



High temperature potentiometric NO₂ sensor with asymmetric sensing and reference Pt electrodes

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ABSTRACT

The focus of this paper is on fabrication of planar potentiometric NO₂ sensors with asymmetric reference and sensing electrodes, both made with Pt, and deposited on yttria-stabilized-zirconia electrolyte. Both electrodes were initially derived from Pt ink. Using a rapid electrochemical method based on surfactant-templated electrodeposition, highly porous Pt was deposited on one of these electrodes and it served as the reference electrode. The increased surface area of the reference electrode leads to asymmetry between the sensing and reference electrodes and the device performed well as a high temperature potentiometric NO₂ sensor. These results also provide direct evidence of the role of non-electrochemical reactions, in this case the equilibration of NO/NO₂ in design of sensors. The simplicity of the sensor design, its compactness, a 1–2 min electrodeposition process, and the use of only two materials (YSZ and Pt) are the attractive features of this device.

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1. Introduction

The difference in heterogeneous catalytic activities of solid-state inorganic materials has been exploited in chemical sensing. Catalytic combustion sensors, for example, were first used for detecting flammable gases five decades ago and currently find considerable use [1,2]. These sensors are essentially calorimeters, composed of two Pt coils that are coated with materials with different catalytic activities toward combustion gases. As gas molecules oxidize on the surface of catalytic activated Pt coils, the heat released changes the resistance of the Pt coil and generates the sensor signal. The second Pt coil with an inert surface serves as the reference.

The concept of dissimilar electrodes has also been used in the design of potentiometric gas sensors based on solid-state electrolytes. Traditionally, the two electrodes of potentiometric sensors, sensing and reference electrodes, are designed to have distinct electrocatalytic activities toward the target gases. The reference electrode is nominally either electrochemically inactive, or physically isolated from the target molecules. The heterogeneous catalytic activities of electrode materials have substantial influence on the sensor signal [3–6]. In a previous study, we have shown that potentiometric sensing devices composed of WO₃ sensing electrodes, YSZ electrolyte, and Pt-loaded zeolite Y coated reference electrodes possess high sensitivity toward NO_x [7]. The asymmetry

in heterogeneous catalytic activities for NO_x equilibration between Pt clusters stabilized in microporous zeolite cages and WO₃ surfaces was responsible for NO_x sensing. Engineering differential heterogeneous catalytic activities of the two electrodes is a promising approach to design potentiometric NO_x sensors operating at high temperatures and in the presence of oxygen.

Electrochemically fabricated mesoporous Pt has received much attention because of its high catalytic activities and good thermal/mechanical stability [8–10]. Various sensing applications like nonenzymatic glucose detection, selective hydrogen-ion sensing, and calorimetric gas sensing have been reported [2,11–13]. General approaches for fabricating mesoporous Pt include the replication of porous alumina or lyotropic liquid–crystal templates with electrochemical reduction of Pt complexes, and potential-controlled surfactant assembly [14].

In this paper, we explore fabrication of compact sensors using only two materials (YSZ and Pt). For the first time, a rapid surfactant-templated solution based electrodeposition process is used to fabricate an effective reference electrode by manipulating the surface catalytic activity of Pt. Both sensing and reference electrodes consist of Pt but the different surface areas and catalytic activities lead to sensing of NO₂ at high temperatures. NO_x sensors are currently one of the key elements in the development of high fuel-efficiency internal combustion engines operating at high air/fuel ratio [15,16]. Though we have only focused on NO₂ in this paper, the sensors developed here can also act as a NO sensor, and with the aid of a catalytic filter at a different temperature than the sensor, the device transforms into a total NO_x (NO + NO₂) sensor [7,17].

