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Four Steps to the Hydrogen Car

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1. Introduction

Hydrogen has long been touted as the fuel of the future; however, it is becoming increasingly clear that the next generation of cars will be hybrid vehicles - combining a small, conventional petrol or diesel engine with a battery-powered electric motor - and that these hybrid vehicles are a stepping stone to the purely electric vehicle, which will be powered by a battery that can be quickly and easily recharged at home or on the road. From the point of view of hydrogen-powered vehicles, this leads us to four critical research questions that we will attempt to cover in this chapter. Does this mean that the hydrogen car has been squeezed out of the picture? Just why are hydrogen vehicles taking so long to realise as a viable form of transport? And what changes or improvements in terms of science and technology are required before our roads see hydrogen cars and, of course, the hydrogen filling stations required to fuel these vehicles? Here we have identified the four critical barriers that need to be overcome before the hydrogen car becomes a reality and have assessed each one in terms of the likelihood of success. Before there is a hydrogen future for the car we need to solve the problems related to on-board hydrogen storage, developing a hydrogen infrastructure, simple and clean hydrogen production and a cheaper fuel cell for converting the hydrogen into electricity.

Of these, storing enough hydrogen in the car is already a practical reality. Toyota is one of a number of companies that has successfully demonstrated a passenger vehicle with a range in excess of 600 km on a single tank of hydrogen. They have achieved this not with a heavily insulated storage vessel that contains liquid hydrogen at –253°C, nor by using some exotic hydrogen-storage material like a rare-earth transition-metal alloy or carbon nanotubes, but instead by developing an extremely strong, carbon-fibre tank that can safely store hydrogen in gaseous form at pressures of up to 680 bar. Of course compression is still an expensive process, but compared to liquefaction or the weight costs of metal-hydride stores, a pressurised-gas tank looks like the best solution. In Section 2 we look at the properties of hydrogen and point to the reasons why other forms of hydrogen storage will find it hard to compete with the pressurised tank.

A hydrogen infrastructure could be introduced quickly, provided there is sufficient financial investment. There is, of course, the obvious chicken-and-egg situation: who will build this infrastructure if there are no vehicles, and who will invest in a hydrogen car if there is nowhere to re-fuel it. But the position is changing. Germany plans to have more than 1000

refuelling stations by 2020. In the United States, efforts are underway to have 50+ hydrogen stations in the Los Angeles area. Estimates for the whole of the US suggest that the country will need tens of thousands of hydrogen stations to provide access for the majority of the population, with the costs expected to be a massive – but still realisable – $35 billion (a figure similar to that quoted for the Alaska North Slope gas pipeline). Carrying pure hydrogen down steel pipes also carries with it the substantial risk of hydrogen embrittlement. This is a well-know problem associated with many steels, whereby relatively small amounts of hydrogen are absorbed by the steel, but the expansion caused either by the presence of interstitial hydrogen atoms of the reformation of hydrogen molecules in the voids in the materials can lead to cracking and subsequent leaking from the pipeline. In this part of the chapter, Section 3, as well as looking at some of the regional-based efforts to construct an infrastructure in Germany, the UK and the US, we also devote some space to some of our recent work on dramatically reducing the amount of hydrogen permeation into the steel by using a very thin coating of conventionally applied TiAlN.

An appropriate and economically viable fuel cell requires technological improvements that will take time and money. Unlike conventional internal-combustion engines fuel cells are anything but robust and durable. In particular, fuel cells contain delicate membranes and expensive catalysts. However, the past 10 years have seen a series of improvements that mean fuel-cell vehicles can operate in low-temperature environments – something that was not possible until very recently. Furthermore, the introduction of nanotechnology in the production of platinum catalysts is driving down prices, making the materials costs similar to those associated with conventional catalytic converters. Section 4 looks at the problems of expensive catalyst materials and points to research which is currently underway to substantially reduce these costs.

However, hydrogen production remains as the most difficult problem to solve, requiring a scientific breakthrough to produce hydrogen sufficiently easily and cleanly. Today, the vast majority of the world's hydrogen is produced by the steam reforming of fossil fuels, but taking into account the depletion of fossil fuels and the associated harmful environmental effects, the production of hydrogen from renewable sources is the most critical problem to overcome. For this reason there are huge development projects focusing on renewable paths for hydrogen production, including some of the following: fermentation, biological water splitting, conversion of biomass and wastes, solar thermal water splitting, renewable electrolysis, photo-electrochemical water splitting – and all these options need to be explored, since it is unlikely that a single solution will be appropriate for every situation. Solar energy is, of course, a virtually inexhaustible and widely available energy source, which leads to the idea of renewable hydrogen in which the large-scale use of solar cells would be coupled to an electrolyzer. However, there is another option, which has been neglected for far too long, and is actually the most attractive and cleanest approach to solar hydrogen: the use of photo-electrochemical cells. The operating principle is simple, the photo-active semiconductor material is immersed in water and photo-generated electrons are directly used to reduce and oxidise water. Within this system the functions of the solar cell and the electrolyzer are combined in a single device. However, the material requirements and the complex mechanism of photo-electrochemical splitting with which a highly efficient solar-to-hydrogen conversion in the visible part of spectra would be achieved are far from simple. Any photocatalyst material has to meet several criteria, i.e., it has to absorb visible light, have a good level of conductivity for photo-exiton transfer, has to straddle the electrochemical potential for reduction and oxidation, has to be very stable in the various media and last - but not least -

should be economically acceptable. In Section 5 we look at the photo-electrochemical splitting of water and recent developments to increase the efficiency of the process.

2. How can we store enough hydrogen in a car?

Before looking more closely at the storage options for hydrogen, it will be useful to look first at the characteristics of the Universe's most common element. Hydrogen in the form of a gas was first recognised as a discrete substance by Henry Cavendish (1731-1810) in the 18th century; although others, like Robert Boyle (1627-1691), had probably prepared it earlier. Cavendish, like his French rival Antoine Lavoisier (1743-1794), also made the important discovery that hydrogen (which he referred to as "inflammable air") reacted with oxygen to produce water. He also made the observation that the reaction produced no chemical by-products. Although this turns out not to be completely true when hydrogen burns in air. In this case small quantities of nitrogen oxides are normally produced as well. An important characteristic of hydrogen as a potential fuel is that it is almost entirely non-polluting in terms of emissions associated with the on-board fuel and the vehicle – emissions that might be associated with the production of hydrogen at some other location are, of course, a completely different question.

Another very important characteristic of hydrogen is that it does not occur naturally. Despite being the most abundant element in the Universe, representing some 75% of matter in terms of mass, hydrogen gas is extremely rare on Earth, quite simply because its light weight means that it can escape the gravitational pull of the planet much more easily than heavier gases. However, this is not to say that the element hydrogen is in anyway rare on Earth: two of water's three atoms are hydrogen, hydrogen is a major constituent of all the flora and fauna on the planet, and hydrogen makes up 61 percent of all the atoms in the human body.

Hydrogen has physical and chemical properties that suggest it is a good candidate for a fuel: it is odourless, colourless, stable, and does not react with oxygen until sufficient energy is inputted to begin an exothermic reaction that results in the production of water.

Hydrogen is the lightest of the elements and stores a lot of energy in its chemical bond. In terms of being useful as a fuel, we need to note a few of its physical characteristics. The density of hydrogen gas is 0.0899 grams per litre, which is about two-thirds the density of air. In liquid form, hydrogen has a density of 70.99 g/l and it boils at –253°C. These properties are part of the reason why hydrogen has the highest energy-to-weight ratio of commonly available fuels. For example, 1 kg of hydrogen contains the same amount of energy as 2.1 kg of natural gas or 2.8 kg of petrol. Putting it in simple terms, if we think about energy per gram of fuel, hydrogen is an easy winner – hydrogen stores more than two and a half times more energy than petrol if we compare equal weights of the two substances. But in terms of volume, hydrogen looks a little less promising: hydrogen has an energy density of 9 MJ/litre, while petrol has an energy density of 31 MJ/litre. In other words, even if we think of hydrogen in the liquid state (and we will ignore all the low-temperature factors for now) a hydrogen fuel tank would need to be at least three times larger than a petrol tank if our vehicle is going to have the same range on the road.

So, storing enough hydrogen – and in an easily accessible form – is one of the four major challenges that need to be overcome. Detailed on-board hydrogen-storage-system requirements were drawn up by the FreedomCAR and Fuel Partnership (a collaboration among the DOE, the U.S. Council for Automotive Research, and the major energy and utility companies), with the most recent revision being in 2009. These requirements are very

detailed; however, it is generally considered that a car needs a minimum of 5kg of hydrogen on board in order to provide a practical range of 500 km. Although this is much less than the 50 kg or so of petrol or diesel that a car currently carries around when the tank is full, hydrogen is not available to us in such a convenient form. Under conditions of standard temperature and pressure, hydrogen is a gas. This means that storing enough hydrogen gas at a pressure of around 1 bar would involve a huge balloon-like tank that is a totally impractical proposition.

The most obvious solution appears to be liquid hydrogen. In theory, only about 14.2 MJ/kg (and here we talk about a kg of liquid hydrogen) have to be removed to cool hydrogen gas from room temperature (298 K) to 20.3 K and then condense the hydrogen gas into the liquid form at atmospheric pressure. In practice, hydrogen is liquefied in a complex, multi-stage process involving compression and expansion that is combined with a counter-flow heat exchange and a certain amount of heat recovery using expansion turbines. The whole procedure makes use of other liquefied gases: first, a three-stage vapour-compression system is used for the initial cooling from room temperature; second, using a multi-stage nitrogen expansion the hydrogen gas is cooled to 77 K; and third, there is a multi-stage helium compression and expansion to obtain liquid hydrogen at 20.3 K.

