a bright surface. AFM observations of the active areas performed at a higher resolution provide more detail (Figure 2). The locally observed increase in surface roughness is a consequence of mezoscopic protrusions with a characteristic element that form in these locations, which we have called star-like structures. They are an effect of stress generated within the film, and of its relaxation. The cause lies in the increased lattice constant and the film surface area associated with the formation of hydride. The development of single star structure is an effect originating from one separated active place. It is interesting to note that the height of the observed structures can reach 1 μm, which is 20-40 times higher than the thickness of the Pd film. This observation indicates that the film is separated from the substrate at the active sites. In spite of these huge changes in the film structure the protrusions disappear when the palladium hydride decomposes in an oxygen atmosphere, confirming the high elasticity of thin palladium film in this reaction.

Using AFM we are thus able to distinguish between active and inactive sites in the process of hydride formation. Studies performed with thin Pd films deposited on atomically flat substrates enable us to propose a model of the film response in this process. Results have been reported in the publications listed below. This work is still in progress and focuses on answering the important question of the nature of active sites. ■

Further reading:

R. Nowakowski, P. Grzeszczak, R. Duś (2002). AFM studies of the catalytic reaction of hydrogen with oxygen on thin Pd and Pt films under pressure similar to 101 kPa. *Surface Sciences, 507*, 813

R. Nowakowski, R. Duś (2003). AFM studies of thin Pd film response to palladium hydride formation and its reaction with oxygen. *Langmuir 19*, 6750