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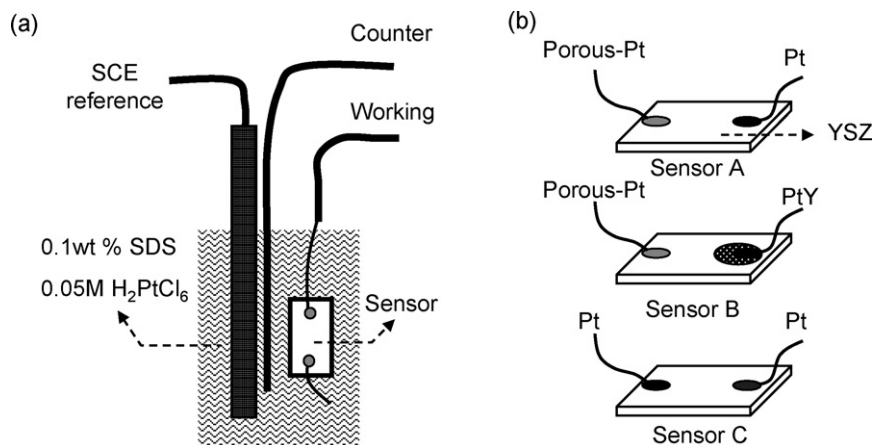


Fig. 1. (a) Apparatus for electrodeposition and (b) the three potentiometric sensors composed of an YSZ electrolyte and two Pt electrodes that are the focus of this study. For Sensor A, porous Pt was deposited on one of the ink-generated Pt electrodes, in Sensor B, the ink-generated Pt electrode was covered with a layer of Pt-zeolite Y and Sensor C was fabricated with two ink-generated Pt electrodes.

2. Experimental

2.1. Sensing device fabrication and characterization

The three sensor structures and the apparatus of electrodeposition are illustrated in Fig. 1. The YSZ substrate was prepared from tetragonal YSZ green sheets obtained from NexTech Materials (Columbus, OH). Two holes that fit Pt wires (99.95%, 0.13 mm in diameter, Fischer Scientific) were punched on the 10 mm by 5 mm YSZ green sheets. The Pt wires were inserted into the hole on YSZ green sheets before sintering in air at 1450 °C for 2 h. The Pt wires were held tightly due to the shrinkage of YSZ after sintering. A small amount of commercial Pt ink (Englehard, A4731) was applied to the junction between sintered YSZ and Pt wires to increase the contact area. The Pt ink was cured at 1200 °C for 2 h. This structure assures good mechanical durability of electrodes during the electrodeposition process.

The electrodeposition solution was prepared with 0.05 M H_2PtCl_6 (Aldrich) and 0.1 wt.% SDS (sodium dodecyl sulfate, MP Biomedicals), following the procedure developed by Choi et al. [14]. As shown in Fig. 1, one of the Pt wires on the YSZ substrate was used as the working electrode in the electrodeposition process. A saturated calomel reference electrode (SCE) and Pt-coil counter electrode were used to construct the electrochemical cell. A cathodic potential of -0.22 V was applied to the Pt electrode for 1–2 min. After deposition, the Pt electrode was rinsed thoroughly with ethanol and deionized water to remove the SDS and Pt complexes on the electrode and YSZ.

FEI XL30 FEG ESEM was used to investigate the nanostructure of Pt electrodes. High-resolution SEM micrographs were acquired by FEI Sirion with the through lens detector (TLD). The cross-section was cut by FEI DB235 focused ion beam. A thick layer of Pt was deposited prior to FIB milling to protect the surface nanostructure.

Pt-loaded zeolite Y (PtY) reference electrodes were also fabricated to compare the performance with the electrodeposited electrodes. Ion-exchange was performed to embed Pt nanoparticles into zeolite Y crystals. 1.0 g of H^+ zeolite Y (Si/Al = 30, CBV720, Zeolyst International) was added to 2.5 mM $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ solution followed by stirring for 24 h at room temperature. The zeolite powder was then centrifuged and washed with distilled water. After repeating the ion-exchange process three times, Pt-exchanged powder was calcined at 300 °C for 3 h and exposed to 5% H_2 at 400 °C for 5 h to reduce Pt^{2+} to metallic Pt. The Pt content determined by ICP-OES was 3.25 wt.%. The resulting powder was mixed with α -terpineol and painted on the top of Pt lead wires. The PtY layer was around 50 μm thick after heating at 550 °C for 2 h.

