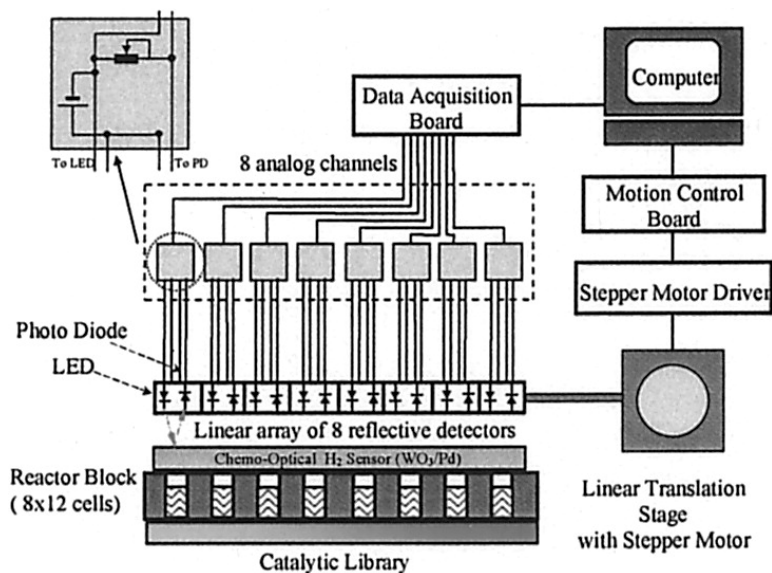


## High-Throughput Screening System for Catalytic Hydrogen-Producing Materials

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# Articles

## High-Throughput Screening System for Catalytic Hydrogen-Producing Materials

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A high-throughput screening system and methodology were developed for libraries of hydrogen ( $H_2$ ) producing catalytic materials. The system is based on the chemo-optical properties of  $WO_3$ , which give rise to reflectance changes in the presence of  $H_2$ . Pd-coated  $WO_3$  sensors were synthesized and examined for their hydrogen sensitivity, wavelength-dependent reflectance, and performance in the presence of water vapor. For high-throughput screening, a polypropylene reactor block was designed and constructed to house  $8 \times 12$  catalyst libraries deposited as thin films. When the library and reactor block are assembled together, 96 independent microreactor units are formed. A large-area Pd/ $WO_3$  sensor film covers and seals all microreactors, forming a 96-element 2-D  $H_2$  sensor array. As  $H_2$  is produced differentially across the library, the reflectance changes of the Pd/ $WO_3$  film are monitored by reflectivity sensors that scan the surface every 30 s. The time-dependent changes in reflectance indicate relative rates of  $H_2$  production. A library of cathode electrocatalysts was synthesized from Ti, Pt, Ni, Au, Pd, Al, Ag, Ge, and mixtures thereof to demonstrate the  $H_2$  high-throughput screening system. The results of the electrolytic screening are in agreement with expected literature trends: mixtures of Ni and samples containing Pt and Pd generated  $H_2$  at the greatest rates, while Ge- and Ti-based materials were the least effective electrocatalysts. A mixture of 80% Al and 20% Pt was found to have the highest rate of  $H_2$  production. This high-throughput screening system is applicable in a variety of catalytic screening applications where hydrogen is the desired product.