However, the situation is not so simple or energy efficient as we have just described. A typical medium-sized liquefaction plant, one producing about 200 kg of liquid hydrogen per hour will consume about 50 MJ/kg, well over three times the theoretical figure. The reason for this is that the theoretical figure does not contain all the electrical, thermal and mechanical losses. A large plant, producing a 1000+ kg of hydrogen per hour can reduce this energy-consumption figure to about 35 MJ/kg, and feasibility studies for plants producing 10,000+ kg of hydrogen per hour have suggested that this figure could be reduced to about 30 MJ/kg.

A graph showing how the amount of energy required for the liquefaction of hydrogen for different liquid-hydrogen-plant facilities is shown below.
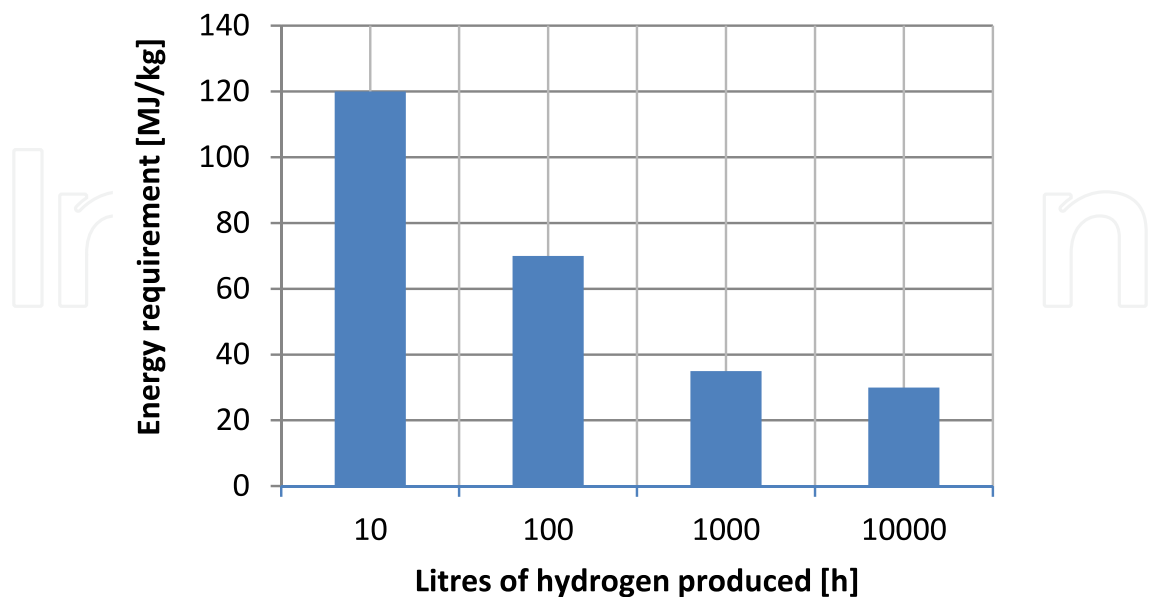

Fig. 1. Amount of energy required for the liquefaction of hydrogen for different liquid-hydrogen-plant facilities

Of course the absolute energy costs for producing the hydrogen are not the only consideration. It is important that we consider how much energy we use to liquefy the hydrogen compared to how much energy we can get out of the stored liquid hydrogen to drive our car.

For very small operations producing less than 10 kg per hour the energy needed to liquefy the hydrogen may exceed the energy available for use in the liquid hydrogen. Such a situation clearly makes no practical sense. However, even for a plant producing 10,000+ kg of hydrogen per hour (and no such plant currently exists) we would consume at least 25% of the available energy for the engine or the fuel cell of the car. The best practical figure for us to use would be 30%. In other words, 1.3 units of energy would have to be supplied during the hydrogen liquefaction process in order to have available 1 unit of energy.

A graph showing the percentage of available energy required to liquefy the hydrogen from room temperature for different liquid-hydrogen-plant facilities is shown below.
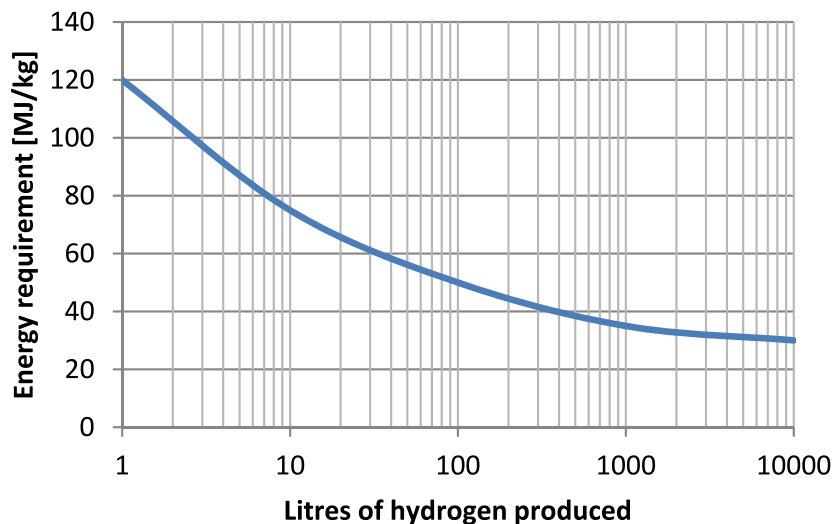

Fig. 2. Percentage of available energy required to liquefy the hydrogen from room temperature for different liquid-hydrogen-plant facilities

The best known problem, although not well understood, is that of boil-off. It occurs because the liquid-hydrogen tank cannot be perfectly insulated and pressure must not be allowed to build up inside the tank because the pressures would very quickly become impossible to contain safely. The extent of these losses depends on many factors, but a few percent per day is as low as we can realistically expect. This means that if our car was parked in a – well ventilated – garage it would lose about a quarter of a full tank in a week.

Perhaps the most elegant way of storing hydrogen is to form a reversible metal hydride. Some of the best researched examples include MgH_2, $NaAlH_4$, $LaNi_5H_6$, and $TiFeH_2$. These materials have an excellent energy density by volume – for example, the hydrogen atoms in $LaNi_5H_6$ are closer together than the hydrogen atoms in liquid hydrogen – however, their energy density by weight is often poor. The best metal-hydride stores are close to about 1.5 weight percent. That means to be able to store 5 kg of hydrogen we will need a metal-hydride storage tank weighing in excess of 330 kg – about the weight of two Ducati 848 Superbikes.

Most metal hydrides require high temperatures to desorb the hydrogen for use in the car. This energy cost is reduced with some of the more popular alloys, which require lower

desorption temperatures; however, if this interaction is too weak the re-hydriding pressure becomes too high. This problem appears to be the most difficult to overcome.

The most obvious, but for a long time overlooked, method of storing hydrogen is simply to compress the gas. The conventional gas cylinders found in any laboratory are filled to a maximum pressure of about 150 bar. To get a sufficient driving range and a reasonable size to fit within the confines of a car's structure, we require much higher pressures of 700-800 bar. Furthermore, in order to withstand everyday abuse and to facilitate handling these conventional cylinders are made from steel. This makes them far too heavy for automotive use. Recent advances in carbon-fibre technology have led to the practical realisation of such tanks. Quantum Technologies, a company based in California, is one of the leaders in this field. They recently demonstrated an all-composite 700-bar hydrogen tank, known as the QUANTUM TriShield, which has been bust tested to 1650 bar, making it comply with the European Integrated Hydrogen Project (EIHP) specifications. The EIHP is one of the main drivers of global regulatory standards.

The main problems associated with hydrogen gas tanks relate not just to the high pressures involved, but also to weight, volume, shape and cost. Weight is the least problematic. The use of carbon fibre and lightweight alloys puts compressed-hydrogen tanks streets ahead of solid-state storage and relatively close to the weights associated with conventional fuel tanks. In terms of weight, there are two directions currently being pursued. The first of these are the so-called cryo-compression tanks. These tanks use a liquid-nitrogen jacket to cool the tank to 77 K, so increasing its volumetric capacity by a factor of four. The second approach involves making the tank a more integral part of the car's structure, making use of the strength of other parts of the car to store the hydrogen, possibly by keeping the hydrogen within cellular load-bearing structures.

These storage tanks also require very safe and reliable pressure-management systems, able to allow the hydrogen to flow smoothly out of the tank to the fuel cell or internal combustion engine. Many companies have patented and proprietary systems for preventing any dangerous release of hydrogen during use. Quantum's patented 700-bar tank includes an in-tank regulator that provides additional safety by containing the high pressure in the tank and allowing a maximum delivery pressure of just 10 bar.

Such tanks are very sophisticated and, of course, expensive. This will be a major hurdle that needs to be overcome before these tanks could become widely available, but history shows that once technologies have been proved to work, if the demand is high, then the price will fall rapidly.

3. How will we introduce a safe and reliable hydrogen infrastructure?

At present there is no country anywhere in the world with any serious intention to introduce a hydrogen infrastructure for fuelling a transport system. In fact, a few years ago there were fewer than 4000 km of low-pressure hydrogen pipelines in the United States and Europe, combined. The pipelines that exist in the US are primarily for the transportation of hydrogen for use in the de-sulphuring of crude oil to produce diesel and petrol. The longest of these is the Texas-Louisiana pipeline that runs along the Gulf Coast.

A hydrogen pipeline infrastructure is basically the same as the pipeline infrastructure used for the transport of natural gas; it would have to involve similar components, such as transmission pipelines and compressor stations. Although there are several thousands of kilometres of hydrogen pipelines throughout the world, they are only designed to transport

the hydrogen over relatively short distances, with the production facility being located relatively close to the site of the end user. With the exception of a few longer stretches of pipeline, most of the world's several thousand kilometres of pipeline are made up of relatively short sections of a few hundred metres, carrying hydrogen at quite low pressures, typically less than 100 bar. However, the safety records associated with these pipelines are very good.

