

Trace Detection of Dissolved Hydrogen Gas in Oil Using a Palladium Nanowire Array

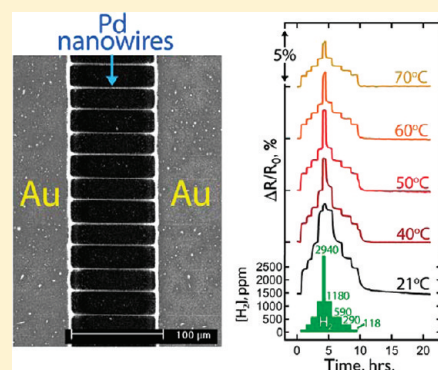
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ABSTRACT: The electrical resistance, R , of an array of 30 palladium nanowires is used to detect the concentration of dissolved hydrogen gas (H_2) in transformer oil over the temperature range from 21 to 70 °C. The palladium nanowire array (PdNWA), consisting of Pd nanowires ~ 100 nm (width), ~ 20 nm (height), and $100\ \mu\text{m}$ (length), was prepared using the lithographically patterned nanowire electrodeposition (LPNE) method. The R of the PdNWA increased by up to 8% upon exposure to dissolved H_2 at concentrations above 1.0 ppm and up to 2940 ppm at 21 °C. The measured limit-of-detection for dissolved H_2 was 1.0 ppm at 21 °C and 1.6 ppm at 70 °C. The increase in resistance induced by exposure to H_2 was linear with $[H_2]_{\text{oil}}^{1/2}$ across this concentration range. A PdNWA sensor operating in flowing transformer oil has functioned continuously for 150 days.



The most important technological application for dissolved gas analysis (DGA) is the detection of incipient faults in utility scale oil-filled power transformers.^{1–8} Failure of a power transformer is known to be preceded by the evolution of hydrogen, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetylene caused by corona discharges, insulation degradation, and the decomposition of oil at “hot spots”.^{1,7–11} The identity and concentrations of these dissolved gases enables the type of fault that will occur to be classified.^{10,12}

Until recently, DGA has involved the off-line measurement of gases in aliquots of oil using gas chromatography.^{1,3,9,13} This process is time-consuming, expensive, and prone to sampling error caused by temporal and spatial fluctuations in dissolved gases within the enormous oil volume of the transformer. These considerations have motivated the development of oil-immersed gas sensors that are capable of the continuous, real-time monitoring of dissolved gases (see Table 1).^{4,5,14–19} A unique set of analytical challenges exists for these sensors. In the case of dissolved H_2 , a limit-of-detection well below 100 ppm is required, the dynamic range of the sensor should extend to at least 1000 ppm, and the sensor should not be damaged by exposure to higher H_2 concentrations.²⁰ The sensor must survive exposure to a wide range of ambient temperatures from -30 to 110 °C while immersed in the oil of an idle transformer. It must detect hydrogen over a temperature range from 50 to 70 °C, the temperature range encountered in an operating transformer.²⁰ Stable calibration of the sensor response to hydrogen on the time scale of a year or more, and across this entire operational temperature range, is critically important. Because oil is typically circulated to the sensor by pumping, the sensor must contend with noise

produced by pressure and flow fluctuations and it must survive the shear forces imparted by the flowing oil to the sensor surfaces.

Resistors based upon single palladium nanowires out-perform palladium film resistors for the detection of hydrogen gas in air and nitrogen.^{21–24} In recent work, we have achieved a limit-of-detection for hydrogen gas, LOD_{H_2} , of 2 ppm in nitrogen and a dynamic range extending to 40 000 ppm. Response and recovery times for these devices, ranging from 3 s ($[H_2] = 4\%$) to 10 s ($[H_2] = 200$ ppm), are the fastest that have been observed for palladium resistor-based devices.²³ These experiments have also revealed that Pd nanowire-based H_2 sensors reliably detect H_2 at elevated temperatures of 80 – 90 °C.²³ These results suggest that palladium nanowires might also be useful for the detection of dissolved H_2 in liquids. As compared with planar films, nanowires have two distinguishing advantages for the detection of molecules in liquids: First, efficient cylindrical diffusion to the nanowire surface provides for rapid equilibration between the nanowire surface and the bulk of the liquid. If we approximate a nanowire supported on a planar surface as a hemicylinder with a radius, r_o , then at long times, the diffusion-limited flux, j , at the surface of the nanowire is inversely proportional to r_o :²⁵

$$j = \frac{2DC^*}{r_o \ln \tau} \quad \text{where} \quad \tau = \frac{4Dt}{r_o^2} \quad (1)$$