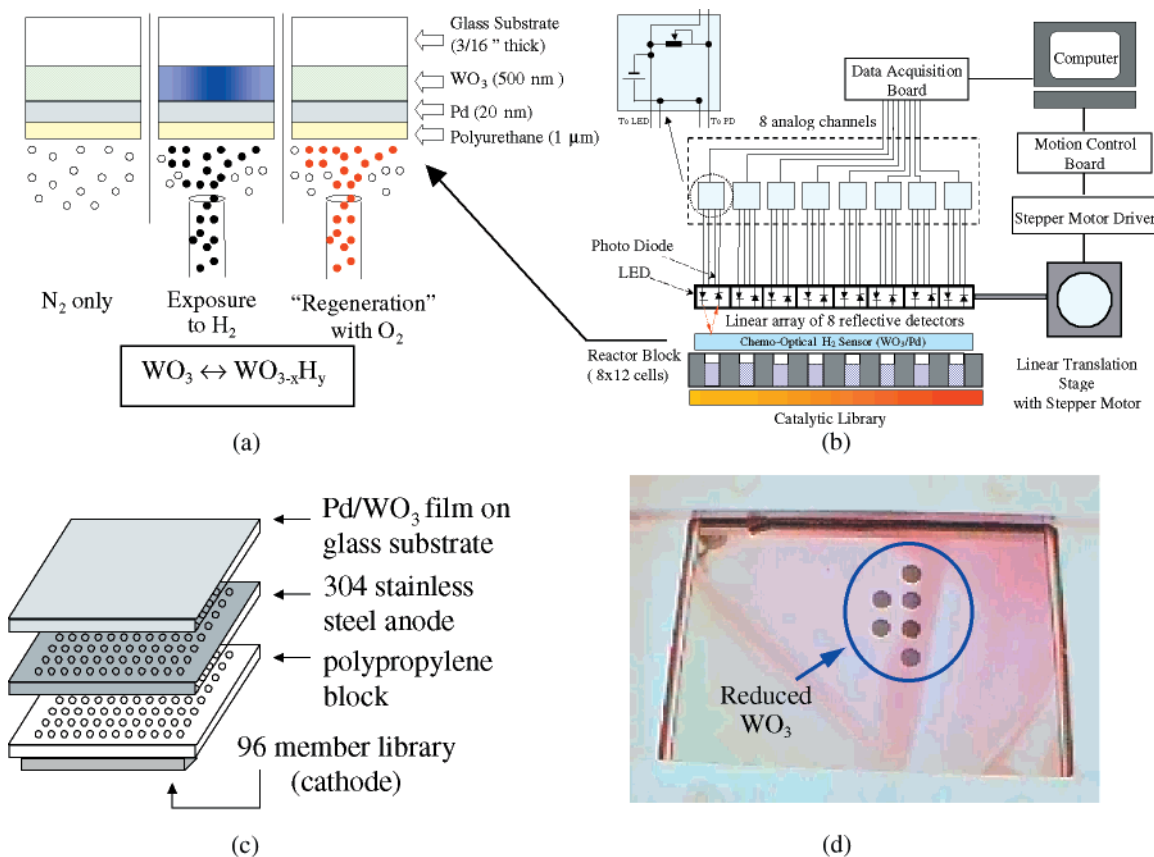
### Introduction

The measurement and detection of molecular hydrogen is of long-standing general interest. Mass spectroscopy and gas chromatography are widely used and accurate; however, they are often relatively expensive and/or impractical for many applications.<sup>1,2</sup> Solid-state hydrogen sensors are viable alternatives in selected applications including process monitoring, safety monitoring, and research. Hydrogen sensors are utilized in the development and use of materials and systems for batteries,  $H_2$  storage, fuel cells, and catalysts. Most solid-state  $H_2$  sensors are based on changes in either electrical or optical properties of transition metals (e.g., Pd) or in metal oxides (e.g.,  $SnO_2$ ).<sup>3,4</sup> Ito and Ohgami developed a colorimetric sensor for room-temperature detection of  $H_2$ , which utilized a Pd/ $WO_3$  bilayer.<sup>5–7</sup> In this design, molecular  $H_2$  dissociates on the Pd surface and diffuses as atomic hydrogen to reduce  $WO_3$  to a tungsten bronze,  $H_yWO_{3-x}$ , Figure 1a.<sup>6</sup> The reduced tungsten oxide is photometrically distinct from  $WO_3$  because of a decreased index of refraction; this effect is readily detected by changes in optical reflectance,

and after significant reduction, the effect is clearly visible to the eye (Figure 1d).<sup>7</sup> In their original work, Ito and colleagues detected optical changes in the sensor by reflecting monochromatic light off the Pd surface at an angle of incidence of  $5^\circ$  and into a spectrophotometer. Reflectance was measured at wavelengths between 300 and 3000 nm as the sensor was exposed to  $H_2$  concentrations between 0.1% and 1.0%. The reduction is reversible, and the sensor can be regenerated in  $O_2$ . We have extended the design of Ito and Ohgami for our large-area multisample array applications in high-throughput screening.