2.2. Sensing measurements

The gas sensing experiments were performed in a tube furnace (Lindberg Blue, TF55035A) as in our previous work [7]. Briefly, computer-controlled mass flow controllers (MFC) were used to introduce the test gases. A certified 2000 ppm N_2 -balanced NO_2 cylinder (Praxair) was used as the NO_x source. Sensor tests were carried out with mixtures of dry air, NO_2 , and nitrogen with total gas flow rates of 200 cm^3/min at 500 °C. The open circuit potential of sensors was recorded by HP 34970A data acquisition system with 10 G Ω internal impedance. The negative terminal was attached to the porous electrode in Sensor A or the PtY electrode in Sensor B in the sensing tests.

3. Results

3.1. Surface nanostructure of electrodeposited Pt electrodes

As shown in Fig. 1a, the sensing device started with two Pt electrodes on YSZ, formed by using Pt ink. This was followed by electrodeposition of Pt only on one of the electrodes (designated henceforth as porous Pt), and the dramatic difference of the Pt surface before and after electrodeposition can be seen from the SEM images in Fig. 2. The electrodeposited Pt (Fig. 2c and d) is significantly more porous than the initial Pt (Fig. 2a and b). The surface area of the Pt film was not measured in this study but was reported in literature to be between 40 and 50 $\text{m}^2 \text{g}^{-1}$ [14]. It can be seen clearly in Fig. 2c that a piece of Pt (shown by arrow) that was isolated from the Pt electrode did not have the electrodeposited layer, as noted by the contrast. The boundaries of the grains of ink-generated Pt beneath the porous Pt are recognizable from the electrodeposited surface (Fig. 2d).

From the high-resolution cross-section (FIB) SEM image shown in Fig. 3a, the thickness of the electrodeposited layer with 60 s deposition is found to be around 200 nm. In Fig. 3b, periodic features (hexagonal) with 5 nm width can be observed on the electrodeposited surface without any Au or Os conductive coating. It is likely that the 5 nm feature represents the mesopores templated by SDS, since it was reported that mesochannels could be observed by high-resolution SEM [18]. After heating at 550 °C in air for 2 h, there was no apparent change in surface morphology (Fig. 3c, compared with Fig. 2d). It has been reported that the mesoporous structure is stable at 500 °C for 2 h [14], though the sensing data as discussed below does exhibit changes with heating.

Fig. 1b shows the three sensors that were fabricated using the electrodeposited Pt electrodes. In Sensor A, the device recovered