In eq 1, D is the diffusion coefficient, C^* is the bulk concentration of H_2 , and t is the time. For example, 100 s after the exposure of a

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Table 1. Palladium-Based Sensors for the Detection of Dissolved H₂ in Transformer Oil

sensor type	mechanism of H ₂ detection	detection range (ppm)	temp. range (°C)	ref.
electrochemical cell	electrochemical oxidation of H ₂	200–15 000	–30–70	3, 5, and 14
Pd/Pt gate MISFET	voltage shift caused by the formation of dipole layer at the metal–semiconductor interface	65–585	50	15
12–15 nm thick Pd film	resistance increase and optical reflectivity change	200–1500	20–120	16
Pt–GaN Schottky diode	voltage shift caused by the formation of dipole layer at the metal–semiconductor interface	0–1000	15–70	18
MIS (Pd/SiO ₂ /n-Si)	Voltage shift caused by the formation of dipole layer at the metal–semiconductor interface	0.5–405	62	19
Pd nanoparticles	resistance decrease	50–4000	80	6
Pd nanowire array	resistance increase	1–4000	20–70	this work

nanowire with $r_0 = 50$ nm to a $C^* = 1.0$ μ M solution of H₂ with $D = 4 \times 10^{-5}$ cm²/s (at 20 °C in transformer oil),²⁶ eq 1 predicts $j \approx 8 \times 10^{-4}$ mol/(cm² s) whereas at a planar palladium film:²⁵

$$j = \frac{D^{1/2} C^*}{\pi^{1/2} t^{1/2}} \quad (2)$$

and under the same conditions, $j = 3.6 \times 10^{-7}$ mol/(cm² s), smaller by a factor of 2200. Second, the diminutive size of the diffusion layer at the nanowire surface (approximately 10 wire radii) reduces or eliminates the influence of convection on the rate of surface limited processes, such as chemisorption and absorption, occurring at the nanowire surface thereby reducing noise.^{27,28} Both of these advantages have the potential to impact the performance of palladium nanowire array (PdNWA) for the detection of H₂ in transformer oil.

Here, we evaluate the performance of arrays of ~30 palladium nanowires for the detection of dissolved hydrogen in transformer oil from 21 to 70 °C. The palladium nanowire array (PdNWA), consisting of nanowires with dimensions of ~100 nm (width), ~20 nm (height), and 100 μ m (length), was prepared using the lithographically patterned nanowire electrodeposition (LPNE) method.^{21,29–31} The unprotected PdNWA with its electrical contacts was exposed directly to flowing transformer oil, and the electrical resistance of this array was monitored as the dissolved hydrogen concentration in a flowing oil stream was varied. We measure a LOD_{H₂} of 0.90 ppm at 21 °C (1.6 ppm at 70 °C) and a dynamic range extending to 2900 ppm at 21 °C (3800 ppm at 70 °C). In principle, the advantage of an array of nanowires as compared with a single nanowire is the durability of the sensor conferred by many redundant nanowire conductors. No advantage relating to sensitivity or sensor performance exists in the absence of failure. However, as our study proceeded, it became apparent that nanowire failure was an extremely rare occurrence. In fact, nanowire fracture, induced by either hydrogen exposure or the forces imparted by flowing oil, was not observed for any of the more than 20 PdNWAs prepared for this study. We further demonstrate the stability of one PdNWA for a period of 150 days in flowing transformer oil.

EXPERIMENTAL SECTION

Materials. Glass slides (2.54 cm \times 2.54 cm) were purchased from Fisher and used as substrates. Nickel wire (Ni, 99.99%) was used as received from Aldrich. A positive photoresist, S1808, and developer, MF319, were both purchased from Microchem. Palladium chloride (PdCl₂, 99.999%, ACS grade), potassium chloride (99.3%, ACS grade), EDTA (disodium ethylenediaminetetraacetate, 99.8%), and acetone (GR, ACS grade) were used as received from Fisher. The transformer oil in the test is a mineral

oil from Hyundai Heavy Industry Co. Ltd. conforming to the ASTM D3487-09 standard³² for electrical apparatus.