Essential to the success of any application of combinatorial materials science is a high-throughput screening system. Senkan used laser-induced resonance-enhanced multiphoton ionization (REMPI) to screen solid-state catalyst libraries for benzene from the dehydrogenation reaction of cyclohexane.<sup>8</sup> Cong and co-workers at Symyx Technologies developed a scanning mass spectrometer for screening heterogeneous catalysts for the gas-phase products of several oxidation reactions.<sup>9</sup> This instrument operates in a serial manner measuring single samples, relatively slowly albeit thoroughly, for all reaction products. For investigating libraries with very large numbers of samples or products not amenable to mass

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**Figure 1.** Chemo-optical H<sub>2</sub> detection system. (a) Upon exposure to H<sub>2</sub> the reflectance of the Pd/WO<sub>3</sub> film decreases. The film appears blue. The reduced tungsten oxide can be slowly regenerated in O<sub>2</sub>. (b) For high-throughput screening (HTS), the film is sealed above an array of 96 microreactors and the time-dependent changes in reflectance of all 96 locations are monitored by a linear array of eight reflectivity sensors scanned across the film surface every 30 s. (c) HTS assembly for cathodic electrolysis. O-rings are used to seal a perforated block of polypropylene to the 96-member library (cathode); a perforated stainless steel block (anode) is then sealed to the polypropylene block. This yields 96 electrolytic microreactors, and a Pd/WO<sub>3</sub> sensor is sealed above them, forming the 2-D array. (d) Digital image of the sensor after a typical experiment showing visible changes in the sensor surface for a cluster of active materials.

spectroscopy or REMPI, there exists a need for other parallel high-throughput screening systems. For our research in catalytic hydrogen production, we required a large-area hydrogen screening system capable of mapping relative H<sub>2</sub> production rates for libraries of at least 96 samples. In the development and testing of a system for our applications, the following questions were addressed:

(1) Can the reflectance change of the Pd/WO<sub>3</sub> film be utilized in a large-area two-dimensional format for evaluating libraries of catalysts for H<sub>2</sub> production?

(2) What are the H<sub>2</sub> detection limits of such a chemo-optical system?

(3) Can the Pd/WO<sub>3</sub> sensor array be made stable in the environment of an electrochemical reactor, in particular, exposure to water vapor?

(4) Will known trends for electrolytic hydrogen production from metal electrocatalysts be reproduced in the high-throughput system?

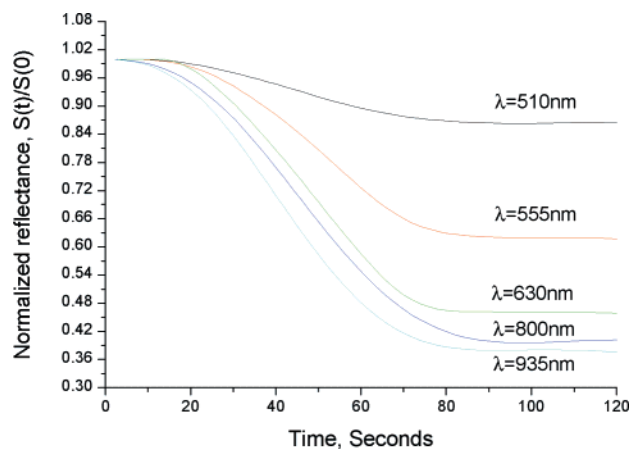
## Experimental Methods

**1. Sensor Fabrication.** Sensors were fabricated in a Class 10 000 cleanroom environment. Glass substrates, typically 110 mm × 80 mm × 4 mm, were meticulously cleaned prior to deposition of WO<sub>3</sub> and Pd. After ultrasonic cleaning in acetone and 2-propanol, the glass substrates were immersed

in a Piranha solution (45% H<sub>2</sub>SO<sub>4</sub>/15% H<sub>2</sub>O<sub>2</sub>/40% H<sub>2</sub>O) at 130 °C to chemically remove organic residues.

The glass substrates were placed under vacuum (approximately 10<sup>-6</sup> Torr) immediately after cleaning, and the active sensor layers were deposited by electron beam evaporation. A total of 500 nm of WO<sub>3</sub> was deposited at a rate of 0.5–1.0 nm/s on the glass substrates. A 20 nm Pd overlayer was then deposited at 0.2 nm/s. The entire metalized surface was covered with a ~1 μm thick commercial polyurethane by spin-coating at 3000 rpm to protect the sensor material from water while still allowing H<sub>2</sub> gas diffusion.<sup>10</sup>

