Development of Fiber Optic Sensors for Downhole pH Measurement

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Cover Illustration: Field exploitation of unconventional hydrocarbon resources.


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Development of Fiber Optic Sensors for Downhole pH Measurement

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<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>AuNPs</td>
<td>Gold nanoparticles</td>
</tr>
<tr>
<td>BCP</td>
<td>Bromocresol purple</td>
</tr>
<tr>
<td>BCG</td>
<td>Bromocresol green</td>
</tr>
<tr>
<td>BPB</td>
<td>Bromophenol blue</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>F⁻</td>
<td>Fluoride</td>
</tr>
<tr>
<td>GCS</td>
<td>Geological CO₂ sequestration</td>
</tr>
<tr>
<td>H₃O⁺</td>
<td>Hydronium ion</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>Sulfate</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
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Acknowledgments

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EXECUTIVE SUMMARY

This report describes a need for practical pH measurements in the context of geological fluids under elevated pressures and temperatures, and reviews current strategies to address this challenge. Several alternative approaches based on emerging materials and fiber optic technology are herein proposed, and preliminary results from gold nanoparticle-based sensors are presented to demonstrate a promising pH sensing system under elevated temperature conditions up to 80°C in acidic conditions as well as in saturated salt solutions. The role of solution refractive index on the measured sensing response has been determined to be relatively weak as compared to the direct interaction between the sensing material and the fluid, although the mechanism is still currently under investigation. A provisional patent application based upon the approach has been filed (Application # US 61987528 Plasmonic Nanoparticle Based pH Sensors in Aqueous Environments).
1. INTRODUCTION

As one of the most basic parameters that characterize chemical properties of aqueous solutions, pH is the generally accepted measure for acidity or basicity. Since almost all biological, ecological, environmental, and geological activities rely on specific pH conditions, and are influenced by changes in pH, the measurements of pH are important for disciplines such as life sciences, environmental sciences, earth sciences, marine sciences, and civil engineering (Dickson, 1993; Wolfbeis, 2002; Korostynska et al., 2008; Wencel et al., 2014). Accurate identification of pH values is therefore a prerequisite for successfully estimating and assessing the outcomes of associated events, for example, pathological characterization, food contamination, water pollution, and geological formations.

While techniques for sensing pH in biological and physiological systems have noticeably matured (Korostynska et al., 2008), their counterparts in environmental and geological contexts remain a challenge due to complicated compositions and other variables including temperature (Bates, 1962) and pressure (Hopkins et al., 2000; Bortoluzzi et al., 2011). For example, the pH of seawater (Dickson, 1993) is basically defined by the interplay of dissolved carbon dioxide (CO₂), ionic strength and protonatable anions such as sulfate (SO₄²⁻) and fluoride (F⁻), and also fluctuates as local temperature and pressure change. Such complication deepens in subsurface geological fluids (Raghuraman et al., 2006a), which are subject to extreme temperatures (>350 K) and pressures (> 1,000 psi), as well as dynamic exchanges of ions with sedimentary minerals.

Table 1: Physical conditions of downhole drillings and geological CO₂ sequestration

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Downhole Drilling</th>
<th>Deep/Ultra-deep</th>
<th>Geological CO₂ Sequestration (Vilarrasa et al., 2013)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth of interest (feet)</td>
<td>1,500–13,500</td>
<td>30,000–40,000</td>
<td>6,000–7,000</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>Up to 470</td>
<td>Up to 580</td>
<td>Up to 370</td>
</tr>
<tr>
<td>Pressure (psi)</td>
<td>Up to over 10,000</td>
<td>Up to 30,000</td>
<td>Up to 3,000</td>
</tr>
<tr>
<td>Typical pH</td>
<td>4–8</td>
<td>4–8</td>
<td>2–6</td>
</tr>
</tbody>
</table>

