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Solar-hydrogen: Unresolved problems in solid-state science

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Abstract

The present work considers unresolved problems that need to be addressed for the development of photo-electrodes for photo-electrochemical generation of hydrogen from water using solar energy. The present work is focused on photo-electrodes based on oxide semiconductors, including TiO_2 and TiO_2-based materials, which are the most promising candidates for photo-electrodes. The properties of photo-sensitive oxide semiconductors are considered in terms of the concepts of photo-electrochemistry and the concepts of defect chemistry. The role of defect chemistry as a framework for the development of photo-electrode is considered. The effect of defect disorder on the performance-related properties of TiO_2-based photo-electrodes are discussed. The major challenges in the development of materials with optimized performance are considered in terms of both collective and local properties that must be assessed and modified simultaneously.

Keywords: Solar-hydrogen; Water photolysis; Titanium dioxide; Photo-electrode; Charge transfer; Defect chemistry; Photo-electrochemistry; Solar energy conversion

1. Introduction

There is a growing consensus that hydrogen has the potential to supplement and possibly replace fossil fuels for the production of energy by 2010–2020 (Thomas et al., 1998). It is estimated that the potential market for hydrogen as a fuel is comparable to the present markets for coal and gasoline combined. Therefore, the availability of hydrogen will have a major impact on the global energy scenario and the environment.

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The major driving forces for the replacement of gasoline by hydrogen include:

- *Price*: The price of hydrogen is expected to decrease while that of oil is expected to increase.
- *Energy capacity*: Hydrogen is the fuel with the highest energy capacity per unit mass.
- *Amount of pollution*: The absence of pollution (during combustion) will make hydrogen-powered vehicles pollution-free.
- *Location of pollution*: Even hydrogen produced from methane has an advantage in that urban pollution will be reduced by facilitating removal of power generation plants to less populated areas.

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- *Security of resources*: Fossil fuel reserves are limited in quantity and they are concentrated in politically uncertain regions.

Hydrogen generated from water using renewable sources of energy can resolve the issue of the availability of a fuel that is 100% environmentally safe (Fujishima and Honda, 1972; Maruska and Gosh, 1978; Bak et al., 2002; Nowotny et al., 2005). Consequently, the development of hydrogen technologies using renewable sources of energy will reduce the dominance of resource-rich nations in international energy markets. Such technologies also will provide these nations with increased energy security.

The most critical issue in the development of hydrogen energy, and specifically the technologies for the conversion of renewable energy into other forms of energy, such as chemical energy (hydrogen), is the development of a special class of materials required for efficient and clean conversion of energy. Development of these materials, which will need to exhibit sophisticated functional properties, will require application of the most recent progress in the science of materials interfaces and solid-state science. The purpose of the present paper is to consider the main challenges in these areas.

2. Solar-hydrogen

One of the most promising renewable energy technologies is the production of hydrogen by water photolysis (Veziroglu, 1998, 2000; Bockris et al., 1991; Bockris, 1999; Bak et al., 2002). Current predictions indicate that the production of hydrogen will skyrocket by 2010 (Thomas et al., 1998). According to a recent comprehensive review, the method of photo-electrochemical water decomposition using solar energy is the most promising method for the generation of hydrogen (Bak et al., 2002). The key functional element in photo-electrochemical devices that will allow the exploitation of this technology is the photo-electrode (PE). However, there is a need to enhance the performance of this element in order to achieve the level required for commercialization of the device technology. Therefore, the primary goal of the R&D activities of many research groups is the development of PEs with maximal efficiencies of conversion of solar energy into chemical energy, viz., hydrogen.

3. Concept of solar-hydrogen generation

The pioneers of solar-hydrogen include Fujishima and Honda (1972) and Fujishima et al. (1975), who first reported photo-assisted water electrolysis using rutile (TiO_{2-x}) as the photo-anode of a photo-electrochemical cell (PEC). An important adjunct to this feature of rutile is that, unlike other photo-sensitive materials, such as valence semiconductors (Si, GaAs, etc.), it is resistant to both corrosion and photo-corrosion in aqueous environments.

The scientific foundation for the solar-hydrogen process was established mainly by Bockris and Uosaki (1976a,b), Bockris (1980, 2003), Bockris et al. (1981), Gerischer (1977, 1997), and Chandra (1985). Bockris' activity in this field encompasses a sustained period of work spanning over four decades.

Fujishima and Honda (1972) and Fujishima et al. (1975) reported the concept and performance of a PEC involving a TiO_{2-x} single crystal as photo-anode and Pt as cathode. They showed that solar irradiation of TiO_{2-x} results in the evolution of oxygen at the anode and hydrogen at the cathode. Their reports, which are cited extensively in the authors' recent review (Bak et al., 2002), have resulted in an ongoing search for candidate materials and design models for PEs. However, the lack of success in increasing the energy conversion efficiency (ECE) of TiO_{2-x} above ~1% during the last 30 years has resulted in skepticism concerning the potential to increase the ECE above ~10%, which is the level that the US Department of Energy (USDOE) considers to be the benchmark for commercialization (Service, 2002). However, the recent report of Khan et al. (2002), who reported an increase in the ECE for commercial TiO_{2-x} to 8.5% by exposing it to a natural gas flame, revived expectations of commercialization of this technology. The authors (Khan et al., 2002) considered that carbon incorporated into the TiO_{2-x} lattice is responsible for the reduction in the band gap from ~3 eV to 2.32 eV and the observed increase in the ECE.

The concept of photo-electrochemical hydrogen generation is based on the splitting of the water molecule on the surface of a PE using photo-energy. Fig. 1 shows the basic components of a photo-electrochemical circuit for water photolysis. Fig. 2 shows the charge transfer associated with the electrochemical chain of a photo-electrochemical device based on TiO_{2-x} as the photo-anode. The experimental approaches used to assess the electrochemical properties of the chain include the determination of the effect of light on the open-cell voltage (EMF) and the current-voltage characteristics. The latter can be used to evaluate the ECE.

The ECE depends not only on the properties of the PE but also on the construction of the PEC and its equivalent circuit as well as the source of light. Although many studies provide the data on the ECE, their physical meaning is frequently quite different. This has the effect of precluding direct comparison of ECE data from different experimental systems.

An essential part of the device for hydrogen generation using solar energy is the semiconducting PE. In the case of photo-anode the PE conventionally consists of an n-type semiconductor. Exposure to light results