**2. Sensor Characterization.** The sensor's wavelength dependence, H<sub>2</sub> detection limits, and performance in the presence of water vapor were evaluated in a 5 cm<sup>3</sup> flow cell. Wavelength-dependent reflectivity measurements were performed with a 150 W quartz–tungsten halogen lamp coupled through an optical fiber onto the glass surface of the sensor at an incident angle of 15°. The wavelength dependence of the Pd/WO<sub>3</sub> film reflectance was examined between 400 and 1000 nm (in 1 nm increments) during exposure to a mixture of 1.0% H<sub>2</sub> in N<sub>2</sub>.<sup>11</sup> Reflectance was monitored with an optical-fiber-coupled spectrophotometer (Ocean Optics S2000).<sup>12</sup>



**Figure 2.** Reflectance change of Pd/WO<sub>3</sub> films in a flow cell observed for several wavelengths during exposure to 1% H<sub>2</sub> in N<sub>2</sub>.

## Results and Discussion

**1. Chemo-optical Response.** The reflectance during exposure to 1.0% H<sub>2</sub> in N<sub>2</sub> is shown in Figure 2 at five representative wavelengths. The greatest sensitivity was found at wavelengths between 900 and 1000 nm, consistent with the results from prior studies.<sup>7</sup> On the basis of this finding and the commercial availability, the wavelength of the reflectivity sensor diode used in the high-throughput screen was selected to be 935 nm.

The transient reflectance of the Pd/WO<sub>3</sub> film was measured at 1 s intervals during exposure to gas mixtures of 0.1%, 0.2%, and 0.3% H<sub>2</sub> diluted in N<sub>2</sub> and in air (parts a and b of Figure 3). Reflectance changes were observed within 20 s. By measurement of the maximum rate of change in reflectance for each concentration of H<sub>2</sub> and taking into consideration a noise level of  $\pm 0.002 \text{ min}^{-1}$ , the detection limit of the system was determined to be approximately 0.07% H<sub>2</sub>. The observed reflectance changes from H<sub>2</sub>, both in N<sub>2</sub> and in air, were approximately the same; however, since O<sub>2</sub> will reoxidize the film, there is a slightly larger net response in N<sub>2</sub> than in air. Nevertheless, the palladium overlayer greatly limits oxygen diffusion to the WO<sub>3</sub>, and thus, the presence of O<sub>2</sub> in air does not markedly inhibit performance, an important feature because H<sub>2</sub> may be cogenerated with O<sub>2</sub> on other oxidizing agents in several catalytic reactions of interest.