Nanowire and Sensor Fabrication. Arrays of linear palladium nanowires were first prepared by LPNE as previously described.^{21,23,24} The electrodeposition of palladium was carried out in a 50 mL, one-compartment, and three-electrode cell. Pd nanowires were obtained from 0.1 M KCl, 0.2 mM PdCl₂, 0.22 mM EDTA (pH 4.9). Plating solutions were prepared using Millipore Milli-Q water ($\rho \geq 18$ M Ω cm). Pd nanowire growth from the EDTA plating solution was carried out at –0.80 V vs SCE using a Gamry Instruments model G300 potentiostat/galvanostat. The resulting nanowires were ~100 nm in width, ~20 nm in height, and many hundreds of micrometers in total length. Four gold electrical contacts were then evaporated (60 nm gold on top of 1 nm of chromium) onto a subset of approximately 30 of these nanowires using a contact mask. These contacts electrically isolated a 100 μ m length of this 30-wire array (PdNWA). The four-contact electrical resistivity of the PdNWA was measured using a source meter (Keithley Instruments, model 2400) in conjunction with a digital multimeter (Keithley Instruments, Model 2000). The thermal annealing of PdNWAs was carried out as the last nanowire processing step prior to testing dissolved hydrogen: PdNWAs were annealed at 200 °C for 5 h in a vacuum oven and then exposed to 100% hydrogen gas for 1 h to eliminate signal drift.

Scanning Electron Microscopy and Atomic Force Microscopy Measurements. Scanning electron microscopy (SEM) images were collected on Philips XL-30 FEGSEM (field emission gun scanning electron microscope) using an accelerating voltage of 10 KeV. The samples were mounted on aluminum stubs (Ted Pella) using adhesive carbon tape after sputtering coating. Intermittent contact mode atomic force microscopy (AFM) images were acquired in air using an Asylum Research MFP-3D microscope and Olympus AC240TS tips.

Dissolved Gas Analysis. The concentration of dissolved H₂ in our oil was determined chromatographically⁹ using a Myrkos microGC from Morgan Schaffer in conjunction with Morgan Schaffer PPMreport 3 software. A 100 mL volume of oil was withdrawn for each measurement using this instrument, which was designed specifically for the determination of dissolved H₂ in transformer oil.

Hydrogen Sensing. The PdNWA was located, face up, in a sealed sample holder (volume = 4.7 cm³) that was connected to an oil tank with a total volume of 1.5 L (Figure 2a). Oil was circulated through the sample holder (flow rate = 510 mL/min) using a circulating pump (Hargraves, W312-11). A 100 W cartridge heater (Temco, HDL00001), located at the bottom of the main oil tank, heated the oil to a predetermined temperature in conjunction with PID control provided by a graphic user

interface (M2I, XTOP12) with a built-in logic control system (KDT System, Cimon). To provide feedback to the heater and PID circuit, the oil temperature was monitored using a resistance temperature detector based upon a platinum resistor sensing element (RTD) (model Pt-100 RTD, US sensor, H3476, -20 to 130 $^{\circ}\text{C}$, precision 0.1 $^{\circ}\text{C}$). All gas concentrations in this work are volume/volume denominated. H_2 gas (Airgas, $\geq 99.998\%$) was mixed with N_2 (Airgas, $\geq 99.995\%$) to a predetermined concentration using mass flow controllers (MKS Inc., model 1479A), and pulses of this gas mixture were switched (Parker Valve, cycle time 25 ms) into a stream of pure N_2 (Airgas, $\geq 99.995\%$) while maintaining a total flow rate of 500 sccm ("sccm" refers to standard cubic centimeters per minute; 1.0 sccm $= 4.5 \times 10^{17}$ atoms/s). H_2 mixture was injected into the oil tank through a gas dispersion tube (Figure 2a). Instrument control and data acquisition were both coordinated by a computer equipped with Labview in conjunction with a National Instruments interface (model BNC 2110). All H_2 sensing measurements were carried out using dry gases at atmospheric pressure.

RESULTS AND DISCUSSION

Hydrogen sensors consisted of an array of ~ 30 palladium (Pd) nanowires onto which four gold electrodes were deposited by through-mask evaporation (Figure 1a,b). These Pd nanowires, prepared by lithographically patterned nanowire electrodeposition (LPNE)^{29–31} on glass substrates, had dimensions of