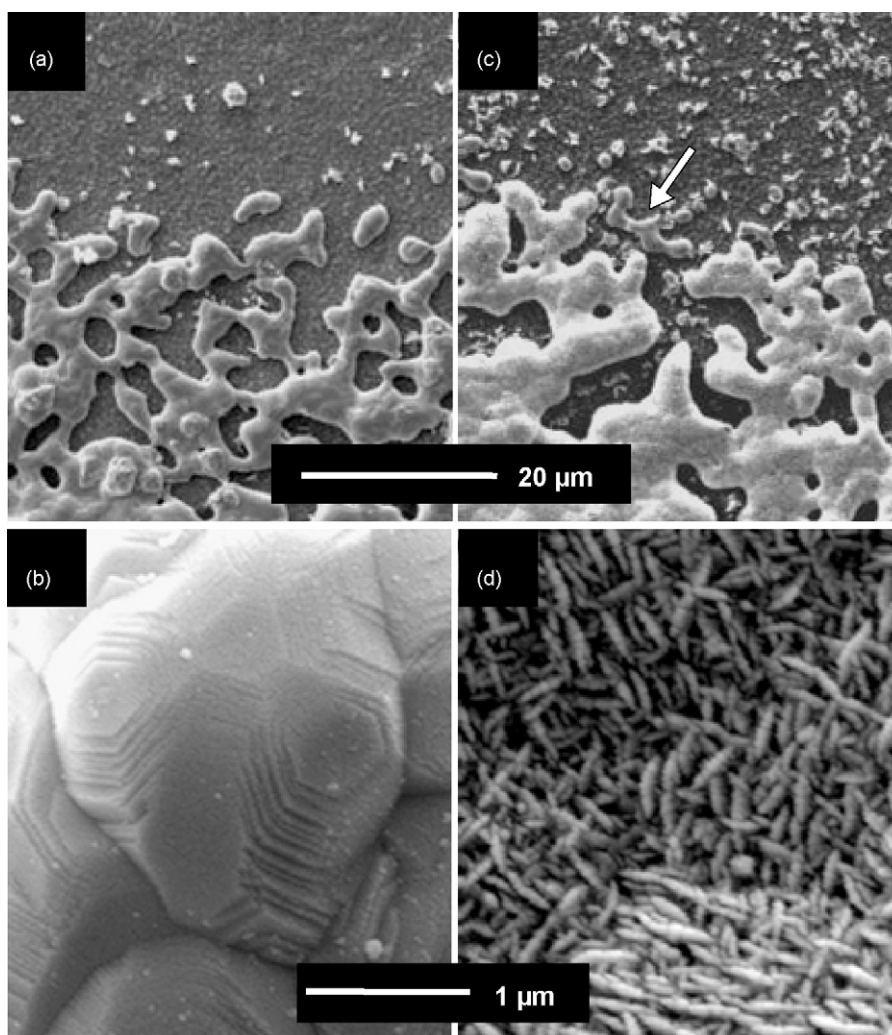


Fig. 2. SEM micrographs. (a and b) Ink-generated sintered Pt electrodes at two magnifications; (c and d) the porous Pt layer after 60 s electrodeposition at two magnifications. The arrow in (c) indicates a piece of Pt that was not electrically connected to the Pt electrode.

after electrodeposition was used. In Sensor B, the dense unreacted Pt electrode was covered with Pt-zeolite Y, which consists of Pt clusters in zeolite Y, details of which, including the microstructure can be found elsewhere [7]. A third Sensor C that had no electrodeposition, i.e. with the bulk Pt electrodes was also examined. Plot (a)

in Fig. 4 shows the signal for Sensor B exposed to 40–800 ppm NO_2 at 500 °C. Very weak signal was observed even for 800 ppm NO_2 (<5 mV), indicating similar catalytic activities of electrodeposited Pt and Pt-loaded zeolite layers coated on the Pt electrodes. Plots (c) and (b) show the response toward 40–800 ppm NO_2 for Sensors C