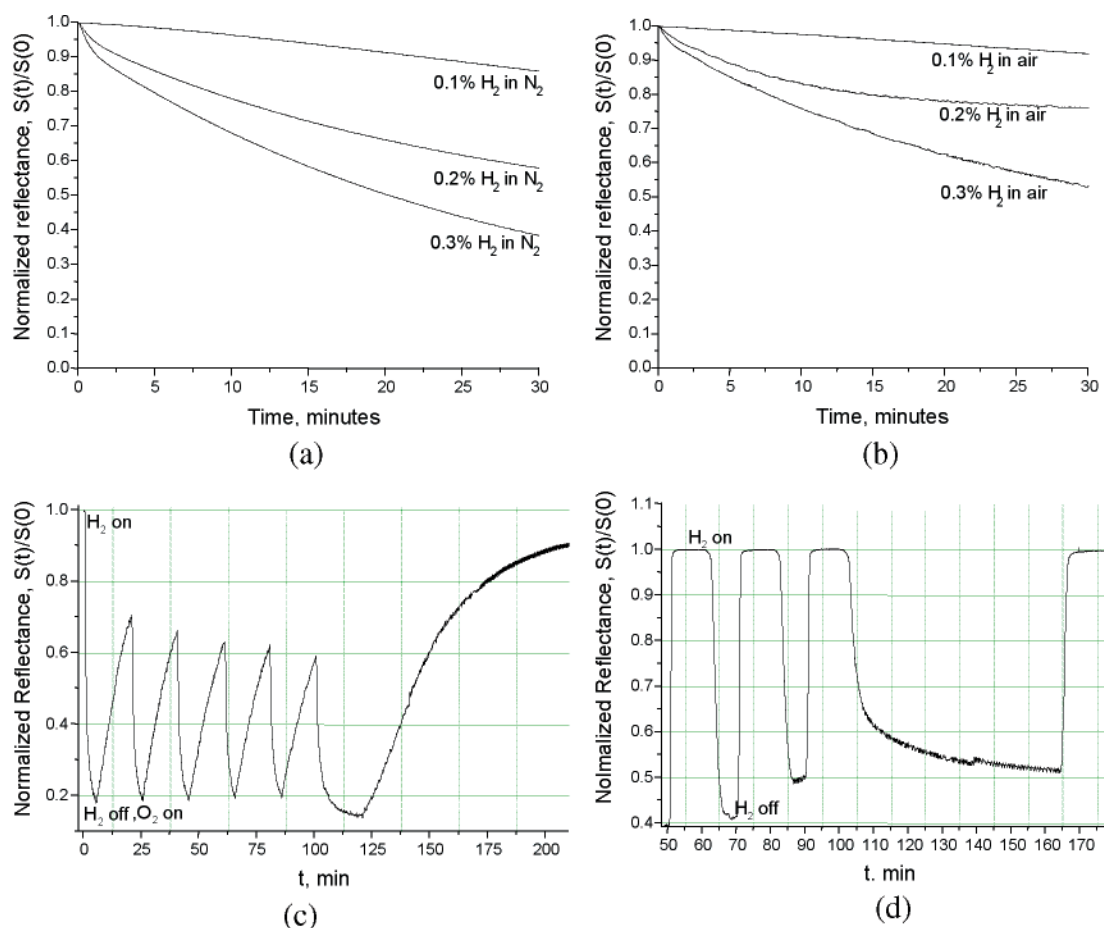
The reflectance change of the film in response to repetitive reduction–oxidation cycles is shown in Figure 3. While sealed in the flow cell, the film was exposed to repeated pulses of 1.0% H<sub>2</sub> in N<sub>2</sub> (5 min) followed by 99.5% O<sub>2</sub> (10 min) (parts c and d of Figure 3). Figure 3c shows the response to dry gas streams. The transient changes in reflectance following gas stream switching indicate that neither the process of WO<sub>3</sub> reduction nor the process of oxidative regeneration had reached steady state before the gases were changed. When the H<sub>2</sub> and O<sub>2</sub> gas streams were saturated with water, the response time of the sensor was considerably faster; steady state was reached well before gas streams were changed (Figure 3d). Unfortunately, after longer exposure times (approximately 30 min), the water-saturated streams caused observable microscopic cracks on the palladium surface presumably because of partial delamination

of the films. These nonuniformities can lead to inaccurate and unreliable reflectivity data, especially across a large surface as utilized in our high-throughput screen. Application of a commercial polyurethane coating protected the sensor in the presence of water vapor without sacrificing its sensitivity to H<sub>2</sub>. Although different coating materials were not exhaustively studied, the polymer selected was easy to apply and gave satisfactory performance.

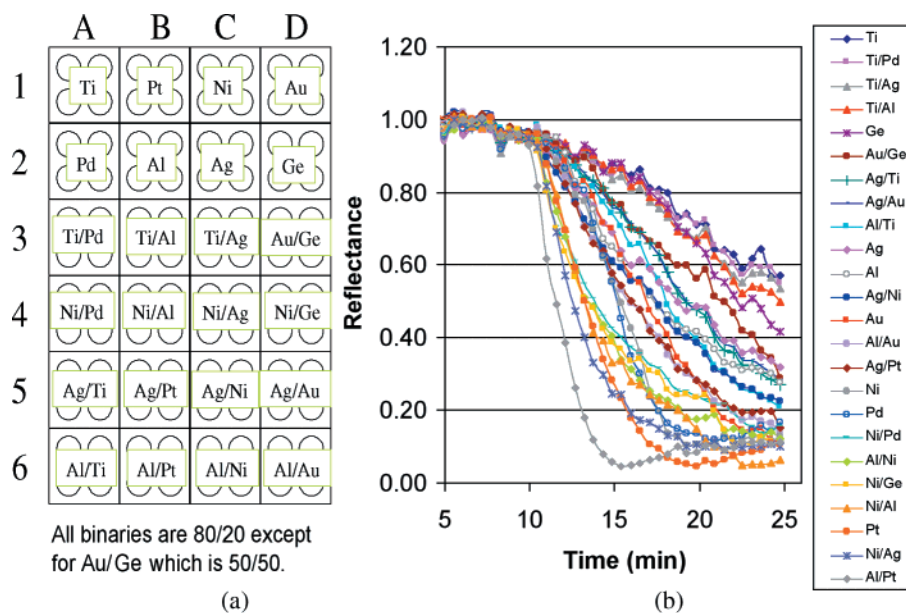
**2. High-Throughput Screening System. 2.1. Two-Dimensional H<sub>2</sub> Mapping with Reflectivity Sensor Array.** In the high-throughput screening system, a linear array of small, commercial IR reflectivity sensors was used to map reflectance changes over the surface of the large-area Pd/WO<sub>3</sub> film covering the library (Figure 1b). Each reflectivity sensor package is about 200 mm<sup>3</sup> in volume and contains both a photodiode and an infrared light-emitting diode (LED) operating at 935 nm.<sup>13</sup> Eight sensor packages were assembled together to simultaneously measure the reflectance of eight distinct, linear points on the Pd/WO<sub>3</sub> film. By use of a linear translation stage driven by a stepper motor, the linear array was scanned repeatedly over the Pd/WO<sub>3</sub> film to achieve semiparallel screening for H<sub>2</sub> production in a 96-well library; the reflectance measurements of all 96 members of the library are recorded every 30 s. The entire process of scanning and data acquisition is under software control (LabView).