90 – 120 nm in width, 19 – 21 nm in height, and many hundreds of micrometers in total length. The electrically isolated length, defined by the evaporated gold contacts, was 100 μm (Figure 1b). The Pd electroplating solution contained a small stoichiometric excess of EDTA relative to Pd^{2+} because we have demonstrated^{21,23,24} that the nanowires produced using this procedure resist fracture upon exposure to gaseous H_2 at concentrations exceeding 1% in air or nitrogen, the threshold for the α to β phase transition of PdH_x .³³ These "PdNWAs" differed in two ways from the Pd nanowire-based sensors we have studied for the detection of H_2 in air and nitrogen:^{21,23,24} First, thirty nanowires were used in parallel instead of a single nanowire in order to ensure the reliability of the device, and second, four electrical contacts were employed for the resistance measurement instead of two in order to maximize the precision with which the wire resistance could be measured. On the basis of the data presented below, however, it is reasonable to expect that a single Pd nanowire with just two electrical contacts could produce detection metrics for dissolved hydrogen that are similar to those we obtained using 4-contact PdNWAs; however, we did not evaluate such single wire sensors in this study.

The solubility of H_2 in transformer oil was directly measured as a function of temperature using the apparatus shown in Figure 2a in conjunction with a gas chromatograph (GC) designed for H_2 analysis in transformer oil. Mixtures of nitrogen and hydrogen were prepared using calibrated mass flow controllers, and the transformer oil was purged with each gas mixture

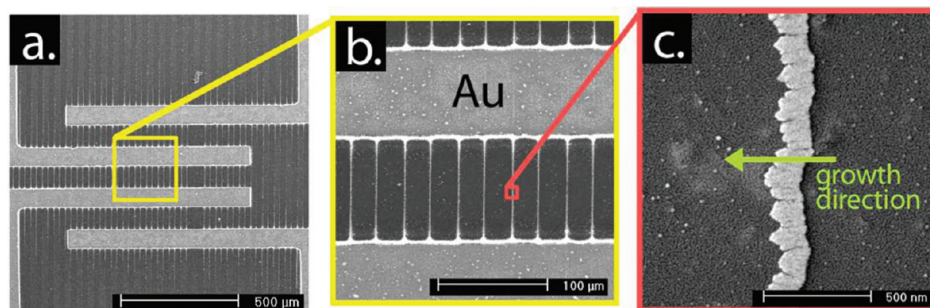


Figure 1. Scanning electron microscopy (SEM) images of PdNWAs: (a) Low magnification SEM image showing array of palladium nanowires, oriented vertically, and the evaporated gold four-point probe isolating 30 nanowires. Nanowires that do not contact all four electrical contacts are not included in the 4-contact resistance measurement circuit and do not contribute to the measured resistance of the other nanowires. Note also, two nanowires are missing from this array as a consequence of a photolithography defect. (b) Higher magnification SEM image showing ten nanowires. (c) Higher magnification SEM image of a single Pd nanowire in the PdNWA. The direction of growth during electrodeposition is indicated by the arrow.

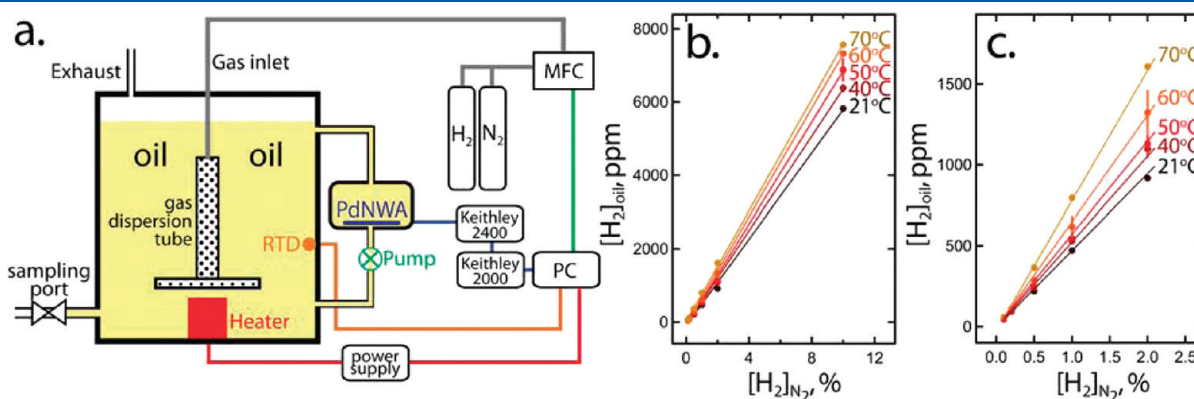


Figure 2. (a) Schematic diagram of the apparatus constructed for testing of PdNWAs. In this diagram, MFC denotes mass flow controller, PC denotes personal computer, and RTD is a resistance temperature detector. (b) Plots of $[\text{H}_2]$ in oil ($[\text{H}_2]_{\text{oil}}$), measured by gas chromatography, versus $[\text{H}_2]$ in nitrogen ($[\text{H}_2]_{\text{N}_2}$) at five temperatures from 21 to 70 $^{\circ}\text{C}$ as indicated. (c) Same data as shown in (b), rescaled to show the low concentration regime.