Difficult as it appears, the quantification of pH under these reservoir conditions is yet crucial to understanding geological CO₂ sequestration (GCS), safety in downhole drilling, and prevention of scaling and corrosion, among others. Despite the vast availability of pH measurement techniques under biological or ambient conditions, few qualify to meet the aggressive requirements set by GCS or downhole conditions, and these are limited by the stability of sensing materials (Raghuraman et al., 2005, 2006b; Raghuraman and O’Keefe, 2007; Fujisawa and Yamate, 2013). This has prompted the investigation of novel approaches to practical, accurate and reliable pH sensing methods by taking advantages of the combination of material chemistry (Basabe-Desmonts et al., 2007; Hatchett and Josowicz, 2008; Mujahid et al., 2010) and fiber optics (Wolfbeis, 2002, 2004, 2008; Rayss, 2005; Wang, 2013). An ideal pH sensor (Wencel et al., 2014) should be able to selectively reflect real-time pH values with both high accuracy and precision under varying extreme conditions. This report provides an overview of
current techniques for pH measurements, especially those related to conditions of interest; and presents the design of optical fiber-based sensors, and preliminary results.
2. BACKGROUND

Originally introduced by S. P. L. Sørensen to evaluate the “power of hydrogen”, pH is now officially defined as the decimal cologarithm of the activity of proton $a(H^+)$, or more exactly, hydronium ion ($H_3O^+$), in any given solution, which is also dependent on temperature $T$, pressure $P$, and ionic strength $I$. Conventionally, methods for pH determination can be categorized into two types: electrochemical (i.e., potentiometric) (Buck et al., 2002) and optical (Himmel et al., 2010).

Common pH indicators for laboratory use are pH strips, paper with immobilized dye indicators that change color in response to environmental pH. Ion selective electrodes that allow for measurement of $H_3O^+$ concentrations, and thus pH, are now extensively equipped in pH meters that enable convenient, quantitative measurements. In the setup of a typical pH meter, a probe made from glass membrane with specific sensitivity towards $H_3O^+$ ion can measure the changes of electric potential in the electrode system as a function of activity changes of $H_3O^+$, which can be processed to yield pH readings with appropriate calibrations. Despite the capability of potentiometric techniques for measuring pH under ambient conditions, they usually fail to maintain their performance under more aggressive conditions as in GCS and downhole drilling. This is caused by electrode damage as a result of pressure and temperature change from GCS conditions to normal conditions, as well as drifts that are challenging to calibrate (Shao et al., 2013b).

In optical pH sensing, direct or indirect chemical changes of sensing materials in response to pH changes are coupled with corresponding optical properties, which can subsequently be transduced into pH values. Broadly speaking, techniques such as pH strips and dye indicators used in acid-base titrations, are examples of optical pH sensing, in which visual estimation is based on distinct pH-dependent colorimetric properties of dyes. As modern optical techniques evolve, optical pH sensors now rely on spectroscopic methods, most commonly in absorption and emission modes, based on planar or fiber-optic platforms. On the other hand, the scope of pH-sensitive materials is no longer limited to organic dye indicators, and has been expanded to include polymers (Hatchett and Josowicz, 2008) and nanoparticles (Basabe-Desmonts et al., 2007) among other advanced materials (Wencel et al., 2014).
Dye indicators are mostly organic molecules that can be protonated and/or deprotonated as pH changes. The intensity (hyperchromic and hypochromic shifts) and wavelength (hypsochromic and bathochromic shifts) in absorption and/or emission spectra will change when dye indicators such as bromocresol purple (BCP) are subject to protonation or deprotonation, which can be ratiometrically correlated to pH values (Figure 1). For fluorescent dye indicators, changes in emission lifetime ($\tau$, or its inversion, the fluorescence decay rate, $1/\tau$) can also be used for pH measurements because, unlike emission intensity, lifetime is less susceptible to environmental factors other than pH, because it does not suffer from fluctuations in light intensity, detector sensitivity, leaching, photobleaching and so on (Wencel et al., 2014). However, applications of dye indicators for pH measurements under GCS and downhole conditions are currently mainly based on absorption methods. While bromophenol blue (BPB) (Shao et al., 2013b) and bromocresol green (BCG) (Shao et al., 2013a) have been demonstrated to measure acidic pH in rock-brine-CO$_2$ systems under simulated GCS conditions, phenol red (Raghuraman et al., 2006b) and other dyes or dye combinations (Raghuraman et al., 2005; Raghuraman and O’Keefe, 2007) have already been used to determine downhole pH; all of which have required the direct dissolution of indicator dyes in the aqueous solutions of interest. In the context of real world applications, these spectrophotometric methods require specialized instrumentation, such as corrosion and pressure-resistant vessels and dedicated spectrophotometers, which raises technical difficulties, as well as cost. Moreover, long-term reliability presents a problem because most indicator dyes are not immune to either the thermal or the chemical environment as above mentioned.
Similar to dye indicators, pH sensors based on polymers also rely on acid/base sensitive functional groups, but polymers can intrinsically address stability issues that widely exist in small molecules. Therefore, polymers have been extensively used in pH sensing in the form of films (or doped films) (Jin et al., 2000; Itagaki et al., 2008), sol-gels (Mujahid et al., 2002; Duong et al., 2006), optical fiber coatings (Song et al., 1997; Hotra et al., 2007; Socorro et al., 2012; Raoufi et al., 2012; Hu et al., 2013), and other forms (Lee and Braun, 2003; Wong et al., 2014; Paek et al., 2014). Another advantage of polymers is the signal amplification effect (McQuade et al., 2000; Rochat and Swager, 2013) that is commonly found in highly conjugated polymeric structures, where changes (e.g., absorption shifts or fluorescence quenching) caused by local interactions between monomeric units and analytes can be significantly amplified through conjugation. Despite their enhanced performance towards environmental conditions relevant to CGS or downhole pH sensing, any reported examples that take advantage of polymers in such applications have not yet been identified.