It is important to consider hydrogen's density when we make comparisons with natural gas pipelines. For any given pressure the density of hydrogen is about one-third that of natural gas. However, for an equivalent pipe diameter and gas pressure, the flow of hydrogen is approximately three times faster than that of natural gas. On this basis, and assuming large-scale hydrogen compressors could be made to operate as effectively as the natural-gas variants, we can envisage similar pipeline diameters of 1–2 m. The actual diameters would of course depend on other factors, particularly demand, achievable pressures and the regulations in force in any particular country or locality.

A lot of people have put forward the idea that we could make use of the existing natural gas infrastructure as the basis for a new hydrogen infrastructure. Natural-gas pipelines could be used in an unmodified form to transport 20% hydrogen in natural gas. However, modifying these same pipelines to carry pure hydrogen would require a number of issues to be addressed: many of the steel components in these pipelines could begin to suffer from embrittlement, and the sealing requirements for hydrogen are much stricter than for natural gas.

We have recently been involved in a major European project, called Hy-NANO-Im, funded by the EU as part of MNT.ERA-NET programme to look closely at the problem of preventing the permeation of hydrogen into steel structures in order to reduce the problems associated with the embrittlement of hydrogen pipelines based on steel. The starting points for the project were that the coating must be effective, cheap, stable and easy to apply. There have been many attempts to produce such anti-permeation coatings in the past, but all of them have failed in at least one aspect of the requirements for widespread application.

The experimental proof of a barrier's efficiency is the relative reduction of the steady permeation flux. Its definition is the ratio of the steady permeation rate through the uncoated membrane, i.e., the steel, versus the steady permeation rate through the coated membrane, termed "the permeation reduction factor" (PRF):

$$PRF = \frac{j_{uncoated}}{j_{coated}} . \tag{1}$$

Both permeation rates must be obtained under identical conditions in terms of the driving pressure and the temperature.

When the hydrogen migration through the planar, homogenous membrane, i.e., the steel, is limited by hydrogen atom diffusion in the material, the steady-state permeation rate j follows the Richardson equation

$$j = \frac{P}{d}\sqrt{p} , \tag{2}$$

where P is the permeability coefficient, p is the hydrogen driving pressure and d is the membrane thickness. The coefficient P is a material property and is a product of the hydrogen diffusivity and solubility. Applying the Richardson equation to a composite (coated) planar membrane enables the calculation of an effective permeation coefficient. The

effective permeability $P_{eff.}$ is based on the sum of the permeation resistances for each layer, analogous to electrical resistors in series. For a two-layered membrane, i.e., a hydrogen-resistant coating on steel, it is then

$$\frac{d}{P_{eff.}} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \, , \tag{3}$$

where the indices denote layer 1 and 2, while the membrane thickness is $d = d_1 + d_2$.

The permeability coefficient of a coating material can thus be obtained from the known layer thicknesses and the steady-state permeation rates through the coated and uncoated membranes.

The coatings reported prior to our Hy-NANO-Im project included dense alumina, only 1 µm thick, which produced a permeation reduction factor (PRF) of 1000 at 800°C, as reported by Levchuk et al. (2004). Erbium oxide, again 1 µm thick, has also been recognized as an efficient barrier, with a PRF of the order of 1000 (Levchuk et al. 2007). And an even more efficient barrier was made from Al–Cr–O, giving a PRF between 2000 and 3500 at 700°C (Levchuck et al. 2008). However, these coatings would not be particularly cheap or easy to apply.

In the Hy-NANO-Im project we decided to look at transition-metal-nitride hard coatings, which have been employed since the early 1980s for the protection of tools. Such coatings are most commonly prepared by physical vapour deposition (PVD) at a typical deposition temperature of around 450°C. Starting from the ubiquitous TiN, several ternary coatings have been developed, with the greatest usage probably achieved by TiAlN. This coating is distinguished by a high hardness (3300 HV), a good oxidation resistance (up to 850°C), a chemical inertness and a low thermal conductivity (PalDey et al. 2003). In its basic form, a TiAlN coating has an atomic ratio of approximately Ti:Al = 50:50, a columnar microstructure and a B1 cubic structure. Several TiAlN-based coatings have been developed over the past 10 years or so, including AlTiN (with an increased share of aluminium) and nanolayer TiAlN/TiN.

Among the diffusion-related properties, oxidation resistance (Inoue et al. 1997) and thermal stability (L Hultman, 2000) have been studied extensively. With the aim being to enhance the coating's performance in cutting operations, several options have been explored, such as multilayers or the addition of another element. However, in contrast to TiN, where there are many reports on its application as a diffusion barrier (M.Y. Kwak et al. 1999), the data on TiAlN is scarce. Of specific interest is the study by Man et al., (2004) who deposited TiAlN coatings on AISI 316L steel and measured the hydrogen permeation flux. They obtained the lowest permeation flux of $1.2 \ 10^{-11}$ mol cm^{-2} s^{-1} for an aluminium share of x=0.4.

These permeation results combined with our experience in depositing dense films as hard coatings made us interested in testing the effectiveness of TiAlN barriers with respect to hydrogen when applied to steel for infrastructure and hydrogen-pipeline applications. In the Hy-NANO-Im project we looked at applying a TiAlN film of 5 µm, deposited on Eurofer steel samples using magnetron sputtering, which resulted in a PRF of 5800 to 20,000 at 400°C.

A cross-section TEM study provided valuable information on the microstructure and the phase composition of the coating. A qualitative EDS analysis confirmed the TiAlN composition of the film. Figure 3 shows the TiAlN/Eurofer interfacial region. The interface between the substrate and the film is smooth and abrupt. TiAlN crystallites extend from the interface in the form of elongated, columnar grains. They become clearly visible after 100 nm or so. The width of these parallel grown columnar grains is 20-50 nm and they are up to 500

nm long. Close to the thin edge of the film we observe, in weak contrast, wavy horizontal bands, *i.e.*, TiAlN growth zones. These bands are a consequence of the sample rotation. In the two-fold rotational geometry the sample travels along a complex trajectory within the deposition chamber, and thus periodically approaches towards and moves away from the target (Panjan et al. 2008). Although the targets are identical, a multilayer character becomes visible, as a consequence of the differences in the growth rate. The typical width of the bands is 10-15 nm, which corresponds to the amount of material deposited in each cycle.
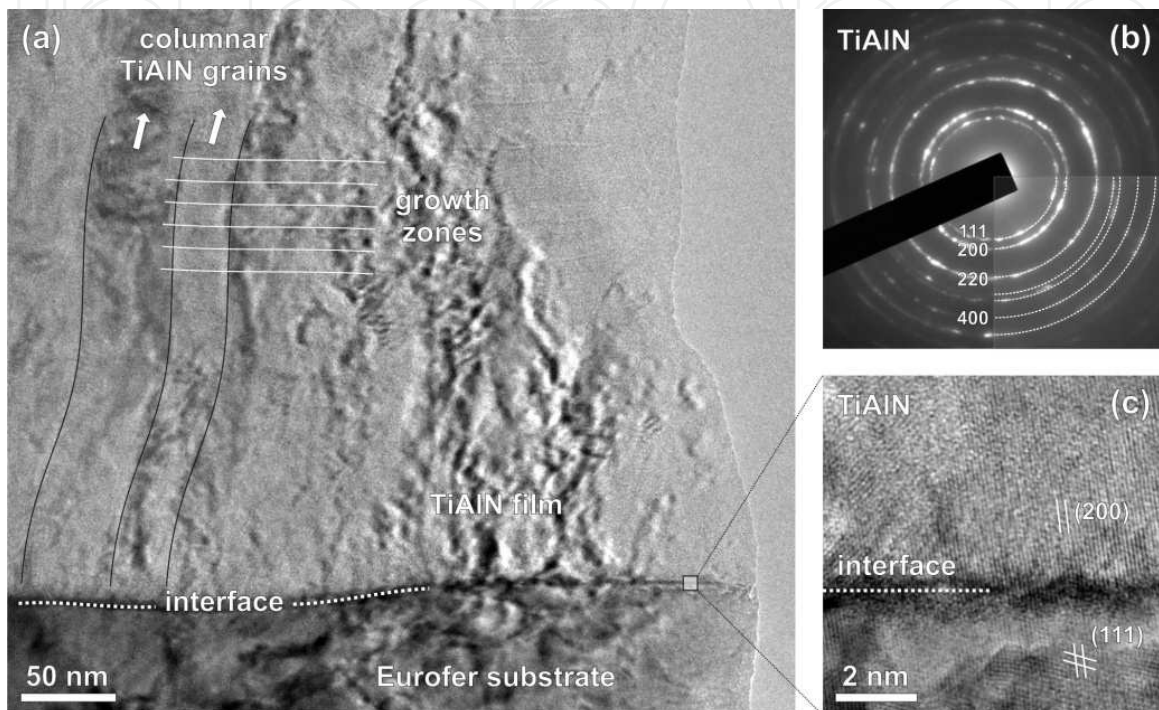
Fig. 3. Bottom part of the TiAlN film at the contact with the Eurofer substrate. (a) TiAlN grows in the form of 20-50-nm-wide columnar grains that extend from the TiAlN/Eurofer interface. Growth zones are parallel with the interface. (b) SAED pattern recorded from the TiAlN film shows diffraction rings stemming from randomly oriented TiAlN crystallites. Measured d-values correspond to the TiN-related cubic structure. (c) A high-resolution TEM image of the TiAlN/Eurofer interface shows that columnar TiAlN grains in the film grow on the top of the Fe grains of the substrate in a semi-epitaxial relation.