for 1 h after which 100 mL of oil was withdrawn for immediate GC analysis. A linear increase in $[H_2]_{oil}$ was observed with increasing $[H_2]_{N_2}$ in accordance with Henry's Law (Figure 2b,c): $P_{H_2} = k_H[H_2]_{oil}$, where P_{H_2} is the partial pressure of H_2 in nitrogen, k_H is the Henry's Law constant, or equivalently, the molar solubility of H_2 in the oil, and $[H_2]_{oil}$ is the concentration of H_2 in the oil. k_H increased with oil temperature from 460.2 ppm/%, (corresponding to 0.001908 M/atm) at 21 °C to 824 ppm/% (or 0.00294 M/atm) at 70 °C. These k_H values are somewhat higher as compared with previous measurements: $k_H = 0.00154$ M/atm was reported at 20 °C¹⁶ and $k_H = 0.00263$ M/atm was reported at 70 °C.⁹

The electrical resistance of PdNWAs, R , was used to determine $[H_2]_{oil}$. A relationship between $[H_2]_{oil}$ and R can be obtained if it is understood that two contributions to R are the nanowire resistance in the absence of hydrogen, $R_0(T)$, and the

extra resistance imparted by hydrogen absorption, $\Delta R([H_2]_{oil}, T)$:

$$R([H_2]_{oil}, T) = R_0(T) + \Delta R([H_2]_{oil}, T) \quad (3)$$

The temperature dependence of $R_0(T)$ is described in terms of the temperature coefficient of resistance, α :

$$R_0(T) = R_0(300K) + \alpha \Delta T \quad (4)$$

We shall show that $\Delta R([H_2]_{oil}, T)$ can be expressed in terms of a sensitivity factor, $S(T)$, as follows:

$$\Delta R([H_2]_{oil}, T) = S(T)(\sqrt{[H_2]_{oil}})R_0(T) \quad (5)$$

Using eqs 3–5, $[H_2]_{oil}$ can be related to R if we know both α and $S(T)$ as well as the temperature.

We determined α for PdNWAs immersed in oil using the measurement apparatus of Figure 2a by varying the oil temperature from 21 to 80 °C and measuring R in the absence of hydrogen (Figure 3a). Across this temperature range, R increased linearly with T with a slope of $\alpha = 3.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ (Figure 3b). This α value is comparable to the value obtained for Pd nanowires in a gaseous ambient by Offermans et al.²² ($\alpha = 5.6 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$) and that which we measured previously for a 94×183 nm Pd nanowire ($\alpha = 1.3 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$).²³ The bulk α value for Pd metal is significantly higher: $3.2 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$.³⁴

The response of PdNWAs to dissolved hydrogen was determined at 21 °C by increasing $[H_2]_{oil}$ in a stepwise fashion from 0 ppm to 118, 290, 590, 1180, and 2940 ppm with a dwell time at each $[H_2]_{oil}$ value of 1 h (Figure 4a) and then stepping down the $[H_2]_{oil}$ to these same values in reverse order (Figure 4c). This procedure was then repeated at each of four higher temperatures as indicated (Figure 4a,c), but because of the higher solubility of H_2 at these higher temperatures, the $[H_2]_{oil}$ programs shown in Figure 4 were scaled to higher values in accord with the data of Figure 2b,c. For the highest $[H_2]_{oil}$ value at 21 °C of 2940 ppm, the PdNWA produced a $\Delta R/R_0 = 8.4\%$ whereas, at 70 °C, $\Delta R/R_0 = 4.7\%$ for $[H_2]_{oil} = 3780$ ppm. Thus, $\Delta R/R_0$ is smaller at