As an area of emerging research interests, nanomaterials exhibit distinct properties from their microscopic and macroscopic counterparts. For example, free electrons in metal nanoparticles can couple with light having far greater wavelengths relative to their size, a phenomenon known as localized surface plasmon resonance (LSPR) that is highly dependent on the refractive index of environment among other factors. Nanosized materials, such as silica-, silver- and polymer-based nanoparticles (Sun et al., 2006; Yin et al., 2011; Climent et al., 2013), dendrimers (Niu et al., 2003), carbon nanotubes (Ghini et al., 2010, 2013; Gou et al., 2014), and quantum dots (Snee et al., 2006; Maule et al., 2010) have been developed into pH sensors, mostly targeting in vivo pH measurements. Meanwhile, nanomaterials can be used as host matrices to immobilize and protect dye molecules from leaching or passive decomposition, in addition to forming hybrid composites with inorganic or polymer materials. The flexibility and modularity of nanomaterials make them promising candidates for building selective and reliable pH sensors.

As one example of nanomaterial based pH sensors, gold nanoparticles (AuNPs) exhibit very strong size-dependent LSPR with the absorption maxima centered around 500 to 600 nm, which is also highly dictated by the environment. Upon directed functionalization, the environment dependence of the LSPR of AuNPs can be engineered selectively towards pH. There are several alternative approaches to pH-responsive AuNPs in the literature. Sun et al. (2008) modified the surface of Au nanorods with bifunctional molecules in a regioselective manner, which enabled them to undergo pH-induced assembly and disassembly in end-to-end or side-by-side fashion. Jiang et al. (2009) developed a gold nanocrescent array coated by a polymer hydrogel thin film that would swell upon pH increase, leading to blue-shift in the LSPR peak of the array. Hong et al. (2010) reported a pH sensor that consisted of a pyrene-based fluorophore and AuNPs connected by a pH-sensitive polysulfonamide linker. The polysulfonamide linker showed pH-controlled coil-globule transition, which could change the proximity between the fluorophore
and AuNPs, and thus the emission quenching efficiency of AuNPs. More recently, Guan et al. (2014) demonstrated the use of poly-(γ-glutamic acid)-stabilized AuNPs as a “naked-eye” colorimetric pH probe, where the degree of aggregation of AuNPs was governed by environmental pH. Despite promising applications for pH sensing, these metal nanoparticle based approaches still require the use of linker or dye molecules that are inherently incompatible with the demanding temperature and pressure requirements for downhole sensing.

This research is currently pursuing a practical fiber optics approach to pH sensor development that exploits engineered functional sensor materials as pH-responsive materials. To this end, this study explores the potential of a variety of materials for optical pH sensing, both traditional and emerging ones, and identifies the pathway to optical pH sensing in harsh environments such as those encountered in GCS and downhole sensing applications. Herein, this research demonstrates the capability of achieving such goals with the initial efforts of fabricating pH fiber-optical sensors based on plasmonic Au nanocrystal embedded in a robust and high temperature stable matrix.
3. **EXPERIMENTAL APPROACH**