**2.2. High-Throughput Screening Assembly.** In one manifestation, libraries of materials to be screened for H<sub>2</sub> production are deposited as thin films on glass or metal substrates in a 12 × 8 array. For high-throughput electrolytic screening, a 1/2 in. thick polypropylene reactor block and a 1/4 in. 304 stainless steel plate (counter electrode) were constructed with 96 holes (7 mm diameter) designed to accept O-rings to form a gas/liquid sealed cell (Figure 1c). One side of the polypropylene reactor block forms a liquid seal with the library substrate, while the other side is liquid-sealed to the stainless steel plate. The uptake of hydrogen into the solid phase of the sensor is expected to be rapid compared to the production rate; thus, no significant pressure increase is expected. The holes align to form 96 wells, each with a volume of approximately 1.0 mL. Each well is then filled with an electrolyte (for electrolysis we used 0.2 M sodium acetate pH = 8.1), which makes contact with both the library member (working electrode) and the stainless steel plate (common counter electrode). The 96 wells cover an area of 100 mm × 70 mm, dimensions that are slightly smaller than the dimensions of our large-area 2-D chemo-optical film. The multilayered structure consisting of the library substrate, the perforated polypropylene block, and the perforated stainless steel counter electrode was then gas-sealed to the polymer-coated Pd/WO<sub>3</sub> sensor plate, forming 96 sealed microreactors.

**2.3. Demonstration Library: Cathode Electrocatalysts.** To demonstrate operation of the sensor, a 96-member library of potential cathode electrocatalysts was studied (Figure 4a). A total of 24 different materials were synthesized (4 samples of each) by electron beam evaporation. Eight distinct elemental sources of 99.99% purity were used to create the library: Ti, Pt, Ni, Au, Pd, Al, Ag, and Ge. Of the 24 different materials spanning the library, 8 were pure elements