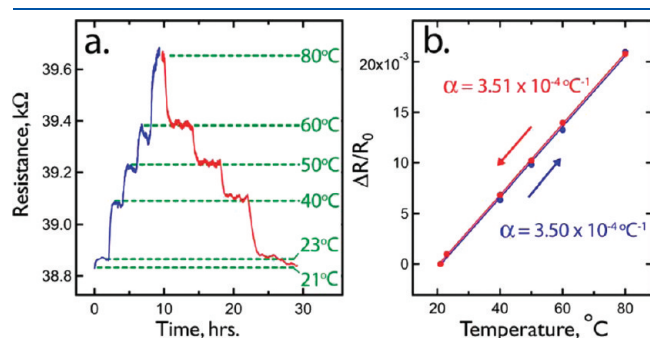


Figure 3. Calibration of a PdNWA for use as a resistance temperature detector (RTD). (a) Resistance of the PdNWA in the transformer oil as the temperature of oil was stepped up (blue) and down (red) across the range from 21 to 80 °C. (b) Plot of the resistance change ratio versus temperature, T ; the resistance change ratio, $\Delta R/R_0$, is defined as the change in resistance, ΔR , divided by the resistance at 21 °C, R_0 . The temperature coefficient of resistance for the PdNWA (shown) is just the slope of this line.

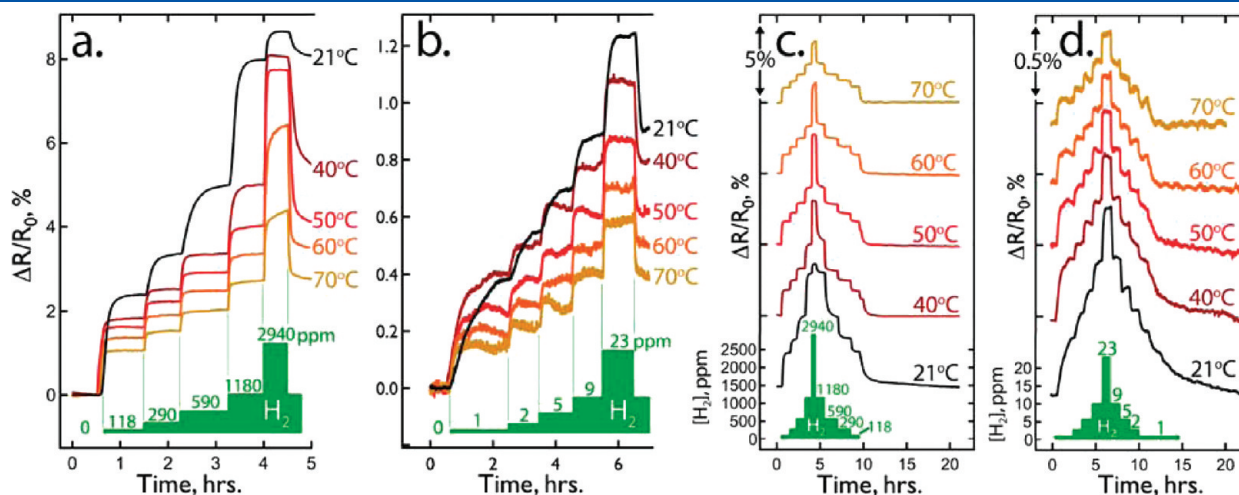


Figure 4. Hydrogen sensing data in transformer oil. (a) Plots of $\Delta R/R_0$ versus time for five hours encompassing the “high concentration” hydrogen program shown at bottom in green ranging from $[H_2]_{oil} = 118$ ppm to 2940 ppm, as graphically indicated. The $[H_2]_{oil}$ at higher temperatures ($T = 40$ °C, 50 °C, etc.) were higher than the values plotted at 21 °C in accordance with data of Figure 2b,c. (b) Plots of $\Delta R/R_0$ versus time for 5 h encompassing the “low concentration” hydrogen program shown at bottom in green ranging from $[H_2]_{oil} = 1$ ppm to 23 ppm, as graphically indicated. Again, the $[H_2]_{oil}$ at higher temperatures ($T = 40$ °C, 50 °C, etc.) were higher than the values plotted at 21 °C in accordance with data of Figure 2b,c. Note that the first stepwise increase in $\Delta R/R_0$ at $t = 0.6$ h was caused by the exposure of the PdNWA to $[H_2]_{oil} = 1.0$ ppm. (c) Plots of $\Delta R/R_0$ versus time for 20 h of the “high concentration” hydrogen program shown (green) at bottom. (d) Same experiment for the “low concentration” program.

