II.E.3 Discovery of Photocatalysts for Hydrogen Production

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Objectives

- Design and construct tools for high-throughput screening
- Employ modeling to prioritize material candidates for analysis
- Prepare for commercialization of photoelectrochemical (PEC) water splitting through a materials discovery process

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- M. Material Durability
- N. Materials and System Engineering
- O. Photoelectrochemical Efficiency

Approach

- Develop tools for the high-throughput analysis
- Use modeling to identify candidate materials for further study via high-throughput screening

Accomplishments

- Screened over 60 samples under 9 different experimental conditions (>540 samples)
- Evaluated complementary metal oxide semiconductor (CMOS)-based hydrogen sensor for direct hydrogen measurement
- Modeling effort indicates ferroelectric materials of interest

Future Directions

- Complete 25-cell electrochemical analysis module
- Employ modeling to identify material candidates
- Explore core-shell nanoparticulate materials

Introduction

The conversion of the dominant energy source from one that is petroleum-based to one based on hydrogen will have a profound effect on the reduction of greenhouse gasses being emitted by current technologies. Furthermore, if the hydrogen is generated from a non-carbon containing feedstock, such as water, using an energy source that is not carbon-based, such as solar radiation, the reduction in emitted gasses will be enhanced even further. The key hurdle to overcome in the development of such a technology (photolytic generation of hydrogen from water) is a materials-related issue that can be solved by the discovery of materials with the appropriate energetics and stability upon solar irradiation.

The key material requirements for efficient PEC hydrogen production are A) a semiconductor with a band gap relevant to the solar spectrum so as to maximize solar utilization; B) band edge energies relevant to the reduction and oxidation potentials of water to minimize energy mismatch; C) fast interfacial electron transport to minimize recombination; and D) stability in the presence of an aqueous electrolyte. The key technical barriers to the implementation of PEC hydrogen production relate to the fact that materials that satisfy all of these requirements simultaneously, needed to fully enable this technology, have not been found.

Approach

The use of high-throughput techniques to speed the discovery process has been in place for a number of years, the pharmaceutical companies being the first to invest heavily into the combinatorial synthesis and high-throughput analysis concept. The key to the concept is to test as many samples as possible as quickly as possible for a specific property rather than to do a complete characterization on a specific material or class of materials. In this manner, candidates for further study can be culled from very large sample sets. In developing tools for the high-throughput screening of materials for properties relevant to PEC hydrogen production, we have designed and built a 25-cell module to analyze the photolysis products generated upon illumination of samples with a simulated solar spectrum. The basic design incorporates a vacuum-sealed sample module
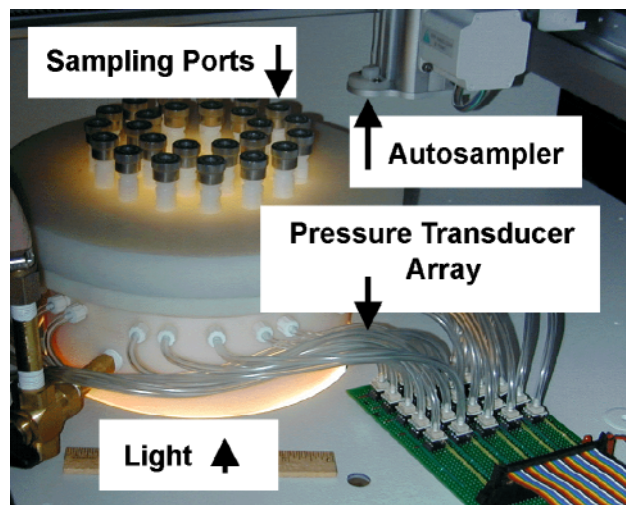

Figure 1. 25-Cell Photolysis Analysis Module In Use
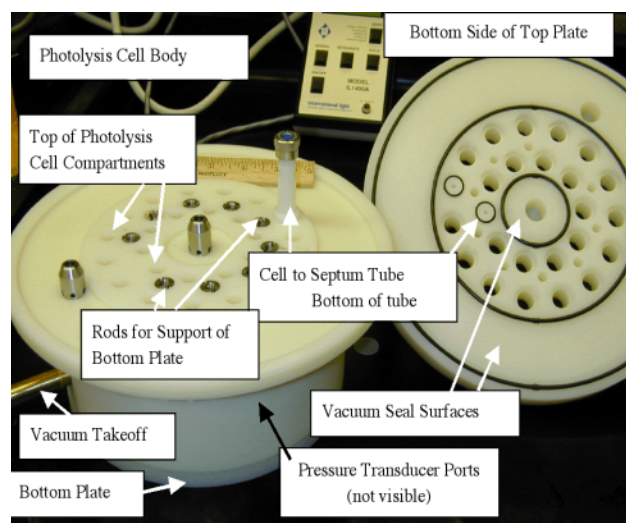

Figure 2. Open Picture of 25-Cell Photolysis Analysis Module Showing Vacuum Plate Seal Design

with a pressure transducer to monitor the pressure as a function of photolysis time (see Figures 1 and 2). The vacuum seal component of this design ensures that each cell is isolated, and the quick release and seal capability make loading quick and easy.

In order to determine which materials to investigate, we have begun a modeling effort to assist in the identification and prioritization of candidate materials.