The fabrication of the plasmonic pH sensors started with the preparation of a coating solution using a sol-gel technique. Briefly, 0.04 g of HAuCl₄ was mixed with 1.0 ml deionized water, 4.5 ml ethanol and 4.5 ml tetraethoxysilane (TEOS). The mixture was stirred at 60°C for 1 hr. To deposit Au nanoparticle film on a planar substrate, the Au/silane solution was spin-coated on the substrate and heated to 200°C for 45 min in air. To prepare an optic fiber coated with Au nanoparticles, an optic fiber was first heated in air at 550°C for 60 min to remove the polymer coating and then etched in a buffered oxide hydrofluoric acid (HF) etchant solution for 50 min. The etched fiber was subsequently coated with the Au/silane solution and then calcined at 200°C for 45–60 min in air. The preparation of sensors using other metal nanoparticles such as Pd was performed in a similar manner with different metal salts such as PdCl₂ as the Pd source. As control experiments, planar films and optical fibers were also coated with pure TEOS in H₂O/ethanol using the exact same procedure.

![Figure 2: Schematic illustration of the experimental setup for pH sensing.](image)

The pH sensing response was measured by monitoring the transmission spectral changes using an OceanOptics spectrometer of an optic fiber coated with different sensing materials in a solution as the solution pH was varied by adding 0.1 M NaOH and 0.1 M H₃PO₄. Alternatively, 0.1 M KOH and 0.1 M H₂SO₄ were also used for pH adjustment. NaCl was used to test the response to changes in the refractive index of the solution and to demonstrate the capability of pH sensing using plasmonic optic fibers in high-salinity conditions, which are also ubiquitous in downhole and geological environments. Finally, experiments at temperatures up to 80°C at 1 atmospheric pressure were carried out to demonstrate the potential of these materials for high temperature pH sensing.
4. RESULTS AND DISCUSSION

4.1 PH SENSING USING PLASMONIC AU NANOPARTICLE COATED OPTIC FIBER

The formation of Au nanoparticles after the calcinations is confirmed by the appearance of the characteristic plasmon absorption band around 530 nm (Figure 3). The absorption feature associated with the Pd nanocrystals is also observed for Pd coated fibers (Figure 3). In contrast, the transmission spectrum of a fiber treated with pure TEOS is essentially featureless in the visible spectral range (Figure 3).

![Figure 3: The transmission spectra of three optic fibers coated with pure TEOS (black curve), Au nanoparticles/TEOS (red curve), and Pd nanoparticles/TEOS (blue curve).](image)

To demonstrate the pH sensing capability of plasmonic Au nanocrystal coated optic fiber, the transmission spectra of the fiber at various pH values are shown in Figure 4a. The plasmon absorption band grows significantly as pH increases. Only change in intensity is observed and no spectral shift or broadening/narrowing is seen. This observation suggests that the optical response is not a result of the change of the refractive index ($n$) of the solution, although more in-depth experiments will be discussed later in this section to definitively rule out any significant role of the change in $n$. The sensor is responsive in wide pH ranges from at least 2 to 12, but seems to be more sensitive towards basic pH values as the optical change is more significant under high pH conditions (Figure 4b). However, despite the general observation of higher sensitivity at higher pH values, there is also variation from fiber to fiber due to subtle changes in the preparation conditions, such as fiber etching. Therefore, the sensitivity at acidic pH values can be further enhanced by optimizing the sample preparation processes. The response of the plasmonic pH sensor is fast, robust, and highly reversible (Figure 5). These attributes make them promising for real time pH measurement under harsh environmental conditions.
Figure 4: (a) The transmission spectra of an Au nanoparticle coated optic fiber at different pH values. (b) The transmission at the peak plasmon absorption band wavelength as a function of solution pH.

Figure 5: The transmission at the peak plasmon absorption band as a function of time showing fast, robust and reversible response to pH variations. The solution pH is indicated in the figure.
4.2 CONTROL EXPERIMENTS PROVING THE SENSOR RESPONSE IS A RESULT OF PH CHANGE

A series of control experiments were performed to ensure that the strong optical response is indeed a result of the response of the plasmonic absorption band of Au nanoparticles towards changes in pH. First, a fiber coated with pure TEOS was tested and the fiber exhibits no response to solution pH changes (Figure 6). Second, an experiment using 0.1 M H₂SO₄ and 0.1 M KOH as the acid/base pair for pH adjustment was carried out and the Au/TEOS coated fiber demonstrates qualitatively similar response to pH irrespective of the specific acid/base pairs used (Figure 7).