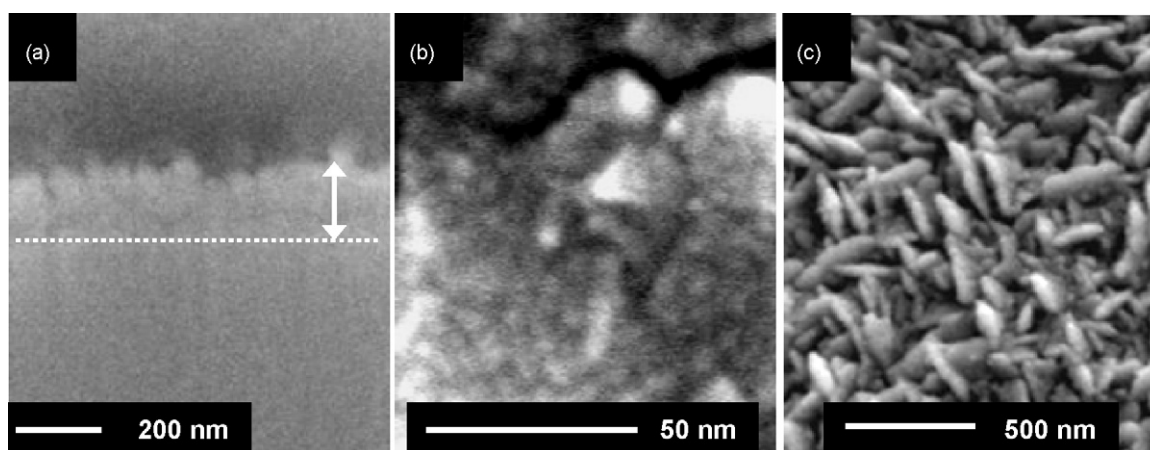


Fig. 3. SEM micrographs of electrodeposited porous Pt (60 s deposition): (a) FIB-cut cross-section; the arrow indicates the thickness of the electrodeposited porous layer, (b) high-resolution SEM of the electrochemically deposited Pt, (c) after heat treatment at 550 °C in air for 2 h.

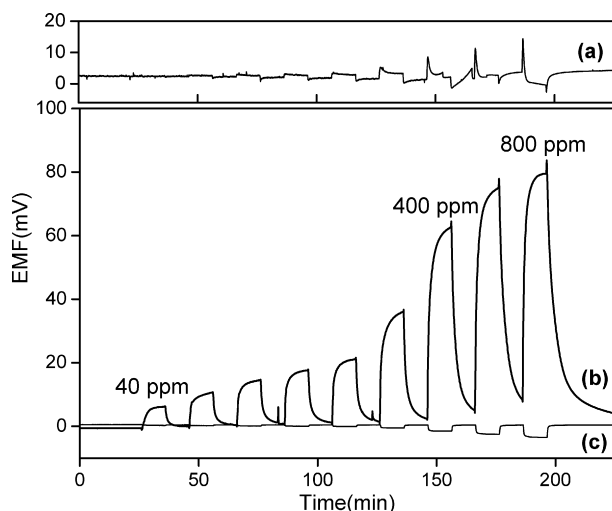


Fig. 4. Signal transient in 3% oxygen and 40–800 ppm NO₂ at 500 °C (concentrations of NO₂: 40, 60, 75, 90, 110, 200, 400, 600, 800 ppm). Plot (a): Sensor B; Plot (b): Sensor A with 60 s electrodeposition for Pt; Plot (c): Sensor C before electrodeposition. Plots (b) and (c) were obtained from the same device.

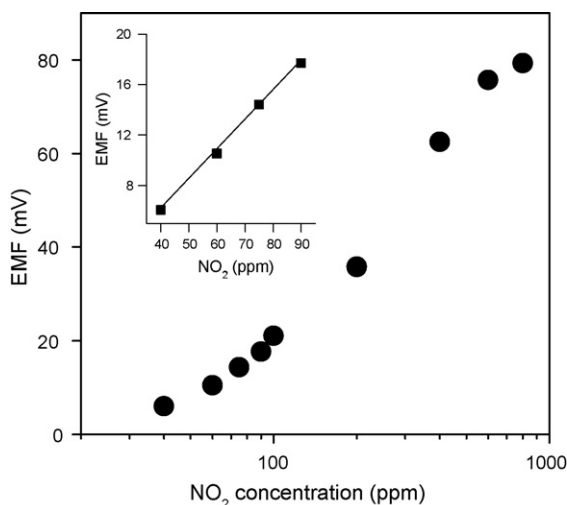


Fig. 5. EMF–log[NO₂] plots of Sensor A (after 60 s electrodeposition) in 3% O₂ at 500 °C (inset shows a linear fit to the low concentration range).

and A (before and after the electrodeposition process, respectively). With the two similar ink-generated Pt electrodes (Sensor C, no electrodeposition), the sensor exhibited a small signal of ~4 mV with 800 ppm NO₂ (Plot c). After depositing the ~200 nm porous Pt layer on one of the Pt electrodes (Sensor A), the signal increased to 80 mV (Plot b). The NO₂ was left on for 10 min, and the sensor response did not stabilize during this time, especially at the high concentrations. The plot of the potential with gas concentration (EMF – log NO₂) for Sensor A is shown in Fig. 5. EMF does not have a strict logarithmic relation to NO₂ concentration, however, as the inset shows, in the low concentration range of 40–90 ppm, a linear response is indeed observed.