The SAED pattern recorded from a larger area of the TiAlN film shows the diffraction rings characteristic for a face-centred cubic TiN-related structure with slightly larger *d*-spacings. All of the diffraction rings can be attributed to the cubic phase; therefore, we could exclude the possible presence of any hexagonal AlN- or TiN-related phase. Along the interface we can regularly observe a certain degree of epitaxy between the Fe grains in the substrate and the TiAlN grains in the film. One such situation is shown in the close-up in Fig. 4c, where (111) lattice planes of iron continue into the (200) lattice of TiAlN. Because of the structural dissimilarity in the other directions a full-scale epitaxial growth cannot be expected in this system. The columnar texture of the TiAlN coating is retained throughout the film's cross-section all the way to the surface. Figure 4 shows the surface area of the TiAlN film. The surface itself is smooth with a roughness comparable to the roughness of the substrate (Fig. 4a). In the ion-milled parts of the TiAlN surface we can clearly recognize the columnar grains and the growth zones, which are characteristic for the film's method of deposition (Fig. 4b).
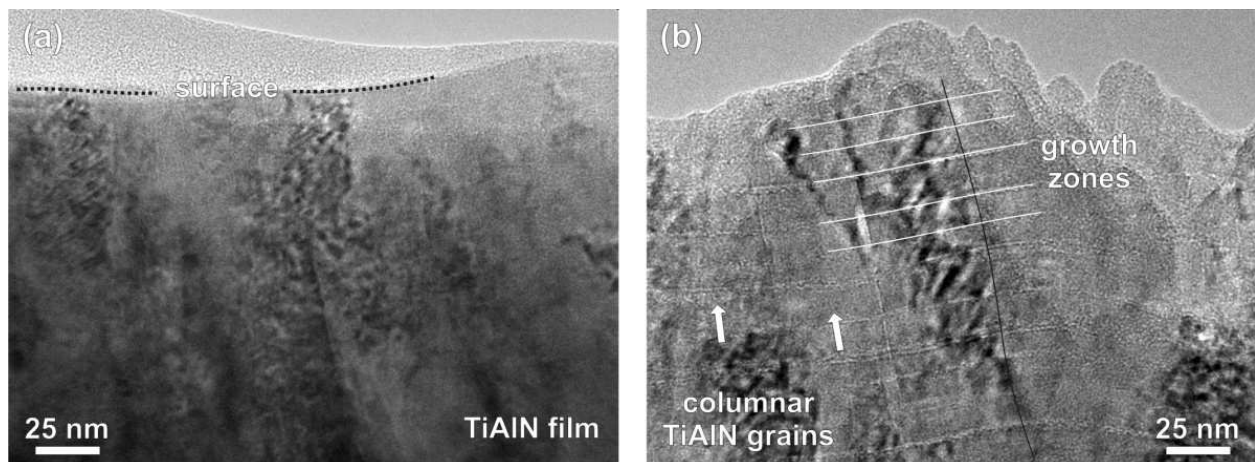
Fig. 4. Top part of the TiAlN film. (a) Smooth surface embedded in epoxy resin visible as amorphous layer above the surface line. (b) ion-milled surface region showing columnar TiAlN grains and distinct growth zones.

The measurements made on the uncoated membrane were performed to test the system's performance, reproducibility and to compare our data with previously published data. Since our system has a very high sensitivity, but the measurements with such a sensitivity last a long time, we decided to fix the temperature of the experiments at 400°C. The permeation flow of hydrogen through the uncoated membranes was observed immediately on a 5-Pa FS CM (capacitance manometer) gauge after the hydrogen was suddenly introduced to the upstream side. The steady flows at various values of the upstream pressure from p_{up} = 60–120 kPa are shown in Fig. 5 for the uncoated steel. The measured flow is proportional to the square root of the upstream pressure, indicating a diffusion-limited permeation regime. The small differences between the flows through the three uncoated samples can be related to slight variations in the surface composition or to impurities in the hydrogen gas. These impurities were kept at a low level by leading the gas through a trap chilled by liquid nitrogen. The average time-lag of 6.5 s was determined from several repeated cycles giving us a diffusivity constant of D(400°C) = 6.4·10^{-9} m^2/s. The permeability coefficient was determined to be P(400°C) = 1.7·10^{-11} mol H$_2$/m s $\sqrt{Pa}$ and the hydrogen solubility was S(400°C) = 2.6·10^{-3} mol H$_2$/m^3 $\sqrt{Pa}$. The obtained parameters are in very good agreement with the published transport parameters for hydrogen and deuterium in Eurofer steel (Esteban et al (2007) and Levchuck et al. (2004b)). When testing the TiAlN-coated sample at 1 bar of H$_2$ we observed that the permeation flux was both substantially lower and that the time to reach a maximum flow value was longer. The first exposure to 1 bar and the subsequent pressure change on the downstream side is given in Fig. 6.

Three repeated exposures of the steel to approximately 1 bar of hydrogen were conducted and the exposure lasted for some hours. Between those exposures the membrane was allowed to outgas in UHV for some tens of hours, which was sufficient to restore the low background. Two values for the PRF were recorded within the first 4 days: 13,300 and 20,000. During this period the membrane was kept at 400°C all the time.

However, an evaluation of a barrier's effectiveness is not simple and no unique criterion has been accepted (Perujo & Forcey 1995). Nevertheless, using the PRF as a means of assessing the capability of a given coating to act as a permeation barrier is still the most common way to enable such a comparison. It is generally determined in similar permeation devices, but at various temperatures and pressures. This makes any PRF comparison and prediction of its

long-term operation even less reliable. In any case, we made a comparison of our PRF value measured at a planned 400 °C against the highest published values of PRF for different barrier-film materials deposited by various techniques.
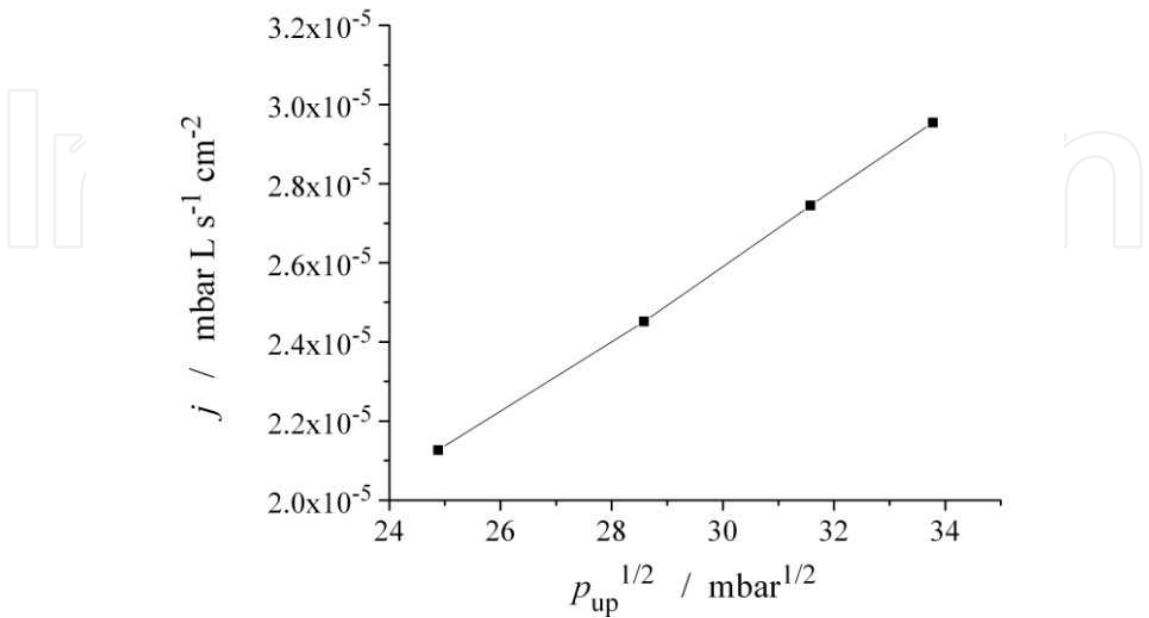

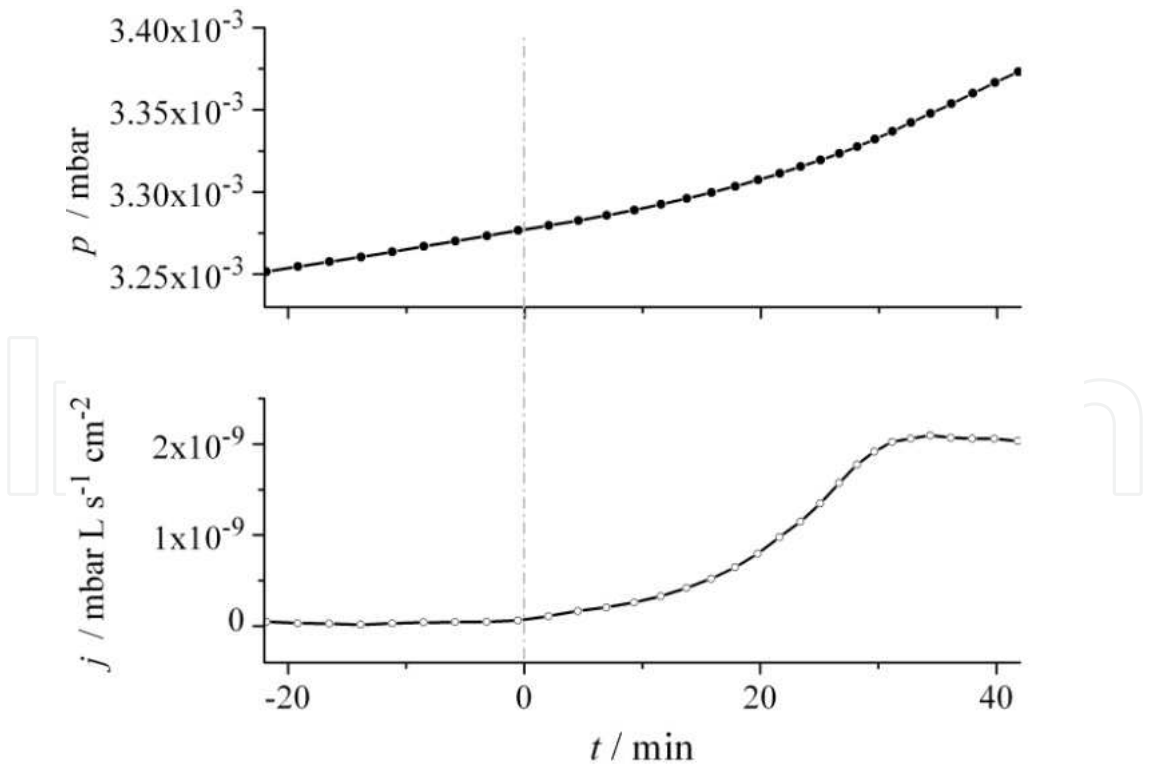Fig. 5. Permeation rate versus square root of the upstream pressure from 62 000 Pa to 114 000 Pa