70 °C in spite of the fact that $[H_2]_{oil}$ is $\sim 30\%$ higher than at 21 °C. This loss of sensitivity, which is seen across the entire concentration range of $1 \text{ ppm} < [H_2]_{oil} < 2940 \text{ ppm}$, parallels the behavior seen for gas phase sensing of H_2 using a single Pd nanowire²³ and is caused by the reduced solubility of H in PdH_x at elevated temperatures.³⁵ Also for single Pd nanowires, we have previously reported^{24,36} that, at 21 °C, ΔR saturates at 10–12% R_0 for $[H_2]_{N_2} \approx 1\%$; higher $[H_2]_{N_2}$ do not induce a higher R for the nanowire while at elevated temperatures, and R saturation is not observed.²³ Even this idiosyncrasy is observed in the data of Figure 4a,c: A smaller-than-expected ΔR is measured for $[H_2]_{oil} = 2940 \text{ ppm}$ at 21 °C (Figure 4a) while, at higher temperatures of $T = 40$ °C and above, the incremental ΔR is much larger. For gas phase H_2 sensing, R saturation at $[H_2]_{N_2} \approx 1\%$ coincides with the α -to- β phase transition of PdH_x ³⁷ and it may be that, in transformer oil, this phase transition occurs at a slightly lower concentration of 0.2–0.3%.

The response and recovery times measured from the data of Figure 4 of 15–30 min represent maximum values for the PdNWA since these are limited by the rate at which it was possible to change $[H_2]_{oil}$ within the 1.5 L volume of transformer oil by gas purging and circulation. For this reason, response and recovery were virtually unchanged across the temperature range explored here, except for some acceleration of the response at higher temperatures that can be attributed mainly to more rapid diffusive contributions to mixing. A more sophisticated oil flow system would be required to measure the sensor-limited response and recovery, but the rapidity of the response demonstrated in Figure 4 is already sufficient for DGA.^{1–8}

PdNWAs also detect and discriminate between lower dissolved H_2 concentrations, ranging from $[H_2]_{oil} = 0.9$ to 23 ppm (21 °C). In fact, at $T = 21$ °C, $[H_2]_{oil} = 0.9 \text{ ppm}$ is detected as a $\Delta R/R_0$ of 0.40% on a baseline with rms noise of $\approx 0.03\%$, a signal-to-noise (S/N) of 10 (Figure 4b). In our testing system, $[H_2]_{oil} = 0.9 \text{ ppm}$ is the lowest concentration that can be generated but the projected limit-of-detection based upon a $S/N = 3$ is estimated to be $LOD_{H_2} \approx 0.3 \text{ ppm}$. At 70 °C, the lowest $[H_2]_{oil}$ tested was 1.6 ppm which generated $\Delta R/R_0 = 0.15\%$ on a baseline with rms noise of $\approx 0.06\%$, a signal-to-noise of 2.5 (Figure 4b). These LOD_{H_2} values are among the lowest reported for H_2 sensors in transformer oil (Table 1).

Plots of $\Delta R/R_0$ versus $[H_2]_{oil}$ (Figure 5a) show curvature that resembles the behavior of single Pd nanowires operating in gaseous H_2 mixtures with N_2 , below $[H_2]_{N_2} = 1.0\%$.²⁴ In this concentration regime, the PdH_x remains α phase³⁷ and we have demonstrated²⁴ that $\Delta R/R_0$ is linear with $[H_2]_{N_2}^{1/2}$ in accordance with Sievert's Law.³⁸ If the R data of Figure 5a is replotted against $[H_2]_{oil}^{1/2}$, we again find linear plots at all temperatures (Figure 5c). This is strong evidence that the Pd nanowires within the PdNWA remain α phase across this range of $[H_2]_{oil}$. The slope of these lines equals the sensitivity factor, $S(T)$, which is required for the calculation of $[H_2]_{oil}$ using eqs 3–5. A plot of $S(T)$ versus T (Figure 5d) is linear with a negative slope, a direct consequence of the reduced solubility of H_2 in PdH_x with increasing temperature.³⁵

The durability of PdNWAs in flowing transformer oil is an issue of critical importance. One indication of the durability of PdNWAs is the fact that we suffered no failures of nanowires in any of the more than 20 PdNWAs prepared for this study once these devices were mounted within the oil tank and covered with oil. Beyond this baseline, we carried out a preliminary stability assessment by measuring the R for a PdNWA in flowing