4. Discussion

The electrochemical NO/NO₂ half-reaction at the sensing electrode:



is responsible for the sensing response. Ideally, at the reference electrode, reaction (1) should be minimized. This can be done by increasing the NO_x heterogeneous catalytic activity at the reference electrode, such that an equilibrated mixture of NO/NO₂ reaches the triple point boundaries. We have demonstrated that Pt-loaded zeolite Y coated electrodes are efficient reference electrodes due to their high NO_x catalytic activities [7,17]. However, the mechanical stability of zeolite Y coated on the Pt electrode by screen printing is often unsatisfactory, and was the motivation for this study.

General approaches for fabricating mesoporous Pt include the replication of porous alumina or lyotropic liquid–crystal templates with electrochemical reduction of Pt complexes, and potential-controlled surfactant assembly [14]. In the surfactant method, with a potential on the electrode surface, micelles can be formed on the surface even when the surface surfactant concentration is lower than the critical micelle concentration (cmc) [19,20]. Surfactant-inorganic aggregates can be induced and stabilized by controlling the electrochemical potential. The SEM images in Fig. 2a and b indicate that the electrodes made with Pt ink were dense after sintering. However, when these sintered Pt electrodes are used as the substrate for surfactant-templated electrodeposition, a porous deposit of Pt is formed on the sintered Pt electrode, as can be seen in Figs. 2c and d, and 3. The increase of the Pt surface area should greatly enhance the equilibration of NO/NO₂, reaction (2) on the surface of the electrodeposited electrode:



The presence of equilibrated NO and NO₂ around the triple phase boundary decreases the thermodynamic driving force of the NO_x electrochemical half-reaction (reaction (1)), leading to a much weaker potential change toward NO₂ on the electrodeposited Pt electrodes as compared to the ink-deposited Pt electrodes.

Although there have been studies suggesting the non-electrochemical reaction is one of the key issues of sensor performance, the comparisons were mostly done between different materials [21,22]. Sensor A in the study uses electrodes of the same metal, but with different catalytic activities. The structure of Sensor A is compact and simple. Only Pt and YSZ are needed to construct the sensor. Electrodeposited Pt has good adhesion with the Pt substrate so the device is mechanically durable.

At low NO₂ concentrations (40–200 ppm), the sensor response is linear with concentration, suggesting that a mass transport limited process is occurring [23], presumably through the porous network of Pt surrounding the reference electrode.

However, we did notice an issue with drift. A long-term test shows that the 200 ppm NO₂ signal decreases slowly up to ~40% after testing at 500 °C in air for nine days and only then reached a steady state (<0.1% change in one day). Our hypothesis is that morphological change (coarsening) of the mesoporous Pt is the cause of the decrease in signal due to a decrease in catalytic activity. With electron microscopy, these morphological changes were not obvious.

5. Conclusions

The porous Pt layer generated by a rapid surfactant-templated electrodeposition method significantly increased the surface area and catalytic activity of Pt electrodes. The large catalytic activity difference between the electrodeposition-treated and untreated Pt electrodes resulted in strong potentiometric signal toward NO₂. This study provides evidence of the role of non-electrochemical reactions for optimizing sensor performance. With the solution-phase electrochemical methods, highly catalytically active porous Pt layer can be formed in less than 1 min with simple apparatus. This technique is well suitable for future applications on fabricating

reference electrodes of micromachined electrochemical devices. A disadvantage is the coarsening of the mesoporous Pt with time resulting in drift at 500 °C, which only stabilizes after a finite time.

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Biographies

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