Fig. 6. Pressure evolution and permeation flux obtained from pressure derivative versus time before and after introducing 83000 Pa H_2 at the upstream side. Hydrogen was introduced at t = 0.

Table 1 summarizes the results on the barriers reported so far on the Eurofer substrate. Among the three published reports, all used arc evaporation for the deposition of the barrier film. One of the features of arc evaporation is the incorporation of droplets into the growing film, which may have a negative influence on the film's permeability. Nevertheless, the authors applied two varieties of arc evaporation, where this problem is significantly reduced. In magnetron sputtering, applied in our case, the droplet problem is largely irrelevant and the resulting compact microstructure contributes to the permeability of the film. Therefore, it is not surprising that our tested TiAlN film exhibited the highest PRF of any reported barrier materials applied so far to a Eurofer substrate.

Material	Deposition method	Thickness	Evaluation temperature	PRF	Ref
Al_2O_3	Filtered arc evaporation	1 μm	700, 750, 800°C	1000	Levchuck et al. (2004)
Er_2O_3	Filtered arc evaporation	1 μm	400-700°C	800	Levchuck et al. (2007)
Al-Cr-O	Pulse enhanced electron emission arc evaporation	2 μm	600-700°C	2000-3000	Levchuck et al. (2008)
TiAlN	Magnetron sputtering	5 μm	400°C	5800-20000	McGuiness et al. (2010)

Table 1. Comparison of the highest achieved PRF values for various barrier types applied on Eurofer.

Despite the common usage of PRF to assess a film's capability, it is not the best quantity for an intercomparison since it does not take into account the substrate's properties (material, thickness) and the film thickness. When the permeation through a coated membrane is assumed to be diffusion limited, then the permeability coefficient P of the film is the proper quantity that is independent of the substrate and dimensions. The permeation coefficient at 400°C for our measurements on the TiAlN film give P_{TiAlN} = 2.9·10^{-17} mol H_2/m s $\sqrt{Pa}$, 1.3·10^{-17} mol H_2/m s $\sqrt{Pa}$ and 8·10^{-18} mol H_2/m s $\sqrt{Pa}$ corresponding to the following PRF = 5800, 13300 and 20000. From ref. [9] (the only publication on permeation measurements through a TiAlN film deposited on AISI 316L steel) we calculated the P_{TiAlN}(550°C)= 4.5·10^{-16} mol H_2/m s $\sqrt{Pa}$ for the least permeable film investigated. The references [2-4] used in Table 2 unfortunately do not provide sufficient data to calculate P in the temperature range close to 400°C. The exception is ref. [3], where P_{Er2O3}(600°C) = 4.1·10^{-16} mol H_2/m s $\sqrt{Pa}$ could be calculated. From a rough extrapolation of $P_{eff.}$ for an Al_2O_3-coated membrane [2], the permeability coefficient P_{Al2O3} (600°C)≈2·10^{-16} mol H_2/m s $\sqrt{Pa}$ and P_{Al2O3} (400°C)≈4·10^{-17} mol H_2/m s $\sqrt{Pa}$ could be extracted. The latter value is in good agreement with the P_{TiAlN} obtained on our sample, while the P values at ≈600°C lie in the (2-5)·10^{-16} mol H_2/m s $\sqrt{Pa}$ range for TiAlN [9], Er_2O_3 [3] and Al_2O_3 [2], suggesting that all three coating materials could have similar effectiveness as a hydrogen permeation barrier.

Our present approach seems a good choice, since TiAlN films are today deposited routinely as hard coatings. We also believe that the deposition parameters may be further optimized to fulfil the demands for barrier films as required for hydrogen pipelines as part of an international hydrogen infrastructure that could be used for automotive refuelling stations.

So far, hydrogen infrastructures for transport systems have been developed only at the regional level. The best-known and oldest pipeline is the Rhine-Ruhr pipeline that runs for a distance of more than 200 km. It was completed in 1938 and carries hydrogen through 30-cm diameter pipes at a pressure of approximately 15 bar. The original pipeline is still working, although the complete network is now much extended. In 2009 the organisation H2-Netzwerk-Ruhr set out a plan to become the "Silicon Valley" of hydrogen technology. The region of North Rhine Westphalia is the centre of many hydrogen-related activities. In Bottrop and Herten, the regenerative production of hydrogen takes place, industrial hydrogen is available in a pipeline from Marl, and Duisburg provides know-how through its centre for fuel-cell technology. In addition, the region operates a fleet of fuel-cell vehicles (Hychain) and in 2010 the city of Essen hosted the world hydrogen conference.

Other early starters in the regional pipelines were Isbergues in France (1973), Zeebrugge in Holland (1985), Rotterdam (1997). There are many other regional pipeline infrastructures in the planning stage or beginning construction. There are ideas to produce hydrogen in Iceland, with the plan to use a pipeline to transport it to Scotland, although at the moment this remains only as an idea, with the costs being described as prohibitive. In Germany, the National Organization Hydrogen and Fuel Cells Technology (NOW) is convinced that hydrogen will play a key role in the future and that hydrogen and battery technologies are in fact complementary rather than competitive. However, they admit that one of the primary difficulties of introducing to the market an alternative to gas-powered cars—whether powered by a battery or fuel cell—is building up the number of new cars on the road while creating a new fuelling infrastructure. They have said that hydrogen supplies could be trucked in initially, but eventually pipelines carrying the fuel to filling stations would be required. Daimler, who work closely with NOW, have admitted that fuelling infrastructure has not become real to the extent that is required, but they believe that the German government's stimulus plan is expected to fund new hydrogen filling stations to complement the four already located within the country. Four is not very many, but it is a start.

In the UK, Wales has taken a very forward-looking view on the subject of hydrogen and a hydrogen infrastructure. The organisation H2Wales has already identified that the transition to a hydrogen economy will require a number of intermediate steps, rather than a single-step change. These transition steps include the adoption of hydrogen as an additive to conventional fuels like diesel or CNG for internal combustion engines, electric vehicle drive development, hydrogen storage improvement and fuel-cell developments. In February 2010 the Welsh Secretary, Peter Hain, announced that the M4 motorway in south Wales is to become a "hydrogen highway". The scheme, to extend into south west England, is aimed at making hydrogen and electric-powered vehicles a viable alternative to petrol-driven machines. Under the plan, Wales will lead in developing alternative fuels, including hydrogen from renewable sources. The aim is to create an extensive renewable refuelling infrastructure.

In California, the California Hydrogen Infrastructure Project, led by Air Products and Chemicals, Inc. and the DOE, aims to conduct a comprehensive, California-based, multi-year hydrogen infrastructure demonstration project to develop and demonstrate strategically located fuelling stations. The infrastructure is expected to include flexible modes of supply to deliver liquid and gaseous hydrogen. A key feature of this project is that

it will demonstrate "real-world" performance and generate data to help assess the feasibility of achieving the DOE's infrastructure goals. Honda, Nissan, and Toyota have agreed to provide a sufficient number of fuel-cell vehicles to the project at no expense, and BMW will also provide vehicles at no expense, operating with hydrogen internal combustion engines (H2-ICE) and onboard liquid-hydrogen storage to allow the project to demonstrate yet another important infrastructure component – liquid hydrogen refuelling. By encompassing a variety of vehicles, customer profiles, and fuelling experiences, this proposed infrastructure project will obtain a picture of real market needs.

The above examples are just a few of the many projects that are being carried out on relatively local scales by a wide range of different groups with the funding coming from a mix of public and private sources, which more or less input from car makers. It is clear that the technology is sufficiently mature, much can be taken from the existing natural-gas pipelines, and improvements like our own high PRF coatings to reduce permeation and embrittlement, means that all that is required to have a fully operating hydrogen infrastructure is the political initiative. It has been suggested that a country like China, which does not as yet have a massive "petrol/diesel" infrastructure is in the best place to leapfrog straight to a hydrogen-based fuelling infrastructure. However, the fact that we still have plenty of oil and that it is still very cheap means that for the moment this does not look economically attractive to the Chinese.