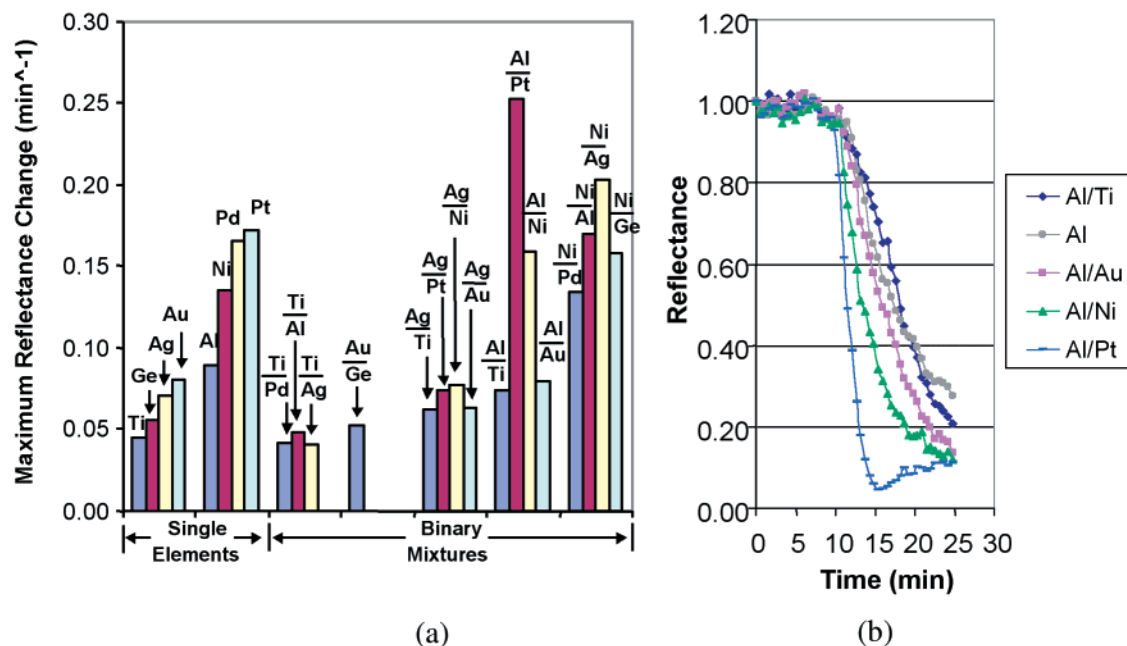
**Figure 3.** Infrared (935 nm) reflectance change of the Pd/WO<sub>3</sub> film following exposure to (a) 0.1%, 0.2%, and 0.3% H<sub>2</sub> in N<sub>2</sub>, (b) 0.1%, 0.2%, and 0.3% H<sub>2</sub> in air, (c) alternating dry 1.0% H<sub>2</sub> and 99.5% O<sub>2</sub>, and (d) H<sub>2</sub> and O<sub>2</sub> streams both saturated with water vapor. Data are obtained at 1 s intervals.



**Figure 4.** (a) Library design for 96 electrocatalysts. A total of 24 different elemental and binary metal cathode materials were deposited as 4 identical library members each for consistency. (b) Raw reflectance data taken at 30 s intervals for the 24 different materials (each curve reflects the mean signal from the four identical library samples of a given material). Relative H<sub>2</sub> production rates are listed in the legend from low to high, as determined by the transient reflectance changes of the Pd/WO<sub>3</sub> film sensor during water electrolysis at  $-2.8$  V potential vs common 304 stainless steel anode.

and the remaining 16 were binary compounds coevaporated in a ratio of approximately 80/20, with the exception of Au/Ge, which was 50/50. Though a native oxide of variable

thickness would be expected to form on many of the materials, any additional overpotential would be expected to be negligible compared to the overpotential drop in the



**Figure 5.** (a) 2-D bar graph representing the maximum change in reflectance for each material. Expected trends are validated because materials containing Ni, Pd, and Pt were the most effective H<sub>2</sub> producers while materials consisting of Ti or Ge performed poorly. The Al/Pt mixture was clearly the best electrocatalyst of those studied. (b) Reflectance data for the subgroup of the aluminum-containing materials.

cathode Helmholtz layers. The surface native oxide represented the surface expected in an actual working electrocatalyst.

Electrolysis in a 0.2 M sodium acetate solution was conducted for 20 min with the library at  $-2.8$  V with respect to a common 304 stainless steel anode located between the library and the Pd/WO<sub>3</sub> film. In this configuration, hydrogen is produced on the library cathode materials in a 2:1 ratio with O<sub>2</sub> produced on the stainless steel anode. Materials delivering the greatest rate of H<sub>2</sub> production were identified by their relatively high rate of reflectance change as measured by the sensor system above that material. The raw reflectance data measured during the experiment can be found in Figure 4b). There are 24 different curves; each represents the mean signal acquired from the four identical samples of a given material. A faster decrease in reflectance indicates a greater H<sub>2</sub> production rate. The legend of Figure 4b lists the 24 materials in order of their relative H<sub>2</sub> production rates, from low to high. Figure 5a is a 2-D bar graph representation of the H<sub>2</sub> production rate within each microreactor, as measured by the slope of the time-varying reflectance of the Pd/WO<sub>3</sub> film. The Al/Pt mixture showed the greatest rate of H<sub>2</sub> production, higher than either Pt or Al alone. Since the surface Al is certainly present as an oxide, the Al/Pt electrode is likely a composite of Pt and alumina, which is known to be a particularly active catalyst.<sup>14</sup> Several known trends in cathodic electrolysis can be verified in Figures 4b and 5a. Of the eight elements used to create this library, Pt, Pd, and Ni are expected to be the most effective for cathodic electrolysis because of their relatively high work functions and ability to bind H and facilitate surface H recombination.<sup>15,16</sup> Ag, Al, and Au would also be expected to perform well, albeit not at the same level as Pt, Pd, or Ni.<sup>15,16</sup> Ti and Ge are known to be poor electrocathode materials.<sup>15</sup> The data from the eight pure elements are in agreement with these