Results

Photolysis Results

We have investigated a number of systems with respect to photocatalytic water splitting. These systems consisted of a semiconductor nanoparticle with a transition metal—Ni, Ru, and/or Pt— deposited on the surface and immersed in an electrolyte. The particles studied to date include titanium, niobium and tantalum oxides, oxysulfides, carbides and nitrides. In no case have efficiencies greater than 1% (solar photons to hydrogen) been observed. As such, we are shifting our focus to core-shell materials where the core consists of a material that has shown efficient conversion of sunlight to hydrogen but has lacked the stability required for sustained production. The shell will consist of a material that will protect the surface and facilitate charge transfer, such as the ferroelectric materials discussed in our modeling results.

We are currently using pressure transducers to monitor the development of photolysis products in our analysis module. This requires that background subtraction be done, which can introduce error into the data. A more direct means to measure the gas generation would be via a hydrogen sensor. Preliminary evaluation of a CMOS-based hydrogen sensor, PowerKnowz^{TM} (Neodym Technologies, www.neodymsystems.com, Vancouver Canada), was conducted to determine the response curve and reliability of the device in the direct measurement of headspace gas of the 25-cell photolysis unit. The sensor response to a known concentration of hydrogen was analyzed using the maximum sensor signal and, as the signal versus time response is broad, the integrated signal as well. The integrated signal, Figure 3, proved to show a more linear response, R = 0.98, than the data analysis using the signal maximum, R = 0.93. The results of these experiments are encouraging and we will be further evaluating the sensors.

Modeling Results

A modeling effort was initiated to try to identify new candidate materials. Our initial efforts began with an attempt to understand results reported by
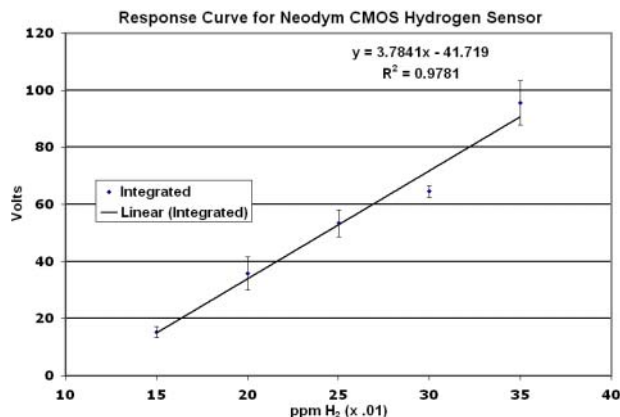

Figure 3. Response Analysis of Neodym Technologies Hydrogen Sensors

Kato et al. [1] in which $NaTaO_3$ is doped by a few percent lanthanum. The material surface has a zigzag nanostructure with step size 10-15 nm, with the peaks having excess positive charges (*p*-regions) and the grooves having excess negative charges (*n*-regions). They attribute increased photoactivity to this structure as it facilitates separation of electrons and holes at the surface, reducing surface charge recombination. A literature search found that $NaTaO_3$ was claimed to be ferroelectric [2], meaning it has a dielectric polarization even in the absence of an electric field. Although this claim was challenged later [3], it is fair to say that $NaTaO_3$ tends to have a strong dielectric polarization under perturbations such as electric fields, strains, and doping, which is supported by that fact that both $KTaO_3$ and $Na_xK_{1-x}TaO_3$ are ferroelectric.

We carried out a first-principles calculation to determine whether La will substitute Na or Ta in La-doped $NaTaO_3$. We considered a supercell with 2x2x2 unit cells (the corresponding doping concentration is 1/8) and compared the energies of configurations with La in different locations (see Figure 4) at fully relaxed geometry. Substitution into the Na over the Ta site was found to be more energetically favorable by 16.5 eV and, due to charge difference, undoubtedly creates a strong electric field on nearby Ta and O ions, producing a further polarization. We also found that La doping induces considerable strain in the $NaTaO_3$ lattice. Thus, these theoretical calculations indicate that a La-doped $NaTaO_3$ likely has a macroscopic dielectric
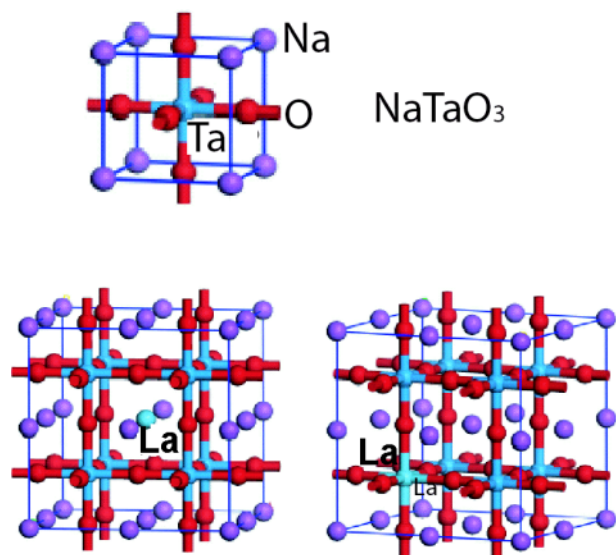
Figure 4. Modeling Results of Unit Cell Distortion of $NaTaO_3$ Alloyed with Lanthanum

polarization. Also, according to a theory by Zhirnov [4], the thickness of the transition region between two 90° domains in $BaTiO_3$ is about 5-10 nm. As $NaTaO_3$ and $BaTiO_3$ have the same crystal symmetry, the observed step size of 10-15 nm in La-doped $NaTaO_3$ reflects the length scale of ferroelectric domain structures in the material.

Conclusions

- Results to date are poor.
- Modeling indicates potential of ferroelectric class of materials.
- A core-shell approach is being used to evaluate known materials with functional shell.

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