4. Is it possible to make the fuel cells cheaply enough?

The fuel cell is an electrochemical cell that converts chemical energy from a fuel into electricity. This electricity is generated from the reaction between hydrogen and an oxidizing agent, usually the oxygen in the air. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate continuously as long as the necessary reactant and oxidant flows are maintained. This makes fuel cells very different to conventional batteries, because they consume the reactant, in this case hydrogen, from an external point, rather than carrying all the fuel within the device itself. Figure 7 shows a schematic diagram of a fuel cell.
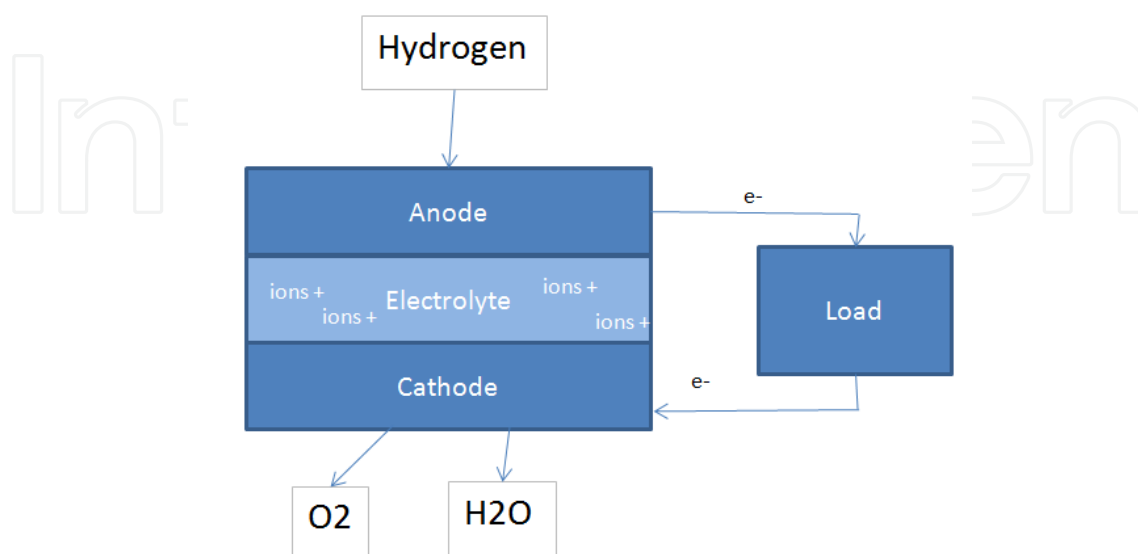

Fig. 7. Schematic diagram of a fuel cell

The first fuel cell was demonstrated by the Welsh scientist Sir William Robert Grove (1811-1896) in 1839. Interestingly, this makes the fuel cell an older technology than either the four-stroke or two-stroke internal combustion engine. Over the past 170 years many different types of fuel cells have been developed, with each type of fuel cell having a particular electrolyte, efficiency, working temperature and cost. Solid-oxide fuel cells (SOFCs), for example, have an electrolyte of O^{2-} - conducting ceramic oxide, and an efficiency of approximately 65%, a working temperature of up to 1100°C and are relatively cheap compared to other types of fuel cells. They also have the advantage that they can tolerate a lot of impurities in the hydrogen fuel, but the very high operating temperature makes them completely unsuitable for automotive applications. Molten carbonate fuel cells (MCFCs) operate in a similar manner, except that the electrolyte consists of molten carbonate, which is a negative ion and an oxidizing agent. Of the existing 10+ types of fuel cell, only the proton-exchange-membrane fuel cell has a realistic possibility of being used as the source of electricity to drive a car.

Proton-exchange-membrane fuel cells, sometimes referred to as polymer-electrolyte membrane fuel cells (PEMFCs) were developed in the 1960s for the NASA Gemini space missions, although were not – as is often said – used on the first flights to the moon on the Apollo missions. The key features of PEMFCs are their low weight, the low gas pressures required, and their relatively low operating temperatures. However, the critical material with respect to this type of technology is the special polymer electrolyte membrane (PEM). A PEM is a semipermeable ionomer membrance which is impermeable to gases, but is able to conduct protons – the basic function in a fuel cell. The most common PEM goes by the trade name Nafion and is made by the company DuPont. These membranes are not cheap, but the real cost problem associated with PEMFCs is the catalyst material – platinum. The positions of the various elements in the fuel cell are shown in the schematic diagram below (Figure 8).
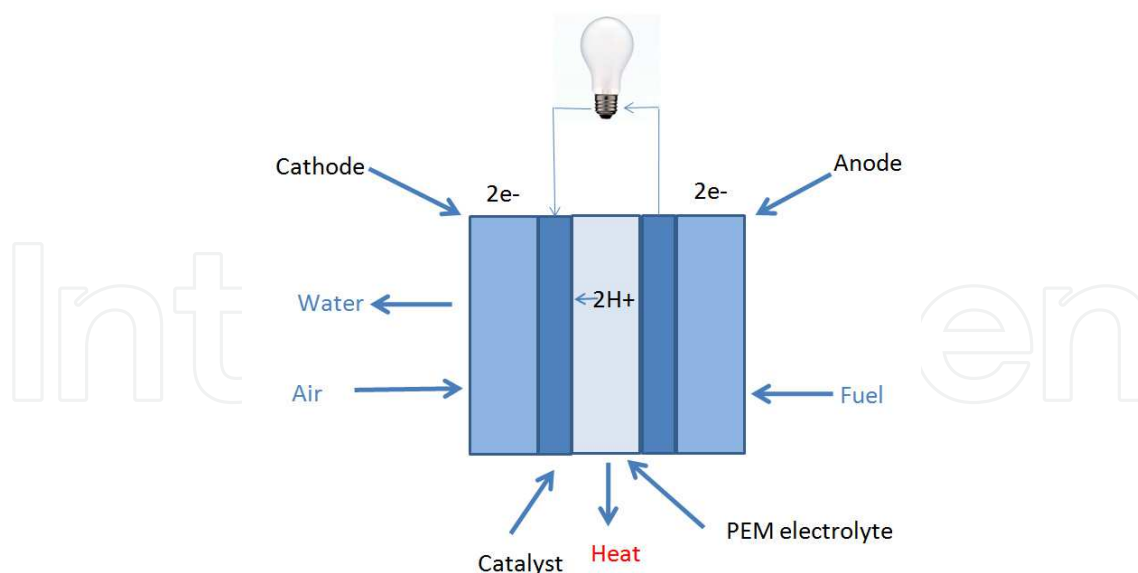

Fig. 8. Schematic diagram of a polymer-electrolyte membrane fuel cell

Platinum is prohibitively expensive, the current price is over $1,800 per ounce (about €50/gram). Even being able to reduce the amount of platinum in an automotive fuel cell to 10 grams will make it very hard to compete with the battery-based systems. However, recently, researchers at Alamos National Laboratory have developed a platinum-free fuel

cell that employs carbon, iron and cobalt on the cathode of the PEM cell. During tests these fuel cells yielded high power, good efficiency and promising longevity. However, this is just one in a line of many such announcements that have been made over the years, there have been reports of replacing platinum with nickel and cobalt, titatnium dioxide nanocrystals and even carbon nanotubes, but all of these failed to live up to a lot of the early promise. Nevertheless, it is clear that progress is being made, and if scientists can also overcome the problems associated with robustness, then fuel cells could fulfil the promise that they have been showing for more than 100 years.

5. How can we produce the hydrogen easily and cleanly?

Currently, energy is cheap, but it is also environmentally polluting, and even if global warming remains a matter of debate, it is surely an illusion that the emission of carbon dioxide, which exceeded 30 billion metric tonnes in 2010, will have no effect on the planet. So the issue of solving humanity's number one problem during the next 50 years, the energy needed for an increasing population, is no longer just the depletion of fossil fuels but also the steam age alert. (Grimes et al. 2008) In addition to the fact that hydrocarbons have extraordinary value as the source of chemicals used to produce goods and other essentials for living, depletion is occurring rapidly. In a collective effort we succeeded in depositing vast amounts of CO_2 in the atmosphere, today reaching the highest concentrations in at least 500 000 years. If we keep burning fossil fuels to provide more than 40 Terawatts of energy we use every year the earth's atmospheric CO_2 can reach levels so that we end up cooking ourselves alive. Therefore, most of the energy scenarios predict, as the only solution, the use of renewable sources. The most fundamental of the sustainable energy sources is incident solar radiation and actually all others are simply a consequence of the sun's power: wave, wind, biomass and even fossil fuels, which is, by photosynthesis, solar energy stored over a geological time scale. At a power of 1000 W/m^2, the solar incident energy on the earth's surface by far exceeds all human energy needs. If 0.16% of the earth's surface would be covered with photovoltaic (PV) panels of 10% efficiency, this would meet the world's total energy demand. While 0.16 % appears to be a small number, it still corresponds to a huge surface area. (Gratzel 2005) It is a matter of scale and economics. And where would hydrogen be important in this scenario? Hydrogen already plays a vital role in our life, e.g., in fertilizer, chemicals and the petrol industry, but the real scenario is that today, 96% of production is based on the steam reforming of natural gas, and therefore it is dirty.

However, solar cells only generate electricity during daytime, so even mesoscopic solar cells require a practical way to store such large amounts of energy. Also, in the case of electricity from wind turbines, it is a fact that wind is inherently unreliable and so faces similar similar problems to PV electricity, i.e., that the grid cannot handle it if the wind blows at too many places at once. Therefore, in Hamburg they will install facilities with electrolysis to produce hydrogen and so keep the grid stable. Costs are still an issue for such solutions, but actually it is question of whether we can afford not to have hydrogen infrastructure if we want to be renewable.

Fuel from sunlight can be achieved by the reaction of splitting water $2H_2O \rightarrow H_2 + O_2$, which is a 4-electron reaction and therefore not so complicated and efficient as a 6- or 8-electron evolved reaction for producing methanol or methane. The route to solar hydrogen can therefore be coupled to PV and an electrolyser. Actually, if we connect an efficient solar cell with an efficient electrolyzser, the total efficiency for standard

technology is estimated to be between 8 to 10 % and the estimated hydrogen cost would be €8 per kg. The main issue is again cost!