known trends.<sup>17</sup> Indeed, the sensor response to cathodic electrolysis on Pt, Pd, and Ni showed the most rapid changes in reflectance, whereas for Ti and Ge slow changes in reflectance were observed. The rates for Ag, Al, and Au electrolysis were between the two groups.

Binary mixtures also validated expected trends. Since the evaporated films were not annealed and many of the mixtures do not form thermodynamically stable phases, it is expected that the metals were largely amorphous dispersions. Nevertheless, expectations on performance remained the same; mixtures containing Pt, Pd, and Ni were predicted to generate H<sub>2</sub> at a greater rate than those with Ti or Ge. The row of Al mixtures (row 6) shows that electrolysis is improved when Al is mixed with either 20% Pt or Ni. Mixing Al with 20% Au or Ti showed little change. A similar trend is seen for the Ag mixtures (row 5). All Ti-based mixtures performed poorly and with little difference among them; the strong presence of Ti (a poor cathodic material) dominates any effect of mixing with other elements. On the other hand, all Ni-based mixtures demonstrated high relative hydrogen production rates, as in the case of pure Ni. Figure 5b shows reflectance data from the subgroup of Al-based mixtures. The Al/Pt mixture was observed to be the most active material followed by Al/Ni and then Al/Au, both of which behaved similarly to pure Al. In the case of the Al/Ti mixture, the presence of Ti appears to slightly inhibit the electrocatalytic reaction because the Al/Ti mixture exhibited a lower rate of H<sub>2</sub> generation than Al alone. This should be expected because Ti shows poor electrolytic performance in its pure form.

In the electrolysis process both hydrogen and oxygen are produced. For several of the most active materials (Al/Pt, Pt, and Ni/Al) the signal increases once the minimum is reached (Figure 4b). Though not confirmed in detail, we expect that reoxidation of the reduced tungsten oxide by the

kinetically slower process of oxygen diffusion (through the Pd overlayer) and subsequent reaction with the reduced tungsten oxide are responsible for beginning the regeneration process. A verification of the spatial uniformity of the system response was performed by conducting an electrolysis experiment on a library of 96 identical Au electrodes. The responses were found to be equal in all cells to within 5%.

### Conclusion

A system for high-throughput screening of libraries of H<sub>2</sub>-producing catalytic materials has been developed on the basis of a large-area Pd/WO<sub>3</sub> chemo-optical H<sub>2</sub>-sensing film. The wavelength dependence and performance in the presence of water vapor gave rise to a system design consisting of infrared reflectance measurement and a polyurethane-coated Pd/WO<sub>3</sub> film. The system is sensitive to H<sub>2</sub> concentrations as low as 0.07% in either N<sub>2</sub> or air, and in a semiparallel manner it captures 96 data reflectance data points every 30 s across the 2-D array. Demonstration of the system on a 96-member cathode electrocatalyst library confirmed known trends in H<sub>2</sub> electrosynthesis. A mixture of Pt and Al was found to be the most active for H<sub>2</sub> synthesis.

### Library Synthesis

A cathode electrocatalyst library was synthesized using electron beam evaporation onto a titanium (99.5%) foil substrate of dimensions 90 mm × 110 mm × 0.8 mm. A high-vacuum dual gun evaporation system was used with a total of eight sources. Binary mixtures were created by simultaneous codeposition. After ultrasonic cleaning of the substrate with acetone and 2-propanol, 500 nm of titanium (99.99%) was deposited on the entire substrate to ensure a clean uniform surface. Each material on the library was evaporated from elemental targets through a mask that was manually changed to create the 96-member library. Each sample, circular in geometry with a diameter of 8 mm, was evaporated at an overall rate of 0.5 nm/s (0.4 and 0.1 nm/s for 80/20 binary mixtures) for a total thickness of 100 nm. Energy-dispersive X-ray spectroscopy was used to confirm that the binary materials were within ±10% of the desired ratios.

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