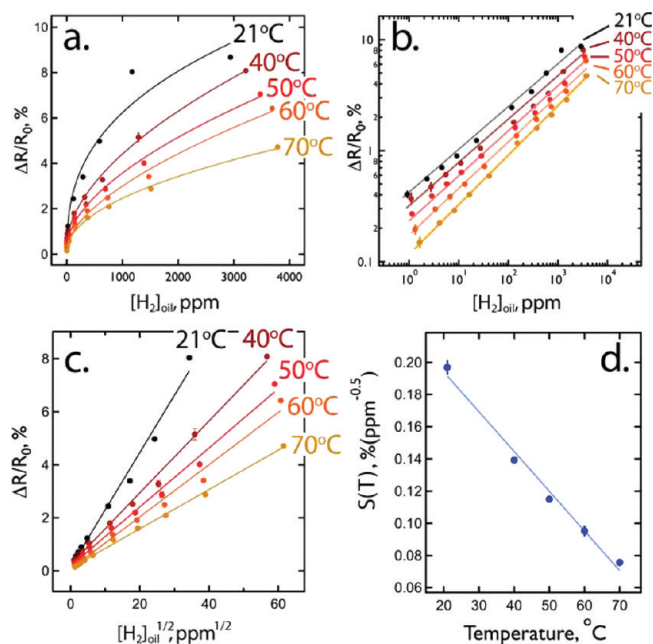


Figure 5. Summary of H_2 sensing responses observed at five temperatures. (a) Plots of mean $\Delta R/R_0$ versus $[H_2]_{oil}$ for five temperatures as indicated. Solid lines represent the best fit to the equation, $\Delta R/R_0 = [H_2]_{oil}^x$ where the best fit value of x varied from 0.35 to 0.60. (b) Log–log plot of the same data shown in (a), emphasizing linearity of the data in the low $[H_2]_{oil}$ regime. (c) Plot of $\Delta R/R_0$ versus $[H_2]_{oil}^{1/2}$ for the same data shown in (a) and (b). (d) Plot of the slope of the lines shown in (c) as a function of temperature.

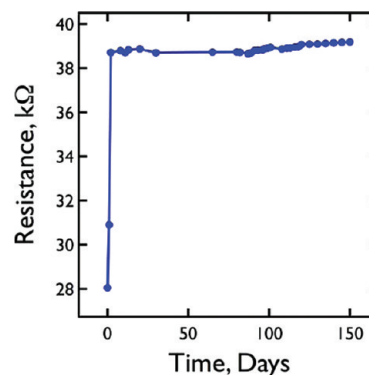


Figure 6. Long-term resistance stability monitoring for a PdNWA in flowing transformer oil. R is plotted as a function of time for 150 days. The temperature was changed from $T = 21$ °C to $T = 70$ °C during the first 90 days of this trial. After day 90, the temperature remained at 20–21 °C for the remainder of the trial.

transformer oil over a range of temperatures from 21 to 70 °C for an extended period of 5 months (Figure 6). On day 1 of this trial, the PdNWA was damaged during its loading into the oil tank and several nanowires were fractured (first two data points). After day 1, R increased gradually from 38.7 k Ω to 39.2 k Ω on day 150, an increase of 1.2%. This change in R is too small, and too gradual, to be caused by loss of even a single nanowire. Instead, it is likely due to an actual increase in $[H_2]_{oil}$ resulting from trace oil decomposition since just $\sim 0.5 \text{ ppm}$ H_2 is required to account for this ΔR . Much more testing of PdNWAs for longer durations will be required in order to determine whether these

devices possess the necessary ruggedness and resistance stability for real-time H₂ testing in operating transformers.

CONCLUSIONS

We describe a new application for metal nanowires involving the detection of a dissolved gas in a liquid. In our demonstration of this concept, we have exploited an application with direct technological relevance: The detection of dissolved H₂ in transformer oil. Our data support the conclusion that PdNWAs are sensitive, durable sensors for dissolved hydrogen in transformer oil. Specifically, we measured LOD_{H₂} values in the 1–2 ppm range from 21 to 70 °C, among the lowest reported to date (Table 1). Even lower LOD_{H₂}, down to 0.30 ppm at 21 °C, can be projected on the basis of the noise present in these devices. PdNWAs also discriminate [H₂]_{oil} above this LOD_{H₂} up to 2900 ppm at 21 °C (3800 ppm at 70 °C). Striking parallels are observed between the behavior of PdNWAs operating in transformer oil and single Pd nanowires functioning in gaseous ambients including linear $\Delta R/R_0$ versus [H₂]_{oil}^{1/2} behavior and R saturation at the α -to- β phase transition of PdH_x.

The redundancy provided by multiple nanowires was intended to increase the durability of the sensor but nanowire failure during sensing was not observed in a single instance in this study, suggesting that multiple nanowires are superfluous and unnecessary. Additional research will be required, however, to determine whether PdNWAs have the necessary R stability and durability to function within transformers for periods of a year or more.

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