The Hydrogen Economy, which is a short name for obtaining fuel from sunlight and water, is actually here, we can do it using electrolysers powered by renewable energy. But the direct splitting of water/artificial photosynthesis is a much better way. So, here is the idea, which was neglected for far too long, the so-called Holy Grail of material science, a Direct Photoelectrochemical Water Spliting by sunlight with PEC cells. The photoelectrolsis of water is the direct splitting of water into hydrogen and oxygen using only sunlight as the input. The semiconductor material is placed into water and illuminated with sunlight, driving water splitting directly, and this configuration combines the solar cell and the electrolyzer into a single device. Although this approach is certainly a step into the right direction, there is still plenty of development research needed. We know it will work because nature has been doing it for billions of years, but we have different obstacles than nature, we do not have time, which means we must be concerned by efficiency and cost and that we need better light-harvesting semiconductors. (Turner 2008)

The splitting of water into hydrogen and oxygen, the sustainable and removable fuels of H_2-based economy, involves the following reactions:

$$\text{Reduction}: 2H_2O + 2e^- \rightarrow H_2 + 2OH^-, E°(H_2/H_2O) = -0.41/0.0 \text{ V at pH} = 7/0 \text{ (vs NHE)}$$

$$\text{Oxidation}: 2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E°(H_2O/O_2) = -0.82/+1.23 \text{ V at pH} = 7/0 \text{ (vs NHE)}$$

$$E°_{overall} = E°(H_2O/O_2) - E°(H_2/H_2O) = 1.23 \text{ V}$$

Thus, the overall reaction $H_2O \rightarrow H_2 + \frac{1}{2} O_2$ is endothermic with an increase in Gibbs free energy ($\Delta G° = 237$ kJ mol). Water absorbs solar light in the IR region ($\lambda = 1008$nm) with a photon energy too low to drive the splitting. An advanced possibility to overcome thermodynamic potential is the use of a photo-electrochemical cell (PEC) with a photo-active catalyst (inorganic semiconductor), which is immersed in water. The basic principle of PEC is that when the semiconductor is illuminated with photons with an energy that is equal to or larger than the band gap, electrons are excited from the valance band (VB) into the conduction band (CB). These photo-generated electrons are directly or even better, through a cocatalyst, used to reduce water to hydrogen at the catalyst/water interface. The electron hole that remains in the valance band migrates to the surface, where it oxidizes water to form oxygen gas. The designed targets of water-splitting researchers in that field is rather ambitious. An estimated price of 3 \$/kg H_2 would be possible to achieve with photoelectrode materials that would cost round for 160 \$/m^2 if the solar-to-hydrogen efficiency would be 10 % and the life time would exceed 15 years.

This simple principle operates only if many material requirements are completely fulfilled simultaneously. Firstly, suitable band-edge positions of the photocatalyst are required to enable the reduction/oxidation of water. The photochemical water reduction occurs if the flat band potential (for doped semiconductors, this equals the bottom of the CB) exceeds the water reduction potential, $E°(H_2/H_2O)$. For water oxidation the VB edge should exceed the potential of water oxidation $E°(H_2O/O_2)$. The high chemical stability of the photocatalyst in different corrosive media and under illumination as well as long life-time is of crucial importance. Hence, chemical reactivity/stability depends on of the type of molecular orbitals that the CB and VB are composed of and is the definite characteristics of oxide semiconductors. These requirements limit the use of most of non-oxide semiconductors with a small band gap since they either dissolve or passivate in water. Furthermore, strong visible light absorption is required.
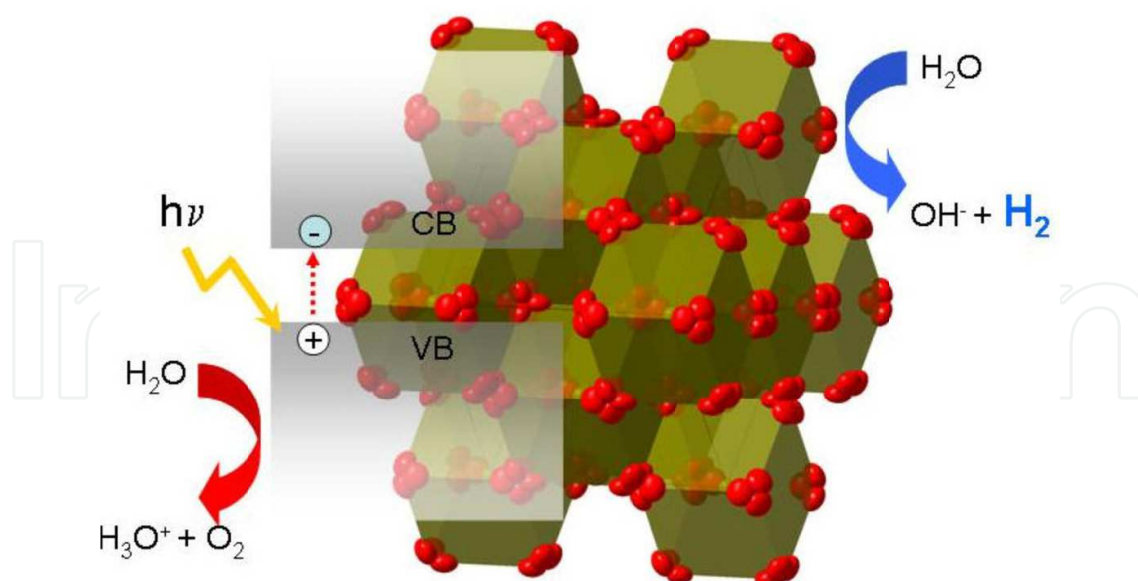
Fig. 9. Schematic presentation of water splitting by semiconductor photocatalysis

The first step in the photochemical solar-to-hydrogen conversion is the light absorption process and it has a definite energy limit, the value of which is the band gap. Also, the spectral region, in which the semiconductor absorbs light, is determined by the band gap. For this reason large band-gap materials only absorb at short wave lengths (UV region) and will not absorb as many photons from the solar spectrum as small-band-gap semiconductors. The optimum value of the band gap considering the energy required for splitting and the absorption within the visible range of solar light, should be somewhere around 1.9 and 3.1 eV. In addition, an efficient charge transport in the bulk is important to avoid any trapping of the photogenetared holes and the recombination of the exitons.

The problem is that as a consequence of the co-dependence of all the limiting material requirements, the energy efficiency of the solar-to-hydrogen conversion using suspended photocatalysts is low. Exclusive principles for the absorption of visible light versus the chemical stability of photocatalysts are the basic problem for low photoactivity. The fact is that stable materials that can split water with strong photoactivity have band gaps too large (> 3eV) and do not respond to visible light. In contrast, efficient light absorbers with small bad gaps are more chemically and photo reactive. Additional problems related to electronic band structure are unfavourable band-edge positions.

Photocatalytic splitting also requires an efficient charge separation and charge transport to the semiconductor surface, where at the semiconductor/water interface the reduction/ oxidation takes place. Therefore, another problem that appears as a consequence of low conductivity is the slow kinetics of charge transfer. This can cause the electrons or electron holes not to reach the surface or the oxidation of the semiconductor itself. Finally, the performance of such a system could also be hindered due to either electrochemical resistance at the interface or/and backward reaction.

Most of the photocatalysts have so far been prepared by solid-state synthesis and the effects of variable material preparation conditions have not been fully investigated. From the chemical viewpoint there is a number of phase systems, which have never been subject of photocatalytic studies. A significant opportunity for improving water splitting is also within an investigation of the cocatalyst effect.

The pioneers of solar-hydrogen are Fujisima and Honda, who first reported photo-assisted water electrolysis using rutile (TiO_{2-x}) as photocatalyst of a Photo-Electrical Cell (PEC) (Fujisima 1972) An important additional characteristics of rutile is that unlike other photo-sensitive semiconductor materials such as non-oxide valance semiconductors (Si, GaAs, etc.) it is resistant to both corrosion and photo-corrosion in an aqueous environment. Consequently, extensive investigations of TiO_2 as a photo-electocatalyst for water-splitting have followed.

In the late 1970s after the general photocatalysis concepts were reported the titania catalysts were improved significantly. The enhanced evolution of H_2/O_2 took place on a TiO_2 catalyst to which a Pt cocatalyst had been added via photodeposition. Importantly it was shown that the spectral response of a TiO_2 single crystal can be extended into the visible range by doping. The presence of Cr^{3+} in the rutile lattice has been found to shift the optical absorption from 415 to 550 nm and a 10 % increase in sunlight conversion was measured. Although doping with Al^{3+} did not have a significant response in the visible range, it enhances the absorption in the UV region.

The Gratzel group published studies in the 1980s on the development of a multicomponent catalysts composed of colloidal TiO_2 particles doped with Nb_2O_5 and joined with Pt or RhO_2 particles as a cocatalyst. The next important improvement was achieved with the addition of $[Ru(bpy)3]^{2+}$ as a visible-light sensitizer – dye – and the system was able to split water under visible-light irradiation. The overall result of the Gratzel group showed that catalytic activity is strongly dependent on doping levels of the catalyst, the pH, temperature, etc.

Parallel to investigations of TiO_2 the same kinds of investigations were performed on other potential photocatalysts such as Fe_2O_3, WO_3, $SrTiO_3$. Also semiconductors based on tantalates, niobates, other mixed-oxide semiconductors and non-oxide semiconductors such us CsS, GaAs, etc, were the subject of the same interest, i.e., the direct splitting of water under visible-light irradiation. (Lewis)

The new millennium has brought progress in nanoscience with new, advanced techniques that can be applied to the fabrication of semiconductors (van de Krol et al. 2008). At the same time environmental concerns and awareness have continued to grow together with increasing energy demands. For that reason the interest in the solar generation of hydrogen and oxygen, the renewable and sustainable future energy carriers, has dramatically increased.