![Figure 6: Transmission through an optic fiber coated with pure TEOS as the pH of the solution is varied over time (the pH of the solution is indicated as colored numbers in the figure).](image1)

![Figure 7: Transmission at the peak plasmon absorption band wavelength of an Au/TEOS coated optic fiber at different pH values using H₂SO₄/KOH and H₃PO₄/NaOH acid/base pairs for pH adjustment.](image2)
Furthermore, extensive experiments were also performed to eliminate the possibility of the change in the refractive index $n$ of the solution as the cause of the observed optical response. One set of experiments comparing the response by intentionally changing the refractive index $n$ of the solution with the change observed by varying pH demonstrated that the optical response during the pH sensing measurements is indeed a result of change in pH rather than small, even negligible, variation of $n$ of the solution under test in these experiments.

These extensive control experiments offer convincing evidence that the optical response of the plasmonic Au sensors is truly a result of variation of solution pH.

### 4.3 DEMONSTRATION OF PH SENSING AT ELEVATED TEMPERATURE AND WITH SATURATED NaCl SOLUTION

Under neutral to acidic conditions, the plasmonic Au coated optic fiber pH sensor is robust, thermally stable, and highly responsive even under high salinity conditions, all of which are essential to successful deployment in realistic geological and/or downhole sensing environments. As shown in Figure 8, pH sensing experiments using the plasmonic Au optic fiber sensor at 80°C and in saturated NaCl solutions demonstrate measurable responses under these conditions at neutral to acidic pH ranges, which are expected for geological and downhole environments. The temperature of 80°C is only limited by the fact that it is approaching the solution boiling temperature at 1 atmospheric pressure as the sensing material is expected to be stable at significantly higher temperatures than the testing conditions employed. For example, the Au nanoparticles are stable at temperatures approaching 1000°C and the polymer matrix is anticipated to be stable at temperatures of at least 300°C, above the temperatures required for downhole sensing applications. It is also optimistic that this approach should also be suitable for high temperature and high pressure pH sensing and an elevated pressure and temperature reactor is currently under construction to allow for testing in the near future.

![Figure 8: Optical pH sensing using a plasmonic Au/TEOS coated optic fiber at 80°C and in saturated NaCl solution. The pH of the solution is indicated in the figure.](image)

<table>
<thead>
<tr>
<th>Elapsed Time (s)</th>
<th>Transmission at 550 nm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>23.85 % (sat.) NaCl</td>
</tr>
<tr>
<td>200</td>
<td>5.93</td>
</tr>
<tr>
<td>300</td>
<td>5.60</td>
</tr>
<tr>
<td>400</td>
<td>5.35</td>
</tr>
<tr>
<td>500</td>
<td>4.46</td>
</tr>
<tr>
<td>600</td>
<td>5.60</td>
</tr>
<tr>
<td>700</td>
<td>6.29</td>
</tr>
<tr>
<td>800</td>
<td>7.65</td>
</tr>
<tr>
<td>900</td>
<td>2.69</td>
</tr>
<tr>
<td>1000</td>
<td>2.59</td>
</tr>
<tr>
<td>1100</td>
<td>2.15</td>
</tr>
<tr>
<td>1200</td>
<td>4.61</td>
</tr>
<tr>
<td>1300</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Figure 8: Optical pH sensing using a plasmonic Au/TEOS coated optic fiber at 80°C and in saturated NaCl solution. The pH of the solution is indicated in the figure.
5. CONCLUSION AND OUTLOOK

A clear need exists for higher temperature stable pH sensors in elevated pressure aqueous solutions. A number of potential optical sensing material design approaches compatible with optical fiber based sensors are being investigated and a novel plasmonic Au nanoparticle nanocomposite sensor approach has successfully been developed showing great promise for applications. The response of the plasmonic pH sensor is fast, robust, reversible, and sensitive towards a wide pH range. The plasmonic pH sensor also demonstrates excellent capability for pH sensing at elevated temperatures and in saturated salt solutions. These properties are promising for applications in high temperature and high pressure conditions relevant for downhole sensing environments and may overcome the limitations of previously existing classes of pH sensing materials. While conducting in-depth investigation into the sensing mechanism of these newly developed plasmonic pH sensors, the scope of materials will be expanded to polymers, other nanoparticles and nanocomposites, and hybrid formula, targeting robust, efficient and selective pH sensing capability tailored towards broad, especially extreme temperature and pressure ranges.
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6. REFERENCES