The new results in visible-light photocatalytic activity were published by a few of the world's top scientific groups. Even though the primary work of Gratzel is focused on photovoltaic cells, the principles that govern the visible-light photoactivity as well as the processing of semiconductor catalysts are the same as for solar hydrogen production. An important contribution from scientific and technological point of view is the tandem cell for water splitting by visible light. The low-cost tandem device is composed of a WO_3 or Fe_2O_3 nanocrystalline thin film on top (absorbs the blue part of vis-spectra and creates exciton and oxidize water) of the dye-sensitized TiO_2 cell above (absorbs the green and red parts of the visible spectra and generates hydrogen).

According to some recent studies the visible-light activity can be significantly increased using $BiVO_4$, $AgNbO_3$, $PbBi_2Nb_2O_9$ and $InMO_4$, M = Nb, Ta, due to a more appropriate band gap (Kudo et al. 1999). The narrower band gap of these compounds occurs due to the formation of a valance band consisting of the O_{2p} orbital hybridized with either Pb_{6s}, Bi_{6s} or

Ag_{4d}. The electronic excitation from this valence band to the Nb_{4d} conduction band is reported to facilitate the direct water splitting. $InTaO_4$ and $InNbO_4$ with band gaps in the range 2.8-2.4 eV were found to split water, too. (Osterloh 2008) The difference in unit-cell volumes for both TaO_6 and NbO_6 octahedral leads to a change in the lattice parameters, slightly affecting their photocatalytic activity, mainly due to a variation in the conductance-band levels formed by Ta_{5d} and Nb_{4d} orbitals.

Direct splitting under visible-light irradiation with $In_{(1-x)}Ni_xTaO_4(x = 0-0.2)$ was reported. The solid solution, prepared with a solid-state reaction, was impregnated with a Ni cocatalyst. The authors stressed that the Ni doping reduced the band gap from 2.6 eV (undoped) to 2.3 eV (doped) and that this is attributed to internal d-d transitions in partly filled d shells. A significant achievement was reported by Kato et al. for 0.2 wt % of co-catalyst NiO and 2 wt % of doped with La, the $NaTaO_3$ in comparison to undoped $NaTaO_3$ a nine times increase in H_2 and O_2 was found under the UV light illumination. The quantum yield was reported to be 56% at 270 nm - the best ever reported. The authors obtained 100-700-nm sized nanoparticles, which is smaller in contrast to undoped $NiO/NaTaO3$ (2-µm). They showed that with a controlled particle size, crystallization and surface topology an important improvement can be achieved. They created a nano-step morphology, which helped to reduce the unwanted electon-hole recombination. In addition, by loading the cocatalyst in the form of "ultra-fine" particles they created the separate active sites for H_2 and O_2 evolution, avoiding any back-reaction during water splitting.[18]

Recently, Osterloh published an overview on his research on inorganic materials as catalysts for photochemical water splitting. He stressed that many photocatalysts that work under UV light irradiation have been discovered, but only recently, in the past ten years or so, the investigation focused on enhancing photocatalytic performance in the visible range and photocatalytic materials interesting for solar hydrogen production. He pointed out that the effects of material preparation conditions, catalysts (nano)structures, nano-scale morphology, cocatalyts loading and similar are insufficiently investigated and, actually, that this topic is in its early stages of research and development. A new challenge is also in the application of quantum-size effects to tailor the electronic structure and photoactivity, since all these system were not so much fabricated using nanotechnology techniques.

The current record holder for the splitting of pure water in terms of quantum efficiency is NiO-modified $La/KTaO_3$. Unfortunately, this excellent 56 % efficiency is achieved under UV illumination.[18] For water splitting under visible light, to date the best solar-to-hydrogen efficiency of 2.5 % has been obtained with Cr/Rh-modified GaN/ZnO (Maeda 2006)

6. Conclusions

The situation is still far from certain; however, hydrogen vehicles still have a very strong chance, even though the competition, especially from pure electric vehicles, will be tough. Some of the difficulties have almost been overcome. The situation with storage suggests that the use of modern materials will provide the answer to high-pressure gaseous storage, as a better alternative to the liquid or solid-state options. In terms of infrastructure and distribution, this is largely a question of making the appropriate investments. Many well-funded projects around the world, which are at the regional rather than national level, show

that this can be done. And although transporting hydrogen through steel pipes is not completely without problems, our own work has shown that we can reduce the problem of hydrogen permeation into steel to the point where it can be described as negligible. Fuel cells are an old technology, and one that works well, but the fragility of the device and the expense of some of the components are dampening interest, but once these problems are overcome with better materials and processes there is no reason to believe that fuel cells will always be too expensive. The big one is making the hydrogen cheaply and in a renewable form. The science is well understood, but so far we do not have the materials. Nevertheless, we believe that what it comes down to in the final analysis is whether direct photo-electrochemical water splitting can be sufficiently well developed over the next 5-10 years to produce cheap, plentiful and environmentally acceptable hydrogen that can be made readily available where it is required. If it can, then it will be hydrogen that fuels the car of the future.

7. References

G.A. Esteban, A. Pen~a, I. Urra, F. Legarda, B. Riccardi, J. Nuc. Mater. 367–370 (2007) 473–477

Fujisima, Honda, Electrochemical Photolysis of Water at Semiconductor Electrode, Nature, 238, (1972) 37-38

Gratzel, Mesoscopic Solar Cell for Electricty and Hydrogen Production from Sunlight, Chemistry Letters, 34, 1, (2005) 8-13

Grimes, Varghese, Ranjan, Light, Water, Hydrogen. The solar Generation of Hydrogen by Water Photoelectrolysis, Springer (2008)

L. Hultman, Vacuum 57 (2000) 1–30

S. Inoue, H. Uchida, Y. Yoshinaga, K. Koterazawa, Thin Solid Films 300 (1997) 171–176

Kudo, K. Omri, H. Kato, A novel aqueous process for preparation of crystal form-controlled and highly crystalline BiVO4 powder from layered vanadates and its photocatlytic properties. J. Am. Chem. Soc. 121, (1999) 11459-11467

M.Y. Kwak, D.H. Shin, T.W. Kang, K.N. Kim, Thin Solid Films 339 (1999) 290–293

D. Levchuk, F.Koch, H.Maier, H.Bolt, J. Nuc. Mater. 328 (2-3) (2004) 103-106

D. Levchuk, F. Koch, H. Maier, H. Bolt, J. Nuc. Mater. 328 (2004b) 103–106

D. Levchuk, S. Levchuk, H. Maier, H. Bolt, A. Suzuki, J. Nuc. Mater. 367–370 B (2007) 1033-1037

D. Levchuk, H. Bolt, M. Doebli, S. Eggenberger, B. Widrig, J. Ramm, Surf. Coat. Technol. 202 (2008) 5043-5047

Lewis, Light work with water, Nature, 414,(2001) 589-590

Maeda, K. Teramura, D. Lu, T. Tanaka, N. Saito, Y, Inoue, K. Domen, Photocatalyst releasing hydrogen from water splitting in sunlight. Nature, 440, (2006) 295

P. J. McGuiness., M Čekada, V Nemanič, B Zajec, A Rečnik. Surf. coat. technol., 205 (2011) 2709-2713, doi: 10.1016/j.surfcoat.2010.08.133.

B.Y. Man. L Guzman, A Miotello, M Adami, Surf. Coat. Technol. 180-181 (9) (2004) 9-14

Osterloh, Inorganic Materials as Catalyst for Photochemical Splitting of Water, Chem. Mater., 20, (2008) 35-54

S. PalDey, S.C. Deevi, Mat. Sci. Eng. A 342 (2003) 58–79

M. Panjan, M. Čekada, P. Panjan, A. Zalar, T. Peterman, Vacuum 82 (2008) 158–161
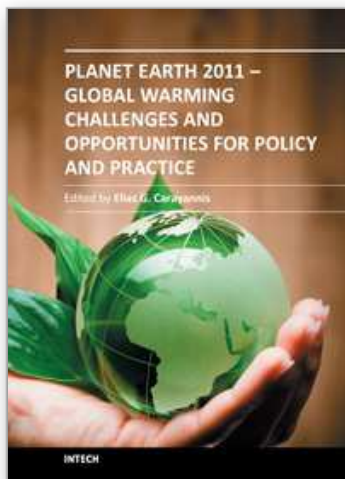
A. Perujo, K.S. Forcey, Fus. Eng. Des. 218 (1995) 224-230

Turner, The other half of the equation, Nature materials,7, (2008) 770-771

R. van de Krol, Y. Liang, J. Schoonman, Solar hydrogen production with nanostructural metal oxides, J. Mater. Chem., 18, (2008) 2311-2320

Planet Earth 2011 - Global Warming Challenges and Opportunities for Policy and Practice

Edited by Prof. Elias Carayannis

The failure of the UN climate change summit in Copenhagen in December 2009 to effectively reach a global agreement on emission reduction targets, led many within the developing world to view this as a reversal of the Kyoto Protocol and an attempt by the developed nations to shirk out of their responsibility for climate change. The issue of global warming has been at the top of the political agenda for a number of years and has become even more pressing with the rapid industrialization taking place in China and India. This book looks at the effects of climate change throughout different regions of the world and discusses to what extent cleantech and environmental initiatives such as the destruction of fluorinated greenhouse gases, biofuels, and the role of plant breeding and biotechnology. The book concludes with an insight into the socio-religious impact that global warming has, citing Christianity and Islam.

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